Theoretical, Physical, and Chemical Studies of Oxouranium(v) and Related Species.

David Glen Durrett
Louisiana State University and Agricultural & Mechanical College

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OF OXOURANIUM(V) AND RELATED SPECIES

A Dissertation
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy
in
The Department of Chemistry

by
David Glen Durrett
B.S., University of Southwestern Louisiana, 1964
Th.M., New Orleans Baptist Theological Seminary, 1968
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To Dianne
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LIST OF ABBREVIATIONS

BP ................................ benzo[a]phenazine
Bu .................................. butyl
DBP .................................. dibenzo[a,c]phenazine
dipy .................................. 2,2′-bipyridyl
DMA .................................. N,N-dimethylacetamide
DMF .................................. N,N-dimethylformamide
DMSO .................................. dimethylsulfoxide
dpm .................................. 2,2,6,6-tetramethyl-3,5-heptanedione
DPyQ .................................. 2,3-di(2-pyridyl)quinoxaline
EBDPP .................................. ethylenebis(diphenylphosphine)
EPA .................................. ethyl ether-isopentane-ethanol mixture
Et .................................. ethyl
HMPA .................................. hexamethylphosphoramide, [(CH₃)₃N]₃PO
HT .................................. tropolone
MB .................................. methylene blue
Me .................................. methyl
oxine .................................. 8-quinolinolate anion
oxine H .................................. 8-quinolinol
P .................................. phenazine
Ph .................................. phenyl
o-phen .................................. o-phenanthroline
Pr .................................. propyl
i-Pr .................................. isopropyl
PrenCO₃ .................................. propylene carbonate
PT........................................phenothiazine
Py........................................pyridine
Qi........................................quinoline
i-Qi....................................isoquinoline
T........................................tropolonate anion
TGAC....................................trichloroacrylyl chloride
THF......................................tetrahydrofuran
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\text{CH}_2\text{OH} \\
\text{CH}_2\text{COOH}
\end{align*}
\]

Thiolactic Acid
\[
\begin{align*}
\text{CH}_2\text{SH} \\
\text{CH}_2\text{COOH}
\end{align*}
\]

Mandelic Acid
\[
\begin{align*}
\text{OH} \\
\text{CHCOOH}
\end{align*}
\]

Thiosalicylic Acid
\[
\begin{align*}
\text{COOH} \\
\text{SH}
\end{align*}
\]

 Anthranilic Acid
\[
\begin{align*}
\text{COOH} \\
\text{NH}_2
\end{align*}
\]

Anisole
\[
\begin{align*}
\text{OCH}_3
\end{align*}
\]

Tropolone
\[
\text{OH}
\]

8-Quinolinol
\[
\begin{align*}
\text{N} \\
\text{OH}
\end{align*}
\]

Pyrazine
\[
\begin{align*}
\text{N} \\
\text{N}
\end{align*}
\]

Isoquinoline
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\begin{align*}
\text{N} \\
\text{N}
\end{align*}
\]

Phthalazine
\[
\begin{align*}
\text{N} \\
\text{N}
\end{align*}
\]

2,2'-Bipyridyl
\[
\begin{align*}
\text{N} \\
\text{N} \\
\text{N} \\
\text{N}
\end{align*}
\]

ß-Phenanthroline
\[
\begin{align*}
\text{N} \\
\text{N} \\
\text{N} \\
\text{N}
\end{align*}
\]

Phenazine
ABSTRACT

The data available for characterization of pentavalent uranium are relatively meager because this oxidation state of uranium is very unstable. The ground state electronic configuration, \([\text{Rn}]^{5f^1}\), of uranium(V) makes it important both chemically and spectroscopically.

The first definitive preparation of compounds of the \(\text{UO}^{3+}\) species was done in 1971 when salts of \(\text{UOX}_5^{2-}\) (X = F, Cl, Br) anions were reported. The present work was undertaken to explain the observed spectral properties of the \(\text{UOCl}_5^{2-}\) entity and to study the chemical properties of this unusual air-stable species.

In order to explain the electronic spectrum of \((\text{Et}_4\text{N})_2\text{UOCl}_5\), the theory of tetragonal \(5f^1\) complexes was developed. A semiempirical calculation of the transitions of \(\text{UOCl}_5^{2-}\) was carried out by beginning with the \(5f^1\) energy levels of \(\text{UCl}_6^-\) split by the \(O_h\) crystal field and by spin-orbit coupling and then considering the effects of the lower symmetry field. In addition to the four band groups observed in the visible-near-I.R. region, two additional groups were sought (as a result of the theoretical predictions) and observed at lower energies. A new salt, \(\text{Cs}_2\text{UOCl}_5\), was synthesized to aid in these spectral studies. An understanding of the electronic and ESR spectra of \(\text{UOX}_5^{2-}\) and other \(\text{U(V)}\) compounds was gained from this study.

A new and simpler preparative route to \((\text{Et}_4\text{N})_2\text{UOCl}_5\) was developed; the method involved hydrolysis of the versatile \(\text{UCl}_5^-\text{TCAC}\) complex. (TCAC = Trichloroacryloyl Chloride, \(\text{Cl}_2\text{C}=\text{OClCOCl}\)). In efforts to prepare additional compounds of the \(\text{UO}^{3+}\) species, there were carried
out reactions in which UC\textsubscript{5}·TCAC was hydrolyzed in the presence of various ligands, and three new adducts of UOCl\textsubscript{5}\textsuperscript{2-} were prepared. These compounds are believed to contain free radicals complexed to U(V).

Hydrolyses of two compounds of general formula UC\textsubscript{5}·xL were performed; (Et\textsubscript{4}N)\textsubscript{2}UOCl\textsubscript{5} was the product in both cases. The direct reactions of (Et\textsubscript{4}N)\textsubscript{2}UOCl\textsubscript{5} with some ligands resulted in disproportionation of the U(V). The reaction of (Et\textsubscript{4}N)\textsubscript{2}UOCl\textsubscript{5} with phenazine resulted in the isolation of the unexpected free radical salt of phenazine(P), \textcolor{red}{\text{PH}}\textsubscript{2}Cl. Because of this fascinating result, analogous reactions were carried out with several phenazine-like compounds and with other uranium(V) compounds, and several stable solid free-radical salts were isolated. Studies were also conducted in order to understand the unusual reaction which produces the \textcolor{red}{\text{PH}}\textsubscript{2}Cl radical.

Due to importance of molybdenum(V) and of free radicals in biological systems, the above work was extended to Mo(V) compounds. Several new Mo(V) compounds were isolated, and free radical formation was found to occur in Mo(V)-phenazine reactions.
HISTORY

Uranium has a long and fascinating history. It was discovered in 1789 by Martin Klaproth (1743-1817), a German analytical chemist. Klaproth's research efforts were directed toward devising improved analytical methods in order to establish the composition of minerals.¹ He undertook an investigation of the mineral pitchblende, which was thought to be an ore of zinc and iron. Dissolving the mineral in nitric acid and neutralizing the resulting solution with potash, Klaproth separated a yellow precipitate which dissolved in excess potash. He then heated a linseed oil paste of the yellow solid in a charcoal crucible and obtained a black powder that had a metallic luster. Thinking that he had isolated a new element, Klaproth named it "uranium" in honor of the discovery of the planet Uranus by Hershel in 1781.² The elemental nature of this product was accepted for over fifty years until Peligot showed in 1841 that Klaproth had actually obtained uranous oxide, UO₂.

In 1823, J. A. Arfwedson also obtained UO₂ by heating green uranium oxide in a current of hydrogen gas. Since hydrogen failed to reduce the product, Arfwedson also concluded that it was uranium metal.

Eugene-Melchoir Peligot (1811-1890) isolated the pure metal. He demonstrated that Klaproth's "uranium" was in reality an oxide. Peligot heated it with carbon in a current of chlorine, obtained carbon monoxide, carbon dioxide, and uranium tetrachloride, and concluded that the "element" isolated by Klaproth contained oxygen. Peligot then heated uranium tetrachloride with potassium metal in a platinum crucible.
The violent reaction caused the crucible and contents to become white-hot, and it was fortuitous that Peligot was not injured by pieces of potassium thrown out. By dissolving the potassium chloride, he obtained black metallic uranium.  

The radioactivity of uranium was discovered by Antoine-Henri Becquerel (1852-1908) in 1896. Having learned of the discovery of x-rays by Röntgen, Becquerel investigated the relationship between x-rays and fluorescence. He placed each compound being investigated on a wrapped, unexposed photographic plate in direct sunlight and then developed the plate. Becquerel inadvertently failed to expose one compound, potassium uranyl sulfate, to sunlight, but the photographic plate nevertheless became fogged.

In 1934 Enrico Fermi (1901-1954) and his associates undertook the neutron bombardment of uranium. The radioactivity thus produced indicated that a new element of atomic number greater than 92 had been produced. Other workers, however, challenged the results of Fermi, and the situation became somewhat cloudy during the subsequent several years. Physicists assumed that a nuclear reaction was likely to result only in the ejection of particles of small mass. The fission of the uranium nucleus was thus completely overlooked.

Otto Hahn and Fritz Strassman were the first to recognize the shortcomings of previous work and sought to identify the fragments of the neutron bombardment of uranium. The result was the discovery of nuclear fission in 1939.

Einstein's relation for the equivalence of mass and energy suggested the possibility of large energy releases in nuclear reactions.
The result was feverish investigative activity during the next several years. Uranium-235 was prepared in essentially pure form during the Manhattan Project.²

Uranium is sure to be an important nuclear power source in the future. The fission of one kilogram of U²³⁵ produces energy equivalent to the combustion of 6.6 million kg of coal.⁴
CHAPTER I

INTRODUCTION

A. Stability and Importance of Pentavalent Uranium

The available data on pentavalent uranium are sparse compared with those on the other oxidation states of uranium, except possibly trivalent uranium. This scarcity of literature on uranium(V) is due in part to the great instability of the pentavalent state; U(V) is very susceptible both to oxidation by atmospheric oxygen and to disproportionation that is frequently caused by the presence of trace quantities of water. The driving force in both modes of decomposition of uranium-(V) is the phenomenal stability of the uranyl ion, UO$_2^{2+}$.

In spite of these difficulties, uranium(V) is quite important both chemically and spectroscopically. The nuclear instability of most of the actinides lends importance to the chemical study of those such as uranium that have more stable nuclei. The ground state electronic configuration of uranium(V) is [Rn]$^5f^1$. The lack of interelectron repulsions should simplify spectroscopic interpretations and thereby aid structural and bonding studies.

B. Survey of the Literature on Pentavalent Uranium

A recent comprehensive review has summarized the literature on uranium(V). It is the purpose of this survey to briefly summarize
the review and to provide a survey of the literature which has become available since that review. For convenience, the order of the review article will be followed.

1. Compounds of Uranium(V)

a. Halogen compounds and halo complexes

Uranium pentachloride has been prepared by chlorine oxidation of uranium tetrachloride at high temperatures and by the action of organic chlorinating agents such as CCl₄ on UO₃ or U₃O₈. A recent report claims that UCl₅ is produced by the chlorination of UO₂ and U₃O₈ by Cl₂-CCl₄ in a static bed reactor at 350-500°C. The other product of the reaction is UCl₆. Uranium pentachloride has also been prepared by reacting uranium with chlorine gas in the presence of excess liquid chlorine at 298°K. The standard enthalpy of formation of solid UCl₅, \(-247.7 \pm 0.5\) kcal/mole, was determined by means of this reaction.

Uranium pentachloride decomposes thermally into UCl₄ and Cl₂ below 100°C, and decomposes by disproportionation into UCl₄ and volatile UCl₆ under high vacuum at 120-150°C.

The crystal structure of UCl₅ shows that UCl₅ crystallizes as a dimeric molecular unit, U₂Cl₁₀. Gruen and McBeth have studied the reaction between UCl₄ and Cl₂ and have identified the gaseous U₂Cl₁₀ dimer. The reaction at 450-650°C K was found to be

\[ 2\text{UCl}_4(s) + \text{Cl}_2(g) = \text{U}_2\text{Cl}_{10}(g) \]  

The visible-near I.R. (electronic) absorption spectrum of the compound changes drastically above 650°C K. These changes are thought to be due to the equilibrium
U_2Cl_{10}(g) = 2UCl_5(g) \quad (2)

Uranium pentafluoride has been prepared by reacting UC_1_5 with anhydrous HF, UC_1_6 with anhydrous HF, UF_4 with F_2, UF_4 with UF_6, and UF_6 with anhydrous HBr. Uranium pentafluoride can also be prepared by the reaction of uranium tetrafluoride with ClO_2F. The reaction also results in the formation of intermediate fluorides. \(^3\)

\[
nUF_4 + ClO_2F \rightarrow nUF_X + ClO_2 \quad (4 < X \leq 5) \quad (3)
\]

\[
nUF_4 + ClO_2F \rightarrow nUF_X + 0.5 Cl_2 + O_2 \quad (4)
\]

A recent study\(^{10}\) reveals that UF_5 and several intermediate fluorides are formed in the system UF_4-ClF, in which the following reactions are significant.

\[
nUF_4 + ClF \rightarrow nUF_X + 0.5 Cl_2 \quad (4 < X \leq 5) \quad (5)
\]

\[
2UF_5 + 2ClF \rightarrow Cl_2 + 2UF_6 \quad (6)
\]

\[
UF_6 + nUF_X \rightarrow (n + 1) UF_5 \quad (7)
\]

Uranium pentafluoride is formed by the reaction of UF_4 with ClF_3\(^{10}\) and by reduction of UF_6 with H, CO, SO_2, O, or Xe when UV radiation is used to accelerate the reaction.\(^{11}\) The role of O and Xe in the reduction was not determined.

The intermediate fluorides U_{4}F_{17} and U_{2}F_{9} have been formed\(^5\) along with \(\alpha\)-UF_5 and \(\beta\)-UF_5 in the reaction \(\text{vide supra}\) of UF_4 with UF_6. The reactions of UF_6 with PF_3, MoF_5, or WF_4 have produced\(^12\) UF_5, U_{2}F_{9}, and U_{4}F_{17}. The actual composition of the product depended on the ratio of reactants.

There are at least two crystal modifications of UF_5.\(^5\) The crystal structure of U_{2}F_{5} has recently been refined\(^13\) and shows that
U$_2$F$_3$ crystallizes in space group I$4_3$m with an average U-F distance of 2.30 Å.

Uranium pentafluoride disproportionates violently in the presence of moisture.$^5$ The reactions$^{14}$ of UF$_5$, U$_2$F$_5$, and U$_4$F$_{17}$ with BCl$_3$ and of UF$_5$ with PF$_3$, AsF$_3$, SbF$_3$, PCl$_3$, TiCl$_4$, and AsCl$_3$ are all attributed to an initial disproportionation, and UF$_4$ is a product of all the reactions.

Other recent studies on uranium(V) fluorides include calculations of thermodynamic values for UF$_5$,$^{15,16}$ U$_2$F$_9$,$^{16}$ and U$_4$F$_{17}$.$^{16}$

The report$^5$ of the preparation of uranium pentabromide has recently$^{17}$ been challenged in an investigation which claims that the compound can be isolated by the reaction of elemental uranium or UBr$_4$ with boiling bromine or with bromine and catalytic amounts of acetonitrile at room temperature. The pentabromide is isostructural with α-PaBr$_5$.$^{17}$ It is somewhat unstable$^5$ and decomposes quantitatively to uranium tetrabromide when it is heated in a vacuum.$^{18}$

Uranium pentaiodide has not been prepared and is evidently too unstable to be isolated.$^5$

Several salts of the hexachlorouranate(V) species, UC$_{16}^-$, have been prepared, generally from thionyl chloride solutions of U(V).$^5$ A simple method of preparation of these solutions involves heating UO$_3$ in thionyl chloride$^{19,20}$ or benzoyl chloride.$^{19}$ The desired solutions may also be conveniently prepared by dissolving the complex UC$_{15}^-$·TCAC (vide infra) in thionyl chloride.$^5,21$ Addition of the appropriate chloride to these solutions produces the desired salt. A new method$^{22,23}$ for the preparation of these salts involves the chlorine oxidation of the corresponding uranium(IV) complex in nitromethane. This method seems to be
more rapid and convenient than that which uses thionyl chloride solutions. It suffers, however, from the following disadvantages. First, there is lack of flexibility because a different U(IV) complex must be prepared for each cation desired. Second, there is restricted scope because only the Et₄N⁺ and Ph₄As⁺ salts have been prepared, and the Ph₃PH⁺, Cs⁺, PyH⁺, and Me₄N⁺ salts could not be prepared. However, salts containing Ph₄As⁺, Et₄N⁺, (n-Pr)₄N⁺, Na⁺, K⁺, Rb⁺, Cs⁺, and NH₄⁺ have been prepared from thionyl chloride solutions of UCl₅·TCAC, and those containing Me₄N⁺, (n-Bu)₄N⁺, Ph₄P⁺, Tl⁺, Ag⁺, and Ba⁺⁺ have been isolated from solutions prepared by refluxing UO₃ in SOCl₂. Third, the presence of trace amounts of water will cause oxidation of U(V) to UO₂Cl₄²⁻; this oxidation will not occur, however, if thionyl chloride is used.

Stoichiometric and conductometric evidence has been presented for the existence of the ions UCl₇⁻ and UCl₈³⁻. Preparation of the analogous protactinium complex (NO)₃PaCl₈ has also been claimed. Recent ESR and electronic spectral evidence cast considerable doubt upon the existence of these ions.

Several salts of the hexafluorouranate(V) species have been prepared. Ammonium hexafluorouranate(V) may be prepared by reacting liquid UF₆ with ammonium fluoride for extended periods. A great number of MUF₆ salts are prepared by adding MF to a solution of UF₅ in anhydrous or 48% HF. Dissolution of uranium metal in N₂O₄-HF mixtures results in the formation of NOUF₆. The reaction of UF₅ and ClO₂F at 0° produced UF₆ClO₂, but at 25° the product is UF₆. Hydrazinium difluoride reacts with UF₆ in anhydrous HF at room temperature to yield N₂H₆(UF₆)₂. Pure hydrazine and UF₆ react explosively at
but they easily form $N_2H_5UF_6$ at 70° when they are diluted with nitrogen. The use of hazardous fluorinating agents for the preparation of $UF_6^-$ compounds is avoided in a new method. The $Ph_4As^+$ salt is formed by the addition of $Ph_4AsUCl_6$ to 48% HF, whereas $CsUF_6$ can be prepared by the addition of CsF to a solution of $Et_4NUCl_6$ in 48% HF.

Data from the powder diffraction investigation of many $UF_6^-$ salts have been obtained. In addition, the crystal structure of $CsUF_6$ has been determined. The uranium atom is surrounded by a slightly distorted octahedron of fluorine atoms. In a recent ESR study, this distortion was observed in the case of the $Na^+$, $Li^+$, $Cs^+$, and $NO^+$ salts, and the extent of the distortion was calculated. The $NH_4^+$, $K^+$, and $Rb^+$ salts, however, possess a different coordination geometry. They are isostructural with $RbPaF_6$; the crystal structure of $RbPaF_6$ has been determined. This compound is orthorhombic (Cmma), and each Pa is bonded to eight F atoms in a dodecahedron of $D_{2d-L2m}$ symmetry. The dodecahedra form chains by sharing edges; the Pa-F bond lengths are 2.34 Å for F atoms in the shared edges and 2.09 Å for those in the unshared edges. Spectral results indicate that the coordination geometry of the $Ph_4As^+$ salt is similar to that of the $Cs^+$ salt, i.e., distorted octahedral.

Complexes corresponding to the formula $MU_2F_{12}·4H_2O$ ($M = Co$, Ni, Cu) have been prepared by mixing a solution of $UF_5$ in 48% HF with a solution of the hydrated metal fluoride in 48% HF. Those complexes, like most U(IV) compounds, are unstable in air. The $Co^{2+}$ salt crystallizes in the triclinic system.

The reaction of $UF_6$ with $N_2H_5F_2$ at room temperature forms the complex $N_2H_5UF_7$. Thermal decomposition of these compounds and of some $UF_6^-$ salts ultimately yields the very stable $UF_4$. 
In addition to the foregoing fluoro complexes, the octafluoro-uranate(V) ion is known, and several salts have been prepared.\textsuperscript{35} The crystal structure of Na\textsubscript{3}PaF\textsubscript{8}, which is isostructural with Na\textsubscript{3}UF\textsubscript{8}, has recently been determined.\textsuperscript{36} The protactinium compound is tetragonal (I\textsubscript{4}/mmm); each protactinium is surrounded by eight F atoms which lie at the corners of an almost perfect cube. The U-F bond lengths in Na\textsubscript{3}UF\textsubscript{8} have been calculated\textsuperscript{36} to be 2.21 Å; the same positional parameters as those of Na\textsubscript{3}PaF\textsubscript{8} were used. In a recent NMR study,\textsuperscript{37} however, it was concluded that Na\textsubscript{3}UF\textsubscript{8} is not isostructural with Na\textsubscript{3}PaF\textsubscript{8} because the uranium complex contains inequivalent fluorine atoms; however, the structures of Na\textsubscript{3}UF\textsubscript{8} and Na\textsubscript{3}PaF\textsubscript{8} are probably quite similar. The study also found that there is hindered molecular rotation of the UF\textsubscript{8}\textsuperscript{3-} units.\textsuperscript{37} A theoretical treatment of the magnetism of various UF\textsubscript{8}\textsuperscript{3-} salts assumed a trigonal deformation of the coordination sphere surrounding the uranium.\textsuperscript{38}

The disproportionation of U(V) in molten fluorides has been studied electrochemically.\textsuperscript{39}

Compounds of the type MUBr\textsubscript{6} (M = Ph\textsubscript{4}As\textsuperscript{+}, Et\textsubscript{4}N\textsuperscript{+}) have been made by Br\textsubscript{2} oxidation of the corresponding M\textsubscript{2}UBr\textsubscript{6} salts\textsuperscript{22,23} or by reaction of liquid boron tribromide with the corresponding MUC\textsubscript{6} salts.\textsuperscript{40} It is interesting to note that the Cs\textsuperscript{+} salt can not be prepared by either of these methods.\textsuperscript{22,40} Salts of the UBr\textsubscript{6}\textsuperscript{-} ion with M = Me\textsubscript{4}N\textsuperscript{+}, Et\textsubscript{4}N\textsuperscript{+}, n-Bu\textsubscript{4}N\textsuperscript{+}, and Ph\textsubscript{4}As\textsuperscript{+} have also been formed by adding the appropriate MBr to a solution prepared by dissolving UO\textsubscript{3} in thionyl bromide.\textsuperscript{20}

Salts of the UI\textsubscript{6}\textsuperscript{-} species have been formed by condensing anhydrous HI onto either hexachlorouranate(V) salts or UO\textsubscript{2}Cl\textsubscript{4}\textsuperscript{2-} salts.\textsuperscript{22}
The hexaiodo compounds are very unstable and decompose above -30°C to U(IV) and free iodine.22

b. Addition compounds of halides

The number of compounds of the type $UX_5 \cdot L$ ($X =$ halogen, $L =$ ligand other than halogen) has, until recently, been very small.5 The "adduct" $UCl_5 \cdot PCl_5$ was prepared by Panzer and Suttle by reacting $UO_3$ with $PCl_5$.5 The same compound has also been made19 by heating $UO_3$ with $PCl_5$ in benzoyl chloride, from which the complex crystallizes on cooling. The electronic spectrum indicates19 that the complex exists as $PCl_4^+ \cdot UCl_6^-$ in benzoyl chloride.

Heating $UO_3$ with $SOCl_2$ results5 in the formation of $UCl_5 \cdot SOCl_2$. The benzoyl chloride analog of this compound was formed19 in solution by heating $UO_3$ with benzoyl chloride, but a definite compound could not be isolated.

The complexes $UCl_5 \cdot Ph_3PO$ and $UCl_5 \cdot (C_6H_{17})_3PO$ have been made5 by reacting a suspension of $CsUCl_6$ in dichloromethane with the phosphine oxide. Addition of isopentane to a dichloromethane solution of $UCl_5 \cdot Ph_3PO$ and triphenylphosphine oxide produces41 $UCl_5(Ph_3PO)_2$. The bromo complexes $UBr_5 \cdot L$ ($L =$ $Ph_3PO$ or hexamethylphosphoramide) have been prepared5,40 by bromine oxidation of $UBr_4$ in acetonitrile containing the appropriate ligand or by the reaction

$$3UCl_5(Ph_3PO) + 5BBr_3 \rightarrow 3UBr_5(Ph_3PO) + 5BCl_3 \quad (8)$$

The complex $UCl_5 \cdot AlCl_3$ has been detected spectroscopically8 in the gas phase but has not been isolated. The spectral data were interpreted in terms of the reaction
\[
\text{UCl}_4(s) + \frac{1}{2} \text{Al}_2\text{Cl}_6(g) + \frac{1}{2} \text{Cl}_2 = \text{UCl}_5\cdot\text{AlCl}_3(g)
\] (9)

A series of ether complexes \(\text{UCl}_5\cdot\text{THF}, \text{UCl}_4\cdot(1,4\text{-dioxane}),\) and \(\text{UCl}_4\cdot\text{OR}_2\) (\(R = \text{Me, Et, } i\text{-Pr, } n\text{-Bu, } i\text{-C}_5\text{H}_{11}\)) have recently\(^4^2\) been made by the reaction of uranium pentachloride with the appropriate ether in carbon disulfide. Attack by water causes ether cleavage in the monomeric non-ionic complexes and produces the corresponding alcohol and chloride.\(^4^2\)

The unusual complexes \(\text{UF}_5\cdot\text{XeF}_6\) and \(\text{UF}_5\cdot1.75\text{XeF}_6\) have been prepared\(^4^3\) by the treatment of solid \(\text{UF}_4\) or \(\text{UF}_5\) with xenon hexafluoride at room temperature. The air-sensitive \(\text{UF}_5\cdot\text{XeF}_6\) can be recrystallized from anhydrous hydrogen fluoride, in which it forms bluish green solutions.

The pentachloro complex \(\text{UCl}_5\cdot\text{TCAC}\) (TCAC = trichloroacryloyl chloride, \(\text{Cl}_2\text{C} = \text{CClCOCl}\)) is made\(^5\) by heating \(\text{UO}_3\) or \(\text{U}_3\text{O}_8\) in hexachloropropene. An improved preparative procedure for this important compound has recently been described by this author, Sherrill, and Selbin.\(^2^1\) The unusual compound serves as a starting material for the preparation of a variety of compounds of pentavalent uranium. Although the compound is extremely sensitive to oxygen and moisture, it is conveniently stored \textit{in vacuo} and can be manipulated quite easily in an inert atmosphere enclosed in a dry box or dry bag. The usefulness of this complex as a starting material apparently stems from the poor coordinating ability of the TCAC ligand, which is displaced by most other ligands.

The \(\text{UCl}_5\cdot\text{TCAC}\) complex has been used to prepare\(^4^4, 4^5\) a series of eighteen new addition compounds of \(\text{UCl}_5\), including ligands with donor atoms which had not been previously complexed to uranium(V). Among these
donor atoms are several "soft base" donors. Since the actinides are considered to be Chatt-Ahrland Class "A" acceptors, the existence of these complexes has considerable importance in the study of actinide chemistry in general. The complexes are formed by adding a benzene solution of the ligand to a benzene solution of \( \text{UCl}_5 \cdot \text{TCAC} \). Some of the most interesting properties of these complexes are their EPR spectra (vide infra).

Another series of complexes of general formula \( \text{UCl}_5 \cdot x \text{L} \) (\( x = 1, 2, 3 \) and \( L = \text{N-} \) or \( \text{O-donor ligands} \)) has been prepared\(^{25,46} \) by addition of petroleum ether to a solution of \( \text{U}(\text{V}) \) and the ligand in thionyl chloride. As in the case of the majority of uranium(\( \text{V} \)) compounds, these complexes disproportionate rapidly when exposed to air or moisture.\(^{25} \)

c. Alkoxides, halide alkoxides, and related compounds

This group contains the greatest number of compounds of pentavalent uranium.\(^{5} \) These compounds may be classified into the following types.\(^{5,48-51} \)

1. \( \text{U} (\text{OR})_5 \), where \( R = \text{alkyl}, \text{fluoroalkyl}, \text{aminoalkyl}, \) or thioalkyl.
2. \( \text{U} (\text{OR})_{5-x} (\text{OR'})_x \), where \( R \) and \( R' = \text{alkyl} \).
3. \( \text{U} (\text{OR})_5 \cdot \text{L} \), where \( L = \text{ligand} \) and \( R = \text{alkyl} \).
4. \( \text{U} (\text{OEt})_6 ^- \), where cation is \( \text{Na}^+ \), \( \text{Ca}^{2+} \), or \( \text{Al}^{3+} \).
5. \( \text{U} (\text{OSiR}_x \text{R'}_{3-x})_5 \) where \( R \) and \( R' = \text{alkyl} \).
6. \( \text{U} (\text{OR})_{5-x} x \text{X}_x \), where \( X = \text{Cl} \) or \( \text{Br} \), and \( R = \text{alkyl} \).
7. \( \text{U} (\text{OCH}_2 \text{CF}_3)_5 x \text{amine} \).
8. \(\text{U(OR)}_5 - x\text{L}_x\), where \(L = \text{β-diketonate, β-ketoester, carboxylate, thiocarboxylate, or thioglycollate ion.}\)

9. \(\text{U(OEt)}_5 - 2x\text{L}_x\), where \(L = \text{lactate, mandelate, thiolactate, thiosalicylate, or glycollate ion.}\)

10. \(\text{U}_2\text{L}_5\), where \(L = \text{lactate, mandelate, thiolactate, or thiosalicylate ion.}\)

11. \(\text{U}\text{L}_2(\text{HL})\), where \(L = \text{lactate, mandelate, thiolactate, thiosalicylate, or glycollate ion.}\)

Uranium pentaalkoxides have been prepared\(^5\) by oxidation of uranium(IV) alkoxides by \(\text{Br}_2\) or \(\text{O}_2\), by reacting uranium pentachloride with ammonia and the appropriate alcohol, by exchange of alkoxide groups, and by the following method.

\[
\text{(PyH)}_2\text{UOCl}_5 + 5\text{NH}_3 + 3\text{ROH} \rightarrow \\
\text{UO(OR)}_3 + 5\text{NH}_4\text{Cl} + 2\text{C}_5\text{H}_5\text{N} \quad (10)
\]

\[
n\text{UO(OR)}_3 \xrightarrow{\text{heat}} \text{U(OR)}_5 + \text{U}_{n-1}\text{O}_n(\text{OR})_{3n-5} \quad (11)
\]

The starting material was produced by treating \(\text{UCl}_5\cdot\text{SOCl}_2\) with pyridine in an alcoholic solution. Recent evidence\(^22\) indicates that the starting material obtained in this way is not uranium(V) at all, but an equimolar mixture of uranium(IV) and uranium(VI). In the light of this evidence the formulation of the product as a uranium(V) compound must be viewed with skepticism. It should be emphasized that no proof of the oxidation state of the product was given;\(^5\) only the elemental analysis was presented, and an equimolar mixture of U(IV) and U(VI) would give the same analysis as a U(V) compound.

Molecular weights of many of the pentaalkoxides have been determined,\(^7\) and many of these compounds are thought to be dimers. A
recent NMR study\textsuperscript{47} of U(OEt)\textsubscript{5} in CFCl\textsubscript{3} and CDCl\textsubscript{3} indicates that from room temperature to -65$^\circ$ C the compound is dimeric and has a double alkoxide bridge and 6-coordinate uranium. At lower temperatures, however, there is thought to be an increase in the molecular complexity. The NMR spectrum\textsuperscript{47} of U(Oi-Pr)\textsubscript{5} in CDCl\textsubscript{3} suggests that there is a mixture of monomers and dimers at room temperature but that there are only dimers at low temperature.

Reaction of the pentaalkoxides with acetyl chloride or bromide produces the corresponding halide alkoxide.\textsuperscript{5}

Various oxygen-donor ligands react with uranium pentaethoxide in benzene and replace the ethoxide groups. $\beta$-Diketones,\textsuperscript{5,51} $\beta$-keto esters,\textsuperscript{5,51} thioglycols,\textsuperscript{49} thiobenzoic acid,\textsuperscript{49} and carboxylic acids\textsuperscript{50} yield derivatives of the type U(OEt)\textsubscript{5-x}L\textsubscript{x} (where L = anion of ligand; x = 1-5, depending on the particular ligand as well as the reaction conditions). Compounds having the general formula U(OEt)\textsubscript{3-x}L\textsubscript{x} (where x = 1,2) are obtained with mandelic acid,\textsuperscript{48} lactic acid,\textsuperscript{50} glycols,\textsuperscript{49} thiolactic acid,\textsuperscript{49} and thiosalicylic acid.\textsuperscript{49} Reactions with mandelic acid,\textsuperscript{48} lactic acid,\textsuperscript{50} thiolactic acid,\textsuperscript{49} and thiosalicylic acid\textsuperscript{49} also yield compounds having the formula U\textsubscript{2}L\textsubscript{5}, whereas derivatives with the general formula UL\textsubscript{2}(HL) can be formed when L is the anion of mandelic acid,\textsuperscript{48} lactic acid,\textsuperscript{50} various glycols,\textsuperscript{49} thiolactic acid,\textsuperscript{49} and thiosalicylic acid.\textsuperscript{49}

When refluxed with $t$-butyl alcohol, many of the above compounds will exchange their ethoxy groups for $t$-butoxy groups. Some of the compounds are dimeric, and coordination numbers of 5, 6, 7, and 8 have been suggested\textsuperscript{5,50,51} for several compounds of this type as well as for the amine complexes, Type 7 (vide supra).
It is important to point out that alkoxide compounds of uranium(V) have not been satisfactorily characterized. In general, elemental analyses and molecular weights are the only analytical data obtained. These data are not sufficient to establish the oxidation state of the metal, and, as the case of $\text{U}(\text{OEt})_5$ illustrates (vide supra), even the formulation of these compounds as uranium(V) species is open to question.

d. Oxides and oxo compounds

There are known several uranium oxides in which the presence of uranium(V) is possible. Among these are $\text{U}_2\text{O}_5$, $\text{U}_3\text{O}_8$, $\text{U}_4\text{O}_9$, $\text{U}_3\text{O}_7$, and $\text{U}_5\text{O}_{13}$ as well as some nonstoichiometric oxides, $\text{UO}_x$, in which $2 < x < 3$.

Uranium pentoxide has been prepared by dissolution of $\text{U}_3\text{O}_8$ or $\text{UO}_3$ in $10\text{-}15\% \text{H}_2\text{SO}_4$ or in $\text{H}_2\text{S}$. Dissolution of $\text{U}_3\text{O}_8$ in 7.0 M acetic acid, $0.25$-$2.0 \text{N HClO}_4$, or $1 \text{N HNO}_3$ containing anthranilic acid has been used to produce $\text{U}_2\text{O}_5$, although use of higher concentrations of acetic acid caused formation of higher oxides. Magnetic susceptibilities (vide infra) indicate that $\text{U}_2\text{O}_5$ contains the $\text{UO}_2^+$ species. The thermal stability of $\text{U}_2\text{O}_5$ has been studied, and an attempt has been made to correlate infrared spectra with oxygen content of the oxides.

Studies of magnetic properties (vide infra) also indicate that $\text{UO}_2^+$ is present in $\text{U}_3\text{O}_8$, although it is claimed that $\text{U}_3\text{O}_8$ behaves as a mixture of $\text{UO}_3$ and $\text{UO}_2$. Recent investigations of $\text{U}_3\text{O}_8$ involve its preparation, reduction, and thermal decomposition.

The previous supposition that $\text{U}_4\text{O}_9$ contains uranium(V) has received support from a recent spectroscopic study, although magnetic
properties indicate\textsuperscript{32} that there is no uranium(V) in U\textsubscript{4}O\textsubscript{9}. The recent literature pertaining to U\textsubscript{4}O\textsubscript{9} includes an electron diffraction study\textsuperscript{36} as well as investigations of its formation,\textsuperscript{58} oxidation,\textsuperscript{67} and reduction.\textsuperscript{56,59,68-71}

Pentavalent uranium may also be present in U\textsubscript{3}O\textsubscript{7},\textsuperscript{58,67} U\textsubscript{5}O\textsubscript{13},\textsuperscript{5,52} and several non-stoichiometric oxides UO\textsubscript{x}, in which 2 < x < 3.\textsuperscript{5,54,57,59,61-64,70,72-75}

In general, the above oxides have not been well characterized. The oxidation state of the uranium is difficult to determine, and the presence of uranium(V) has, in most cases, not been conclusively demonstrated.

There are several reports of compounds of the monoxouranium(V) species, UO\textsuperscript{3+}, but very little definitive work has been done on compounds of this entity. The oxochloro compound, UOCl\textsubscript{3}, has been prepared by the reaction of UCl\textsubscript{4} with UO\textsubscript{2}Cl\textsubscript{2}.\textsuperscript{5} The same compound has been reported\textsuperscript{5} to result from treatment of UO\textsubscript{3} with molybdenum pentachloride.

\[
UO_3 + MoCl_5 \rightarrow UOCl_3 + MoO_2Cl_2
\]  \hspace{1cm} (12)

The product was obtained in pure form by distillation of the volatile MoO\textsubscript{2}Cl\textsubscript{2} and collection of the UOCl\textsubscript{3} residue. The compound was described as a brown powder, extremely hygroscopic and soluble in absolute alcohol; it was characterized by elemental analysis and its infrared spectrum. Unfortunately, no data were given to show that this is a uranium(V) compound rather than a mixture of uranium(IV) and uranium(VI).

Uranium(V) oxobromide, UOBr\textsubscript{3} has also been reported.\textsuperscript{5} It was prepared by reacting UO\textsubscript{3} with CBr\textsubscript{4} at 110\textdegree\ in an inert atmosphere. The formulation of this compound as a uranium(V) entity was also based on scanty
evidence. Lux, et al.,\textsuperscript{17} prepared a yellow-green solid by the addition of DMA (N,N-dimethylacetamide) to an acetone solution of UBr\textsubscript{5}. On the basis of elemental analyses, the compound was formulated to be UOBr\textsubscript{3}.\textsuperscript{2.5} DMA. Infrared and electronic spectra revealed the presence of both uranium(IV) and UO\textsubscript{2}\textsuperscript{2+}, and the authors claimed to have prepared "Apart from the actinide oxides and halides... the first coordination compound containing an actinide element in two different oxidation states". If the substance were actually a mixed oxidation-state compound, the color would be expected to be black or at least very intense. It appears, then, that the material is a mixture of UO\textsubscript{2}Br\textsubscript{2} and UBr\textsubscript{4} (which have been prepared many times) that contains coordinated DMA.

In a brief preliminary report,\textsuperscript{76} it was claimed that treatment of CsUCl\textsubscript{6} with antimony trioxide yielded the salt CsUOCl\textsubscript{4}. No additional information has been published.

The preparation of (PyH)\textsubscript{2}UOCl\textsubscript{5} was reported\textsuperscript{5} by Bradley, et al. The compound was made by dissolving UCl\textsubscript{5}·SOCl\textsubscript{2} in ethanol, saturating the solution with dry HCl, and adding pyridine. The green compound was characterized by elemental analyses, but no additional data were given to support the claim that this was a uranium(V) complex. This report has been shown by Ryan\textsuperscript{22} to be in error. The analysis and pale green color would result from an equimolar mixture of UCl\textsubscript{6}\textsuperscript{2−} and UO\textsubscript{2}Cl\textsubscript{4}\textsuperscript{2−}. Furthermore, immediate and complete disproportionation occurs when Et\textsubscript{4}NUCl\textsubscript{3} is added to absolute ethanol. Saturation of this solution with HCl does not cause the mixture of UCl\textsubscript{6}\textsuperscript{2−} and UO\textsubscript{2}Cl\textsubscript{4}\textsuperscript{2−} to be reconverted to uranium(V). It is fairly certain, then, that what Bradley, et al., actually produced was an equimolar mixture of (PyH)\textsubscript{2}UCl\textsubscript{6} and (PyH)\textsubscript{2}UO\textsubscript{2}Cl\textsubscript{4}.
In contrast to these ambiguous and erroneous reports, Ryan has recently described the first definitive preparation of compounds of the UO\(_{3+}\) species. The compounds prepared were bright blue (Et\(_4\)N)\(_2\)UOCl\(_5\), violet-blue (Ph\(_4\)As)\(_2\)UOCl\(_5\), blue (PyH)\(_2\)UOCl\(_5\)·2.5PyHCl, green (Ph\(_4\)As)\(_2\)-UOBr\(_5\), green (Et\(_4\)N)\(_2\)UOBr\(_5\)·2.5Et\(_4\)NBr, pink (Et\(_4\)N)\(_2\)UOF\(_5\)·2H\(_2\)O, and bright pink (Et\(_4\)N)\(_2\)UOF\(_5\). The preparation of (Et\(_4\)N)\(_2\)UOCl\(_5\) illustrates the general procedure: undried Et\(_4\)NCl was dissolved to approximate saturation in undried nitromethane, diluted ten-fold with undried acetone, and filtered. The product was formed by addition of Et\(_4\)NUCl\(_6\) to the solution at -78\(^\circ\) C. The solution evidently contains enough water to cause the hydrolysis to proceed, but disproportionation of the uranium-(V) is prevented both by the low temperature and the insolubility of the product in the reaction medium. The other salts were prepared by similar methods with appropriate changes in the solvent system, temperature, and other variables. The products were characterized not only by elemental analyses but also by their electronic spectra (vide infra), which are markedly different from those of uranium(IV) and uranium(VI) and demonstrate conclusively that the products are uranium(V) compounds. The electronic spectra are intriguing, and a significant part of the present research is concerned with the spectrum of the UOCl\(_5^{2-}\) ion. Equally interesting is the unusual stability of these compounds. The complex (Et\(_4\)N)\(_2\)UOCl\(_5\), for example, is stable for several months in a laboratory atmosphere. In solution, however, these compounds undergo disproportionation rapidly in the absence of excess halide, if traces of moisture are present. The preparation of (PyH)\(_2\)UOCl\(_5\)·2.5PyHCl was given as further evidence against the reported preparation\(^5\) of (PyH)\(_2\)-UOCl\(_5\) by Bradley, et al.
Several compounds containing the \( \text{UO}_2^+ \) entity have been isolated. The bromide, \( \text{UO}_2\text{Br} \), was prepared by the action of \( \text{HBr} \) on uranium trioxide.\(^5\)

\[
\text{UO}_3 + 2\text{HBr} \xrightarrow{250^\circ} \text{UO}_2\text{Br} + \tfrac{1}{2}\text{Br}_2 + \text{H}_2\text{O}
\]  

(13)

The brown product was reported to be stable to \( 500^\circ \) and to have an infrared spectrum similar to that of the \( \text{UO}_2^{2+} \) entity.\(^5\) Magnetic susceptibility measurements have recently been used\(^7\) to establish the oxidation state. The chloro compound, \( \text{UO}_2\text{Cl} \), has been made\(^7\) by reduction of \( \text{UO}_2\text{Cl}_2 \) with \( \text{UO}_2 \) at \( 590^\circ \) or by heating \( \text{UCl}_4 \) with \( \text{U}_3\text{O}_8 \) at the same temperature under argon for 72 hours. The brown-violet crystalline product is stable in an inert atmosphere to \( 600^\circ \); at higher temperatures it decomposes into \( \text{UO}_2 \) and \( \text{Cl}_2 \). Magnetic susceptibility measurements showed that \( \text{UO}_2\text{Cl} \) is a uranium(\( V \)) compound. This compound was detected\(^7\) in the \( \text{LiCl}-\text{UO}_2\text{Cl}_2 \) system and is produced by the dissociation of \( \text{UO}_2\text{Cl}_2 \) into \( \text{UO}_2\text{Cl} \) and \( \text{Cl}_2 \). The compound was not found in systems containing \( \text{RbCl} \) or \( \text{CsCl} \), and this absence was ascribed to the stabilizing effect of the larger ionic radii of \( \text{Rb}^+ \) and \( \text{Cs}^+ \).\(^7\) Caligari, \textit{et al.},\(^7\) studied the reaction

\[
\text{UO}_2\text{Cl}_2 \rightarrow \text{UO}_2\text{Cl} + \tfrac{1}{2}\text{Cl}_2
\]

(14)
in molten \( \text{LiCl}-\text{KCl} \) eutectic and found it to be first order. A series of uranium oxyfluorides has been formed\(^1\) by heating \( \text{UF}_4 \) with \( \text{U}_3\text{O}_8 \) or \( \text{UO}_2 \) and \( \text{UO}_3 \) in the absence of air at \( 400-550^\circ \). The products had the general formula \( \text{UO}_x\text{F}_y \) \( (x = 2.00-2.50, y = 0.25-1.00) \). The composition of the products was found to depend on the ratio of the reactants. In a study of the magnetic properties, electronic spectra, and crystallographic properties of these compounds, it was reported\(^1\) that the
structures of the oxyfluorides are very similar to those of several uranium oxides such as $U_2O_5$ and $U_3O_8$. The compounds contain O-U-O chains ($D_{2h}$).

The very unstable dioxouranium(V) ion, $UO_2^+$, has been studied quite extensively in solution. This species has been generated by reduction of $UO_2^{2+}$ electrochemically or with zinc amalgam or hydrogen, by dissolving $UCI_5$, or by mixing solutions of $U(IV)$ and $U(VI)$.

Formal oxidation potentials of the following reactions have been determined in 1 M HClO$_4$ at $25^\circ$.

\[
U^{4+} = UO_2^+ + e^- \quad E = -0.58 \text{ V} \quad (15)
\]
\[
UO_2^+ = UO_2^{2+} + e^- \quad E = -0.063 \text{ V} \quad (16)
\]
\[
U^{4+} = UO_2^{2+} + 2e^- \quad E = -0.32 \text{ V} \quad (17)
\]

In a recent study, a correction has been estimated for adjusting the formal potential of the $UO_2^+/UO_2^{2+}$ couple to a true $E^0$ value. A value of $-0.163 \text{ V}$ was found for $E^0$. It has been found that the $U^{4+}/UO_2^+$ reaction is irreversible, but the $UO_2^+/UO_2^{2+}$ couple is reversible. The reversible nature of the latter couple has been attributed to the fact that no strong metal-oxygen bonds are formed or broken during redox and is considered to be strong evidence for the existence of the $UO_2^+$ species. The potential of this couple is only slightly affected by complexation by the $Cl^-$ ion.

The disproportionation of $UO_2^+$ has been extensively studied. The above potentials show that $UO_2^+$ has a strong tendency to undergo disproportionation into $U(IV)$ and $UO_2^{2+}$. It has been reported that
the UO$_2^+$ entity is somewhat stable only in the pH range 2.0-4.0, but in recent studies it is claimed that UO$_2^+$ undergoes disproportionation rapidly in acetate buffers at low pH and that disproportionation is negligible in aqueous carbonate solutions (at high pH) and in solutions of monochloroacetic acid and pyridine. The uranium(V) is thought to form complexes with the last two compounds in solution. The mechanism of disproportionation is thought to involve OH radical transfer, and the equilibrium constant for the reaction has been determined. The periodicity of the equilibrium constants of the disproportionation of MO$_2^+$ ions of the actinides has been reported to be the result of the parity of the electronic configurations of the ions. The U(IV) product of the disproportionation in molten acetamide has been identified to be UO$_2^{2+}$. The effects of a number of variables on the rate of disproportionation have been studied. Recent investigations of the disproportionation reaction have dealt with determination of the activation energy, processes at the electrode surface, and rate measurements by cyclic chronopotentiometry.

Studies of the UO$_2^+$ species have also involved its formation in LiCl-KCl eutectic, its reduction, its complexation, its behavior at high pH, and its spectral properties (vide infra).

Uranium(V) oxo compounds containing the anions UO$_3^-$, UO$_4^{3-}$, UO$_5^{5-}$, UO$_6^{7-}$, U$_2$O$_6^{2-}$, U$_2$O$_4^{3-}$, U$_2$O$_7^{4-}$, U$_2$O$_9^{8-}$, and certain nonstoichiometric anions have been prepared.

Compounds containing the UO$_3^-$ anion have been formed by heating UO$_2$ with M$_2$UO$_4$ (M = alkali metal) or with Na$_2$CO$_3$ and by heating...
BaUO$_3$ with UO$_3$. Studies of this species have involved determination of crystal structures, thermal and solution stability, and the extent of covalency in the U-O bond by means of $^{17}$O NMR.

The preparation of the UO$_4^{3-}$ species has been accomplished by heating M$_2$O$_3$ ($M = Bi$, Cr, Fe, or lanthanide element) with a mixture of UO$_2$ and UO$_3$ or with U$_3$O$_8$ to yield compounds having the general formula MUO$_4$. The compound Na$_3$UO$_4$ has been prepared by heating Na with UO$_3$, U$_3$O$_8$, or Na$_2$U$_2$O$_7$ or by heating Na$_2$O with UO$_2$ or with UO$_2$ and Na$_2$UO$_4$. The compound Na$_{11}$U$_5$O$_{16}$ has been produced by the reaction of Na$_2$O with NaUO$_3$ or of Na$_2$CO$_3$ with UO$_2$, but the oxidation state of the uranium in this compound has not been definitely established. A study of covalent bonding in BiUO$_4$ has been conducted by means of $^{17}$O NMR, and the crystal structure of FeUO$_4$ has shown it to be isostructural with CrUO$_4$.

Compounds of the general type MUO$_5$ ($M = V$, Nb, Mo) have been prepared and are thought to contain pentavalent uranium. Investigations of the crystallographic properties of these compounds have been carried out, but as yet there are no magnetic nor spectral data to confirm the presence of uranium(V).

The UO$_6^{7-}$ ion has been obtained in the compounds Li$_7$UO$_6$, Sr$_2$InUO$_6$, Ba$_2$FeUO$_6$, Ba$_2$CrUO$_6$, Ba$_2$Mn$_{1-x}$In$_x$UO$_6$ ($x = 0$, 0.33, 0.67, 0.89), and Ba$_2$Fe$_{1-x}$M$_x$UO$_6$ ($M = Ga$, In, Mg, Zn; $x = 0.33$, 0.67, 0.89, 1.00). Crystallographic studies show that the compounds are ordered perovskites, and spectroscopic and magnetic measurements indicate the presence of pentavalent uranium. At low temperatures the iron compounds are ferrimagnetic.
Several compounds containing the \( U_2O_8^{2-} \) anion have been made with \( \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Mg}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \) and \( \text{Cd}^{2+} \) cations. The compounds were prepared by heating the appropriate diuranate(VI) compound (containing the \( U_2O_7^{2-} \) ion) or by reducing it with \( \text{NH}_3 \) at 600°C. The calcium compound, \( \text{CaU}_2O_6 \), has also been prepared by the thermal decomposition of \( \text{CaUO}_3.5O \) (vide infra) at 1500°C in the presence of \( \text{H}_2 \) or at 700°C in the presence of \( \text{H}_2\text{S} \).

\[
2\text{CaUO}_3.5O \xrightarrow{1500°C} \text{CaU}_2O_6 + \text{CaO}
\]  

The crystal structures of the \( \text{Co}^{2+} \) and \( \text{Ni}^{2+} \) compounds have recently been solved and show that both oxides crystallize hexagonally in space group \( D_{3h}^-\text{P}321 \), the \( \text{Na}_2\text{SiF}_6 \) structure. Measurements of the magnetic susceptibility of \( \text{CaU}_2O_6 \) have revealed the presence of \( \text{UO}_2^+ \) groups (vide supra) and suggest that the compound should be formulated as \( \text{Ca}^{2+}(\text{UO}_2^+)\text{O}_2(\text{O}^2-)\). The \( \text{U}_2O_8^{2-} \) species has been obtained in compounds of the type \( \text{MM}'\text{U}_2O_8\text{F} \) (\( \text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Tl}; \text{M}' = \text{Sr}^{2+}, \text{Pb}^{2+}, \text{Ba}^{2+} \)) and in the compound \( \text{Pb}_{1.5}\text{U}_2O_6\text{F} \). In addition, a series of non-stoichiometric compounds having the general formula \( \text{M}_{0.33}\text{PbU}_2O_5.67\text{F} \) (\( \text{M} = \text{K}, \text{Rb}, \text{Tl} \)) has been prepared. According to magnetic and spectroscopic measurements (vide infra), the last two types of compounds contain the \( \text{UO}_2^+ \) group. Similar investigations of the compounds \( \text{MM}'\text{U}_2O_8\text{F} \) indicate that when \( \text{M} = \text{K} \) or \( \text{Rb} \) and \( \text{M}' = \text{Sr} \) or \( \text{Ba} \), the uranium is surrounded by a regular octahedron of oxygens, but the octahedron is distorted in the other compounds.

Thermal decomposition of the uranium(VI) compound \( \text{MgUO}_4 \) has been used to prepare \( \text{Mg}_2\text{U}_2O_7 \). This reaction is reversible; the \( \text{MgUO}_4 \)
is regenerated when Mg₂U₂O₇ is cooled in air.\(^{116}\) When the reaction is carried out with excess MgO present, a compound having the composition MgUO₃ is formed.\(^{117}\) Reduction of CaUO₄ with H₂ or H₂S produces\(^{52}\) CaUO₃\(^{86}\) and CaU₂O₇ (CaUO₃\(^{3}\)). Magnetic susceptibility measurements indicate\(^{52}\) the presence of UO₂\(^{+}\) groups in the Ca²⁺ compounds. The compounds Pb₂U₂O₇ and Ba₂U₂O₇ have also been prepared.\(^{5}\)

Oxo compounds which may contain uranium(V) also include U₂Th₂O₉,\(^{65,118}\) the solid solutions M₀.₅⁻ₓThₓO₂ (M = Y or lanthanide, 0 ≤ x ≤ 0.938),\(^{119}\) pentavalent uranium doped into crystals of LiNbO₃ and LiTaO₃,\(^{120}\) and NUO, which has been identified in the mass spectrum of the U-N-O system but has never been isolated.\(^{121}\)

e. Other compounds

A recent report\(^{122}\) describes the preparation of the first uranium(V) sulfide, KUS₃. The compound was made by heating an excess of sulfur with KUS₂ at 750°C for several days in an inert atmosphere. The black crystalline compound is less hygroscopic and less susceptible to oxidation than KUS₂. Magnetic susceptibility measurements were used to support the formulation of KUS₃ as a uranium(V) compound, and the compound was found to crystallize in the orthorhombic system.

In a study of atomic radii, it has been concluded\(^{123}\) that the compounds UX (X = N, P, As, Sb, S, Se, Te) contain pentavalent uranium, although the nature of the bonding in these compounds is not certain.

2. Magnetic Susceptibilities and EPR Studies

Magnetic susceptibilities of a wide variety of uranium(V) compounds have been determined. These measurements often prove to be quite useful
**TABLE I**

RECENT MAGNETIC DATA FOR URANIUM(V) COMPOUNDS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp, °K</th>
<th>$\chi_m^{corr} \times 10^6$</th>
<th>$\mu_{eff}$, B.M.</th>
<th>Behavior</th>
<th>Ref</th>
</tr>
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<tbody>
<tr>
<td>UCl$_5$·OR$_2$</td>
<td>298</td>
<td>1.4-2.2</td>
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<td></td>
<td>42</td>
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<tr>
<td>UCl$_5$·xL</td>
<td>298</td>
<td>1.70-3.77</td>
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<td></td>
<td>45</td>
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<tr>
<td>UCl$_5$·xL</td>
<td>298</td>
<td>1.635-1.792</td>
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<tr>
<td>UCl$_5$·2Py</td>
<td>87.0</td>
<td>1911</td>
<td>2.772$^e$</td>
<td>C-W</td>
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</tr>
<tr>
<td></td>
<td>295.2</td>
<td>1252</td>
<td>2.668</td>
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<tr>
<td>UCl$_5$·3Py</td>
<td>89.5</td>
<td>1506</td>
<td>2.467$^e$</td>
<td>C-W</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>294.9</td>
<td>937</td>
<td>2.308</td>
<td></td>
<td></td>
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<tr>
<td>UCl$_5$·2QI</td>
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<td>2555</td>
<td>2.189$^e$</td>
<td>C-W</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>294.6</td>
<td>1263</td>
<td>2.126</td>
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<tr>
<td>UCl$_5$·3QI</td>
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<td>1674</td>
<td>1.856$^e$</td>
<td>C-W</td>
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<td></td>
<td>294.1</td>
<td>980</td>
<td>1.902</td>
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<td>UCl$_5$·3(QI)</td>
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<td>1820</td>
<td>1.649$^e$</td>
<td>C-W</td>
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<td>947</td>
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<td>298</td>
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<td>(in SOCl$_2$)</td>
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<tr>
<td>U(OEt)$_3$</td>
<td>298</td>
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<td>47</td>
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<tr>
<td>UO$_2$Cl</td>
<td>86-295</td>
<td>1.86$^f$</td>
<td>C-W</td>
<td>77</td>
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<tr>
<td>UO$_2$Br</td>
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<td>1.76$^f$</td>
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<td>UO$_{x\text{F}_y}$</td>
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<td>125</td>
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<tr>
<td>MM'U$_2$O$_6$F</td>
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<td>758-986</td>
<td>0.71-0.81</td>
<td>Non-C-W</td>
<td>113</td>
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<td></td>
<td>453</td>
<td>422-589</td>
<td>1.24-1.47</td>
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<td>X$_{0.33}$Pb$_2$U$<em>2$O$</em>{5.67}$</td>
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<td>1479-1704</td>
<td>0.99-1.07</td>
<td>Non-C-W</td>
<td>115</td>
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<td></td>
<td>453</td>
<td>613-688</td>
<td>1.50-1.59</td>
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<tr>
<td>NaUO$_3$·Pb$_2$U$_2$O$_7$</td>
<td>83</td>
<td>1431</td>
<td>0.98</td>
<td>Non-C-W</td>
<td>115</td>
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<tr>
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<td>1.48</td>
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<td>801</td>
<td>1.04</td>
<td>Non-C-W</td>
<td>115</td>
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<td></td>
<td>453</td>
<td>517</td>
<td>1.37</td>
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<td>KUS$_3$</td>
<td>90-300</td>
<td>2.23</td>
<td>C-W</td>
<td>122</td>
<td></td>
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</tbody>
</table>

*a. Seven addition compounds of UCl$_5$ with ethers are reported.*

*b. Data reported are for a series of eighteen addition compounds of UCl$_5$ with various ligands.*

(Continued)
c. Data reported are for UC$_{15}$·2(α-Picoline) and for UC$_{15}$·3L (L = α-Picoline, Isoquinoline).
d. Obeys Curie-Weiss Law.
e. This moment has little significance due to the large value of the Weiss Constant.
f. μ$^{\text{eff}}$ was calculated from μ$^{\text{eff}}$ = 2.828 $\sqrt{\sigma}$, where $\sigma$ is the slope of a plot of $1/\chi_m$ vs T.
g. Data reported are for a series of nine compounds of general formula UO$_x$F$_y$ (x = 2.00-2.50, y = 0.25-1.00).
in structural and bonding studies, and many of these values are reported in the recent review.\textsuperscript{5} Data which have been reported since the review are summarized in Table I. Most compounds of pentavalent uranium obey the Curie-Weiss Law,\textsuperscript{5,25,43,52,77,122} but the Weiss constants of most compounds are large. For this reason, many of the magnetic moments reported are not very significant. Compounds which do not obey the Curie-Weiss Law include some oxides,\textsuperscript{5} compounds of the general formula $\text{MU}_2\text{O}_6$,\textsuperscript{5} $\text{Ba}_2\text{FeUO}_6$,\textsuperscript{109} the compounds $\text{Ba}_2\text{MUO}_6$ ($M = \text{Fe, Ga, In, Mg, Zn}$),\textsuperscript{111} compounds containing the $\text{U}_2\text{O}_6\text{F}^{3-}$ anion\textsuperscript{113,114} or other oxo-fluoro anions,\textsuperscript{115} and other oxofluorides.\textsuperscript{125} Ferromagnetism has been detected\textsuperscript{109,111} in the compounds $\text{Ba}_2\text{Fe}_{1-x}\text{M}_x\text{UO}_6$ ($M = \text{Ga, In, Mg, Zn}$) at low temperatures.

Magnetic susceptibilities have been employed\textsuperscript{109} as evidence that $\text{Ba}_2\text{FeUO}_6$ is a compound of Fe(III) and U(V), rather than Fe(II) and U(VI). Karraker, et al.,\textsuperscript{47} explained the low magnetic moment of $\text{U(OEt)}_5$ by dimer formation, which is known\textsuperscript{5} to occur in the case of the pentethoxide. Magnetic data have also been used\textsuperscript{43} to show that $\text{UF}_5\cdot\text{XeF}_6$ is ionic. It is claimed that magnetic susceptibilities indicate octahedral coordination in $\text{Pb}_2\text{U}_2\text{O}_7$\textsuperscript{115} and some compounds of $\text{U}_2\text{O}_6\text{F}^{3-}$.\textsuperscript{113} Magnetic properties are also used to infer distorted coordination spheres in some $\text{U}_2\text{O}_6\text{F}^{3-}$ compounds\textsuperscript{113} and in the eight-coordinate compounds $\text{M}_3\text{UF}_6$ ($M = \text{NH}_4^+, \text{Na}^+, \text{Rb}^+, \text{Cs}^+$).\textsuperscript{38} The oxides $\text{U}_2\text{O}_5$ and $\text{U}_3\text{O}_8$ have been formulated\textsuperscript{5} as U(V) compounds on the basis of magnetic susceptibilities. Finally, the presence of $\text{UO}_2^+$ groups in $\text{U}_3\text{O}_8$, $\text{U}_3\text{O}_{13}$, $\text{U}_2\text{O}_5$, $\text{CaUO}_3$,\textsuperscript{88} $\text{Ca}_2\text{U}_2\text{O}_7$, $\text{Ca}_2\text{U}_2\text{O}_6$,\textsuperscript{52} $\text{UO}_2\text{Cl}$, $\text{UO}_2\text{Br}$,\textsuperscript{77} $\text{Pb}_{1.5}\text{U}_2\text{O}_6\text{F}$,\textsuperscript{114} and other oxo-fluoro compounds\textsuperscript{115,125} has been claimed on the basis of magnetic susceptibilities.

The paucity of electron spin resonance data on compounds of pentavalent uranium is somewhat surprising in view of the valuable
information which can be obtained by this method. The available information on EPR spectra of uranium(V) compounds is summarized in Table II. EPR spectra have been used to deduce the symmetry of the uranium coordination sphere. Symmetrical signals have been reported in the case of compounds of general formula MUCl₆ as well as in the case of UCl₅SOCl₂, UCl₅PCl₅, Et₄NUBr₆, and Bu₄NUBr₆. The asymmetric signals obtained for the complexes MUF₆ (M = Li⁺, Na⁺, Cs⁺, NO⁺) have been interpreted on the basis of a slight axial distortion of the fluorine octahedron. The strength of this distortion has been calculated, and crystal field theory has been used to interpret the experimental g-values. It should be noted that CsUF₆ is known to have a distorted octahedron of fluorine atoms. Similarly, U(V) doped into LiNbO₃ is claimed to have nearly octahedral symmetry, whereas in LiTaO₃ and BiNbO₄ the octahedra are distorted. Most uranium(V) compounds give very broad (> 1200 gauss wide) ESR signals with g-values less than 1.2 (Table II). Both the signal widths and g-values indicate that the 5f¹ electron is highly localized on the uranium atom. In contrast, a series of addition compounds of UCl₅ with various ligands having organic pi-systems has EPR spectra with g ≈ 2 and narrow signal widths (2-39 gauss). The g-values obtained are very close to the free-electron value (2.0023), and the narrow signals are also consistent with the presence of a free electron. It appears, then, that the lone electron is delocalized into the pi-systems of the coordinated ligands and is no longer a 5f electron. It is somewhat surprising that a similar series of addition compounds possesses neither the free-electron g-values nor the narrow signal widths, but the compounds seem to have localized 5f electrons. Finally, the g-values of (Et₄N)₃UCl₆ and Et₄NUCl₆ are identical, a fact which
# TABLE II

**EPR DATA FOR URANIUM(V) COMPOUNDS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>g value</th>
<th>Signal width, gauss</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCl$_5$·TCAC</td>
<td>1.1</td>
<td>~ 1200</td>
<td>5</td>
</tr>
<tr>
<td>UCl$_5$·SOCl$_2$</td>
<td>1.1</td>
<td>~ 1200</td>
<td>5,19</td>
</tr>
<tr>
<td>UCl$_5$·PCl$_5$</td>
<td>1.1</td>
<td>~ 1200</td>
<td>5,19</td>
</tr>
<tr>
<td>RbUCl$_6$</td>
<td>1.1</td>
<td>~ 1200</td>
<td>5,19</td>
</tr>
<tr>
<td>Pr$_4$NUCl$_6$</td>
<td>1.1</td>
<td>~ 1200</td>
<td>5</td>
</tr>
<tr>
<td>MUC$_6$</td>
<td>1.1-1.2</td>
<td>~ 1200</td>
<td>19</td>
</tr>
<tr>
<td>(Et$_4$N)$_3$UCl$_8$</td>
<td>1.1</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>U(V)$^d$</td>
<td>1.25</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>UF$_5$</td>
<td>-0.7</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>MUF$_6$</td>
<td>-0.7(0.709-0.768)</td>
<td></td>
<td>5,32</td>
</tr>
<tr>
<td>MUF$_6$</td>
<td>-0.7</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Na$_3$UF$_6$</td>
<td>1.2</td>
<td></td>
<td>120</td>
</tr>
<tr>
<td>U(V)$^e$</td>
<td>-0.7</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Et$_4$NUBr$_6$</td>
<td>1.39</td>
<td>&gt; 2000</td>
<td>20</td>
</tr>
<tr>
<td>Bu$_4$NUBr$_6$</td>
<td>1.31</td>
<td>&gt; 2000</td>
<td>20</td>
</tr>
<tr>
<td>U(V)$^h$</td>
<td>0.727</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>U(V)$^i$</td>
<td></td>
<td>250</td>
<td>120</td>
</tr>
<tr>
<td>U(V)$^j$</td>
<td>0.773(g</td>
<td></td>
<td>) 0.685(g⊥)</td>
</tr>
<tr>
<td>UCl$_5$·xL$^k$</td>
<td>1.124-1.138</td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>UCl$_5$(oxineH)$_4$</td>
<td>2.286</td>
<td>1124</td>
<td>45</td>
</tr>
<tr>
<td>UCl$_4$·HT</td>
<td>1.980</td>
<td>&gt; 2000</td>
<td>45</td>
</tr>
<tr>
<td>UCl$_5$·xL$^l$</td>
<td>1.990-2.022</td>
<td>2-39</td>
<td>45</td>
</tr>
</tbody>
</table>

---

*a.* Unless otherwise noted, data are for powder samples at ambient temperature.

*b.* The sign of most g-values is undetermined, but is probably negative.$^5$

*c.* M = Na$^+$, K$^+$, NH$_4$$^+$, Ti$^2+$, Ag$^+$, Ba$^{2+}$, Cs$^+$. Spectra were obtained at -170° for powders and SOCl$_2$ solutions.

*d.* For U(V) ions in a matrix of ThO$_2$.

*e.* M = Li$^+$, Na$^+$, Cs$^+$, NO$^-$. Temperature = 77° K.

(Continued)
TABLE II (Continued)

f. For single crystals.
g. For single crystals of NaSbF₆ doped with U(V).
h. Single crystals of LiNbO₃ containing 1% U(V) at 7³ K.
i. Single crystals and polycrystalline samples of LiNbO₃ containing 1-5% U(V) at 297⁰ K.
j. For LiTaO₃ doped with U(V).
k. For six compounds with x = 2,3 and L = pyridine, quinoline, and isoquinoline.
l. For 14 compounds with x = 0.5,1,2. The ligands L contain organic pi-systems as well as a variety of donor atoms.
militates against the reported existence of the $\text{UCl}_3^{3-}$ ion (vide supra).

3. Spectral Studies

a. Vibrational spectra

The normal vibrational modes of an octahedral molecule are

\[ 2T_{1u}(\nu_3, \nu_4) \quad ; \text{infrared-active} \]
\[ A_{1g}(\nu_1), E_g(\nu_2), T_{2g}(\nu_5) \quad ; \text{Raman-active} \]
\[ T_{2u}(\nu_6) \quad ; \text{inactive} \]

Assignments of the uranium-chlorine stretching frequency ($\nu_3$) for several compounds of pentavalent uranium have been made to bands around $300 \text{ cm}^{-1}$; these frequencies are about $50 \text{ cm}^{-1}$ higher than the value for $(\text{Et}_4\text{N})_2\text{UCl}_6$. Lowering of the U-Cl stretching frequency of $\text{UOCl}_5^{2-}$ to $254 \text{ cm}^{-1}$ was explained to be due to a weakening of the U-Cl bond because of the strong U=O bond (vide infra). Bands were also found in the far-I.R. spectrum of $\text{UOCl}_5^{2-}$ at 296, 197, and $120 \text{ cm}^{-1}$, but these bands were not assigned. Bands at $525 \text{ cm}^{-1}$ in the case of $\text{Ph}_4\text{AsUF}_6$, at $503 \text{ cm}^{-1}$ in CsUF$_6$, at $526 \text{ cm}^{-1}$ in $\text{N}_2\text{H}_6(\text{UF}_6)_2$ and $(\text{NH}_3\text{OH})\text{UF}_6$, and at $551 \text{ cm}^{-1}$ in NOUF$_6$ have been assigned to the U-F stretch. The frequency of the U-Br stretching vibration ($214 \text{ cm}^{-1}$ for $\text{UBr}_3^{2-}$, $190 \text{ cm}^{-1}$ for $\text{UOBr}_3^{2-}$) is less than the value for the U-Cl stretch. Bands of the $\text{UOBr}_5^{2-}$ complex at $250 \text{ cm}^{-1}$ and $80 \text{ cm}^{-1}$ are also at lower frequencies than corresponding bands of the $\text{UOCl}_5^{2-}$ complex, but these bands have not yet been assigned.

Bands of several of the $\text{UX}_6^{2-}$ complexes have been assigned, and these data are summarized in Table III. In addition, Ryan has
TABLE III

VIBRATIONAL BAND ASSIGNMENTS FOR UX₆⁻ COMPLEXES

<table>
<thead>
<tr>
<th>Frequency, cm⁻¹</th>
<th>UF₆⁻</th>
<th>UC₁₆⁻</th>
<th>UBr₆⁻</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>628 b</td>
<td>345 c</td>
<td></td>
<td></td>
<td>v₁(A₁g)</td>
</tr>
<tr>
<td>503 d</td>
<td>303-315 e</td>
<td>214 f,g</td>
<td></td>
<td>v₃(T₁u)</td>
</tr>
<tr>
<td>526 h</td>
<td></td>
<td>215 f</td>
<td></td>
<td>v₅(T₂g)</td>
</tr>
<tr>
<td>551 j</td>
<td></td>
<td></td>
<td></td>
<td>v₄(T₁u)</td>
</tr>
<tr>
<td>525 k</td>
<td>277 c</td>
<td></td>
<td></td>
<td>v₂(E₉)</td>
</tr>
<tr>
<td></td>
<td>136 c</td>
<td></td>
<td></td>
<td>v₅(T₂g)</td>
</tr>
<tr>
<td>173 k</td>
<td>122 g</td>
<td>87 g</td>
<td></td>
<td>v₄(T₁u)</td>
</tr>
<tr>
<td></td>
<td>125 c</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. Unless otherwise noted, all data are from I.R. spectra.  
b. Raman data for the Cs⁺, NH₃OH⁺, and N₂H₇⁺ salts.  
c. Raman data.  
d. Cs⁺ salt.  
e. Cs⁺, Ph₄As⁺, Me₄N⁺, Et₄N⁺, and Pr₄N⁺ salts.  
f. Et₄N⁺ salt. Not assigned by authors.  
g. Et₄N⁺ salt.  
h. N₂H₆²⁺ and NH₃OH⁺ salts.  
i. Ph₄As⁺ salt. Not assigned by authors.  
j. NO⁺ salt.  
k. Ph₄As⁺ salt.
observed a broad doublet at 05 and 56 cm⁻¹ in the far-I.R. of Et₄NCl₆ and a similar doublet at 68 and 62 cm⁻¹ in the spectrum of Et₄NBr₆. These bands were found to be located at a frequency equal to that of νC (I.R. inactive), but they were assigned²² to cation-anion vibrations. Vibrational matrix elements and force constants of the UCl₆⁻ species have recently been calculated²⁷, and I.R. and Raman bands of the UCl₆³⁻ ion have been assigned.²⁷ The existence of the latter anion is by no means certain (vide supra). Vibration frequencies for the normal modes of trigonal bipyramidal and tetragonal pyramidal structures of UF₅ have been calculated.¹⁵

Upon coordination of phosphine oxide ligands, the P=O frequency is lowered 217 cm⁻¹ in the case of UCl₅·Ph₃PO,⁵ 137 cm⁻¹ in UCl₅(Ph₃PO)₂,⁴¹ 232 cm⁻¹ in UBr₅·Ph₃PO,⁴⁰ 276 cm⁻¹ in UBr₅·HMPA,⁴⁰ and 161 cm⁻¹ in UCl₅·(C₈H₁₇)₃PO.⁵ The absence of P=O and P-H bands in the complexes UCl₅·Ph₃P and UCl₅(EBDPP) was cited⁴⁴,⁴⁵ as evidence for the existence of U-P bonds in these complexes. The U-P vibration of the two complexes was assigned to the 265 and 272 cm⁻¹ bands, respectively.⁴⁵ The absence of a band attributable to As=O stretching was taken to be indicative of a U-As bond in [U₂Cl₉(Ph₃As)]Cl, but the U-As stretching frequency was not found.⁴⁵

Infrared spectra have also been used as evidence for the absence of the uranyl group, UO₂²⁺, in the compounds UCl₅·xL,⁴⁵ and for the coordination of N-donor ligands in another series UCl₅·xL.²⁵ Lowering of the C=O stretching frequency of TCAC by 200 cm⁻¹ upon complexation in UCl₅·TCAC ³ and lowering of the asymmetric C-O-C stretching frequency of various ethers by 38-145 cm⁻¹ upon coordination to UCl₅ ⁴²
have also been reported. Infrared studies indicate\textsuperscript{42} that ether cleavage occurs when the latter compounds disproportionate in the presence of moisture. Vibrational data have been reported for UCl$_5$·SOCl$_2$,\textsuperscript{5} U(OEt)$_5$,\textsuperscript{5} and UF$_5$·XeF$_6$,\textsuperscript{43} but these results have not yet been interpreted with any degree of certainty.

The I.R. spectra of the Et$_4$N$^+$ salts of the UOX$_5^{2-}$ each show\textsuperscript{22} two strong bands of approximately equal intensity in the 750-950 cm$^{-1}$ region; these values are given in Table IV. Ryan\textsuperscript{22} assigned both these bands to U=O stretch. The order F$^-$ < Cl$^-$ < Br$^-$ would be expected because the order of the U-X bond strengths is F$^-$ > Cl$^-$ > Br$^-$ as a result of the "hard acid" behavior of uranium(V) (vide supra). Strengthening the U-X bond should weaken the U=O bond, and this effect is observed. Upon drying the UOF$_5^{2-}·2$H$_2$O salt, the two frequencies decrease. This decrease has been explained\textsuperscript{22} on the basis of the water molecules being hydrogen bonded to fluorine atoms, thus decreasing the U-F bond strength, and, in turn, strengthening the U=O bond. The existence of two U=O bands for such compounds is quite unusual, however, and this assignment is subject to question (vide infra). Bands attributed to U-O vibrations have been reported at 940, 890, and 850 cm$^{-1}$ in the case of UO$_2$Br\textsuperscript{5} and at 916-904 cm$^{-1}$ in the oxides UO$_x$ (x = 2.50-2.67).\textsuperscript{54} In the case of the latter series of compounds, additional bands were found at 720-745, 288, 273, 222, 202, and 196 cm$^{-1}$\textsuperscript{54}

b. \textbf{Electronic and vibronic spectra}

In no area is the scarcity of data on uranium(V) compounds more obvious than in the field of electronic spectral studies. The ultraviolet region presumably contains not only charge-transfer
**TABLE IV**

**URANIUM-OXYGEN VIBRATIONAL FREQUENCIES (IN cm\(^{-1}\))**

**FOR \((\text{Et}_4\text{N})_2\text{UOX}_5\) COMPOUNDS\(^{22}\)**

<table>
<thead>
<tr>
<th>(\text{UOF}_5^{2-} \cdot 2\text{H}_2\text{O})</th>
<th>(\text{UOF}_5^{2-})</th>
<th>(\text{UOCl}_5^{2-})</th>
<th>(\text{UOBr}_5^{2-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>780</td>
<td>760</td>
<td>813</td>
<td>817</td>
</tr>
<tr>
<td>872</td>
<td>853</td>
<td>913</td>
<td>919</td>
</tr>
</tbody>
</table>
transitions but also the Laporte-allowed $5f \rightarrow 6d$ transitions, which have much greater intensities than the Laporte-forbidden $f-f$ transitions. Very little work\textsuperscript{5,22} has been done, however, on the investigation of bands in this region.

Transitions between the $5f$-levels occur in the near-I.R. region as well as in the visible region and are generally very sharp. Interpretation of these spectra is greatly simplified by the lack of interelectron repulsions.

(1) Octahedral and near-octahedral symmetry

In most of the theoretical and experimental spectral studies of uranium(V) compounds, the uranium(V) is in an octahedral or near-octahedral ligand field. The $^2F$ term level which is derived from the $5f^1$ configuration is split by spin-orbit coupling into two levels, $^2F_{5/2}$ and $^2F_{7/2}$, which are six- and eightfold degenerate, respectively. The $^2F_{5/2}$ level has lower energy in accordance with one of Hund's rules. This splitting is shown schematically in Figure 1(a). It can be shown\textsuperscript{5} from group theoretical arguments that, under the influence of an octahedral crystal field, these free ion levels are split in the manner shown in Figure 1(b). The relative ordering of the levels has been ascertained by solving the appropriate wave equations.\textsuperscript{5} The $\Gamma_8$ and $\Gamma_8'$ levels are fourfold degenerate, and the $\Gamma_7$, $\Gamma_7'$, and $\Gamma_6$ levels are doubly degenerate, i.e., Kramer's doublets. The energy of each state as a function of field strength is shown\textsuperscript{5} in Figure 2. Intermediate coupling is usually observed in the case of uranium(V) (as in the case of most actinide species), in which both spin-orbit coupling and the effect of the crystal field are important.
FIGURE 1. Energy Levels for a $\frac{1}{2}f^1$ Electron Split by
(a) Spin-Orbit Coupling and
(b) An Octahedral Crystal Field.
FIGURE 2. The Effects of Octahedral Crystal Field Strength on the Energy Levels of a $\text{f}^2$ System.
From a consideration of Figure 2 and the assumption of intermediate coupling, one would expect to observe four electronic bands due to f-f transitions in the spectra of octahedral uranium(v) compounds: $\Gamma_8 \rightarrow \Gamma_7$, $\Gamma_7' \rightarrow \Gamma_7$, $\Gamma_8' \rightarrow \Gamma_7$, and $\Gamma_6 \rightarrow \Gamma_7$. In practice, however, four groups of bands are usually found. The additional bands result from (1) vibronic transitions and (2) splitting of the quadruply degenerate $\Gamma_8$ and $\Gamma_8'$ levels as a result of the removal of their non-Kramer degeneracies by lowering of the crystal field symmetry below octahedral.

Additional theoretical predictions are summarized in the recent review. These predictions will not be considered here, but they will be mentioned below there they are applicable to interpretation and assignment of the observed bands. These assignments will be considered next.

(a) The $\Gamma_8 \rightarrow \Gamma_7$ transition -- This absorption band is generally broad and weak; both characteristics are predicted by theory. This transition has been observed at frequencies in the range of $3200\text{ to }4600$ cm$^{-1}$ in the spectra of UCl$_6^-$, UCl$_5$, the gaseous U$_2$Cl$_{10}$ dimer, UCl$_5$-TCAC, and UCl$_5$-SOCl$_2$. The transition appears at higher energy ($5000\text{ to }5700$ cm$^{-1}$) in the spectra of CsUF$_6$ and the salts MUF$_2\cdot$2H$_2$O ($M = \text{Co, Ni, Cu}$). The bands at 5405 and 5680 cm$^{-1}$ in the case of [U(0Et)$_5$)$_2$ have been assigned to be this transition, and the broad band at 4050 cm$^{-1}$ in the reflectance spectrum of UBr$_5$ is probably assignable to the same transition. Kemmler-Sack assigned to this transition a broad band at $\sim 4400$ cm$^{-1}$ in the compounds KUO$_3$, RbUO$_3$, and MM$'U_2O_6$F ($M = \text{K, Rb; } M' = \text{Sr, Ba}$). A second broad band occurs at about 5400 cm$^{-1}$ in the spectra of these compounds but has not been assigned. Presumably, it might be a second component of the split $\Gamma_8$ level (vide supra). The
compounds MM'U_2O_5F (M = Na, K, Tl; M' = Sr, Ba, Pb), NaUO_4, LiUO_3, Li_3UO_4, Ba_2U_2O_7, and Li_7UO_6 all have similar bands, although the bands of the last three compounds are shifted considerably. The two bands at 5440 and 6280 cm\(^{-1}\) in the spectra of Ba\(_2\)Mn\(_{1-x}\)In\(_x\)UO_6 have been assigned to the split \(\Gamma_8 \rightarrow \Gamma_7\) transition, and a similar pair of bands is found in the spectra of Ba\(_2\)Fe\(_{1-x}\)M\(_x\)UO_6 (M = Ga, In, Mg, Zn). It should be noted that even small distortions from \(O_h\) symmetry will produce large splittings in the \(\Gamma_8\) and \(\Gamma_8'\) levels, but, in general, this splitting has been largely ignored in assignment of the \(\Gamma_8 \rightarrow \Gamma_7\) transition. Furthermore, it is possible that the band assigned to this transition in several of the above compounds is actually the upper component of the split level. If the lower component falls below 4000 cm\(^{-1}\) it might be easily overlooked in the I.R. region. For instance, Ballhausen has asserted that the band at 4386 cm\(^{-1}\) in the spectrum of the gaseous U\(_2\)Cl\(_{10}\) dimer, assigned to the \(\Gamma_8 \rightarrow \Gamma_7\) transition by Gruen and McBeth, is actually the upper energy component of this transition.

Finally, a doublet with smaller splitting has been found in this region in the spectra of several compounds. The splitting agrees closely with the energy of \(\nu_3\), the highest I.R.-active stretching mode; this value is given in Table III. It is thought that the pure electronic \((0 \rightarrow 0)\) transition is the lower energy (also the more intense) component of the doublet.

(b) The \(\Gamma_7' \rightarrow \Gamma_7\) transition -- This transition displays two important characteristics: (1) the relative invariance of its position with ligand field strength and symmetry and (2) the sharpness and resolution of its vibronic components.
With regard to characteristic (1), the energy of this transition falls within the limits 7050 ± 450 cm\(^{-1}\) in the case of a variety of compounds, including various \(\text{UCl}_5^-\) salts in several media,\(^5,19,22,40\) \(\text{UCl}_5\cdot\text{Ph}_3\text{PO},^5,40\) \(\text{UCl}_5\cdot\text{(CsH}_{17}\text{)}_3\text{PO},^5\) \(\text{UCl}_5\cdot\text{TCAC},^5\) \(\text{UCl}_5\cdot\text{SOCl}_2,^5\) the gaseous \(\text{U}_2\text{Cl}_{10}\) dimer,\(^8\) \(\text{UCl}_5\cdot\text{AlCl}_3\) vapor,\(^8\) \(\text{UBr}_5,^{17}\) \(\text{UBr}_6^-\) salts,\(^{17,22,40}\) \(\text{UBr}_5\cdot\text{Ph}_3\text{PO},^{40}\) \(\text{MU}_2\text{F}_12\cdot\text{H}_2\text{O (M} = \text{Co, Ni, Cu),}^{34}\) \(\text{UF}_6^-\) salts,\(^5,22\) \(\text{MUO}_3 (M = \text{Li, Na, K, Rb}),^{126}\) \(\text{Ba}_2\text{U}_2\text{O}_7,^{126}\) \(\text{Li}_7\text{UO}_8,^{126}\) \(\text{Li}_3\text{UO}_4,^{126}\) \(\text{MM}'\text{U}_2\text{O}_3\) \(\text{F (M} = \text{Na, K, Rb, Tl; M}' = \text{Sr, Ba, Pb}),^{113,126}\) \(\text{Ba}_2\text{Mn}_{1-x}\text{In}_x\text{UO}_6,^{111}\) \(\text{Ba}_2\text{Fe}_{1-x}\text{M}_x\text{UO}_6\) \(\text{(M} = \text{Ga, In, Mg, Zn}),^{111}\) and a variety of compounds with symmetry lower than \(\text{O}_h\). Since this phenomenon is a significant conclusion of the theoretical part of the current research, a further discussion of this point will be deferred until Chapter 3.

The sharpness of the bands within this system has permitted the assignment of vibronic components in the spectra of the hexahalo salts, \(\text{UX}_6^-\). These assignments are summarized in Table V. A comparison of the values in Table V with those in Table III shows that agreement among vibronic, I.R., and Raman data is quite good. Furthermore, the relative order \(\text{F}^- > \text{Cl}^- > \text{Br}^-\) for all vibrational modes is the expected order (vide supra).

The vibrational fine structure in this band group has been exhibited by compounds other than \(\text{UX}_6^-\) salts,\(^5,8,17,19,40,111,113,126\) but vibrational band assignments have not been made in the case of these compounds.

(c) The \(\Gamma_6' - \Gamma_7\) transition -- This transition is a broad doublet in the spectra of most uranium(V) compounds. The center of the doublet is located at 13,715 cm\(^{-1}\) in the spectrum of \(\text{Ph}_4\text{AsUF}_6\),\(^{22}\) is shifted to lower energy \((10,285 \pm 124 \text{ cm}^{-1})\) in the spectra of several
<table>
<thead>
<tr>
<th>Assignment</th>
<th>UF₆⁻</th>
<th>UCl₆⁻</th>
<th>UBr₆⁻</th>
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<tbody>
<tr>
<td>v₁(A₁g)</td>
<td>609ᵃ</td>
<td>300ᵃ</td>
<td></td>
</tr>
<tr>
<td>v₃(T₄u)</td>
<td>503ᵃ  , 524ᵇ  , 526ᵇ</td>
<td>312ᵃ  , 308ᵇ , 215ᵇ , 219ᵇ , 212ᶜ</td>
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<td>325ᶜ  , 310ᶜ , 214ᵉ , 229ᵉ</td>
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<td>292ᵈ  , 326ᵈ , 318ᵈ , 316ᵈ</td>
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<tr>
<td>v₄(T₁u)</td>
<td>150ᵃ  , 166ᵃ , 162ᵇ</td>
<td>121ᵃ  , 119ᵇ , 84ᵇ , 87ᵇ , 94ᶜ , 96ᶜ</td>
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<tr>
<td></td>
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<td>125ᵇ  , 114ᶜ , 120ᵈ , 103ᵈ</td>
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<td>117ᶜ  , 123ᵈ , 127ᵈ</td>
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<tr>
<td>v₅(T₂g)</td>
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<tr>
<td>v₆(T₂u)</td>
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<td>97ᵇ , 84ᶜ , 65ᵈ , 54ᵉ , 56ᵉ</td>
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<tr>
<td></td>
<td></td>
<td>96ᶜᵈ , 95ᵈ , 98ᵈ</td>
<td></td>
</tr>
</tbody>
</table>

a. Reference 5.

b. Reference 22.

c. In CH₂Cl₂ solution.⁴⁰ The original authors did not assign these bands. Assignments are those of the present author.

d. In KBr wafer.⁴⁰ The original authors did not assign these bands. Assignments are those of the present author.

e. For UBr₆⁻ in CH₂Cl₂/HBr solution, in which the U(V) species is thought¹⁷ to be HUBr₆⁻. The original authors did not assign these bands. Assignments are those of the present author.
sults in various media, and to still lower energy (2660 ± 110 cm\(^{-1}\)) in the case of the \(\text{UBr}_6^-\) ion. The transition occurs in the region 8795-10,945 cm\(^{-1}\) in the spectra of \(\text{UCl}_5\), \(\text{U}_2\text{Cl}_{10}\) vapor, \(\text{UCl}_5\cdot\text{TCAC}\), \(\text{UCl}_5\cdot\text{SOCl}_2\), \(\text{UCl}_5\cdot\text{Ph}_3\text{PO}\), \(\text{UCl}_5\cdot(\text{C}_6\text{H}_{17})_3\text{PO}\), \(\text{UBr}_5\), \(\text{UBr}_5\cdot\text{Ph}_3\text{PO}\), \([\text{U(OEt}_5]\)\_2\), \(\text{KUO}_3\), \(\text{RbUO}_3\), \(\text{MM}'\text{U}_2\text{O}_6\text{F} (\text{M} = \text{K, Rb}; \text{M}' = \text{Sr, Ba})\) and is shifted to \(\sim 13,000\) cm\(^{-1}\) in the spectrum of \(\text{Ba}_2\text{Mn}_{1-x}\text{In}_x\text{UO}_6\).

The splitting in this transition is very interesting. The splitting results from the removal of the non-Kramer degeneracies by (even slight) distortions from regular octahedral symmetry. It has been observed that the splitting in the spectra of \(\text{UCl}_6^-\) salts in several media is \(540 ± 20\) cm\(^{-1}\), but that for lower symmetry species such as \(\text{UCl}_5\cdot\text{TCAC}, \text{U}_2\text{Cl}_{10}\) and \([\text{U(OEt}_5]\)\_2\), it ranges from 720 to 1490 cm\(^{-1}\). It has been suggested that the magnitude of this splitting is a measure of the magnitude of the geometrical distortion. This idea is one of the significant conclusions of the theoretical model which is presented in the current research and will be dealt with further in Chapter 3.

The splitting is greater in the case of \(\text{UF}_6^- (\sim 1000\) cm\(^{-1}\)) than in that of \(\text{UCl}_6^-\) but is smaller in the case of \(\text{UBr}_6^- (\sim 400\) cm\(^{-1}\)). Splittings of this transition were not observed in the spectra of \(\text{MUO}_3 (\text{M} = \text{Li, Na, K, Rb}), \text{Ba}_2\text{U}_2\text{O}_7, \text{Li}_7\text{UO}_6, \text{Li}_3\text{UO}_4, \text{MM}'\text{U}_2\text{O}_6\text{F} (\text{M} = \text{Na, K, Rb}; \text{M}' = \text{Sr, Ba}; \text{M} = \text{K, Tl}, \text{M}' = \text{Pb}), \text{Ba}_2\text{Mn}_{1-x}\text{In}_x\text{UO}_6\); the intense charge-transfer or 5f \(\rightarrow\) 6d bands in this region may have obscured some of the structure of the \(\Gamma_8' \rightarrow \Gamma_7\) transition.
(d) The $\Gamma_3 - \Gamma_1$ transition -- This highest-energy transition occurs at 15,000 cm$^{-1}$ in the case of Ph$_4$AsUF$_6$, about 11,500 cm$^{-1}$ in the case of several UCl$_5^-$ salts, and at about 10,000 cm$^{-1}$ in the case of the UBr$_6^-$ species. The band is hidden by a large charge-transfer band in the spectrum of the gaseous U$_2$Cl$_{10}$ dimer but is located at about 12,000 cm$^{-1}$ in the case of UCl$_5$, UCl$_5$-AlCl$_3$, UCl$_5$-TCAC, UCl$_5$-SOCl$_2$, UCl$_5$-Ph$_3$PO, UBr$_5$, KUO$_3$, RbUO$_3$, and MM'U$_2$O$_6$F ($M = K, Rb; M' = Sr, Ba$), whereas it is moved to higher energy in the spectra of [U(OEt)$_5$]$_2$ and the oxides Ba$_2$M$n$$_{1-x}$In$_x$UO$_6$. In spectra of the solid UX$_6^-$ salts, this transition is split into a doublet that has high- and low-energy shoulders. In the case of the UCl$_6^-$ and UBr$_6^-$ salts, it has been suggested that the pure electronic (0-0 transition) is missing and that the observed bands are due to coupling of the $\nu_6(T_{2u})$ and $\nu_3(T_{1u})$ vibrational modes to this missing electronic peak. In spectra of the UF$_6^-$ species the pattern is more complex, and the pure electronic transition is thought to be present in this compound. This suggestion is not unreasonable in view of the fact that the UF$_6^-$ ion is known to be distorted in CsUF$_6$ (vide supra). This point will be discussed further in Chapter 3.

Spectral studies of the ether adducts UCl$_5$-OMe$_2$, UCl$_5$-OEt$_2$, and UCl$_5$-(1,4-dioxane) have also been conducted, but assignments of the bands of these compounds have not been made.

Spin-orbit coupling constants of several uranium(V) compounds have been calculated, and the values range from 1770 cm$^{-1}$ in the case of CsUF$_6$ and several oxo compounds to 2015 cm$^{-1}$ in the case of RbUF$_6$. It has been pointed out that a linear
interpolation of values for Pa(IV) and Np(VI) compounds yields a value of \(10.0\ \text{cm}^{-1}\), in good agreement with most uranium(V) values. The free-ion uranium(V) spin-orbit coupling constant has been calculated to be \(2172\ \text{cm}^{-1}\) from relativistic wave-functions.\(^{128}\)

Finally, a molecular orbital theory for \(5f^1\) complexes has recently\(^{129}\) been developed to include the effects of covalent bonding in intermediate field actinide complexes. The calculation was applied to CsUF\(_6\), and exact agreement with the CsUF\(_6\) spectrum was obtained. Unfortunately, the band assignments of Reisfeld and Crosby\(^{130}\) were used, and these are known\(^{22}\) to be in error.

(2) Axial ligand fields: the \(\text{UO}_2^+\) ion

Spectral studies of the \(\text{UO}_2^+\) ion are few in number. Reflectance spectra of several oxides which are thought to contain isolated \(\text{UO}_2^+\) groups or -O-U-O-chains have been recorded. These oxides include \(\text{U}_3\text{O}_8\),\(^{125}\) \(\text{UO}_x\text{F}_y\) \((x = 2.00-2.58; y = 0.17-1.00)\),\(^{125}\) solid solutions of \(\text{Pb}_2\text{U}_2\text{O}_7\) and \(\text{NaUO}_3\text{F}\),\(^{115}\) \(\text{M}_{0.33}\text{PbU}_2\text{O}_5\text{e}_7\text{F}\) \((M = \text{K}, \text{Rb}, \text{Tl})\),\(^{115}\) \(\text{Pb}_{1.5}\text{U}_2\text{O}_6\text{F}\),\(^{114}\) and solid solutions of \(\text{MUO}_4\) and \(\text{ThO}_2\) \((M = \text{Nd}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Y}, \text{Yb})\),\(^{119}\) \(\text{U}_4\text{O}_9\) and \(\text{ThO}_2\),\(^{65}\) and \(\text{U}_2\text{Th}_2\text{O}_9\) and \(\text{ThO}_2\).\(^{65}\) The spectra of all these compounds are similar and have a prominent band at 6000-7000 \(\text{cm}^{-1}\) (probably corresponding to the \(\Gamma_7' - \Gamma_7\) transition) and several additional bands at higher energy. These additional bands are present as broad maxima or (usually) shoulders on an intense ultraviolet band. A splitting diagram has been developed\(^{119}\) for the uranium(V) energy levels under the influence of both spin-orbit coupling and an axial ligand field. This diagram, reproduced in Figure 3, was used\(^{119}\) to assign
FIGURE 5. Energy Levels for a $5f^1$ Electron Split by
(a) Spin-Orbit Coupling,
(b) A Strong Axial Crystal Field, and
(c) By Both Effects (Intermediate Field).
the bands in the spectra of the solid solutions of MUO₄ and ThO₂, but has not been applied to the spectra of any other compound.

There are only four reports⁵,⁸⁰ of solution spectra of the UO₂⁺ species. The spectrum has been measured in fused salt solutions,⁵ in dimethylsulfoxide solution,⁵ and in concentrated aqueous chloride solutions.⁸⁰ These spectra are similar; they have a prominent band at ~ 6600 cm⁻¹ and two weaker bands at higher energy, and they are somewhat similar to the reflectance spectra of the oxides (vide supra).

(3) Other symmetries

Spectral properties of the eight-coordinate oxides MU₂O₆ (M = Cd, Mg, Mn), MUO₄ (M = Bi, Gd, Y, Nd, Eu), and 0.45 La₂O₃ · 0.55U₂O₅,¹²⁸ and of several systems of unknown symmetries have been obtained, but these results have not yet been interpreted. These systems of unknown symmetries include uranium(V) in aqueous carbonate solutions,⁸⁰ the addition compounds UCl₅ · xL (x = 2, 3; L = py, Q₁, 1-Q₁),²⁵ and another series of addition compounds UCl₅ · xL (x = 0.5-4.0; L = organic molecule).⁴⁴,⁴⁵ Visible-near-I.R. spectral properties of the last series of compounds have been correlated with EPR spectra; the smaller the width of the EPR signal, the fewer and less clear are the electronic spectral bands.⁴⁴ This phenomenon was interpreted⁴⁴ to be due to delocalization of the 5f¹ electron onto the pi-system of the unsaturated organic ligand.

Ryan²² observed four groups of bands in the spectra of UOX₅²⁻ complexes (X = F, Cl, Br) but was hesitant to assign the four transitions found in Oₙ or near-Oₙ uranium(V) compounds to these bands; he suspected that the uranium(V) is influenced by a strongly distorted
crystal field (C\textsubscript{4v}), and the theory had not yet (early 1971) been developed for uranium(V) in a field of this symmetry. The development of this theory and assignment of the observed bands is a significant part of the current research.

C. Scope of the Present Research

The current research was begun as a result of the intriguing report of the preparation of the first oxouranium(V) complexes, UOX\textsubscript{5}\textsuperscript{2-} (X = F, Cl, Br), by Ryan.\textsuperscript{22} The reluctance of Ryan to assign the observed bands in the very interesting electronic spectra of these compounds provided the motivation for the development of a theory to explain the observed spectra. In the present research, a semiempirical calculation of the energy levels of UOC\textsubscript{5}\textsuperscript{2-} was performed by beginning with the 5f\textsuperscript{1} energy levels of UC\textsubscript{16}\textsuperscript{-} split by the O\textsubscript{h} crystal field and then considering the effects of spin-orbit coupling and the lower symmetry (C\textsubscript{4v}) field. In addition to the four groups of bands reported by Ryan,\textsuperscript{22} two additional groups were sought (as a result of the theoretical predictions) and observed at lower energies; the lowest-energy band was found in the NaCl I.R. region. In order to detect this lowest-energy band, the new salt, Cs\textsubscript{2}UOC\textsubscript{5}, was prepared. The I.R. spectrum of this salt is free from interfering bands which are found in the spectra of organic cations.

A new preparative method for (Et\textsubscript{4}N)\textsubscript{2}UOC\textsubscript{5} in which the starting material is the very versatile compound UC\textsubscript{5}:TCAC rather than the UC\textsubscript{16} used by Ryan (vide supra) was developed. As a result of this development, a project in which the preparation of complexes of the UO\textsuperscript{3+} species would be attempted by three methods was envisioned:
\[ \text{I: } \text{UCl}_5 \cdot \text{TCAC } + L \xrightarrow{\text{Et}_4\text{NCl}} \text{"undried" acetone} \quad (19) \]
\[ \text{II: } (\text{Et}_4\text{N})_2\text{UOCl}_5 + L \xrightarrow{} \quad (20) \]
\[ \text{III: } \text{UCl}_5 \cdot xL \xrightarrow{\text{Et}_4\text{NCl}} \text{"undried" solvent} \quad (21) \]

In the above scheme, L is an organic ligand, and the starting materials \( \text{UCl}_5 \cdot xL \) in method III were prepared from \( \text{UCl}_5 \cdot \text{TCAC} \) (vide supra).\(^{44,45}\) Three complexes have been prepared by the first method; phthalazine, \( \text{o-phenanthroline} \), and \( \text{2,2'}\)-bipyridyl were the ligands. These unusual compounds appear to contain free radicals complexed to uranium(V). Only two reactions were attempted by the third method; it appears that \( (\text{Et}_4\text{N})_2\)\( \text{UOCl}_5 \) was the product in both cases.

When L was phenazine in reaction II, the product was the unexpected and not previously well characterized chloride salt of the dihydrophenazine cation radical, \( \cdot \text{PH}_2\text{Cl} \).\(^*\) This fascinating result modified somewhat the objectives given above. Analogous reactions were carried out with several phenazine-like compounds and with other uranium(V) compounds. In addition, due to the importance of molybdenum(V) and of free radicals in biological systems, investigations of free-radical formation by Mo(V) were also undertaken. Several new Mo(V) complexes, some of which also contain free-radicals, resulted from this work.

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\(^*\)The dot above the formula signifies that the compound is a free radical. This convention will be used throughout the remainder of this work.
CHAPTER II

EXPERIMENTAL PROCEDURES

A. Technique

Since most compounds of uranium(V) are sensitive to both \( O_2 \) and \( H_2O \), much of the work with these compounds was carried out in an inert atmosphere. A steel dry box was filled with dry nitrogen. The atmosphere in the box was then circulated through (1) a heated oven packed with copper turnings, (2) a column filled with Linde 13X molecular sieves, and (3) a column packed with manganous oxide, MnO. Manganous oxide, which is pyrophoric, rigorously removes \( O_2 \) from the system.\(^{131,132}\)

In some of the work it was necessary to use solvents or reagents (e.g., \( H_2O \), acetone, etc.) which would badly contaminate the atmosphere in the dry box. For such work, as well as for other work which did not require the rigorous conditions achieved in the dry box, a plastic glove bag was used. The bag was thoroughly flushed and then filled with dry nitrogen.

Compounds which were known (or suspected) to be air-sensitive were dried \textit{in vacuo} in vials equipped with a ground glass cap and side-arm stopcock; these compounds were stored \textit{in vacuo} in the same vial.

Filtration was usually effected by pressure rather than suction. The pressure filtration apparatus consisted of a length of rubber tubing connecting a nitrogen supply to a one-hole rubber stopper sized to fit
the top of a fritted funnel. This technique is more convenient than suction filtration when filtration is done inside a glove bag or dry box. In addition, solids could be dried by allowing the nitrogen stream to pass through the filter for extended periods.

B. Materials

Materials not specifically mentioned below were reagent grade chemicals and were not further purified.

1. Solvents

Acetone, glycerol, methanol, and nitrobenzene were reagent quality materials. In some instances, spectroquality methanol was used. These solvents were dried over anhydrous calcium sulfate or Linde 3A molecular sieves.

Acetonitrile and nitromethane were spectroquality. They were dried over anhydrous CaSO$_4$ or Linde 3A molecular sieves.

Benzene and carbon tetrachloride were reagent quality solvents. They were dried over CaH$_2$, then refluxed over CaH$_2$ under a nitrogen atmosphere for twelve hours, and finally slowly distilled from CaH$_2$ under nitrogen. They were opened only in a glove bag or dry box.

Dimethylsulfoxide (DMSO) was purified by the following procedure. The reagent grade solvent was placed over anhydrous BaO in a flask connected to a vacuum distillation apparatus. The apparatus was evacuated, and there was a concomitant release of a large quantity of gas from the solvent. Pumping was continued for five hours; the vacuum was then relieved with dry nitrogen, and the solvent was allowed
to stand overnight. The evacuation treatment described above was repeated once each day during a period of one week. The solvent was then slowly distilled under vacuum by very slight heating (b.p. 25-26° at < 1 mm). The distillate was clear and colorless. It was found that a poor vacuum (and a correspondingly higher boiling point) resulted in the color of the distillate being pale yellow. The distillate was not stored over BaO because prolonged contact with BaO causes the solvent to develop a slight yellow color. The purified solvent was stored in vacuo in a dark closet.

Ethanol (absolute) was dried over Linde 3A molecular sieves.

Hexachloropropene was obtained from several suppliers and used without further purification.

Hexamethylphosphoramide was dried over Linde 4A molecular sieves. The reagent grade material was clear and colorless and was used without further purification.

Propylene carbonate from Aldrich Chemical Co. was dried first over Linde 4A molecular sieves and then over anhydrous calcium oxide. The solvent was then vacuum distilled (b.p. 141-142° at 34 mm); bumping was quite severe.

Pyridine (reagent grade) was dried and stored over anhydrous KOH pellets.

2. Special ESR Solvents

Acetonitrile-d₃ was dried over Linde 3A molecular sieves; acetonitrile, dimethylsulfoxide, and methanol were purified by the methods described above. The solvents were then degassed in the following manner. In a heavy-walled round bottom flask (fitted with a standard
taper joint and stopcock) the solvent was frozen in the appropriate cooling bath. The following freezing baths were used: ice-water for dimethylsulfoxide, dry ice-acetone for acetonitrile and acetonitrile-d_3, and liquid nitrogen for methanol. After the contents were frozen, the flask was evacuated, the stopcock was closed, and the solvent was allowed to melt at room temperature. The freezing-evacuating-melting cycle was carried out four times. The solvents were stored in vacuo.

3. Reagents and Starting Materials

Anisole (reagent grade) was dried over anhydrous calcium sulfate.

Benzo[a]phenazine and 2,3-di-(2-pyridyl)quinoxaline were kindly supplied by Dr. G. R. Newkome.

Dibenzo[a,c]phenazine (Aldrich) was recrystallized from benzene.

8-Hydroxyquinoline (oxineH) (from Eastman) was recrystallized from petroleum ether.

Phenazine (from Matheson, Coleman, and Bell) was bright yellow and crystalline. The color was identical with that of zone-refined material, and the compound was used without further purification. When received from Aldrich, the material was a reddish-brown powder. This sample was recrystallized twice from absolute ethanol, and bright yellow crystals resulted.

Phthalazine (Aldrich) was recrystallized from ethyl ether, then sublimed in vacuo, and stored over anhydrous magnesium perchlorate.

Potassium diethyldithiocarbamate (Baker) consisted of large yellow crystals coated with a viscous liquid. The TGA of the crude
material indicated that it could not be dried by heating. Attempts to recrystallize the compound from acetone,\textsuperscript{133} ethanol, and ethyl ether were unsuccessful. The viscous liquid was removed by gently boiling ethyl ether in which the compound had been placed. It was then washed twice with small portions of absolute ethanol at -10°. The clear crystals were white and dry in appearance. **Anal.** Calcd. for KS$_2$CN(C$_2$H$_5$)$_2$ - \(1.6\)H$_2$O (C$_{5}$H$_{13}$,KN0$_1$,eS$_2$): C, 27.78; H, 6.16; N, 6.48. Found: C, 27.73; H, 5.90; N, 6.33.

Sodium tetraphenylboron, NaBPh$_4$, was dissolved in an equal-volume mixture of acetone and heptane. The solution was then evaporated on a steam bath to a small volume. The white solid which crystallized upon cooling was isolated by filtration and washed with chloroform.

Tetraethylammonium chloride (Eastman) was dried by evacuation (< 1 mm) at room temperature for three days, then evacuation at 65° over P$_2$O$_5$ for 65 hours.

Tetraethylammonium hydroxide was purchased from Matheson, Coleman and Bell as a 25% aqueous solution.

Tetraethylammonium oxopentabromouranate(V), (Et$_4$N)$_2$UOBr$_5$, was kindly supplied by Mr. H. J. Sherrill, who prepared it by the procedure of Ryan.\textsuperscript{22}

Pentachloro(methyl ether)uranium(V), UCl$_5$$\cdot$OMe$_2$, was kindly supplied by Dr. J. D. Ortego.\textsuperscript{42}

C. Reactions and Preparations of Compounds

1. Preparation of Known Compounds

a. Uranium(IV) compounds
(1) \((\text{Et}_4\text{N})_2\text{UCl}_6\), Tetraethylammonium hexachlorouranate(IV)

Since uranium metal was not readily available, the procedure of Ryan\(^{22,23}\) was modified. Uranium tetrachloride (1.68 g) was dissolved in 20 ml HCl-saturated acetone, and the solution was filtered. This solution was added to a solution of 2.12 g of tetraethylammonium chloride in 20 ml of 12 M HCl. The light green product was isolated by filtration, washed with 12 M HCl and then acetone, and dried \textit{in vacuo}. The somewhat hygroscopic compound was stored over anhydrous Mg(ClO\(_4\))\(_2\).

(2) \((\text{Ph}_4\text{As})_2\text{UCl}_6\), Tetraphenylarsonium hexachlorouranate(IV)\(^{22,23}\)

A solution of 1.17 g of UCl\(_4\) in 10 ml of HCl-saturated acetone was prepared and filtered. To this solution was added 2.05 g of Ph\(_4\text{AsCl}\) in 30 ml of HCl-saturated ethanol. The pale green product was removed by filtration, washed with HCl-saturated ethanol and then acetone, dried \textit{in vacuo}, and stored over anhydrous Mg(ClO\(_4\))\(_2\).

(3) \((\text{Et}_4\text{N})_2\text{UBr}_6\), Tetraethylammonium hexabromouranate(IV)\(^{22,23}\)

Uranium tetrabromide (5.76 g) was dissolved in 25 ml of concentrated aqueous HBr. The solution was filtered, resaturated with HBr gas, and added to a solution of 4.31 g of Et\(_4\text{NBr}\) in 25 ml of HBr-saturated ethanol. Only a small amount of product precipitated; therefore, 25 ml of HBr-saturated ethanol containing Et\(_4\text{NBr}\) to approximate saturation was added. This additional Et\(_4\text{NBr}\) did not cause additional precipitation of the product; consequently, acetone (~ 400 ml) was added until no further precipitation occurred.\(^{134}\) The green product was isolated by filtration, washed with acetone, dried \textit{in vacuo}, and
stored over anhydrous Mg(ClO₄)₂. Higher concentrations of reactants would presumably aid the precipitation of the product.

(4) U(dpm)₄, Tetrakis(2,2,6,6-tetramethyl-3,5-heptane-diono)uranium(IV)

The procedure of Ortego¹³⁵ was followed except that, after the initial drying, the lumpy product was ground to a powder and dried in vacuo for 24 hours. Anal. Calcd. for U(dpm)₄·2H₂O(C₄₄H₈₀O₁₀U): C, 52.17; H, 8.01. Found: C, 52.18; H, 7.68.

b. Uranium(V) compounds

(1) UCl₅·TCAC, Pentachloro(trichloroacrylylchloride)uranium(V)

The following procedure is a modification of the original procedure.¹³⁶ The apparatus shown in Figure 4 was constructed. To the three-necked round bottom flask were added 20 g (0.07 mole) of UO₃ (or U₂O₅) and 175 ml (1.24 mole) of hexachloropropene. The reaction mixture was then rapidly heated without stirring. This "spot heating" initiated the reaction without heating the entire mixture to a high temperature. Heating was continued without stirring until the temperature reached 75°, at which temperature external heating was stopped. The slightly exothermic reaction started at about 75°; the initiation of the reaction was indicated by the evolution of a white gas and a darkening of the reaction mixture. The temperature was allowed to rise until it reached 100° and then was maintained between 100° and 120°. When only a small (~0.5 g) amount of UO₃ remained in the reaction flask, the solution was suction-filtered by tilting the reaction flask and very gradually applying suction to the receiving flask while increasing the nitrogen flow. Careful manipulation of the nitrogen flow and suction.
FIGURE . Apparatus for Preparation of $\text{UCI}_5 \cdot \text{TCAC}$. 

- Nitrogen Inlet
- Vent to Hood
- Oil Bubbler
- Magnetic Stirrer
- Heating Mantle
- Fritted Disk
- Dry Ice-Acetone Trap
- To Vacuum Pump
- 500 ml
were necessary to prevent sucking oil and air from the bubbler into the reaction flask. After filtration was completed the suction was turned off, and the pressure was allowed to equalize through the sintered glass filter. The receiving flask was then removed from the apparatus and quickly stoppered. Dry nitrogen was bubbled through the solution until most of the excess trichloroacrylylchloride was removed and the solution had cooled to ambient temperature. The solution was placed in an ice bath for several hours and then placed in a glove bag containing a nitrogen atmosphere. The orange-to-red crystalline product was isolated by pressure filtration, washed with a small portion of dry, oxygen-free CCl₄, and dried in vacuo.

(2) UC₅(phthalazine)₂, Pentachlorobis(phthalazine)uranium(V)

The procedure of Selbin, et al.,⁴⁵ was used. Their method follows. The work was performed in the dry box. A benzene solution of 0.456 g (3.50 mmol) of phthalazine was added to a benzene solution of 1.07 g (1.76 mmol) of UC₅·TCAC. The orange product was removed by filtration, washed with benzene, and dried in vacuo.

(3) CsUC₁₈, Cesium hexachlorouranate(V)

In a glove bag, iodine monochloride was added to a suspension of 3.41 g (20.2 mmol) of CsCl in 15 ml of SOCl₂ until all of the CsCl dissolved.¹³⁷ A total of about 5.5 g of ICl was required. To the resulting solution was added 12.72 g (20.9 mmol) of UC₅·TCAC with stirring. The precipitate was obtained by filtration, washed with SOCl₂, and dried in vacuo.
(1) Et₄NUCI₆, Tetraethylammonium hexachlorouranate(V)

This compound was prepared by the procedure of Ryan.⁰¹,²²³ Although a yield of 65% was reported by Ryan,²³ two preparations by this method gave yields of 34 and 35%.

(5) Ph₄AsUCI₆, Tetraphenylarsonium hexachlorouranate(V)

The procedure of Ryan²²,²³ was followed. A heterogeneous mixture of large orange crystals and pale yellow crystals was obtained. The two types of crystals were physically separated as much as possible. The orange compound was found to be the desired product. Anal. Calcd. for Ph₄AsUCI₆(C₂₄H₂₀AsCl₆U): C, 34.55; H, 2.42. Found: C, 34.83; H, 2.68.

The visible-near I.R. spectrum of the pale yellow material indicated that most of the uranium was U(VI). Anal. Calcd. for (Ph₄As)₂UO₂Cl₄(C₂₄H₂₀AsCl₄O₂U): C, 48.92; H, 3.42. Found: C, 44.15; H, 3.36. The low carbon and hydrogen percentages are apparently due to the presence of Ph₄AsUCI₆ which could not be removed.

(6) Et₄NUBr₆, Tetraethylammonium hexabromouranate(V)

Ryan's procedure²³ was followed, and a yield of 71% was obtained.

(7) (Et₄N)₂UOCl₅, Tetraethylammonium oxopentachlorouranate(V)

Undried tetraethylammonium chloride was dissolved to approximate saturation in nitromethane. The solution was then diluted ten-fold with undried acetone, filtered, and taken into a glove bag. After the bag was flushed and filled with nitrogen, the solution was poured into
a flask containing solid UCl₅·TCAC (about 50 ml of solution per gram
of solid). The flask was swirled gently until all of the UCl₅·TCAC
dissolved. The blue compound which formed immediately was isolated by
filtration, washed with dry acetone, and dried in a stream of dry nitrogen.
It proved in every way to be the same compound prepared by Ryan, who
used Et₄NCl₆ as starting material. Yields of 75-91% were obtained;
the average yield was 84%. Anal. Calcd. for (Et₄N)₂UOCl₅ (C₁₆H₄₀Cl₅-
N₂O): C, 27.78; H, 5.83; N, 4.05. Found: C, 27.61; H, 5.93; N, 4.06.

(8) (Me₄N)₂UOCl₅, Tetramethylammonium oxopentachlorouranate(V)

Approximately one gram of tetramethylammonium chloride was
added to 50 ml of propylene carbonate. The salt did not dissolve
readily; the solvent was then saturated with Cl₂ gas, and the salt dis­
solved quickly. In a glove bag, this solution was added to a flask con­
taining 1.21 g (2.00 mmol) of UCl₅·TCAC. The resulting blue compound
was separated by filtration, washed with dry acetone, and dried in a
stream of dry nitrogen. When exposed to the air, the compound imme­
diately started to decompose and rapidly turned green with evolution of
smoke. The visible-near I.R. spectrum of the decomposed material showed
the presence of U(IV), U(V), and U(VI). Ryan prepared but did not
analyze this salt by addition of undried chloroform and undried Me₄NCl
to a propylene carbonate solution of Me₄NCl₆ plus chlorine.

(9) (Ph₄As)₂UOCl₅, Tetraphenylarsonium oxopentachlorouranate(V)

This compound was prepared according to the procedure reported
by Ryan.
An attempt was made to prepare this compound by adding 50 ml of acetone saturated with Ph₄AsCl to 1.22 g of UCl₅·TCAC. A green solution resulted, and no product was obtained. Ryan²² found it necessary to cool the reacting solution. It might be possible to synthesize this compound by cooling the Ph₄AsCl solution before adding it to the UCl₅·TCAC, but this was not tried.

c. Molybdenum(V) compounds

(1) MoO(OH)₃, Trihydroxyoxomolybdenum(V) [Molybdenyl hydroxide]

The procedure of Bishop¹³⁸ was used with slight modifications. After mixing the solutions of ammonium paramolybdate and hydrazine sulfate, the dark brown solution was evaporated to a volume of about 100 ml. This evaporation was accomplished by maintaining the temperature very near 100⁰ while blowing dry nitrogen over the surface of the solution. The latter precaution, which served to minimize air oxidation of the compound, was performed by attaching the nitrogen supply to the stem of a funnel which was inverted and suspended just above the surface of the solution. The nitrogen flow was maintained while the solution cooled to room temperature. The slurry containing the extremely fine precipitate is very difficult to filter, and best results were obtained by centrifuging the solution in small batches, washing the product with a small amount of water and then acetone, and drying it in vacuo. The yield was 72%, but the product was not pure (vide infra). Impurities did not present any problems in subsequent use of the product.

(2) (NH₄)₂MoOCl₅, Ammonium oxopentachloromolybdate(V)
This compound was prepared according to the procedure of Palmer. All of the MoO(OH)$_3$ did not dissolve in the HCl; therefore, the insoluble orange material was removed from the solution by filtration. The solution was emerald green, and apparently the impurities in the molybdenyl hydroxide did not interfere with the reaction. The product started to precipitate during the addition of the ammonium carbonate.

**Anal.** Calcd. for (NH$_4)_2$MoOCl$_5$ (H$_2$Cl$_2$MoN$_2$O): N, 8.61; H, 2.48. Found: N, 10.01; H, 2.94. The N:H ratio was found to be 1:4.08. The product is apparently slightly contaminated with ammonium chloride, which could probably be removed by recrystallization from concentrated HCl. This recrystallization was not necessary because the NH$_4$Cl impurity did not interfere with the subsequent reaction of this product.

2. New Compounds and Reactions

This section includes (1) preparations of new compounds, (2) new reactions which produced known compounds, and (3) new reactions which did not result in the isolation of a solid product.

a. New UOCl$_5^{2-}$ salts

(1) Cs$_2$UOCl$_5$, Cesium oxopentachlorouranate(V)

In 60 ml of dry nitromethane was dissolved 0.65 g (3.93 mmol) of undried tetraethylammonium chloride. This solution was saturated with Cl$_2$ and then placed in a glove bag. After the bag was purged and filled with N$_2$, the solution was cooled in a slush bath which consisted of nitromethane which was maintained at its freezing point by periodic additions of liquid nitrogen. This bath was used in preference to a
dry ice-acetone bath because of the danger that CO₂ or acetone dis-
charged into the atmosphere of the bag might cause disproportionation
of the product. The cooled (just above the freezing point) solution
was added to a flask containing 2.31 g (3.96 mmol) of CsUCl₆. The
solution was stirred briefly and then allowed to stand for 15 min. The
blue product was isolated by filtration, washed with dry nitromethane,
and dried in vacuo. The I.R. spectrum (vide infra) of the compound
showed that no Et₄N⁺ or other organic material was present. Although
the visible-near I.R. spectrum (vide infra) showed the product to be
contaminated with U(IV) and possibly U(VI), the spectrum did confirm
the presence of the UOCl₅²⁻ anion. It might be possible to reduce the
extent of disproportionation by maintaining the solution near the
freezing point after mixing the reactants; only a few preparations of
the product were made, and temperature control was not extensively in-
vestigated. It was found that the molar ratio of Et₄NCl to CsUCl₆ must
be very nearly unity; if it is less than one, the desired reaction

\[
\text{Et}_4\text{NCl} + \text{CsUCl}_6 + \text{H}_2\text{O} \rightarrow \frac{1}{2}(\text{Et}_4\text{N})_2\text{UOCl}_5 + \frac{3}{2}\text{Cs}_2\text{UOCl}_5\downarrow + 2\text{HCl}
\]  

(22)
can not proceed to completion. If the ratio is more than one, the ex-
cess Et₄NCl will react with the product.

\[
2\text{Et}_4\text{NCl} + \text{Cs}_2\text{UOCl}_5 \rightarrow (\text{Et}_4\text{N})_2\text{UOCl}_5 + 2\text{CsCl}\downarrow
\]  

(23)

In both Ryan’s²² and this preparation of the UOCl₅²⁻ species,
the traces of H₂O were sufficient to carry out the hydrolysis of UCl₆⁻
to UOCl₅²⁻; the lower solubility of the Cs⁺ salt in nitromethane per-
mitted separation of the Cs⁺ salt from the soluble Et₄N⁺ salt. Ryan²²
made several attempts to prepare salts of UOCl₅²⁻ with metal cations but
was not successful. The cesium salt, Cs$_2$UOCl$_5$, is apparently much less
stable than the tetraethylammonium salt and decomposes rapidly when it
is exposed to the atmosphere; the decomposition is indicated by a color
change from blue to pale green.

(2) Other attempts to prepare metal salts of UOCl$_5^{2-}$

In addition to the successful preparation of Cs$_2$UOCl$_5$ described
above, numerous additional attempts were made to prepare salts of the
UOCl$_5^{2-}$ species with various metal cations. None of these attempts was
successful. The methods used are briefly summarized in Table VI. The
general procedure was to add a solution (as nearly saturated as possible)
of the appropriate metal salt to the solid uranium compound.

b. Hydrolytic reactions of UCl$_5$$^\cdot$TCAC

(1) In the presence of phthalazine

Undried tetraethylammonium chloride was dissolved to approxi-
mate saturation in nitromethane; the solution was diluted ten-fold with
undried acetone and filtered. Phthalazine was dissolved in this solu-
tion, and the resulting solution was added to a flask containing solid
UCl$_5$$^\cdot$TCAC. [An excess (over 1:1 mole ratio) of the phthalazine was used.] The immediate reaction produced a bright green solid which was isolated
by filtration, washed with dry acetone, and dried in a stream of dry
nitrogen. The visible-near I.R. (electronic) spectrum of the product
showed that it contained no more than a few percent U(IV) and U(VI).

Anal. Calcd for (Et$_4$N)$_2$UOCl$_5$·C$_8$H$_6$N$_2$ (C$_{34}$H$_{48}$Cl$_5$N$_4$O$_2$): C, 35.07; H, 5.64;
N, 6.82. Found: C, 33.96; H, 5.61; N, 6.68.
**TABLE VI**

**UNSUCCESSFUL ATTEMPTS TO PREPARE METAL SALTS OF UOCl$_5^{2-}$**

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Solvent</th>
<th>Temperature</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl,$\text{UCl}_5$·TCAC</td>
<td>PrenCO$_3$-Cl$_2$</td>
<td>Ambient</td>
<td>Yellow-green soln.</td>
</tr>
<tr>
<td>LiCl,$\text{UCl}_5$·TCAC</td>
<td>HMPA</td>
<td>Ambient</td>
<td>Mixture of green and black solids</td>
</tr>
<tr>
<td>NaCl,$\text{UCl}_5$·TCAC</td>
<td>CH$_3$NO$_2$-acetone</td>
<td>Ambient</td>
<td>Green soln.$^a$</td>
</tr>
<tr>
<td>NaI,$\text{UCl}_5$·TCAC</td>
<td>CH$_3$NO$_2$-acetone</td>
<td>Ambient</td>
<td>Red soln.$^b$</td>
</tr>
<tr>
<td>NaBPh$_4$,$\text{UCl}_5$·TCAC</td>
<td>CH$_3$NO$_2$-acetone</td>
<td>Ambient</td>
<td>Green soln.$^a$</td>
</tr>
<tr>
<td>NaBPh$_4$,$\text{UCl}_5$·TCAC</td>
<td>Et$_2$-acetone</td>
<td>Ambient</td>
<td>Tan solid$^c$</td>
</tr>
<tr>
<td>NaBPh$_4$,$\text{UCl}_5$·TCAC</td>
<td>CHCl$_3$</td>
<td>Ambient</td>
<td>Tan solid$^d$</td>
</tr>
<tr>
<td>KCl,$\text{UCl}_5$·TCAC</td>
<td>EtOH-glycerol-acetone</td>
<td>Ambient</td>
<td>Yellow-green soln.</td>
</tr>
<tr>
<td>RbCl,$\text{UCl}_5$·TCAC</td>
<td>EtOH-glycerol-acetone</td>
<td>Ambient</td>
<td>Yellow-green soln.</td>
</tr>
<tr>
<td>CsCl,$\text{UCl}_5$·TCAC</td>
<td>Et-OH-glycerol-acetone</td>
<td>Ambient</td>
<td>Yellow-green soln.</td>
</tr>
<tr>
<td>CsCl,$\text{UCl}_5$·TCAC</td>
<td>PrenCO$_3$-ICl</td>
<td>Ambient</td>
<td>Red soln.$^e$</td>
</tr>
<tr>
<td>CsCl,$\text{UCl}_5$·TCAC</td>
<td>CH$_3$NO$_2$-ICl</td>
<td>Ambient</td>
<td>Green solid$^f$</td>
</tr>
<tr>
<td>CsCl,CsUCl$_6$</td>
<td>CH$_3$NO$_2$-ICl-Cl$_2$</td>
<td>-10°</td>
<td>Yellow-green solid</td>
</tr>
<tr>
<td>CaCl$_2$,$\text{UCl}_5$·TCAC</td>
<td>HMPA</td>
<td>Ambient;0°</td>
<td>Blue solid$^g$</td>
</tr>
<tr>
<td>HgCl$_2$,$\text{UCl}_5$·TCAC</td>
<td>Acetone</td>
<td>Ambient</td>
<td>Green soln.</td>
</tr>
<tr>
<td>HgCl$_2$,$\text{UCl}_5$·TCAC</td>
<td>Acetone-benzene</td>
<td>Ambient</td>
<td>Yellow soln.$^h$</td>
</tr>
<tr>
<td>HgCl$_2$,$\text{UCl}_5$·TCAC</td>
<td>Acetone-petroleum ether</td>
<td>Ambient</td>
<td>Green oil</td>
</tr>
<tr>
<td>HgCl$_2$,$\text{UCl}_5$·TCAC</td>
<td>Acetone-CH$_3$NO$_2$</td>
<td>Ambient</td>
<td>Green soln.</td>
</tr>
<tr>
<td>HgCl$_2$,$\text{UCl}_5$·TCAC</td>
<td>PrenCO$_3$-Cl$_2$</td>
<td>Ambient</td>
<td>Brown soln.$^i$</td>
</tr>
</tbody>
</table>

(a) A green oil formed upon addition of petroleum ether.
(b) Excess acetone was added, but no precipitate formed.
(c) The visible-near I.R. spectrum of the product indicates that it is predominantly U(VI) and also contains some U(IV).
(d) Visible-near I.R. spectrum indicates U(VI).
(e) When diluted with undried acetone, this solution became green, then rapidly yellow.

(Continued)
(f) Visible-near I.R. spectrum indicates that this is a mixture of U(IV) and U(VI).

(g) The visible-near I.R. of this product indicates that the UOCl$_5^{2-}$ ion is present and that the product is contaminated with U(IV) and U(VI). The I.R. spectrum, however, contains many bands, presumably due to organic materials. The solvent was probably not removed during drying; HMPA is known to form complexes with uranium(V).

(h) Upon standing, the yellow solution slowly turned green.

(i) Upon dilution with acetone and standing for several hours, the solution developed a deep red color.
The above reaction was also attempted in benzene by adding a solution of UCl₅·TCAC in benzene to a solution of phthalazine in benzene saturated with water and Et₄NCl. An orange precipitate formed immediately. It was not analyzed, but is probably the orange UCl₅(phthalazine). The low solubility of Et₄NCl in benzene apparently prohibited the hydrolysis. When solid UCl₅·TCAC was used instead of a solution, the product precipitated as a coating on the UCl₅·TCAC and prevented its dissolution.

(2) In the presence of o-phenanthroline

Undried tetraethylammonium chloride was dissolved to approximate saturation in nitromethane; the solution was diluted ten-fold with undried acetone and filtered. In 50 ml of this solution was dissolved 0.831 g (4.61 mmol) of o-phenanthroline. The resulting solution was then added to a flask containing 1.251 g (2.06 mmol) of UCl₅·TCAC. The immediate reaction produced a fluffy, iridescent blue precipitate which was isolated by filtration, washed twice with dry acetone, and dried in vacuo. Anal. Calcd. for \((\text{Et}_4\text{N})_2\text{UCl}_5\cdot2\text{C}_{12}\text{H}_8\text{N}_2\cdot\text{C}_{40}\text{H}_{58}\text{Cl}_5\text{N}_8\text{UO})\): C, 45.66; H, 5.36; N, 7.99. Found: C, 44.34; H, 5.34; N, 7.81

(3) In the presence of 2,2'-bipyridyl

Undried Et₄NCl was dissolved to saturation in nitromethane; the solution was diluted ten-fold with undried acetone and filtered. In 50 ml of this solution was dissolved 0.694 g (4.43 mmol) of 2,2'-bipyridyl. The resulting solution was added to a flask containing 1.214 g (2.00 mmol) of UCl₅·TCAC. It was found that the use of larger amounts of UCl₅·TCAC per volume of solution resulted in disproportionation
of the U(V).] The immediate reaction produced a blue solid which was isolated by filtration, washed twice with dry acetone, and dried in vacuo. Anal. Calcd. for \((\text{Et}_4\text{N})_4\text{UOCl}_5\cdot0.5(\text{C}_2\text{H}_5\text{N}_2)\) \((\text{C}_7\text{H}_{14}\text{Cl}_6\text{N}_8\text{UO})\): C, 32.75; H, 5.76; N, 5.48. Found: C, 31.27; H, 5.56; N, 5.16.

**Atomic ratios, C:H:N:** Calcd: 21 : 44 : 3. Found 21 : 44.5 : 2.97.

(4) In the presence of pyridine

The procedure was the same as that for the preparation of the bipyridyl compound except that 0.778 g (9.82 mmol) of pyridine and 0.980 g (1.61 mmol) of \(\text{UCl}_5\cdot\text{TCAC}\) were used. The immediate reaction produced a bright green precipitate which was removed by filtration, washed twice with dry acetone, and dried in a stream of dry nitrogen. The electronic spectrum of the product shows that it is a mixture of \(\text{U(IV)}\), \(\text{U(V)}\), and \(\text{U(VI)}\). The analysis indicates that it contains no pyridine. Anal. Calcd. for \((\text{Et}_4\text{N})_2\text{UOCl}_5\cdot(\text{C}_{18}\text{H}_{40}\text{Cl}_6\text{N}_2\text{OU})\): C, 27.78; H, 5.83; N, 4.05. Found: C, 27.50; H, 6.03; N, 4.02. The product is probably a mixture of tetraethylammonium salts of \(\text{UOCl}_5^{2-}\), \(\text{UCl}_6^{2-}\), and \(\text{UO}_2\text{Cl}_4^{2-}\).

In another preparative attempt, the solution was cooled to \(-78^\circ\) before mixing with \(\text{UCl}_5\cdot\text{TCAC}\). The precipitate was blue, but the characteristic green color of \(\text{UCl}_6^{2-}\) developed rapidly during filtration and washing. The electronic spectrum showed the presence of oxidation states 4, 5, and 6, and the analysis showed the product to be a mixture of the above uranium salts and \(\text{Et}_4\text{NCl}\). Anal. Calcd. for \((\text{Et}_4\text{N})_2\text{UOCl}_5\cdot3.5\text{Et}_4\text{NCl}\cdot(\text{C}_{22}\text{H}_{58}\text{Cl}_8\text{N}_8\text{OU})\): C, 32.64; H, 6.85; N, 4.76. Found: C, 31.73; H, 7.22; N, 5.03. **Atomic Ratios, C:H:N:** pyridine requires \(7 : 5 : 1\); \(\text{Et}_4\text{N}^+\) requires \(8 : 20 : 1\). Found: 8.0 : 21.7 : 1.09.
In the presence of triphenylphosphine

The procedure was the same as that for the preparation of the bipyridyl compound except that 2.156 g (8.22 mmol) of triphenylphosphine and 2.361 g (3.88 mmol) of UCl₅·TCAC were used. The immediate reaction produced a pale green solid which was removed by filtration, washed twice with dry acetone, and dried in a stream of dry nitrogen. The electronic spectrum of the product showed that complete reduction to U(IV) had occurred.

In the presence of phenazine

Undried Et₄NCl was dissolved to approximate saturation in nitromethane; this solution was diluted ten-fold with undried acetone and filtered. In 100 ml of this solution was dissolved 2.660 g (14.8 mmol) of phenazine. An additional 10 ml of nitromethane was added to aid the dissolution. The resulting solution was filtered and mixed with 1.168 g (1.92 mmol) of UCl₅·TCAC; there was the immediate formation of a yellow-green solid which was isolated by filtration, washed with dry acetone, dried in a stream of dry nitrogen, and then dried in vacuo. The electronic spectrum indicated the presence of U(IV), U(V), and U(VI); the amount of U(IV) present was estimated to be greater than the amount of U(V).

In the presence of potassium diethyldithiocarbamate

Undried Et₄NCl was dissolved to approximate saturation in nitromethane; this solution was diluted ten-fold with undried acetone and filtered. In 50 ml of this solution was dissolved 1.68 g (7.76 mmol)
of \( \text{KS}_{4}\text{CNEt}_{4} \cdot 1.0\text{H}_{2}\text{O} \). The resulting yellow solution was filtered and added to \( 1.0\text{g} \) \( (5.87 \text{mmol}) \) of \( \text{UCl}_{5} \cdot \text{TCAC} \). The immediate reaction produced an orange solution containing a gray solid which was separated by filtration, washed with small portions of dry acetone until the orange color was gone from the filtrate, dried in a stream of dry nitrogen, and finally dried \textit{in vacuo}. \textbf{Anal.} Found: C, 16.84; H, 3.57; N, 2.47; U, 61.10; Cl, 22.98, 26.00. It should be noted that the total of the elemental percentages is more than 100%; this material may be a heterogeneous mixture of two or more compounds. \textbf{C:H:N ratio:} Found: 7.97 : 20.1 : 1.00. \( \text{Et}_{4}\text{N}^{+} \) required 8 : 20 : 1; \( \text{S}_{2}\text{CNEt}_{2}^{-} \) requires 5 : 10 : 1. It thus appears that no \( \text{S}_{2}\text{CNEt}_{2}^{-} \) is present in the product, but the analysis could not be fit to a formula.

c. Reactions of \((\text{Et}_{4}\text{N})_{2}\text{UCl}_{5}\)

(1) With triphenylphosphine

In 3.5 ml of dry nitromethane was dissolved 0.292 g (0.422 mmol) of \((\text{Et}_{4}\text{N})_{2}\text{UCl}_{5}\) and 0.223 g (0.850 mmol) of triphenylphosphine. The reaction was monitored for seven hours by measuring the electronic spectrum. The solution slowly changed color from blue to green and then to yellow-green; the electronic spectrum indicated gradual disproportionation to \( \text{U(IV)} \) and \( \text{U(VI)} \). No solid product was obtained.

(2) With pyridine

Pyridine was added to a solution of \((\text{Et}_{4}\text{N})_{2}\text{UCl}_{5}\) in dry nitromethane. Upon addition of the pyridine, the characteristic blue color of the \( \text{UCl}_{5}^{2-} \) disappeared; a yellow solution was obtained, but no
product precipitated. The electronic spectrum indicates that U(VI) was produced in the reaction.

(4) With pyrazine

Upon addition of pyrazine to a solution of \((\text{Et}_4\text{N})_2\text{UOCl}_5\) in dry nitromethane, the blue color of \(\text{UOCl}_5^{2-}\) disappeared, and a yellow solution characteristic of U(VI) resulted. No precipitate was isolated.

(4) With potassium diethyldithiocarbamate

In 3.5 ml of dry nitromethane was dissolved 0.0726 g (0.105 mmol) of \((\text{Et}_4\text{N})_2\text{UOCl}_5\). To this solution was added potassium diethyldithiocarbamate in five increments of 0.0197 g (0.091 mmol) each. The electronic spectrum of the solution was measured after each addition. The first addition resulted in the immediate disappearance of the \(\text{UOCl}_5^{2-}\) bands and the appearance of an intense band in the ultraviolet. This band "tailed over" into the visible region, giving the solution a red-orange color. Further additions of \(\text{K} \text{S}_2\text{CNET}_2\) intensified this band and the color of the solution. After the fifth addition, the visible "tail" disappeared, but the solution remained orange in color. A precipitate could not be isolated by cooling the solution. Evaporating the solution to dryness produced a mixture of materials of different colors.

(5) With 2,2′-bipyridyl

In 2 ml of dry nitromethane was dissolved 0.181 g (1.16 mmol) of 2,2′-bipyridyl. The resulting solution was added to 0.113 g (0.163 mmol) of solid \((\text{Et}_4\text{N})_2\text{UOCl}_5\). A brown solid formed; the solid was removed by centrifugation, washed with dry nitromethane, and dried \textit{in vacuo}.
The electronic spectrum of the solid was similar to that obtained in
the reaction with KSP₂CN₄₀Et₂⁻; there was an intense ultraviolet band that
had a broad "tail" extending into the visible-near I.R. region. This
absorption is not indicative of U(V).

(6) With o-phenanthroline

A solution of 0.196 g (1.08 mmol) of o-phenanthroline in 2 ml
of dry nitromethane was added to 0.104 g (0.151 mmol) of solid (Et₄N)₂-
UOCl₅. A brown solid formed; the solid was removed by centrifugation,
washted with dry nitromethane, and dried in vacuo. The electronic spec­
trum indicated that a mixture of U(IV) and U(VI) was obtained.

(7) With phthalazine

Solutions of (Et₄N)₂UOCl₅ and of phthalazine in nitromethane
were mixed; there resulted a yellow solution which slowly became turbid.
Upon cooling the solution in an ice bath a yellow solid formed; the
solid was removed by filtration, washed twice with dry, ice-cold nitro­
C, 19.59; H, 1.23; N, 5.71. Found: C, 19.88; H, 1.59; N, 5.60.

The above solution was prepared again, and its electronic
spectrum was recorded. Addition of phthalazine to (Et₄N)₂UOCl₅ caused
immediate disappearance of the U(V) bands; the compound appears to have
been oxidized to U(VI).

(8) With phenazine

In 50 ml of dry nitromethane was dissolved 0.500 g (2.78 mmol)
of phenazine. To this solution was added, with stirring, 1.921 g
(2.78 mmol) of (Et₄N)₂UOCl₅. An emerald green solution formed imme-
diately but quickly began to darken. After several minutes, dark green
(almost black) crystals began to precipitate from the dark solution.
The solution was allowed to stand for several hours to allow the product
to form. The compound was isolated by filtration, washed with dry
nitromethane, and dried in vacuo. The product was shown (vide infra)
to be the chloride salt of the dihydrophenazine cation radical. The
ESR spectrum of the polycrystalline powder consists of a single narrow
line with g = 2.005. This indicates that the product is a free radical.
Anal. Calcd. for C₁₂H₁₀ClN₂: C, 66.21; H, 4.63; N, 12.87; Cl, 16.29.
Found: C, 65.39; H, 4.73; N, 12.85; Cl, 16.07.

The filtrate from the above reaction was slowly evaporated
(over a period of several days) by placing it on a warm surface. The
solution was filtered periodically to remove any of the above product
which continued to form. [The product which precipitated in this manner
was discarded, since it is likely to be contaminated with UO₂⁺ (vide
infra).] After all of the above product precipitated, the solution was
yellow, and large greenish-yellow crystals slowly formed in the solu-
tion. These crystals were isolated by filtration, washed with dry
nitromethane, and dried in vacuo. The compound proved to be the well-
known U(VI) complex, (Et₄N)₂UO₂Cl₄. Anal. Calcd. for (Et₄N)₂UO₂Cl₄
(C₁₆H₄OCl₄N₂O₂U): C, 28.58; H, 6.00; N, 4.17. Found: C, 28.59; H,
6.24; N, 4.21.

The chloride salt of the dihydrophenazine radical cation
(₃H₂Cl) was also obtained by mixing a nitromethane solution of phenazine
with a nitromethane solution of (Et₄N)₂UOCl₅. The analysis indicated
that the product is identical with that obtained by mixing a nitromethane
solution of phenazine with solid (Et₄N)₂UOCl₅.
The preparation of $\text{PH}_2\text{Cl}$ was attempted under rigorously anhydrous conditions. The reagents were taken into a dry box where the phenazine was dissolved in the dry nitromethane, and the $(\text{Et}_4\text{N})_2\text{UOCl}_5$ was added to the resulting solution. An emerald green solution was obtained; the solution did not darken, and only a trace of solid product was obtained.

When the above solution was removed from the dry box and exposed to the atmosphere, the color began to deepen within 10 minutes, and the product started to precipitate within 30 minutes. The solution was allowed to stand exposed to the air for 5 hours. The product was then removed by filtration, washed, and dried as described above. The compound obtained in this manner was anhydrous. Anal. Calcd. for $\text{C}_{12}\text{H}_{10}\text{ClN}_2(\text{PH}_2\text{Cl})$: C, 66.21; H, 4.63; N, 12.87. Found: C, 65.80; H, 4.54; N, 13.05.

The compound $\text{PH}_2\text{Cl}$ was formed in the presence of an excess of water. The procedure follows. Nitromethane was saturated with water in a separatory funnel and then separated from the aqueous phase. The reaction was then carried out (in a darkened room) as described above; the wet nitromethane was used. The product formed immediately; the induction period mentioned above was not required. The product was isolated by filtration, washed, and dried as before. This product consists of particles which are smaller and lighter in color than those of other preparations; these characteristics are probably due to the rapidity with which the compound precipitated. Anal. Calcd. for $\text{PH}_2\text{Cl} \cdot 2\text{H}_2\text{O}$ ($\text{C}_{2}\text{H}_4\text{ClN}_2\text{O}_2$): C, 56.51; H, 5.56; N, 11.04. Found: C, 57.09; H, 4.08; N, 11.19.

When this reaction was carried out under conditions intermediate between those described above (i.e., dry nitromethane was used,
but the entire procedure was done on the bench top), the degree of hydration of the compound varied between that of the anhydrous compound and the dihydrate.

This preparation was also done with additional modifications: (1) \(\text{Ph}_4\text{As})_2\text{UOCl}_5\) was substituted for \((\text{Et}_4\text{N})_2\text{UOCl}_5\) and (2) nitrobenzene was substituted for nitromethane (vide infra).

(9) With benzo[a]phenazine

In 55 ml undried nitromethane was dissolved 0.430 g (1.87 mmol) of benzo[a]phenazine. After the yellow solution had been filtered, 1.289 g (1.86 mmol) of solid \((\text{Et}_4\text{N})_2\text{UOCl}_5\) was added slowly with stirring. The solution immediately developed an amber color which slowly darkened. After eight hours, the solution was dark red and contained a small amount of precipitate. No additional precipitate was obtained even though the solution was allowed to stand, open to the air, for several days. The solution was then filtered and saturated with dry HCl gas; there was concomitant precipitation of a reddish-brown solid. The product was removed by filtration, washed with dry nitromethane, and dried in vacuo. Anal. Calcd. for \((\text{BPH}_2)_2\text{UO}_2\text{Cl}_4\) \((\text{C}_{32}\text{H}_{24-}\text{Cl}_{14}\text{N}_4\text{O}_2\text{U})\): C, 43.86; H, 2.76; N, 6.39; U, 27.16; Cl, 16.18. Found: C, 44.13; H, 2.59; N, 6.32; U, 26.42; Cl, 17.41.

This reaction was also carried out using a molar ratio \((\text{Et}_4\text{N})_2\text{UOCl}_5\): BP of 2:1. Upon standing for several days the solution yielded a violet solid, which was isolated by filtration, washed, and dried as in the above procedure. The material was analyzed three times; the analyses were not reproducible and suggest that the product is a heterogeneous mixture of \((\text{BPH}_2)_2\text{UO}_2\text{Cl}_4\) and \(\text{BPH}_2\text{Cl}\). Anal. Calcd. for 1:4
mixture of (BPH₂)₂UO₂Cl₄ and BPH₂Cl (C₉₀H₇₂Cl₆N₁₂O₂U): C, 59.21; H, 3.73; N, 8.65; U, 12.22; Cl, 14.56. Found: C, 61.00, 53.49, 55.88; H, 3.73, 3.69, 3.74; N, 9.47, 8.26; U, 12.38; Cl, 15.91.

(10) With dibenzo[a,c]phenazine (DBP)

Because of the low solubility of dibenzo[a,c]phenazine (DBP) in nitromethane, a mixed solvent system, nitromethane-nitrobenzene, was used. In a mixture of 35 ml of dry nitrobenzene and 40 ml of undried nitromethane was dissolved 0.335 g (1.19 mmol) of DBP, and the mixture was filtered. A solution of 0.829 g (1.19 mmol) of Et₄N₂UOCl₅ in 25 ml of dry nitromethane and 20 ml of dry nitrobenzene was prepared and quickly mixed with the above solution. [Disproportionation of (Et₄N)₂UOCl₅ occurs rapidly in solution in the absence of excess chloride.]²² The resulting bright yellow solution was allowed to stand for several days, but no precipitate formed. Nitrogen which had been bubbled through distilled water was then bubbled through the solution, but there was still no change in the solution. When the solution was saturated with dry HCl, a yellow solid formed at once. The solid was separated by filtration, washed with a mixture of 5 ml of dry nitromethane-10 ml of dry nitrobenzene saturated with dry HCl, dried in a stream of dry nitrogen, and then dried in vacuo. Anal. Calcd. for (DBPH₂)₂UO₂Cl₄ (C₄₀H₂₈Cl₄N₄O₂U): C, 49.20; H, 2.89; N, 5.74. Found: C, 49.10; H, 2.50; N, 5.82.

The above reaction was repeated, and, in lieu of the HCl treatment, an attempt was made to isolate the product by evaporating the filtrate at 60-70°C on a rotary evaporator under a pressure of 30 mm. Two precipitates were obtained successively: the first, a yellow-green
material, contained no DBP and probably consisted of a mixture of U(IV) and U(VI). Anal. Calcd. for (Et₄N)₂UOCl₅ (C₃₁₀H₄₀Cl₅N₂OU): C, 27.78; H, 5.83; N, 4.05. Found: C, 27.35; H, 5.91; N, 4.03. The second precipitate was yellow and is believed to be DBP.

An attempt was also made to carry out the reaction in pure nitrobenzene. A solution of 0.374 g (1.33 mmol) of DBP in 25 ml of dry nitrobenzene was filtered and mixed with 0.919 g (1.33 mmol) of (Et₄N)₂UOCl₅. A brown solution was obtained, but an aqua-colored solid [probable undissolved U(V)] was also present; after allowing the solution to stand for several days, this solid was removed by filtration, washed with nitrobenzene, and dried in vacuo. The electronic spectrum of this product showed it to be a mixture of U(IV), U(V), and U(VI). Anal. Calcd. for (Et₄N)₂UOCl₅ (C₃₁₀H₄₀Cl₅N₂OU): C, 27.78; H, 5.83; N, 4.05. Found: C, 27.86; H, 5.92; N, 3.88. The filtrate was divided into two equal portions. One portion was saturated with dry HCl gas, and there was immediate formation of a bright red precipitate which was separated by filtration, washed with HCl-nitromethane, and dried in vacuo. The compound evidently decomposed upon drying; the color changed from bright red to yellow-brown. EPR and other evidence (vide infra) suggest that the product is probably a mixture of DBPH₂Cl (a free radical, vide infra) and DBP·HCl, a salt of DBP. Anal. Calcd. for DBPH₂Cl (C₂₀H₁₄ClN₂): C, 75.59; H, 4.44; N, 8.81. Calcd. for DBPHCl (C₂₀H₁₃N₂Cl): C, 75.83; H, 4.14; N, 8.84. Found: C, 74.45; H, 3.63; N, 8.45. Upon evaporation (to a small volume) and cooling the second portion of the above filtrate, a yellow solid crystallized. The solid was separated by filtration, washed with dry nitrobenzene, and dried in vacuo. Anal. Calcd. for
DBP (C$_{10}$H$_{12}$N$_2$): C, 85.69; H, 1.32; N, 9.99. Found: C, 85.41; H, 1.07; N, 9.71.

(11) With 2,3-di(2-pyridyl)quinoxaline

To a solution of 0.399 g (1.40 mmol) of DPyQ in 20 ml of undried nitromethane, 0.969 g (1.10 mmol) of solid (Et$_4$N)$_2$UOCl$_5$ was added. This produced a clear, light green solution which quickly became turbid; a brown precipitate then formed. Although only a very small amount of solid formed immediately, clear, light brown crystals began to form after several hours. The solution was allowed to stand for several days to allow the crystals to grow. They were isolated by filtration, washed with dry nitromethane, and dried in vacuo. Anal. Calcd. for (DPyQH$_2$)$_2$UO$_2$Cl$_4$ (C$_{39}$H$_{48}$Cl$_4$N$_8$O$_4$U): C, 43.92; H, 2.87; N, 11.38. Found: C, 43.91; H, 2.63; N, 11.45.

Upon slow evaporation of the filtrate, large yellow-green crystals were obtained. They were removed by filtration, washed with dry nitromethane, and dried in vacuo. Anal. Calcd. for (Et$_4$N)$_2$UO$_2$Cl$_4$ (C$_{16}$H$_{40}$Cl$_4$N$_2$O$_2$U): C, 28.58; H, 6.00; N, 4.17. Found: C, 28.52; H, 6.15; N, 4.06.

(12) With methylene blue

To 50 ml of undried nitromethane, 0.45 g of methylene blue chloride was added; the mixture was stirred for ca. one half-hour and filtered. To this solution, 0.95 g of solid (Et$_4$N)$_2$UOCl$_5$ was added. The reddish-brown solid which formed immediately was isolated by filtration, washed with nitromethane, and dried in vacuo. Anal. Calcd.
for \((\text{MB})_{2}\text{UOCl})_{2}\): C, 38.42; H, 3.63; N, 8.40; U, 23.80; Cl, 17.74. Found: C, 39.01; H, 3.67; N, 8.77; U, 21.89; Cl, 17.97.

(15) With riboflavin

Riboflavin was found to be insoluble in nitromethane and nitrobenzene, so the reaction was done in N,N-dimethylformamide, methanol, and dimethylsulfoxide. In each case, an unwighed amount of solid \((\text{Et}_4\text{N})_2\text{UOCl}_5\) was added to the solution of riboflavin. No solid product was obtained in any case. The \(\text{UOCl}_5^{2-}\) was probably attacked by either the solvent or the hydroxylated side chain (ribose sugar function).

d. Hydrolytic reactions of addition compounds of \(\text{UCl}_5\)

(1) \(\text{UCl}_5\cdot\text{OMe}_2\)

Undried tetraethylammonium chloride was dissolved to approximate saturation in nitromethane; this solution was diluted ten-fold with undried acetone and filtered. In a glove bag, this solution was added to a flask containing an unwighed quantity of \(\text{UCl}_5\cdot\text{OMe}_2\). The immediate blue precipitate was separated by filtration, washed twice with dry acetone, and dried in a stream of dry nitrogen. The electronic spectrum of the product is identical to that of \((\text{Et}_4\text{N})_2\text{UOCl}_5\). \(^{22}\) Anal. Calcd. for \((\text{Et}_4\text{N})_2\text{UOCl}_5\cdot\text{Et}_4\text{NCl}\) (\(\text{C}_{24}\text{H}_{60}\text{Cl}_8\text{H}_9\text{OU}\)): C, 33.62; H, 7.05; N, 4.90. Found: C, 33.13; H, 7.49; N, 4.73.

(2) \(\text{UCl}_5\) (phthalazine)\(_2\)

Undried \(\text{Et}_4\text{NCl}\) was dissolved to approximate saturation in nitromethane; this solution was diluted ten-fold with undried acetone
and filtered. To this solution, solid $\text{UCl}_5(\text{phthalazine})_2$ was added with stirring. The product appeared to form on the surface of the reactant particles; all of the starting material did not dissolve. Nitromethane was then added until all of the product dissolved. The solution was filtered, and acetone was added to precipitate the product. (In another attempt, the product failed to precipitate because too much nitromethane was added.) The green solid was removed by filtration, washed twice with acetone, and dried in a stream of dry nitrogen. The electronic spectrum was identical with that of $(\text{Et}_4\text{N})_2\text{UOCl}_5$ except that a considerable amount of U(IV) and U(VI) was also in evidence.

In a modification of the above procedure, undried Et$_4$NCl was dissolved to approximate saturation in nitromethane; the solution was diluted ten-fold with undried acetone, filtered, and mixed with a solution of $\text{UCl}_5(\text{phthalazine})_2$ in dry nitromethane. Addition of acetone to the resulting solution caused formation of a blue solid, which was separated by filtration, washed twice with acetone, and dried in a stream of dry nitrogen. The electronic spectrum of the product was identical with that of $(\text{Et}_4\text{N})_2\text{UOCl}_5$ and contained some U(IV) and U(VI) but not as much as in the previous preparation. Anal. Calcd. for $(\text{Et}_4\text{N})_2\text{UOCl}_5$ ($\text{C}_{16}\text{H}_{40}\text{Cl}_{5}\text{N}_{2}\text{O}\text{U}$): C, 27.78; H, 5.83; N, 4.05. Found: C, 27.46; H, 5.97; N, 5.95. In another execution of this procedure, the product failed to precipitate because too much nitromethane was used to dissolve the starting material.

e. Other reactions of uranium compounds

(1) The reaction of $(\text{Ph}_4\text{As})_2\text{UOCl}_5$ with phenazine in nitromethane
A solution of 0.068 g (0.270 mmol) of phenazine in 5.5 ml of dry nitromethane was added to a flask containing 0.110 g (0.370 mmol) of (Ph₄As)₂UOCl₅. The resulting green solution slowly darkened and yielded a dark green, almost black, crystalline solid which was removed by filtration, washed with dry nitromethane, and dried in vacuo. Anal. Calcd. for PH₂Cl·0.5H₂O (C₁₂H₁₃ClN₂O₂·5): C, 65.58; H, 4.89; N, 12.36. Found: C, 63.57; H, 4.59; N, 12.42. This is evidently the same product which is formed by the reaction of (Et₄N)₂UOCl₅ with phenazine (vide supra).

(2) The reaction of (Ph₄As)₂UOCl₅ with phenazine in nitrobenzene

A solution of 0.0454 g (0.252 mmol) of phenazine in 11 ml of dry nitrobenzene was added to a flask containing 0.390 g (0.325 mmol) of (Ph₄As)₂UOCl₅. The resulting green solution was filtered to remove a small amount of light-colored solid (probably Ph₄AsCl). After several minutes, a dark solid began to precipitate; this material was removed by filtration, washed with dry nitromethane, and dried in vacuo. Anal. Calcd. for PH₂Cl·1.5H₂O (C₁₂H₁₃ClN₂O₂·5): C, 58.90; H, 5.35; N, 11.45. Found: C, 58.85; H, 4.75; N, 11.06.

(3) The reaction of (Et₄N)₂UOBr₅ with phenazine

Addition of (Et₄N)₂UOBr₅ to a nitromethane (undried) solution of phenazine gave an immediate dark green precipitate which was isolated by filtration, washed with dry nitromethane, and dried in vacuo. Anal. Calcd. for PH₂Br·H₂O (C₁₂H₁₂BrN₂O): C, 51.45; H, 4.32; N, 10.00. Found: C, 51.16; H, 4.07; N, 9.76.
The reaction of \( \text{Et}_4\text{NCl}_6 \) with phenazine

The following reaction was carried out in a glove bag. To a solution of 0.144 g (0.800 mmol) of phenazine in 10 ml of dry nitromethane, 0.590 g (1.025 mmol) of solid \( \text{Et}_4\text{NCl}_6 \) was added. An orange solution containing a yellow solid was produced. Since it was at first assumed that the yellow solid was undissolved \( \text{Et}_4\text{NCl}_6 \), 35 °f dry nitromethane was added to dissolve the material. It did not completely dissolve; therefore, it was removed by filtration, washed with dry nitromethane, and dried in vacuo. Anal. Calcd. for \( \text{UCl}_5\text{P}_2 \) (\( \text{C}_{24}\text{H}_{16}\text{Cl}_5\text{N}_4\text{U} \)): C, 37.16; H, 2.08; N, 7.22. Found: C, 36.81; H, 2.25; N, 7.17.

The same product was obtained by adding (in a glove bag) a solution of 0.516 g (0.889 mmol) of \( \text{Et}_4\text{NCl}_6 \) in 10 ml of dry nitromethane to a solution of 0.123 g (0.685 mmol) of phenazine in 10 ml of dry nitromethane. The yellow product slowly precipitated. It was isolated by filtration, washed, and dried as above. Anal. Calcd. for \( \text{UCl}_5\text{P}_2 \) (\( \text{C}_{24}\text{H}_{16}\text{Cl}_5\text{N}_4\text{U} \)): C, 37.16; H, 2.08; N, 7.22. Found: C, 37.34; H, 2.21; N, 7.27.

A small amount of undried acetone was added to the filtrates from the above reactions. An emerald green color developed, and a dark precipitate slowly formed. This is probably the chloride salt of the dihydrophenazine cation free radical, \( \text{PH}_2\text{Cl} \).

Attempt to prepare \( (\text{Et}_4\text{N})_2\text{USCl}_5 \)

In a glove bag, dry \( \text{Et}_4\text{NCl} \) was dissolved to approximate saturation in dry nitromethane and diluted ten-fold with dry acetone. The resulting slurry was removed from the glove bag (care being taken to minimize contact with laboratory air) and saturated with \( \text{H}_2\text{S} \). The
solution was filtered and placed in a glove bag where 100 ml was added to 3.31 g of UCl₅·TCAC. The immediate reaction, accompanied by evolution of gas, produced a pea-green solid which was isolated by filtration, washed with dry acetone, dried in a stream of dry nitrogen, and then dried in vacuo. The electronic spectrum of the product showed that it was a mixture of U(IV) and U(VI); no U(V) bands were observed. Anal. Calcd. for (Et₄N)₂USCl₅ \( (C_{16}H_{40}Cl_5N_2SU) \): C, 27.15; H, 5.70; N, 3.96. Found: C, 27.55; H, 5.99; N, 3.96.

(6) Attempt to prepare (Et₄N)₃UOCl₅

Undried Et₄NCl was dissolved to approximate saturation in nitromethane; this solution was diluted ten-fold with undried acetone and filtered. To 50 ml of this solution was added 0.590 g of (Et₄N)₂UCl₅; the mixture was stirred for 14 hours. The resulting green solid was then obtained by filtration, washed twice with acetone, dried in a stream of dry nitrogen, and then dried in vacuo. The electronic spectrum of the product was identical with that of the starting material. Anal. Calcd. for \( (Et₄N)_3UCl₅·1.19Et₄NCl \) \( (C_{25.5h₅₈.8Cl₇.2N₃.2U) \): C, 33.74; H, 7.08; N, 4.92. Found: C, 33.89; H, 7.76; N, 4.98.

f. New Mo(V) compounds and reactions

(1) Preparation of Et₄NMoOCl₄·H₂O, Tetraethylammonium oxotetrachloro-
molybdate(V) hydrate

This compound was inadvertently made in attempts to prepare the previously reported¹⁹³,¹⁴¹ complex \( (Et₄N)₂MoOCl₅ \) (vide infra). In 70 ml of conc. HCl, 5.9 g (36.2 mmol) of MoO(OH)₃ was dissolved by gently
warming the solution. The solution was then filtered to remove any insoluble material. To this solution was added 14.4 g (68.5 mmol) of Et₄NBr; a green precipitate began to form at once. The solution was cooled in an ice-water bath and saturated with dry HCl gas. The green solid was isolated by filtration, washed with a small amount of conc. HCl, recrystallized from hot acetone, and dried in vacuo. Anal. Calcd. for Et₄NMoOCl₄·H₂O (C₅H₂₅Cl₄MoN₂O₄): C, 23.90; H, 5.52; N, 3.48. Found: C, 23.68; H, 5.64; N, 3.31.

The same product was obtained by substituting (1) a 25% aqueous solution of Et₄NOH, (2) a solution of Et₄NCl in conc. HCl, or (3) a solution of Et₄NCl in ethanolic HCl for the Et₄NBr and by using ethanolic HCl instead of conc. aqueous HCl to dissolve the MoO(OH)₃.

James and Wardlaw¹⁴⁰ reported that the salt (Me₃NH)MoOCl₄·H₂O was converted to (Me₃NH)₂MoOCl₅ by dissolving the tetrachloro salt in ethanolic HCl, evaporating to a small volume, saturating the solution with dry HCl, and cooling. The tetraethylammonium salt Et₄NMoOCl₄·H₂O was subjected to this treatment but crystallized unchanged. Anal. Calcd. for Et₄NMoOCl₄·H₂O (C₅H₂₅Cl₄MoN₂O₄): C, 23.90; H, 5.52; N, 3.48. Found: C, 23.13; H, 5.44; N, 3.17.

Several salts of the MoOCl₄⁻ species have been prepared¹³⁶,¹⁴⁰,¹⁴²,¹⁴³ but this is apparently the first report of the preparation of the tetraethylammonium salt.

(2) Attempts to prepare (Et₄N)₂MoOCl₅, Tetraethylammonium oxopentachloromolybdate(V)

An attempt was made to prepare this compound by adding a solution of MoCl₅ in absolute ethanol to an alcoholic solution of Et₄NBr, as
described by Bishop.\textsuperscript{138} A fresh sample of MoCl\textsubscript{5} was not available, however, and the material on hand had evidently been hydrolyzed to a considerable extent by atmospheric moisture. Dissolution of this material in absolute ethanol gave a red-brown solution rather than the emerald green color reported by Bishop;\textsuperscript{138} dissolution in ethanolic HCl yielded a yellow solution containing insoluble red particles. Failure to reproduce the results obtained by Bishop may have been due to the poor quality of the MoCl\textsubscript{5}. On the other hand, Bishop's reported results must be viewed with some skepticism; he reports\textsuperscript{138} that the MoOCls\textsubscript{2}\textsuperscript{2-} ion is obtained on dissolution in absolute ethanol, but MoCl\textsubscript{5} is reported\textsuperscript{144} to react with alcohols to form compounds of the type MoCl\textsubscript{3}(OR)\textsubscript{2}.

Another preparative method that was used involved reduction of Mo(VI) with HI. A mixture of 1.00 g (6.95 mmol) of MoO\textsubscript{3}, 2 ml of 47\% HI, and 10 ml of conc. HCl was heated to boiling until evolution of I\textsubscript{2} almost ceased. An additional 10 ml of conc. HCl was then added, and the solution was again boiled until no more I\textsubscript{2} was evolved. The resulting emerald green (characteristic of MoOCls\textsubscript{5}\textsuperscript{2-}) solution was added to a solution of 5.78 g (34.9 mmol) of Et\textsubscript{4}NCl in a small volume of conc. HCl. After several seconds a brown product began to precipitate. This product was separated by filtration, washed with conc. HCl, and dried in vacuo. Anal. Calcd. for Et\textsubscript{4}NMoOCl\textsubscript{4}·H\textsubscript{2}O (C\textsubscript{8}H\textsubscript{22}Cl\textsubscript{4}MoNO\textsubscript{2}): C, 23.90; H, 5.92; N, 3.45. Found: C, 24.43; H, 5.92; N, 3.90. Although the analysis indicates that this compound is Et\textsubscript{4}NMoOCl\textsubscript{4}·H\textsubscript{2}O, the brown color suggests\textsuperscript{138} that a dimeric species has been formed. This preparative method was modified by saturating the two solutions with dry HCl gas before mixing; the brown product was again obtained.
The reaction between $\text{Et}_4\text{NMoOCl}_4\cdot\text{H}_2\text{O}$ and phenazine

In view of (1) the importance of molybdenum in biological systems, (2) the significance of free radicals in these systems, and (3) the formation of stable radicals by $\text{UOCl}_2^2-$, the reaction of $\text{Mo}^{\text{V}}$ with phenazine was also investigated.

In 35 ml of undried nitromethane, 0.521 g (2.89 mmol) of phenazine was dissolved. The resulting solution was then filtered and mixed with 1.586 g (3.95 mmol) of solid $\text{Et}_4\text{NMoOCl}_4\cdot\text{H}_2\text{O}$. The dark green solution was stirred for 30 minutes to insure complete dissolution of the Mo compound and then allowed to stand, exposed to laboratory air. Nitromethane was added as needed to maintain a constant volume of solution. A slight turbidity was noted occasionally, but filtering the solution produced only a very small quantity of dark gray material. After two days, yellow-green crystals were observed. They were isolated by filtration, washed with nitromethane, and dried in vacuo. The ESR spectrum of the polycrystalline solid showed only a Mo(V) signal; no free-radical signal was observed. The best fit obtained was for $\text{MoO}_2\text{Cl} \cdot \text{P}$. Anal. Calcd. for $\text{MoO}_2\text{Cl} \cdot \text{P}$ ($\text{C}_{12}\text{H}_8\text{ClMoN}_2\text{O}_2$): C, 41.95; H, 2.35; N, 8.15. Found: C, 41.26; H, 3.15; N, 10.15.

The above reaction was repeated, but the solvent was removed immediately. In 15 ml of undried nitromethane was dissolved 0.321 g (1.78 mmol) of phenazine. The solution was filtered and added to a flask containing 0.971 g (2.42 mmol) of $\text{Et}_4\text{NMoOCl}_4\cdot\text{H}_2\text{O}$. The resulting deep green solution was quickly filtered, placed in an ampoule, and evacuated. The solvent was evaporated under vacuum (at room temperature) until a substantial amount of light green solid had precipitated.
The solution was then filtered in a glove bag. The solid was washed with dry nitromethane and dried in vacuo. The ESR spectrum of the polycrystalline solid showed only a Mo(V) signal. Anal. Calcd. for Et₄NMoOCl₄·P(C₂₀H₂₉Cl₄MoN₅O): C, 42.58; H, 5.00; N, 7.45. Found: C, 42.64; H, 4.87; N, 7.70. Addition of water to this compound produced a very dark green (almost black) water-insoluble material. Treatment of this dark green material with acetone yielded a green solution and a blue solid. Upon prolonged exposure to air (7 weeks), the original product was found to be contaminated with reddish-brown particles that evidently resulted from slow decomposition by atmospheric oxygen or moisture. The filtrate was again evaporated under vacuum until a large amount of solid had precipitated; the solid was removed by filtration and washed with dry nitromethane. This solid appeared to be a mixture of the first compound obtained and a small amount of a reddish-brown solid. This material did not appear to decompose upon exposure to air for 24 hours (in contrast to Et₄NMoOCl₄·H₂O); it was not analyzed. The filtrate was then evaporated to dryness, and a dark green solid was obtained. The ESR spectrum of the polycrystalline solid showed only a Mo(V) signal. Anal. Calcd. for Et₄NMoOCl₄·2H₂O·0.5P(C₁₄H₂₈Cl₄MoN₂O₃): C, 32.96; H, 5.53; N, 5.49. Found: C, 32.43; H, 5.55; N, 5.42.

Next, the above reaction was carried out in the absence of oxygen or moisture. A solution of 0.500 g (2.78 mmol) of phenazine in 35 ml of dry nitromethane was mixed with 2.23 g (5.56 mmol) of Et₄NMoOCl₄·H₂O. The flask was flushed with nitrogen and stoppered. After several hours, a reddish-brown precipitate slowly formed; after a few days, large yellow-brown tabular crystals had formed. They were removed by filtration (in a glove bag), washed with dry nitromethane and dried in
vacuo. The material started to darken within one-half hour upon exposure to the atmosphere. The ESR spectrum of the polycrystalline solid consisted of two signals: a Mo(V) signal \( g = 1.951 \) and a free radical signal \( g = 2.005 \). Anal. Found: C, 59.96, 61.92, 61.99; H, 4.31, 4.19, 4.21; N, 14.10, 13.76, 13.85. Attempts to fit a formula to these percentages were not successful. The filtrate was exposed to the atmosphere; a bright yellow solid precipitated. It was obtained by filtration, washed with dry nitromethane, and dried in vacuo. The ESR spectrum of the polycrystalline solid contained a Mo(V) signal, but no free radical signal was observed. Anal. Calcd. for \( \text{MoO}_2\text{Cl}\cdot\text{P} (\text{C}_{12}\text{H}_8\text{Cl-MoN}_2\text{O}_2) \): C, 41.95; H, 2.35; N, 8.15. Found: C, 42.45; H, 3.04; N, 8.65.

Due to the failure to fit a formula to the analyses of the first compound isolated in the above procedure, it was repeated. In a glove bag, a solution of 0.500 g (2.78 mmol) of phenazine in 35 ml of dry nitromethane was mixed with 2.23 g (5.56 mmol) of \( \text{Et}_4\text{NMoOCl}_4\cdot\text{H}_2\text{O} \). The dark green solution was filtered, stoppered, and stored in the glove bag. After two days, gold-colored crystals slowly began to form, and the color of the solution became lighter. When the solution was about two weeks old, lighter-colored crystals started to form. The darker ones were removed from the solution, washed with a small amount of dry nitromethane, and dried in vacuo. The ESR spectrum of the polycrystalline powder showed only a signal due to Mo(V) \( \text{vide infra} \). Anal. Calcd. for \( \text{MoO}_2\text{Cl}\cdot\text{P} (\text{C}_{12}\text{H}_8\text{Cl-MoN}_2\text{O}_2) \): C, 41.95; H, 2.35; N, 8.15. Found: C, 42.68; H, 2.99; N, 8.65. After an additional one-week period, the lighter gold crystals stopped forming in the above filtrate. In a glove bag, the product was isolated by filtration, washed with a small quantity
of dry nitromethane and dried in vacuo. The ESR spectrum of the polycrystalline powder showed two signals, due to Mo(V) and a free electron, respectively. The spectrum was somewhat like that of the first product of the previous preparation; the free radical signal for this product is, however, somewhat broader than that of the former material (vide infra). Anal. Calcd. for PHCl (C_{12}H_{9}ClN_{2}): C, 66.52; H, 4.19; N, 12.93; Cl, 16.36. Found: C, 65.92; H, 4.09; N, 13.18; Cl, 16.22, 16.43; Mo, trace (0.10). The amber filtrate was removed from the glove bag and saturated with dry HCl gas. The immediate deep violet crystalline precipitate was removed by filtration, washed with a small amount of dry nitromethane, dried in a stream of dry nitrogen, and finally dried in vacuo. Exposure to the air was minimized; no degradation of the compound was noted except that a green residue formed where the wet compound touched the glass walls of the drying ampoule. The ESR spectrum of the polycrystalline powder showed only a Mo(V) signal. Anal. Calcd. for PH_{2}MoOCl_{5} (C_{12}H_{10}Cl_{5}MoN_{2}O): C, 30.57; H, 2.14; N, 5.94; Mo, 20.35; Cl, 37.60. Found: C, 31.12, 31.19; H, 2.22, 2.30; N, 6.33, 6.48; Mo, 20.02; Cl, 35.07.

(4) The reaction between (NH_{4})_{2}MoOCl_{5} and phenazine

A solution of 0.502 g (2.78 mmol) of phenazine in 55 ml of dry nitromethane was mixed with 0.90 g (2.77 mmol) of (NH_{4})_{2}MoOCl_{5}. Most of the Mo(V) compound did not dissolve. The flask was sparged with dry nitrogen, and the mixture was stirred for a period of twelve hours. During this period, the solid compound darkened considerably. In order to introduce a small amount of O_{2}-free water into the solution, dry nitrogen was first bubbled through a container of distilled water
and then into the solution for one hour. The solid was very dark. It was isolated by filtration, washed with dry nitromethane, and dried in vacuo. The ESR spectrum of the polycrystalline solid showed a Mo(V) signal, but no free radical signal was observed. Anal. Found: C, 15.20; H, 4.55; N, 14.65. No reasonable formula could be devised for this analysis; in view of the procedure followed during the reaction, the product is probably a mixture.

(5) Preparation of Mo(V)-oxine complexes

In view of the interest in and importance of (vide infra) Mo(V)-oxine complexes as model compounds for biological processes, it was desired that a suitable Mo(V)-oxine complex be prepared and reacted with phenazine.

Bishop\textsuperscript{138} reported that MoOCl(oxine)\textsubscript{2} was prepared by mixing an acetone solution of MoCl\textsubscript{5} with an acetone solution of 8-hydroxyquinoline. This procedure was followed; dry acetone was used. All work was done in a glove bag. The acetone solution of MoCl\textsubscript{5} was reddish-brown and contained a large amount of insoluble material; both the color and the presence of the insoluble material were probably caused by the poor quality of the available MoCl\textsubscript{5} (vide supra). The solution was filtered before it was mixed with the oxineH solution. The green product was removed by filtration, washed with dry acetone until the washings were no longer reddish-brown, and dried in vacuo. Anal. Calcd. for MoOCl(oxineH)\textsubscript{2} (C\textsubscript{27}H\textsubscript{25}ClMoN\textsubscript{5}O\textsubscript{5}): C, 54.15; H, 3.53; N, 7.02. Found: C, 54.10; H, 3.50; N, 6.94. When an attempt was made to dissolve the product in nitromethane, a mixture of black and yellow solids in a green solution was obtained. The material is probably a mixture.
Since a pure product could not be obtained with MoCl₄⁻,
Et₄NMOCl₄·H₂O was used as a starting material. In a glove bag, 2.18 g
(5.40 mmol) of Et₄NMOCl₄·H₂O was added to 120 ml of absolute ethanol.
The solution was stirred until saturated, filtered, and added to a
solution of 2.382 g (16.3 mmol) of oxineH in 40 ml absolute ethanol.
A deep violet solution formed immediately. Upon filtration, a deep
violet (almost black) solid was obtained. It was washed with absolute
ethanol and dried in vacuo. Anal. Calcd. for MoO₂Cl(oxineH)₂
(C₁₈H₁₄ClMoN₂O₅): C, 47.65; H, 3.11; N, 6.17. Found: C, 48.14; H, 3.22; N,
6.07. The product yield was poor in the above reaction. An attempt
was made to increase the yield by adding the oxineH solution to solid
Et₄NMOCl₄·H₂O, but a mixture of product and hard lumps of starting
material resulted. The product apparently formed as a coating on
particles of starting material and prohibited further reaction.

It was found that Et₄NMOCl₄·H₂O is much more soluble in
acetone than in ethanol; the reaction of Et₄NMOCl₄·H₂O with oxineH was
then carried out in acetone. In 50 ml of acetone was dissolved 1.93 g
(4.80 mmol) of Et₄NMOCl₄·H₂O. The emerald green solution was filtered
and added to a solution of 1.384 g (9.54 mmol) of oxineH in 10 ml of ace­
tone. The resulting dark green solution was filtered to remove the
immediate precipitate (probably Et₄NCl) and placed in an ice-water bath
for several hours. The dark green crystalline product which formed was
isolated by filtration, washed with acetone, dried in a stream of dry
nitrogen, and finally dried in vacuo. Anal. Calcd. for MoO₂(oxine)
(C₂₀H₂₆MoN₂O₂): C, 39.69; H, 2.22; N, 5.15. Found: C, 40.19; H, 2.20;
N, 5.44.
The reaction of $\text{MoO}_2\text{Cl(oxineH)}_2$ with phenazine

It was thought that, of the oxine complexes obtained above, the complex $\text{MoO}_2\text{Cl(oxineH)}_2$ would have the greatest tendency to produce a free radical (vide infra). A solution of 0.343 g (1.90 mmol) of phenazine in 40 ml of dry nitromethane was added to a flask containing 0.862 g (1.90 mmol) of $\text{MoO}_2\text{Cl(oxineH)}_2$. The resulting deep violet solution was stoppered and stirred for two hours; during this time the color of the solution became dark green, and a light green solid precipitated. The solution was allowed to stand for twelve hours. The light green material was then removed by filtration, washed with a small amount of dry nitromethane, dried in a stream of dry nitrogen, and finally dried in vacuo. The ESR spectrum of the polycrystalline solid consists of an intense Mo(V) signal and a weak free-radical signal (vide infra). Anal. Calcd. for $\text{MoOCl(oxine)}_2$ ($C_{18}H_{12}ClMoN_2O_3$): C, 49.62; H, 2.76; N, 6.43. Found: C, 49.39; H, 2.70; N, 6.86. The color of the filtrate slowly changed from dark green to amber, then red, and finally deep red (wine-colored) upon prolonged (one week) exposure to the atmosphere. The solution was then saturated with dry HCl gas, and a red (about the color of Fe$_2$O$_3$) solid precipitated immediately. The product was isolated by filtration, washed with dry nitromethane, dried in a stream of dry nitrogen, and then dried in vacuo. Exposure to the atmosphere was kept at a minimum. The ESR spectrum of the polycrystalline solid showed a strong Mo(V) signal and a very weak free-radical signal. Anal. Calcd. for $\text{MoO}_2\text{Cl} \cdot 2\text{P} \cdot \text{H}_2\text{O}$ or: (PH)$_2\text{MoO}_3\text{Cl}$ ($C_{24}H_{16}ClMoN_4O_3$): C, 53.20; H, 3.35; N, 10.34. Found: C, 53.80; H, 3.33; N, 10.69.
D. Analyses and Physical Measurements

Carbon, hydrogen and nitrogen analyses were carried out by Mr. R. L. Seab, a staff member in the LSU Department of Chemistry. Samples containing nitrogen were analyzed by means of a Perkin-Elmer Model 240 Elemental Analyzer; samples containing no nitrogen were determined by the use of a Coleman Model 33 Carbon-Hydrogen Analyzer (Coleman Instruments Corp., Maywood, Ill.).

Analyses for uranium, molybdenum and chlorine were conducted by Galbraith Laboratories, Inc., Knoxville, Tenn.

Electronic spectra in the 4,000–50,000 cm$^{-1}$ region were recorded by means of a Cary Model 14 recording spectrophotometer. Solid samples were mulled with Nujol or Kel-F polymer oil. For most samples, grinding the specimen was not necessary; it was merely mixed with the mulling agent. This treatment minimized the possibility of sample decomposition due to grinding. Grinding was done only if light scattering was severe; light scattering was a problem usually only at higher energies (> 20,000 cm$^{-1}$). Filter paper has been used as a support for mulls (the mull is smeared on the filter paper, and a reference of filter paper impregnated with mulling agent is used) with good success. This technique was found to be useful over the wavelength range 200–1700 µm ($\approx$ 30,000–6000 cm$^{-1}$) but presented some problems in the region 4000–6000 cm$^{-1}$. In the first place, filter paper absorbs or reflects rather strongly in this region, and the slits were fully open over much of the range 4000–5000 cm$^{-1}$. Also, spurious bands were noted in this region in the spectra of some samples. Finally, it was noted that in some instances the filter paper in the sample beam actually became charred. This charring was apparently caused by the radiation that strikes the sample before
it enters the monochromator (in this wavelength region). As a result, radiation having a wide range of wavelengths strikes the sample that is exposed to a large amount of energy. The problem is aggravated by samples which absorb strongly in the near-infrared region. Several types of papers were tested in attempts to overcome these problems, but none was completely satisfactory. Best results were obtained by placing the mull between plates of quartz or Suprasil No. 2 and clamping the assembly between brass plates which were suspended in a quartz optical dewar. For some spectra, a spacer consisting of a loop of nichrome wire of appropriate gauge was placed between the plates in order to adjust the thickness of the sample. This arrangement permitted mulls of air-sensitive compounds to be prepared (and placed in the optical dewar) in the dry box, so that these specimens were completely protected from air and moisture until spectral measurements were completed. Spectra at 77° K were obtained by merely opening the dewar and filling it with liquid nitrogen. The entire sample was immersed in liquid nitrogen; no interference from nitrogen bubbles was noted. The reference for solid samples was air; neutral density screens were used to attenuate the reference beam. The slit control was adjusted so that the slits were never fully open; the period control was also used to minimize noise introduced by increasing the slit control setting.

When possible, quartz cells of 1 mm or 1 cm path length were used to obtain electronic spectra of solutions. Solvent bands were eliminated by means of a matched cell filled with solvent in the reference beam. Glasses were obtained by immersing a 1 cm cell filled with an EPA (ethyl ether-isopentane-ethanol in volume ratio of 5:5:2) solution in an optical dewar filled with liquid nitrogen. In some
instances, a cell of very small path length was required. This was achieved by assembling a "sandwich" consisting of a Teflon or polypropylene spacer between two quartz or Suprasil No. 2 plates; this "sandwich" was mounted between brass plates and suspended in an optical dewar. Leakage was usually quite severe and spectra were obtained very tediously; the solution could, however, be frozen in liquid nitrogen.

A Beckman IR 7 or Perkin-Elmer Model 180 infrared spectrophotometer was used to measure infrared spectra in the region 4000-650 cm\(^{-1}\). Spectra in the range 650-300 cm\(^{-1}\) were obtained by means of a Beckman IR 10 or Perkin-Elmer Model 180 instrument. Solids were mulled, or they were pressed into pellets. Nujol or hexachlorobutadiene was the dispersion agent for mulls, which were pressed between salt plates; in the case of air-sensitive compounds, these manipulations were done in the dry box. Pellets were made with spectrographic grade KBr which had been heated in a muffle furnace for four hours at 540\(^\circ\)C, cooled under vacuum (< \(1\) mm) for two hours, and stored in the dry box. Air-sensitive compounds were placed in a dental amalgamator capsule (for grinding the sample) in the dry box. Solutions for infrared analysis were placed in variable-path length cells with Teflon spacers and KBr or CsI windows.

A Dupont Model 900 Thermal Analyzer was used to obtain DTA curves and was used in conjunction with a Dupont Model 950 Thermogravimetric Analyzer for TGA studies. A nitrogen flow was used to protect all samples from air during thermal analyses.

Electron spin resonance spectra were recorded by means of a JEOLCO ESR Spectrometer, Model JES-3BS-X; 100-kc modulation was used. The magnetic field was measured with an NMR precision gaussmeter.
Polycrystalline solids were loaded into 5 mm O.D. quartz tubes. Air-sensitive samples were placed in the tubes in the dry box, and pressure caps were used to prevent leakage of air into the tube. Acid solutions were prepared in a glove bag; dry, degassed solvents (vide supra) were used. Sample tubes were pyrex; small diameter tubes were used to minimize solvent dielectric losses. The diameter of the tube varied with the solvent used: 1 mm (O.D.) for methanol, 2 mm for dimethylsulfoxide, and 3 mm for acetonitrile. Microwave power was maintained below the saturation level. The modulation width that was used was less than one-half the signal width (peak to peak extrema) to prevent signal distortion. Scanning speed and response time were adjusted in such a manner that both signal fidelity and good signal-to-noise ratio were maintained. 148

Raman spectra were obtained by means of a JEOLCO JRS-S1 Laser Raman Spectrophotometer equipped with an Argon-Ion Laser manufactured by Coherent Radiation. Two exciting lines were available: 4880 Å (20492 cm⁻¹) and 5145 Å (19136 cm⁻¹). The polycrystalline samples were placed in melting-point capillaries.

Mass spectra were recorded by means of a Varian Model M-66 mass spectrometer.

A Varian A-60 A or a Varian HA-100 NMR Spectrometer was used to obtain nuclear magnetic resonance spectra.

Magnetic susceptibilities were measured by means of the Gouy method. The apparatus was an Ainsworth type BCT balance equipped with an Alpha Scientific Lab., Inc., Model A17500 electromagnet. A current of 3 amperes was supplied by a power supply that has variable output; the magnetic field was approximately 6000 gauss. The sample
(polycrystalline powder) was placed in a double-ended pyrex tube.\textsuperscript{149}

The tube was equipped with a ground-glass joint for the protection of air-sensitive samples and was suspended from the balance by a plastic cord. The tube and cord were enclosed in a larger pyrex tube for protection for air currents. The apparatus was calibrated with HgCo(SCN)\textsubscript{4},\textsuperscript{149,151,152} Experimental values were corrected for the diamagnetism of the ligands and metal.\textsuperscript{149,151,152}
CHAPTER III

THEORETICAL, SPECTRAL AND CHEMICAL STUDIES OF THE UOCl\textsubscript{5}\textsuperscript{2-} SPECIES

Although he obtained room-temperature spectra in the 4-25 kK region for solid UOX\textsubscript{5}\textsuperscript{2-} (X\textsuperscript{-} = F\textsuperscript{-}, Cl\textsuperscript{-}, Br\textsuperscript{-}) compounds, Ryan\textsuperscript{22} was understandably reluctant to attempt to assign the observed bands (Figure 5). Although the observed spectra and the 5f\textsuperscript{1} theory for the O\textsubscript{h} species UX\textsubscript{6}\textsuperscript{-} (X\textsuperscript{-} = F\textsuperscript{-}, Cl\textsuperscript{-}, Br\textsuperscript{-}) are now (vide supra) in satisfactory agreement, there was no theoretical model available for the lower symmetry UOX\textsubscript{5}\textsuperscript{2-} species. In the following calculation, therefore, the necessary "tetragonal" splittings have been introduced specifically for UOCl\textsubscript{5}\textsuperscript{2-}.

A. Theory

It is observed that the spread of the f-f transitions of hexacoordinated U(V) ions is approximately 11,000 cm\textsuperscript{-1} and that the spin-orbit splitting parameter, \(\zeta\), is approximately 2000 cm\textsuperscript{-1} (hence smaller than the crystal field effects).\textsuperscript{5,136} In the case of species that have field symmetry lower than O\textsubscript{h}, it is reasonable to plot an energy diagram which starts from the 5f\textsuperscript{1} energy levels split by the octahedral "crystal field" and by "spin-orbit coupling" and is perturbed by the effects of the lower symmetry field.

In the equations that follow, \(\Delta\) and \(\Theta\) are the terms of Reisfeld and Crosby\textsuperscript{130} (see Figure 6a), and \(a_{2u}\) (non-bonding), \(t_{2u}\) (\(\pi\)-antibonding) and \(t_{1u}\) (\(\sigma\) and \(\Pi\) antibonding) (Figure 6a) are the irreducible
FIGURE 5. The Electronic Spectrum of Solid (Et₄N)₂UOCl₂ in Nujol Mull at Ambient Temperature.
FIGURE 8. The $f^{1}$-Orbital Energy Levels Perturbed by
(a) the $O_{h}$ Field (Where the $\Delta$ and $\theta$ Values are
those of UC$_{1}Cl_{6}$ and $\zeta$=1770 cm$^{-1}$); (b) the $O_{h}$ Field Plus Spin-Orbit Coupling (Where
the Separations are Those of UC$_{1}Cl_{6}$); (c) the $D_{4}$ Field Plus Spin-Orbit Coupling (Where the
Experimental Separations are Those of UC$_{1}Cl_{6}$); and
(d) the Calculated Energies of the Several Levels
Assuming $\tau$=700 cm$^{-1}$ and $\zeta$=1770 cm$^{-1}$.
representations of the seven f orbitals in $O_h$ symmetry; the appropriate secular determinants after simultaneous diagonalization of both the crystal field and the spin-orbit interactions are $^{153}$ (see Figure 6b and Chapter I)

$$\begin{align*}
\Gamma_4 & \quad \left| \begin{array}{cc}
\Delta + \frac{3}{4} \zeta - W_e & \frac{3 \sqrt{5} \zeta}{4} \\
\frac{3 \sqrt{5} \zeta}{4} & \Delta + \theta - \frac{3}{4} \zeta - W_e
\end{array} \right| = 0 \quad (24) \\
\Gamma_7 & \quad \left| \begin{array}{cc}
-W_\gamma & \sqrt{3} \zeta \\
\sqrt{3} \zeta & \Delta - \frac{1}{2} \zeta - W_\gamma
\end{array} \right| = 0 \quad (25) \\
\Gamma_6 & \quad \left| \begin{array}{cc}
\frac{3}{2} \zeta + \Delta + \theta - W_e
\end{array} \right| = 0 \quad (26)
\end{align*}$$

From equation (25) it can be seen that the $\Gamma_7' - \Gamma_7$ transition energy depends only upon $\zeta$ and $\Delta$. Therefore, one may obtain from (25)

$$\Delta W(\Gamma_7 \rightarrow \Gamma_7') = \sqrt{(\Delta - \frac{1}{2} \zeta)^2 + 12 \zeta^2} \quad (27)$$

Setting the left side equal to 6790 cm$^{-1}$ $^{136}$ and $\zeta$ equal to 1770 cm$^{-1}$, one obtains $\Delta$ as 3810 cm$^{-1}$ and $W(\Gamma_7) = -1940$ cm$^{-1}$; $\Gamma_7$ is the ground state and the zero of energy of the manifold of spin-orbit split levels in $O_h$ symmetry (Figure 6b). It should be noted, however, that $\Delta$ is actually quite poorly determined because small variations in $\zeta$ lead to large variations in the estimated value of $\Delta$ (but not of $\theta$; vide infra). This may be seen from the values summarized in Table VII.

Using the $\zeta$ value of 1770 cm$^{-1}$ and its corresponding $\Delta$ value of 3810 cm$^{-1}$ and solving eq. (26), after putting in 11,520 cm$^{-1}$ $^{136}$ for the $W(\Gamma_6)$, one obtains $\theta$ as 3110 cm$^{-1}$. Next, eq. (24) is solved for
<table>
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the two $\Gamma_{\alpha}$ levels and the transitions specifically for UC1$_5^-$ are then calculated to be $\Delta W(\Gamma_{\alpha} \rightarrow \Gamma_{\gamma}) = 3820$ cm$^{-1}$ and $\Delta W(\Gamma_{\beta} \rightarrow \Gamma_{\gamma}) = 9910$ cm$^{-1}$.

These values are to be compared with the experimental values$^{136}$ of 3800 and 9910 cm$^{-1}$, respectively. Although there is actually quite a large variation of $\Delta$ with small variations in $\zeta$, nevertheless the spectrum is adequately described.$^{154}$

The true octahedral ground-state wave function is

$$\psi = a \psi(\Gamma_{\gamma}) - b \psi(\Gamma_{\gamma}')$$

and evaluating the $g$ factor (spectroscopic splitting factor$^{148}$) leads to$^{153}$

$$g = 2(a^2 + l\sqrt{3} ab)$$  \hspace{1cm} (29)

Introducing "tetragonal" splittings will add three terms to the Hamiltonian in addition to the "octahedral" terms$^{153}$

$$V = \tau V_2^0 + \gamma V_4^0 + \delta V_6^0$$  \hspace{1cm} (30)

Here, $\tau$, $\gamma$, and $\delta$ are parameters which depend on the radical functions, and $V_2^0$, $V_4^0$, and $V_6^0$ transform like the spherical harmonics of order 2, 4, and 6, respectively.

Since little information is available, and $\Delta$ and $\theta$ were poorly determined, it is of course not possible to evaluate $\tau$, $\gamma$, and $\delta$. Therefore, only the term in $V_2^0$ is retained, and thereby the full "tetragonal" Hamiltonian is truncated. Hence all of the tetragonal effects are "lumped" together into one parameter. This aggregation of terms means again that the calculation can only be illustrative, and no efforts can be or should be made to attempt to get exact numerical fits.

The values $\zeta = 1770$ cm$^{-1}$, $\Delta = 3810$ cm$^{-1}$, and $\theta = 3110$ cm$^{-1}$ are taken to be representative and are substituted into the following
tetragonal determinants:

$$\begin{vmatrix}
\Delta + \theta + 2\tau - \frac{3}{2}\zeta - W_7 & \frac{3}{4}\sqrt{2} + \sqrt{5}\tau & \sqrt{10}\tau & 0 \\
\frac{3}{4}\sqrt{2} - \sqrt{5}\tau & \Delta + \frac{3}{2}\zeta - W_7 & 0 & 0 \\
- \sqrt{10}\tau & 0 & \Delta - \frac{3}{2}\zeta - W_7 & \sqrt{3}\zeta \\
0 & 0 & \sqrt{3}\zeta & -W_7
\end{vmatrix} = 0 \quad (31)$$

$$\begin{vmatrix}
\Delta + \theta - 2\tau - \frac{3}{2}\zeta - W_6 & \frac{3}{2}\sqrt{2} + \sqrt{5}\tau & 2\sqrt{2}\tau \\
\frac{3}{2}\sqrt{2} + \sqrt{5}\tau & \Delta + \frac{3}{2}\zeta - W_6 & \sqrt{10}\tau \\
2\sqrt{2}\tau & \sqrt{10}\tau & \Delta + \theta + \frac{3}{2}\zeta - W_6
\end{vmatrix} = 0 \quad (32)$$

The determinants were solved by means of a standard computer program for matrix diagonalization. The results are plotted in Figure 7 for the values of \( \tau = 0-1400 \text{ cm}^{-1} \). Examination of Figure 7 reveals with regard to the excited states of a "tetragonal" \( f^1 \) complex that

1. the \( \Gamma_7' - \Gamma_7 \) transition is nearly unaltered,
2. the \( \Gamma_6 \) and the \( \Gamma_6' \) levels are significantly split,
3. the \( \Gamma_6 \) energy is moved to much higher energy, and
4. there is a very low-lying electronic band. A fifth prediction is that the average \( g \) value should vary only slightly as the symmetry is lowered. All of these predictions are fulfilled, and the results will be described in the following section.

B. Results and Discussion of Spectral Studies

The absorption spectrum of solid \((\text{Et}_4\text{N})_2\text{UOCl}_5\) has been measured in the visible, near-I.R. and I.R. regions (300-25000 cm\(^{-1}\)). The
FIGURE 7. The Splitting of the 5f Manifold of $O_h$ Energy Levels With Increasing Lower Symmetry ($D_4$) Field.
electronic and vibronic band assignments are tabulated in Table VIII. The bands above 6000 cm\(^{-1}\) are taken from the \(77\)° K spectrum (4000-1/000 \(\AA\)) of solid (Et\(_4\)N)\(_2\)UOCl\(_5\) (in Nujol mull) that is shown in Figure 8. The strongest peaks are assigned to the pure electronic (0-0) transitions, and the vibronic bands, most of which, expectedly, are found on the high-energy side of the 0-0 band, are listed along with their separations from the 0-0 band. The two lowest-energy transitions are taken from I.R. and near-I.R. spectra (vide infra). Other bands in the UOCl\(_5^{2-}\) spectrum, not directly attributable to the organic cation, to small amounts of H\(_2\)O or to trace amounts of U(IV), are found at 1740, 917, and 818 cm\(^{-1}\). Each pertinent band in the absorption spectrum of UOCl\(_5^{2-}\) will now be considered; the lowest-energy bands will be considered first.

1. The 818 and 917 cm\(^{-1}\) bands

Ryan\(^{22}\) found two strong, narrow bands at 813 and 913 cm\(^{-1}\) for (Et\(_4\)N)\(_2\)UOCl\(_5\), and he stated that they were both "apparently due to uranium-oxygen vibrations" (see Figure 9 and Table 4). The existence of two such bands for the U=O linkage is somewhat difficult to understand, however. Theoretical and experimental studies for a number of analogous compounds have shown that only one vibration, i.e., the \(\nu_1(A_{1g})\), can have a frequency high enough to occur in the NaCl region. These compounds include (Et\(_4\)N)\(_2\)PaO\(_5\) (X = Cl, Br), 830-840 cm\(^{-1}\);\(^{41}\) M\(_2\)NpOCl\(_5\) (M = Cs, Ph\(_4\)As), 907-921 cm\(^{-1}\);\(^{155}\) Cs\(_2\)ReO\(_5\) (X = Cl, Br), 951-956 cm\(^{-1}\);\(^{156,157}\) M\(_2\)M'OX\(_5\) (M = Et\(_4\)N, Rb, Cs; M' = Nb, Cr, Mo, W; X = Cl, Br), 922-977 cm\(^{-1}\);\(^{158,159}\) and IO\(_5\), 927 cm\(^{-1}\).\(^{160}\)
### TABLE VIII

**THE ELECTRONIC AND VIBRONIC BANDS FOUND FOR \((\text{Et}_4\text{N})_2\text{UOCl}_5\)**

<table>
<thead>
<tr>
<th>Assignment in (D_4) Symmetry(^{(a)})</th>
<th>0-0 Transition</th>
<th>Vibronic Bands</th>
<th>Separation from 0-0</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Gamma_7 \to \Gamma_e(\Gamma_6))</td>
<td>1555(^{(b)})</td>
<td>(\Gamma_7(\Gamma_6)) 5030, 5060</td>
<td></td>
</tr>
<tr>
<td>(\Gamma_7 \to \Gamma_7(\Gamma_7'))</td>
<td>6161vs</td>
<td>5981w</td>
<td>6254s 180</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5935w</td>
<td>6406m 226 245</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(6496)</td>
<td>333</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6623w</td>
<td>462</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(6711)</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6969</td>
<td>808</td>
</tr>
<tr>
<td>(\Gamma_7 \to \Gamma_6(\Gamma_6'))</td>
<td>8584vs</td>
<td>(8475)</td>
<td>8696s 109 112</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(8826)</td>
<td>242 289</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8873m</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>8264w</td>
<td>320 329</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(8913)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7764w</td>
<td>820 814</td>
</tr>
<tr>
<td>(\Gamma_7 \to \Gamma_7(\Gamma_6'))</td>
<td>10616vs</td>
<td>(10834)</td>
<td>218</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11442m</td>
<td>826</td>
</tr>
<tr>
<td>(\Gamma_7 \to \Gamma_6(\Gamma_6))</td>
<td>16835vs</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{(a)}\) The symbol in parentheses represents the irreducible representation of the \(Q_h\) molecular species \(\text{UCl}_6^-\).

\(^{(b)}\) This band was taken from room temperature I.R. spectra obtained by means of a Beckman IR-7; all others are taken from spectra obtained at 77\(^{\circ}\)K by means of a Cary 14.
FIGURE 3. The $^{17O}$K Electronic Spectrum of Solid $\text{Et}_2\text{N}_2\text{UOCl}_6$ in Nujol Mull.
FIGURE 3. The Infrared Spectrum of $\text{(Et}_4\text{N)}_2\text{UOCl}_5$ in (a) Nujol Mull and (b) KBr Pellet. Bands Marked "x" are Due to Nujol; Those Marked "c" are Due to $\text{Et}_4\text{N}^+$ Cation.
Several other possible explanations for the existence of these two bands have been considered. It was first thought that one of the bands might somehow arise from the organic cation. The infrared spectrum (Figure 10) of the cesium salt, Cs₂UOCl₆, contains both of the bands, however, and they are identical in appearance with those in the spectrum of the tetraethylammonium salt (Figure 9). Furthermore, the infrared spectra of Et₄NCl and of (Et₄N)₂UCl₆ were recorded and were found to contain no bands at these frequencies. The possibility that one of these two bands might be due to the lowest-energy electronic transition, \( \Gamma_7 \rightarrow \Gamma_e(\Gamma_0) \) (Figures 6 and 7) was also considered but was rejected for two principal reasons. First, the intensity, width, and overall appearance of the two bands are very similar and are typical of vibrational bands. Also, the observed shift of the bands with change of halogen is not what would be expected for electronic bands. The order of the observed frequencies is F⁻ < Cl⁻ < Br⁻ (Table IV); the reverse order would be expected in the case of electronic bands (on the basis of ligand field strengths), and this reverse order is observed in the case of bands found in the visible and near-infrared regions.²²

It was then proposed that the band at 917 cm⁻¹ might be the U=O stretching mode in the ground (electronic) state, and that the 818 cm⁻¹ band might be the U=O stretching frequency in the first excited (electronic) state. It was further suggested that the first excited electronic state (of very low energy; vide supra, Figure 7 and Table 8) might be sufficiently populated (during infrared analysis) by infrared radiation; commercial infrared spectrophotometers are so constructed that the radiation (consisting of a wide range of wavelengths) passes through the sample before dispersion by the monochromator. This
FIGURE 10. The Infrared Spectra of (a) Nujol, (b) Cs$_2$UOCl$_3$ in Nujol Mull, and (c) Cs$_2$UOCl$_3$ in KBr Pellet.
hypotheses was tested (and disproved) by means of the following experiment. A Nujol mull of \((\text{Et}_4\text{N})_2\text{UOCl}_5\) was pressed between salt plates, and the spectrum in the region 750-950 cm\(^{-1}\) (Figure 9) was recorded. The monochromator was then set at 865 cm\(^{-1}\) (point of maximum transmittance in this region) and a variable density beam attenuator was placed in the sample beam between the source and sample. The attenuator was adjusted so that the transmittance was reduced by 50\%, and an identical device was placed in the reference beam to restore the pen to its original position; thus each beam was attenuated by 50\%. The spectrum was again recorded; there was no change in the intensity of either band. This procedure was then repeated; the intensity of both beams was reduced to 25\% of the original intensity, but there was still no change in the intensity of either band. If one band were caused by population of an excited electronic state, then a change in the relative intensities of the bands would have been observed.

The idea that the existence of these two bands might be due to a peculiarity of the crystal structure (dimeric unit, etc.) was also investigated. Several attempts were made to obtain solution (nitromethane) spectra of \((\text{Et}_4\text{N})_2\text{UOCl}_5\). These were unsuccessful because of several problems, including rapid disproportionation of the compound in solution. Solutions of \(\text{UOCl}_5^{2-}\) can be stabilized somewhat by the addition of excess chloride;\(^{22}\) this stabilization was not done, however, because tetraethylammonium bands at \(~790\) cm\(^{-1}\) and \(~800\) cm\(^{-1}\) would interfere with the band at \(818\) cm\(^{-1}\) (\textit{vide supra}, Figure 9). Another problem is the low solubility of \((\text{Et}_4\text{N})_2\text{UOCl}_5\) in suitable solvents, such as nitromethane. In the case of a saturated nitromethane solution of \((\text{Et}_4\text{N})_2\text{UOCl}_5\), the solute bands did not have adequate intensity to be
useful. The cell path length could not be increased because of interference from a solvent band at 918 cm⁻¹.

It was first thought that a clue to the reason for the existence of the two bands could be drawn from a comparison of the infrared spectra of (Et₄N)₂UOCl₅ in Nujol mull and in a KBr pellet (Figure 9). The 818 cm⁻¹ band is present in the Nujol mull spectrum (Figure 9a) but not in that of the KBr pellet (Figure 9b). The spectrum of the cesium salt (Figure 10) exhibits both bands in both media, however. It appears, then, that the tetraethylammonium salt underwent disproportionation during the grinding and pressing of the pellet; the uranyl ion, UO₂²⁺, has a strong band at ~ 920 cm⁻¹ and a very weak band at ~ 820 cm⁻¹,¹⁶¹ and these are evidently the bands observed in Figure 9b. It was suggested¹⁶² that the single U=O stretch frequency might be split by site symmetry. This splitting cannot be unequivocally rejected, but it is then strange that this same kind of mechanism does not operate in any of the analogous complexes of Nb(V), Cr(V), Mo(V), W(V), Re(V), Pa(V), and Np(V). Another possibility is that the complex is polymeric and contains both terminal and bridging oxygens. The niobium complex NbOCl₃, which is known to contain bridging oxygens,¹⁶³ has a very sharp intense peak at 767 cm⁻¹ that is due to the M-O-M vibration.¹⁵⁹ This idea, of course, is subject to the same objection as the "site symmetry" hypothesis. Thus there is no firm explanation at present for the appearance of two strong bands in this spectral region.

The higher-frequency band can, however, be tentatively assigned to the U=O stretching frequency. Evidence for this assignment follows. (1) The infrared spectrum of U₂O₅ ⁵₄ exhibits a band at 916 cm⁻¹ which can be assigned to the same vibration. (2) The 77⁰ K electronic spectrum
of (Et,N)UOCl. (Figure 8) contains vibronic bands (Table VIII) which are without question due to the UO\textsuperscript{5+} entity and are located ± ~ 820 cm\textsuperscript{-1} from the pure electronic (0-0) band. The M=0 stretch in the ground state is more probably 917 cm\textsuperscript{-1} than 818 cm\textsuperscript{-1}. The M=0 stretching frequencies of the analogous complexes of Nb(V), Cr(V), Mo(V), W(V), Re(V), and Np(V) (vide supra) are all much closer to 917 cm\textsuperscript{-1} than to 818 cm\textsuperscript{-1}.

2. The 1555 cm\textsuperscript{-1} band

This band was discovered in the spectrum of the cesium salt (Figure 11c), although it is also present in the spectrum of the tetraethylammonium salt (Figure 11b). The band is not clearly seen in the spectrum of the tetraethylammonium salt, however. This obscuration is presumably due to interference from the large cation band at ~ 1460 cm\textsuperscript{-1}. In order to observe the band at 1555 cm\textsuperscript{-1}, it was necessary to use a mull with a consistency approximately equal to that of mulls for electronic spectra in the visible-near I.R. regions (more concentrated than mulls for vibrational spectra).

This band can now tentatively be assigned as the lowest energy, \( \Gamma_7 \rightarrow \Gamma_6(\Gamma_8) \), transition. This band is seen (Figure 6) to fit fairly well with the theoretical prediction for \( \tau = 700 \) cm\textsuperscript{-1} and \( \zeta = 1770 \) cm\textsuperscript{-1}, but it should be emphasized that the numerical fit is not as significant as the adherence to the general prediction (number 4) of the model presented above, that there should be a very low-lying electronic band.

It should be noted that a weaker band can be seen (Figure 11) at ~ 1740 cm\textsuperscript{-1}; this may be a combination band (818 + 917 = 1737 cm\textsuperscript{-1}).
FIGURE 11. The Infrared Spectrum of (a) Nujol, (b) (Et₄N)₂UOCl₂ in Nujol Mull, and (c) Cs₂UOCl₂ in Nujol Mull in the Region of the 1595 cm⁻¹ Band.
3. The 5000 cm\(^{-1}\) region

A careful search of the UOCl\(_5^{2-}\) spectrum was conducted throughout the 4000-\(\sim\)5000 cm\(^{-1}\) region. A number of bands were found in this region in the spectrum of the tetraethylammonium salt, but these bands are not present in the spectrum of the cesium salt and are, no doubt, due to the organic cation. The only bands in this region in the spectrum of Cs\(_2\)UOCl\(_5\) are located at \(\sim\)5000 cm\(^{-1}\) (Figure 12a); a similar pattern is exhibited by (Et\(_4\)N)\(_2\)UOCl\(_5\) (Figure 12b). The assignment of spectral bands in this region is complicated by the fact that the strongest bands in the electronic spectrum of the U(IV) complex, UC\(_{16}^{2-}\), occur in this region (Figure 12c). This U(IV) complex is present as an impurity in UOCl\(_5^{2-}\) salts because of slight disproportionation during preparation. It should be noted in Figure 12 that the U(IV) bands are present as a doublet at approximately 5120 and 4960 cm\(^{-1}\) in pure (Et\(_4\)N)\(_2\)UC\(_{16}\) and in both UOCl\(_5^{2-}\) salts. The UOCl\(_5^{2-}\) salts contain additional bands not found in the UC\(_{16}^{2-}\) complex, however. The tetraethylammonium salt has two prominent sharp peaks at 5060 and 5030 cm\(^{-1}\), whereas the cesium salt exhibits only one, somewhat broader band at 5070 cm\(^{-1}\). It was suggested\(^{162}\) that these additional bands are also due to uranium(IV); the center electronic peak is weak in a pure UC\(_{16}^{2-}\) salt (the two bands observed are a vibronic pair) but is greatly intensified by removing the center of symmetry of the ion by hydrogen bonding, impurities, or other effects.\(^{184}\) The following evidence militates against this view, however. The cesium salt is known to be more severely contaminated with U(IV) than is the tetraethylammonium salt (Chapter II), but the 5070 cm\(^{-1}\) peak of Cs\(_2\)UOCl\(_5\) is weaker, relative to the U(IV) bands, than are the 5060 and 5030 cm\(^{-1}\)
FIGURE 12. The 77\textdegree K Near-Infrared Spectrum (5000 cm\textsuperscript{-1} Region) of (a) Cs\textsubscript{2}UOCl\textsubscript{5}, (b) (Et\textsubscript{4}N)\textsubscript{2}UOCl\textsubscript{5}, and (c) (Et\textsubscript{4}N)\textsubscript{2}UCI\textsubscript{5} in Kel-F Oil Mull.
bands of \((\text{Et}_4\text{N})_2\text{UOCl}_5\). Thus the band at \(\sim 5010\) cm\(^{-1}\) is tentatively assigned to the second transition, \(\Gamma_7 \rightarrow \Gamma_7(\Gamma_{11})\) (Figure 5).

4. The 6161 cm\(^{-1}\) band

This band is assigned to the \(\Gamma_7 \rightarrow \Gamma_7(\Gamma_{7}')\) in \(O_h\) transition. The pure electronic (0-0) band at 6161 cm\(^{-1}\) is only 635 cm\(^{-1}\) lower than the \(\Gamma_7 \rightarrow \Gamma_7'\) transition in \(O_h\) and thus bears out the prediction (number 1 in Theory Section) that this transition is left relatively unaltered by the lower symmetry (Figure 7). It has associated with it vibronic components, one of which, namely, that 308 cm\(^{-1}\) from the 0-0 line, is undoubtedly due to the \(U=0\) stretching frequency. Ryan\(^{22}\) recorded the far-I.R. spectrum of \((\text{Et}_4\text{N})_2\text{UOCl}_5\) and found bands at 120 and 253 cm\(^{-1}\); the latter more intense band had weak, narrow side bands at 296 and 197 cm\(^{-1}\). These four bands are probably to be correlated with the low-energy vibronic bands found (Table VIII) at 93, 226, 245, and 180 cm\(^{-1}\). The 15 normal vibrations of the \(\text{MOX}_5^{2-}\) group can be reduced to the following 11 symmetry types: \(4A_1 + 2B_1 + B_2 + 4E\), and therefore no assignment except the \(U=0\) stretch, \(\nu_1(A_1)\), can be unambiguously made with the information presently available.

It is pertinent to point out just how relatively constant the transition assigned as \(\Gamma_7 \rightarrow \Gamma_7'\) in \(O_h\) is in other \(U(V)\) compounds because this is one of the important conclusions of the theoretical model presented here. In Table IX there are collected all of the compound types the spectra of which have been reported and the frequencies (cm\(^{-1}\)) of their \(\Gamma_7 \rightarrow \Gamma_7'\) (in \(O_h\)) bands.\(^3,8,17,19,22,40,80,113,128,130,138,137,154,169,179\) Although the ligand atoms encompass only halogen and oxygen, the crystal field spread among the listed compounds is certainly
### TABLE IX

**THE $\Gamma_7 \rightarrow \Gamma_7'$ TRANSITION IN VARIOUS U(V) COMPOUNDS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Band Wavenumber</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsUF$_6$</td>
<td>7400(a)</td>
<td>22,130</td>
</tr>
<tr>
<td>MUF$_6$ (M = H, Cs, Li, Na)</td>
<td>$\sim$ 7350</td>
<td>165</td>
</tr>
<tr>
<td>MUF$_5$ (M = K, Rb, NH$_4$)</td>
<td>7050</td>
<td>166</td>
</tr>
<tr>
<td>UF$_6^-$ (in CH$_3$CN)</td>
<td>7386</td>
<td>22</td>
</tr>
<tr>
<td>(NH$_3$OH)UF$_6$</td>
<td>7050</td>
<td>167</td>
</tr>
<tr>
<td>N$_2$H$_6$UF$_7$</td>
<td>6990</td>
<td>167</td>
</tr>
<tr>
<td>Rb$_2$UF$_7$</td>
<td>$\sim$ 6770</td>
<td>168</td>
</tr>
<tr>
<td>Rb$_3$UF$_8$</td>
<td>$\sim$ 6770</td>
<td>168</td>
</tr>
<tr>
<td>K$_3$UF$_8$</td>
<td>6849</td>
<td>169</td>
</tr>
<tr>
<td>UC$_{16}^-$ for several cations</td>
<td>6800 ± 10</td>
<td>5,19,136</td>
</tr>
<tr>
<td>UC$_{15}^-$·TCAC</td>
<td>6760</td>
<td>136</td>
</tr>
<tr>
<td>UC$_{15}^-$·Ph$_3$PO</td>
<td>6880</td>
<td>137</td>
</tr>
<tr>
<td>UC$_{15}^-$·SOCl$_2$</td>
<td>6760</td>
<td>136,137</td>
</tr>
<tr>
<td>UC$_{15}^-$·AlCl$_3$ (vapor)</td>
<td>6605(a)</td>
<td>8</td>
</tr>
<tr>
<td>U$<em>2$Cl$</em>{10}$ (vapor)</td>
<td>6658(a)</td>
<td>8</td>
</tr>
<tr>
<td>UBr$_5$</td>
<td>6710</td>
<td>17</td>
</tr>
<tr>
<td>UBr$_6^-$</td>
<td>6825 (6831)</td>
<td>22,40</td>
</tr>
<tr>
<td>UBr$_5$·Ph$_3$PO</td>
<td>6845</td>
<td>40</td>
</tr>
<tr>
<td>UO$_2^+$</td>
<td>6620</td>
<td>80,170</td>
</tr>
<tr>
<td>[U(OC$_2$H$_5$)$_5$]$_2$</td>
<td>6934</td>
<td>154</td>
</tr>
<tr>
<td>MM$'$$U_2$O$_9$F (M = Na,K,Rb; M$'$ = Sr,Ba; M = K,Tl; M$'$ = Pb)</td>
<td>$\sim$ 7000</td>
<td>113</td>
</tr>
<tr>
<td>Mu$_2$O$_6$ (M = Cd,Mg)</td>
<td>$\sim$ 7000</td>
<td>126</td>
</tr>
<tr>
<td>MUO$_3$ (M = K,Rb, Li, Na)</td>
<td>$\sim$ 7000</td>
<td>126</td>
</tr>
<tr>
<td>Li$_2$UO$_6$</td>
<td>$\sim$ 7000</td>
<td>126</td>
</tr>
</tbody>
</table>

(a) The authors did not assign these bands to the 0-0 transition, but it is now thought$^{22,153}$ that they are indeed that transition.
substantial. In spite of this, the energy of this transition is in
the range \( \psi \pm h \lambda \) cm\(^{-1}\), or, excluding the UF\(_{5}\) values, \( (850 \pm 100 \) cm\(^{-1}\). This constancy helps to explain why the \( \Delta \) and \( \Theta \) values are so
poorly determined and the spin-orbit coupling parameter is so critical
in their determination.\(^{127}\)

5. The bands at 8584 and 10,616 cm\(^{-1}\)

These bands are assigned to the split components of \( \Gamma_{5}'(O_{h}) \)
(Figure 7 and Table VIII). The 2030 cm\(^{-1}\) splitting is interesting.
It has been observed\(^{5}\) that the splitting of the \( \Gamma_{7} \rightarrow \Gamma_{8}' \) transition is
540 \pm 20 cm\(^{-1}\) in the case of UC\(_{6}\)\(^{-}\) in various media (indicating that
the 5f\(^{1}\) system is not at a pure \( O_{h} \) site) and that in the case of lower
symmetry species, such as UC\(_{5}\)\(^{-}\)TCAC and \([\text{U(OEt)}\(_{5}\)]_{2}\), it ranges from 720
to 1490 cm\(^{-1}\). It was also suggested\(^{5}\) that the magnitude of the split­
ting is roughly a measure of the geometrical distortion. This sugges­
tion is confirmed by the following evidence. The splitting in the case
of UF\(_{6}\)\(^{-}\) is \(~ 1050 cm\(^{-1}\) compared with the UC\(_{6}\)\(^{-}\) and UBr\(_{6}\)\(^{-}\) splittings\(^{22}\)
of 480 and 370 cm\(^{-1}\), respectively. The UF\(_{6}\)\(^{-}\) species is known\(^{171}\) to
have lower-than-octahedral symmetry. The geometries of UC\(_{6}\)\(^{-}\) and UBr\(_{6}\)\(^{-}\)
are unknown, but it is likely that the octahedrons are much more nearly
regular in these complexes because the ligands are much larger. The
distortion in the fluoro complex may result from the repulsion of the
small fluoride ions (which have a filled shell and high charge density)
by the lone 5f electron of uranium(V). These ideas receive further
support from ESR spectra, which consist of an unsymmetrical signal in
the case of UF\(_{6}\)\(^{-}\)\(^{32}\) and symmetrical signals in the case of UC\(_{6}\)\(^{-}\)
(Figure 13 and ref. 19) and UBr\(_{6}\)\(^{-}\).\(^{20}\) In this connection, it should be
FIGURE 1. The ESR Spectrum of Solid $\text{Et}_4\text{NCl}_2$ at Ambient Temperature.
noted that the ether complex $\text{UCl}_5\cdot\text{OME}_2$ yields an ESR spectrum (Figure 14) which is very similar to that of $\text{Et}_4\text{NUCl}_6$ and indicates that the field symmetry around the uranium(V) is very nearly regular octahedral. The fact that the splitting of the $\Gamma_8'$ of $\text{UCl}_5^{2-}$ is even greater than that of $\text{UF}_6^-$ accords well with the above suggestion. The distortion of the octahedron in $\text{UCl}_5^{2-}$ is reflected in the asymmetry of the ESR signal of $(\text{Et}_4\text{N})_2\text{UCl}_5$, which is shown in Figure 15. It is interesting to note that the splitting of $\Gamma_8'$ in the case of $\text{UF}_6^-$ ($1050 \text{ cm}^{-1}$) is slightly larger than it is in the case of $\text{UOF}_5^{2-}$ ($980 \text{ cm}^{-1}$).

Both components of the split $\Gamma_8'$ of $\text{UCl}_5^{2-}$ possess vibronic bands (Table VIII), and the most prominent ones ($\sim 820 \text{ cm}^{-1}$) surely arise from the U=O stretch.

6. The band at 16,835 cm$^{-1}$

This last $\Gamma_7 \rightarrow \Gamma_6$ transition has moved to a much higher energy in $\text{UCl}_5^{2-}$ (16,835 cm$^{-1}$) compared with its position in $\text{UCI}_6^-$ (11,540 cm$^{-1}$); this movement is in agreement with the theoretical prediction (number 5 and Figure 7). No vibronic components can be observed; perhaps the broadness of the band may cover the vibronic components. This great width ($\sim 1800 \text{ cm}^{-1}$ at half-height) may result from closely-spaced vibrational levels in the $\Gamma_6$ state.

7. Variation of the $g$-factor

Notice (from eq. 31) that the octahedral $\Gamma_7$ states in the lower symmetry are only coupled weakly to the other lower symmetry $\Gamma_7$ states via $V_{2j}$. Therefore the $g$-factors for the distorted and the
FIGURE 1. The ESR Spectrum of Solid UCl$_{2}$·OMe$_{2}$ at Ambient Temperature.
FIGURE 1. The ESR Spectrum of Solid (Et₄N)₂UOCl₆ at Ambient Temperature.
regular $O_h$ complexes cannot differ very much. To a good approximation one can use the formula for $g$ (octahedral), and with a splitting of $T_g'$ equal to $\sim 2000 \text{ cm}^{-1}$ ($\tau = 600 \text{ cm}^{-1}$), the calculation yields $g = -1.04$. The sign of $g$ is of course not revealed by the experiment, but the $g$-values have been measured in the case of both UC$_6$ (Figure 13) and UOCl$_3^{2-}$ (Figure 15); they are 1.12 and 1.09, respectively, and are in quite excellent agreement with the calculated value.

C. The Ultraviolet Spectrum

The absorption spectrum of $(\text{Et}_4\text{N})_2\text{UOCl}_5$ in Kel-F mull at ambient temperature and at 77°K was measured. The region of the Laporte-allowed transitions (17-50 kK, where 1 kK = 1000 cm$^{-1}$) was observed carefully, and the spectrum is shown in Figure 16. The band positions are tabulated in Table X.

Ryan$^{22}$ obtained but did not publish the electron transfer spectrum of $(\text{Et}_4\text{N})_2\text{UOCl}_5$ in dry acetonitrile containing excess dry Et$_4$NCl. The positions of the bands were similar to those of UC$_6^{2-}$, but the relative intensities of the bands were not. An examination of Figure 16, Table X, and reference 13$^4$ reveals that these results have probably been obtained in this work also. Ryan$^{22}$ was not certain whether the bands he observed were those of UOCl$_5^{2-}$ or those of UC$_6^{2-}$; this uncertainty is understandable in view of the fact that UOCl$_5^{2-}$ is known$^{22}$ to undergo disproportionation rapidly in solution. Since Figure 16 is the spectrum of a solid rather than a solution, it is probable that most of the observed bands, particularly the more intense, resolved peaks, are those of UOCl$_5^{2-}$. The weaker shoulders are also given in Table X with the recognition that they may be those of an impurity.
FIGURE 15. The Ultraviolet Spectrum of \((\text{Et}_4\text{N})_2\text{UOCl}_4\) in Kel-F Oil at (a) Ambient Temperature and (b) \(77^\circ\text{K}\).
TABLE X

THE BANDS\textsuperscript{a} OBSERVED FOR (Et\textsubscript{4}N)\textsubscript{2}UOCl\textsubscript{5} IN THE
REGION OF LAPORTE-ALLOWED TRANSITIONS

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\textsuperscript{a} Shoulders are given in parentheses.

\textsuperscript{b} Uranium(IV) exhibits a band near this position.\textsuperscript{134} See text for discussion.

\textsuperscript{c} The optical dewar (even after repeated cleaning) gave rise to a band at 2400 \textmu\textmu m (ambient temperature) which shifted to 2375 \textmu\textmu m at 77\textdegree\ K.
Ryan stated that "no bands attributable to UOCl$_{2}^{2-}$ electron transfer transitions could be obtained". This statement was probably based on the fact that Ryan estimated the half-widths of the observed bands to be about 700 cm$^{-1}$. Half-widths of this magnitude are generally associated with f $\rightarrow$ d-bands, whereas broader bands are generally assigned to electron transfer transitions. It should be emphasized that this is not a rigid distinction. The narrow bands which Ryan apparently observed are also seen in Figure 16, but there are, in addition, broad shoulders at lower energy which are more evident at 77° K. It is possible that Ryan did not observe these bands in solution at room temperature.

It was also observed by Ryan that the energy of the first electron transfer band of UOBr$_5^{2-}$ is about 9300 cm$^{-1}$ higher than that of UBr$_6^{2-}$ and that this difference is equal to the difference in the absorption cutoffs of UBr$_6^{2-}$ and UOBr$_5^{2-}$. If it is assumed that the difference in the absorption cutoffs of Ph$_4$AsUCl$_6$ and (Et$_4$N)$_2$UOCl$_5$ (9550 cm$^{-1}$) is similar to the difference in energy of the first charge-transfer bands of these compounds, then the first charge-transfer band of UOCl$_5^{2-}$ would be expected at about 35 kK, if Ryan's value$^{22}$ of 29.5 kK for the first electron transfer band of UCl$_6^{2-}$ is used. The first band above 33 kK occurs at 35.5 kK (Figure 16), but its intensity and width are those generally ascribed to f $\rightarrow$ d-bands and are remarkably similar to the two bands at 32.6 and 31.5 kK, respectively.

The crystal structure of the analogous complex, (Et$_4$N)$_2$PaOCl$_5$, has recently been determined.$^{172}$ The PaOCl$_5^{2-}$ ion has a distorted octahedral structure in which there are Pa-Cl distances of 2.59-2.72 Å in the case of four chlorides cis to the oxygen and distances of only...
2.42 Å in the case of the chloride trans to the oxygen. As a result of the short Pa-Cl distance of the trans chloride, the "charge-separation effect" is small in the case of this complex, and the difference in energy of the first charge-transfer bands of \( \text{PaCl}_6^- \) and \( \text{PaOCl}_5^- \) is relatively small.\(^\text{162}\) If \( \text{UOCl}_5^{2-} \) has a very short U-Cl distance, then the energy difference of the first electron transfer bands of \( \text{UOCl}_5^{2-} \) and \( \text{UCl}_6^- \) would be much less than the 9.6 \( \text{kK} \) calculated above, and the energy of the first charge-transfer band of \( \text{UOCl}_5^{2-} \) would be much lower than 35 \( \text{kK} \). It should be noted (Figure 16) that at 77° K there appears at 30.0 \( \text{kK} \) a band which looks very much like one that would be expected for a charge-transfer band.\(^\text{164}\) If this is indeed the case, the three bands at 31.5, 32.6, and 35.5 \( \text{kK} \) could be assigned to \( f \to d \)-transitions; such an assignment accords quite nicely with their half-widths and intensities. However, these ideas are quite speculative, and a determination of the (Et\(_4\)N)\(_2\)UOCl\(_5\) crystal structure might be very helpful in interpreting the observed spectrum.

D. Other Physical-Chemical Studies of the UOCl\(_5^{2-}\) Species

1. Magnetic Susceptibility

The magnetic susceptibility of (Et\(_4\)N)\(_2\)UOCl\(_5\) was measured by the Gouy method. The value of \( \chi_M^{\text{corr}} \) was determined to be 1.8 x \( 10^{-3} \) c.g.s., and \( \mu_{\text{eff}} \) was calculated to be 2.1 B.M. Because of the low density of the compound, the weight change due to paramagnetism was only 0.2 mg; hence, only one significant figure was obtained in the case of the magnetic susceptibility and magnetic moment. Because of experimental limitations, it was possible to obtain data only at ambient temperature; therefore,
the Weiss constant is not known. Weiss constants are often very large in the case of uranium(V) compounds, and these large values cause magnetic moments to be very nearly meaningless (*vide supra*, Chapter I). The value obtained does, however, fall between the "spin-only" value of 1.73 B.M. and the $5f^{1}$ "free-ion" value of 2.54 B.M.

2. Thermal Studies

The (Et$_4$N)$_2$UOCl$_5$ complex was studied by differential thermal analysis (DTA) and by thermogravimetric analysis (TGA). These curves are shown in Figure 17; the temperature range was 0-500$^\circ$ C. The TGA curve was obtained over the temperature range 0-1000$^\circ$ C, but there was no further weight loss above 500$^\circ$. The weight of residue that remains after heating above 500$^\circ$ is 41.9% of the original weight of sample. A residue that is UOCl$_2$ would account for this weight of residue; this decomposition would require that Et$_4$NC1 and Cl$_2$ be lost during decomposition. The weight loss occurs at approximately the same temperature as that at which the two DTA peaks occur (395 and 410$^\circ$); the presence of two such peaks accords with the loss of two species during decomposition. For samples prepared by the method of Ryan, a peak was observed at $\sim$285$^\circ$ (Figure 17c); this peak was not observed in the case of samples prepared by hydrolysis of UCl$_5$·TCAC (Figure 17b). A very strong endothermic peak is present at $\sim$297$^\circ$ in the DTA curve of Et$_4$NC1 and may account for the observed peak. Since the reactant solution is cooled to -78$^\circ$ in Ryan's method, it is not unlikely that some Et$_4$NC1 might crystallize with the product. Analyses of samples prepared by Ryan's method show consistently high percentages of carbon, hydrogen, and
FIGURE 1. Thermal Analysis Curves for \((\text{Et}_4\text{N})_2\text{UOCl}_5\): (a) TGA Curve, (b) DTA Curve for the Complex Prepared from UCl\textsubscript{6}·TCAC, and (c) DTA Curve for the Complex Prepared from Et\textsubscript{4}NUCl\textsubscript{6}. Temperatures on the Abscissa are Uncorrected; Corrected Values are Under the Curves.
nitrogen that may indicate the presence of excess Et₄NCl. It should also be noted that tetraethylammonium chloride was evidently present in the product obtained from the hydrolysis of UCl₅·TCAC in the presence of pyridine; during the hydrolysis the reactant solution was cooled to -78° (vide supra, Chapter II).

3. Chemical Properties of UOCl₅²⁻ Salts

Ryan has discussed the chemical properties of the UOX₅²⁻ (X = F, Cl, Br) complexes and has related these to electron transfer spectra. The chemistry of the UOCl₅²⁻ complex has been extended somewhat in this work, and some of this work will be discussed later (Chapter IV). With the preparation of the cesium salt, Cs₂UOCl₅, salts of UOCl₅²⁻ have now been prepared in which the cation is Et₄N⁺, Me₄N⁺, Ph₄As⁺, Cs⁺, and PyH⁺. Of all these salts, the tetraethylammonium salt is by far the most stable; it undergoes no apparent decomposition after months of exposure to laboratory air. The pyridinium complex is extremely unstable; it absorbs water from the air and undergoes subsequent disproportionation. The stabilities of the UOCl₅²⁻ salts of the other cations are: Ph₄As⁺ < Et₄N⁺ > Me₄N⁺ ~ Cs⁺. In the preceding list, the cations were listed in order of decreasing size. Thus, it appears that the size (and/or geometry) of the cation is the predominant factor influencing the stability of UOCl₅²⁻ salts; the tetraethylammonium cation apparently has the optimum size to stabilize the crystal lattice and thus to render the compound stable in air. This same effect is noted in the case of the MoO₃⁺ species (vide infra).

Ryan prepared M₂UOCl₅ salts by low-temperature hydrolysis of MCl₆ in the presence of MCl. This preparative method produces a
product that is essentially free of U(IV) and U(VI) but suffers from an obvious lack of flexibility. Thus, for every $M_2^+\text{UOCl}_5$ salt desired the precursors $M_2\text{UCl}_6$ and $\text{MUCl}_6$ must first be prepared. The method developed in this research, consisting of hydrolysis of $\text{UCl}_5\cdot\text{TCAC}$ in the presence of excess $\text{MCl}$, is much more flexible. Only one uranium starting compound, $\text{UCl}_5\cdot\text{TCAC}$, need be prepared. Thus far, only the $\text{Et}_4^+\text{N}^+$ and $\text{Me}_4^+\text{N}^+$ salts have been prepared by this method, but it may be possible to make other salts if a low temperature is maintained during the reaction.22

4. The Raman Spectrum of $(\text{Et}_4\text{N})_2\text{UOCl}_5$

The Raman spectra of $(\text{Et}_4\text{N})_2\text{UOCl}_5$ and of $\text{Et}_4\text{N}\text{Cl}$ are shown in Figure 18. The lines observed in the case of $(\text{Et}_4\text{N})_2\text{UOCl}_5$ are not Raman lines but are, instead, due to "resonance" Raman.173 The spectrum has not yet been interpreted, but it promises to yield new information about the complex.173

5. NMR Studies

The possible use of $(\text{Et}_4\text{N})_2\text{UOCl}_5$ as a paramagnetic shift reagent was investigated and will be discussed with studies of other uranium compounds (vide infra).
FIGURE 15. The Raman Spectra of (a) $(\text{Et}_4\text{N})_2\text{UOCl}_5$ and (b) $\text{Et}_4\text{NCI}$ Using 4360 Å Exciting Line.
CHAPTER IV

FREE RADICAL FORMATION BY PENTAVALENT METAL IONS

A. The UOCl$_5$ Adducts

It was reported in Chapter II that the hydrolysis reactions of UCl$_5$-TCAC in the presence of various ligands produced three solid products which were isolated and characterized. These products are (Et$_4$N)$_2$UOCl$_5$·(phthalazine), (Et$_4$N)$_2$UOCl$_5$·2(o-phenanthroline), and (Et$_4$N)$_2$UOCl$_5$·½(2,2'-bipyridyl). Due to the unusual nature of these products, a discussion of their formulation will be deferred until their physical properties are presented.

1. ESR Spectra

The ESR spectra of polycrystalline samples of these compounds consist of two signals that have $g$-values of ~2 and ~1.1, respectively. The high-field signals of all three compounds are very similar to that of (Et$_4$N)$_2$UOCl$_5$ (Figure 15) and have $g$-values of 1.09, 1.10, and 1.11 in the case of the phthalazine, o-phenanthroline and 2,2'-bipyridyl compounds, respectively. These $g$-values are subject to some error, however, because of the difficulty of locating the center of such a broad (~1800 gauss) signal.

The low-field signals of these compounds are shown in Figures 19-21. The low-field spectrum of the phthalazine adduct (Figure 19) consists of a weak, narrow (but reproducible) signal that has $g = 2.00$ superimposed on a stronger, broad (~1200 gauss) signal that has $g =$
FIGURE 19. The Low-Field ESR Spectrum of Solid $(\text{Et}_4\text{N})_2\text{UOCl}_5^-$ (phthalazine) At Ambient Temperature.
FIGURE 20. The Low-Field ESR Spectrum of Solid $(\text{Et}_4\text{N})_2\text{UOCl}_5 \cdot \text{(2-phen)}$ At Ambient Temperature.
FIGURE 21. The Low-Field ESR Spectrum of Solid (Et₄N)₂UOCl₆·dipy At Ambient Temperature.
The narrow absorption \((g = 2.00)\) is consistent with a signal that would result from an electron delocalized in the unsaturated \(\pi\)-system of the phthalazine molecule (i.e., a free radical). The broad resonance \((g = 2.35)\) is thought to be that of \(\text{U(IV)}\). The following evidence is cited to support this interpretation. The electronic spectrum of this compound (\textit{vide infra}) indicates the presence of a considerable amount of \(\text{U(IV)}\), whereas this impurity is not present in the \(\alpha\)-phenanthroline and 2,2'-bipyridyl adducts. Ghosh, \textit{et al.},\textsuperscript{174} obtained the ESR of \(\text{UF}_4\) in powder form and observed a broad, weak resonance that had \(g = 2.4\). McLaughlan\textsuperscript{175} found broad, isotropic resonances that had \(g \approx 2\) in the case of \(\text{U(IV)}\) doped into \(\text{CaF}_2\), and these resonances have been attributed\textsuperscript{176} to a \(\text{U(IV)}\) in a cubic field. A \(g\)-value of \(\sim 2.7\) has been reported\textsuperscript{177} for \(\text{U(IV)}\) doped into \(\text{ThO}_2\). While the symmetry of the field of the \(\text{U(IV)}\) is not known, it probably is not octahedral because of the "tetragonal" symmetry of the \(\text{UOCl}_5^{2-}\) and the presence of phthalazine within the crystal lattice. Finally, a signal practically identical with the signal in question was observed (in addition to the high-field signal, \(g = 1.1\)) in the case of \(\text{Cs}_2\text{UOCl}_5\), which is known to contain \(\text{U(IV)}\) as an impurity, but no such pattern was obtained in the case of pure \((\text{Et}_4\text{N})_2\text{UOCl}_5\) (\textit{vide supra}).

The low-field signal of the \(\alpha\)-phenanthroline adduct (Figure 20) is an example of an axially symmetry \(g\)-tensor.\textsuperscript{148,178,179} The line widths are quite narrow, presumably because of exchange narrowing,\textsuperscript{148} and these small widths allow resolution of the \(g\)-values. From Figure 20 one obtains \(g_{\parallel} = 2.043\) and \(g_{\perp} = 2.019\). These values are slightly greater than the free-electron \(g\)-value and may be due to spin-orbit coupling caused by the heavy uranium nucleus.\textsuperscript{180}
In the case of the 2,2′-bipyridyl complex, the low-field signal (Figure 21) has a $g$-value of 2.005, approximately equal to the free-electron value, and indicates the presence of a free radical. The signal is somewhat broader than that one might expect from an organic free radical, and this broadness is perhaps due to loss of electron exchange. Satellite bands are present in the spectrum, but an explanation of their origin is not possible at present because of poor resolution and lack of data with respect to their intensity ratios. It is improbable, however, that they arise from the same species responsible for the center line.

These results indicate the presence of both the $\text{UOCl}_5^{2-}$ species and the free radical of the respective organic ligands in these compounds. Spin concentration measurements have not yet been done in the case of these compounds, and integration of the high-field ($g \sim 1.1$) signals is not possible because of their extreme width. It appears, however, that the ratio of free radical to $\text{UOCl}_5^{2-}$ is very small, particularly in the phthalazine and 2,2′-bipyridyl cases.

2. Electronic spectra

The visible-near I.R. spectra of the three compounds were measured at ambient temperature and at $77^\circ$ K. They are practically identical with the spectra of $(\text{Et}_4\text{N})_2\text{UOCl}_5$ (Figures 5 and 8); small shifts in the positions of the absorption bands are within experimental error. The spectrum of the phthalazine adduct indicates the presence of a few percent of U(IV) and U(VI), whereas the other compounds are virtually free of these contaminants. The non-variance of the electronic spectra
indicated that the o-phenanthroline compound did not decompose upon exposure to laboratory air for ten days and that the phthalazine compound did not decompose upon exposure to air for one month; the stability of the 2,2'-bipyridyl adduct was not monitored.

The ESR results indicate the existence of small quantities of ligand free radicals in these adducts. The electronic spectrum of the 2,2'-bipyridyl anion radical has been determined to have bands in the visible-near I.R. regions; no such bands were found in the spectrum of the 2,2'-bipyridyl adduct. There are two possible explanations for this result: (1) the concentration of radical is too low to be detected in the electronic spectrum or (2) the free radical bands have been shifted into the ultraviolet region. Large shifts of these bands have been observed in the case of metal complexes thought to contain the 2,2'-bipyridyl anion radical.

### 3. Infrared Spectra

The infrared spectra of the adducts and their ligands in the NaCl and CsI regions were obtained, and the band positions are displayed in Table XI. The spectra were compared with spectra of Et₄NCl and (Et₄N)₂UOCl₅ in order to eliminate bands assignable to the cation and to UOCl₅²⁻. The spectra are very complex because both the organic cation and the organic ligand are present. The presence of the U=O³⁺ entity is confirmed by the spectra. Bands due to the UOCl₅²⁻ anion are essentially unperturbed in comparison to those in the parent (Et₄N)₂⁻ UOCl₅. Nevertheless, the spectra do reveal (1) the absence of some ligand bands, (2) shifts in some ligand bands, and (3) the appearance of new bands in the adducts. These results indicate that the ligand is
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</table>

Continued
TABLE XI (Continued)

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Description</th>
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<tbody>
<tr>
<td>895w</td>
<td>872m 685m, br</td>
</tr>
<tr>
<td>817s(U=0)</td>
<td>815w 608m</td>
</tr>
<tr>
<td>803s(C)</td>
<td>540w</td>
</tr>
<tr>
<td>795s(C)</td>
<td>788w 525m</td>
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<tr>
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<tr>
<td>512m</td>
<td>505m 390w</td>
</tr>
<tr>
<td>502w</td>
<td>285w(U-Cl)</td>
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<tr>
<td>470s</td>
<td>468s 255m(U-Cl)</td>
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<tr>
<td>390m</td>
<td>373s</td>
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<tr>
<td>350w</td>
<td>(350)</td>
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<tr>
<td>290m(U-Cl)</td>
<td></td>
</tr>
<tr>
<td>(265)</td>
<td>275w</td>
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<tr>
<td>258s(U-Cl)</td>
<td></td>
</tr>
</tbody>
</table>

a. Abbreviations used are: x = Nujol band; s = strong; m = medium; w = weak; br = broad; C = cation (Et₄N⁺) band. Shoulders are given in parentheses.

b. In Nujol mull.

c. In KBr pellet.

d. The spectrum was not measured in the CsI region.

e. See Chapter III for a discussion of these bands.
somewhat perturbed in the complex while the parent \((\text{Et}_4\text{N})_2\text{UOCl}_5\) is practically unaffected. The significance of these results will be discussed below.

4. Thermal Studies

Each compound was studied by means of DTA, TGA, and melting point measurements. The TGA curve of the phthalazine adduct is shown in Figure 22a. The second weight loss occurs at about the same temperature as that at which the weight loss of \((\text{Et}_4\text{N})_2\text{UOCl}_5\) (Figure 17a) occurred. The initial weight loss corresponds to the loss of \(\text{C}_8\text{H}_8\text{N}_2 + \frac{3}{2}\text{Cl}_2\), and the second loss is that of \(2\text{Et}_4\text{NCl} + \frac{5}{2}\text{Cl}_2\); the residue is UOCl. The DTA curve of this material (Figure 22b) shows endothermic peaks at 135° and 395° which correspond approximately to those of \((\text{Et}_4\text{N})_2\text{UOCl}_5\) (Figure 17b) as well as a peak at 196° which occurs at approximately the same temperature as that of the initial weight loss observed by TGA.

A sample of phthalazine was physically mixed with some \((\text{Et}_4\text{N})_2\text{UOCl}_5\), and the DTA of the mixture was obtained (Figure 22c). It should be noted that the melting of phthalazine at 85° can be seen, whereas the melting is not observed in the case of the adduct (Figure 22b). This evidence indicates that the phthalazine adduct is not a mixture of \((\text{Et}_4\text{N})_2\text{UOCl}_5\) and phthalazine. The adduct was observed to decompose at about 200°.

The DTA and TGA curves of \((\text{Et}_4\text{N})_2\text{UOCl}_5\cdot 2(\text{o-phen})\) are shown in Figures 23 and 24, respectively; both are very complex. The DTA does not show the melting point of free \(\text{o-phenanthroline}\) (114°). The TGA curve shows four weight losses; the initial weight loss corresponds to HCl, and the second loss is that of two molecules of \(\text{o-phenanthroline}\).
FIGURE 23. Thermal Analysis Curves For (Et₄N)₂UOCl₅·(phthalazine): (a) TGA Curve, (b) DTA Curve, and (c) DTA Curve of a Mixture of (Et₄N)₂UOCl₅ and Phthalazine. Temperatures on the Abscissa Are Uncorrected; Corrected Values are Below the Curves.
FIGURE 25. DTA Curve for (Et₄N)₂UOCl₅·2(o-phen). Temperatures on the Abscissa are Uncorrected; Corrected Values are Below the Curve.
FIGURE 2. TGA Curve for \( \text{Et}_2\text{N})_2\text{UOCl}_2 \cdot 2(\text{o-phen}) \). Temperatures on the Abscissa are Uncorrected; Corrected Values are Below the Curve.
The other losses could not be rationalized, nor could the weight of observed residue be explained. The final weight is less than that of uranium metal. It thus appears that some of the uranium volatilizes (probably as a complex), but this volatilization could not be verified. The compound was observed to melt with decomposition at 160-200\(^\circ\)C.

The TGA curve of \((\text{Et}_4\text{N})_2\text{UOCl}_5\cdot\text{dipy}\) is shown in Figure 25a; no further weight loss occurred up to 1000\(^\circ\)C. The three observed weight losses correspond to \(\text{dipy} + 1.5\text{ Cl}, 2\text{ Et}_4\text{NCl},\) and \(1.5\text{ Cl},\) respectively, and the weight of residue corresponds to that of \(\text{UO}\). The second weight loss occurs at approximately the same temperature as the loss in the case of \((\text{Et}_4\text{N})_2\text{UOCl}_5\) (Figure 17a). The DTA curve (Figure 25b) is somewhat more complex than that of pure \((\text{Et}_4\text{N})_2\text{UOCl}_5\) (Figure 17b) and does not show the melting point of \(2,2'\)-bipyridyl (69-70\(^\circ\)C). The adduct was observed to decompose at 180\(^\circ\)C.

5. Magnetic Susceptibilities

The magnetic susceptibilities of the phthalazine and \(o\)-phenanthroline adducts were measured by means of the Gouy method. Values of \(\chi_m^{\text{corr}}\) of \(1.2 \times 10^{-3}\) c.g.s. and \(0.9 \times 10^{-3}\) c.g.s. and \(\mu_{\text{eff}}\) values of 1.7 and 1.5 B.M. were obtained in the case of the two compounds, respectively. As in the case of pure \((\text{Et}_4\text{N})_2\text{UOCl}_5\) (\textit{vide supra}, Chapter III), only one significant figure was obtained in each measurement because of the small weight change due to paramagnetism. Hence, within experimental error, the magnetic moments of these compounds are probably very nearly identical with that of pure \((\text{Et}_4\text{N})_2\text{UOCl}_5\).
FIGURE 2). Thermal Analysis Curves for \( (\text{Et}_4\text{N})_2\text{UOCl}_5 \cdot \text{dipy} \): (a) TGA and (b) DTA. Temperatures on the Abscissa are Uncorrected; Corrected Values are Below the DTA Curve.
6. The Nature of the Adducts

The idea that these materials might simply be mixtures of \((\text{Et}_4\text{N})_2\text{UOCl}_5\) and ligand was considered, but the following evidence indicates that this idea is not the case. (1) Peaks due to the melting points of the ligands are not observed in the DTA curves. (2) The infrared spectra show new bands as well as shifts and disappearances of ligand bands. (3) Microscopic examination of the phthalazine adduct revealed only one color and one type of crystal structure. (4) The ratios of ligand to \(\text{UOCl}_5^{2-}\) in these adducts are not indicative of mixtures. Three preparations of the 2,2'-bipyridyl adduct were done in which varying amounts of ligand and of \(\text{UCl}_5\cdot\text{TCAC}\) were used, but the same product was obtained in each case; washing the compound with benzene (in which the ligand is soluble) produced no change in the analysis.

The ESR spectra reveal the presence of free radicals in these compounds (vide supra). Radical anions are known for phthalazine and 2,2'-bipyridyl, and several metal complexes are thought to contain the radical anion of 2,2'-bipyridyl, analogous complexes of \(\sigma\)-phenanthroline are also known. It was previously pointed out, however, that the concentration of free radical in these adducts may be quite low.

The essential equivalence of the electronic spectra of these materials with that of pure \((\text{Et}_4\text{N})_2\text{UOCl}_5\) was previously noted. If these are true coordination compounds, these similarities would arise if (1) the ligands displace chloride from the coordination sphere and (2) the effects of the ligands on the crystal field strength and symmetry are very nearly identical with the effects of chloride. It appears,
however, that these adducts are best described either as clathrates, in which the ligand is trapped inside the crystal lattice, or as outer-sphere complexes, in which the interaction of the ligand with the uranium(V) is very weak or even negligible. It is generally thought\(^{164}\) that formation of such complexes has very little effect on the f-f spectra of actinide ions because of the small perturbation (compared to first sphere effects) of the field around the metal by such outer-sphere effects.

7. Unsuccessful Preparative Attempts

It was previously noted (Chapter II) that other hydrolysis reactions of UC\(_5\)·TCAC were carried out in the presence of pyridine, triphenylphosphine, phenazine, and potassium diethyldithiocarbamate, respectively. The pyridine did not coordinate; in view of (1) the tendency of U(V) to form free radicals and (2) the fact that pyridine readily forms a radical anion which dimerizes to form the \(4,4'\)-bipyridyl radical anion,\(^{198,199}\) the pyridine may have remained in solution as a radical. The triphenylphosphine may have been oxidized to the oxide, and there may have been concomitant reduction of the uranium to U(IV); thus the product may actually be a U(IV)·Ph\(_3\)PO complex, but this product was not analyzed. In the hydrolysis reaction of UC\(_5\)·TCAC in the presence of phenazine, disproportionation of the U(V) was apparently caused by the large volume of solvent required to dissolve the ligand; the use of a large volume of solvent would cause the U(V) to remain in solution for a relatively long period of time and thus increase the probability of disproportionation.
B. The Dihydrophenazine Cation Radical

The product of the direct reaction of \( (\text{Et}_4\text{N})_2\text{UOCl}_3 \) with phenazine was not the expected complex of phenazine and uranium(V); the compound proved to be the chloride salt of the dihydrophenazine cation radical\(^{200} \) (I):

\[
\begin{align*}
\text{H} & \\
\text{N} & \\
\text{Cl}^- & = \text{Ph}_2\text{Cl} + \\
\text{H} & \\
\text{N} & \\
\end{align*}
\]

I

The dihydrophenazine cation radical has been known for a long time. As early as 1873, Claus\(^{201} \) noted the formation of dark green compounds upon treatment of the colorless 5,10-dihydrophenazine with mineral acids, but he incorrectly formulated these compounds to be salts of a dimeric species (II):

\[
\begin{align*}
\text{H} & \\
\text{N} & \\
\text{N} & \\
\text{H} & \\
\end{align*}
\]

II

It should be pointed out that dimeric complexes of phenazine and 5,10-dihydrophenazine are known; these complexes are the phenazhydrins or meriquinones.\(^ {202,203} \) The two known phenazhydrins of phenazine are blue and violet; phenazhydrins differ from semiquinones in that the former are diamagnetic in the solid state whereas the latter are paramagnetic (vide infra).
Subsequent to the work of Claus, the dihydrophenazine radical cation has been obtained many times in solution by reducing phenazine chemically,\textsuperscript{203-207} photochemically,\textsuperscript{208-210} and electrochemically,\textsuperscript{207,211-216} by electrolytic oxidation of 5,10-dihydrophenazine (PH\textsubscript{2}),\textsuperscript{216} by mixing phenazine and 5,10-dihydrophenazine (PH\textsubscript{2}) in acid solution,\textsuperscript{217,218} and by treating PH\textsubscript{2} with sulfuric acid.\textsuperscript{219} The cation radical has also been adsorbed on solid surfaces by treatment of phenazhydrin with a strong acid ion exchanger.\textsuperscript{220} In addition, several investigators have reported the isolation of the chloride salt of the dihydrophenazine cation radical by reduction of phenazine with stannous chloride in acid solution.\textsuperscript{204,205,221} In a recent report,\textsuperscript{222} however, it is claimed that this procedure produces a stannic chloride chelate of phenazhydrin. It thus appears that the present work is the first definitive isolation and characterization of the pure solid chloride salt of the dihydrophenazine cation radical.

1. Properties of PH\textsubscript{2}Cl

PH\textsubscript{2}Cl is insoluble in benzene, hexane, tetrahydrofuran (THF), and dioxane; slightly soluble in water, nitromethane, and acetonitrile; and very soluble in methanol, ethanol, N,N-dimethylformamide (DMF), and DMSO. Solutions of the radical in dry, deoxygenated solvents are stable for several days, whereas solutions in reagent grade methanol (which was not dried nor degassed) were observed (spectrophotometrically, \textit{vide infra}) to decompose over a period of several hours; the characteristic green color faded and the yellow color of phenazine appeared. Addition of water to an ethanol solution of the radical caused the solution to turn yellow immediately. Attempts to digest the crystalline product
and to recrystallize it from dry spectroquality nitromethane or methanol were unsuccessful; the compound decomposed in solution even though the solution was kept in a nitrogen atmosphere. The radical salt was finally recrystallized by dissolving it in absolute methanol, filtering, bubbling dry HCl gas into the solution, and cooling. The radical chloride precipitated in the form of black needles of the anhydrous (as shown by analysis) compound.

The mass spectrum of \( \cdot \text{PH}_2\text{Cl} \) is identical with that of phenazine, indicating rapid decomposition in the mass spectrometer.

DTA and TGA curves (Figure 26) indicate that water of hydration is lost from \( \cdot \text{PH}_2\text{Cl} \) at about 100°. The compound apparently sublimes and/or decomposes over the range 150-300°; this behavior is shown in Figure 26. During the TGA analysis, a green solid condensed on the cool area of the TGA tube, but it is not known whether this condensate is sublimed \( \cdot \text{PH}_2\text{Cl} \) or a decomposition product. In a capillary melting point tube, this "sublimation" process was observed at 240°, and the residue darkened and melted at 270-275°.

The ESR spectrum of polycrystalline \( \cdot \text{PH}_2\text{Cl} \) consists of a single narrow (0.9 gauss) resonance; the \( g \)-value is 2.005 (Figure 27). The extremely small width is presumably due to exchange narrowing. The signal is very strong, and this intensity is a further indication that previous investigators did not obtain the pure chloride salt since a weak signal was reported. The spectrum of \( \cdot \text{PH}_2\text{Cl} \) in acetonitrile was also obtained and is shown in Figure 28. The radical salt is only sparingly soluble in acetonitrile; a saturated solution (\( \sim 10^{-3}\text{M} \)) was used in the experiment. The spectrum is in agreement with spectra in
FIGURE 2c. Thermal Analysis Curves for PH₂Cl: (a) DTA and (b) TGA.
FIGURE 77. The ESR Spectrum of Solid $\text{PH}_2\text{Cl}$ at Ambient Temperature.
FIGURE 25. The ESR Spectrum of PH\textsubscript{2}Cl in Acetonitrile at Ambient Temperature.
which the radical was generated \textit{in situ} \cite{206,207,212,213,223} and is perhaps the most convincing evidence for the identification of this species. It should be noted that, in addition to the aforementioned reports of the ESR spectrum of this compound, several investigators have reported poorly resolved spectra in which some of the hyperfine components are not observable. \cite{204,205,224}

The infrared spectrum of a KBr pellet of PH$_2$Cl was obtained. In addition to the numerous (shifted) bands of phenazine, new bands at 2500 and 3340 cm$^{-1}$, both of which are due \cite{222} to the $\equiv$N-H linkage, were observed. Several attempts were made to record solution spectra, but solvent bands presented rather severe interferences. Mulls of Nujol or hexachlorobutadiene were not satisfactory either; in dilute mulls only the strongest bands were observable, whereas in more concentrated mulls light scatter was severe. The latter problem was also encountered in the course of electronic spectral measurements (\textit{vide infra}).

In the case of electronic spectra of methanol and ethanol solutions and of Kel-F mulls, the frequency interval 4,000-20,000 cm$^{-1}$ was scanned. In solution at ambient temperature no bands were found in the region 4,000-13,000 cm$^{-1}$. Four bands were observed at 14,200, 15,700, 16,900, and 18,300 cm$^{-1}$; these bands are shown in Figure 29a. The molar absorptivity of the most intense band (15,700 cm$^{-1}$) was estimated to be about 600. Upon freezing the solution at 77$^\circ$ K, two new bands appear at $\sim$ 9,600 and $\sim$ 11,900 cm$^{-1}$, respectively (Figure 29b). Similar phenomena have been observed in the case of other radicals and were attributed to the formation of dimeric $\Pi$-complexes at low temperatures. \cite{225} These complexes are said to differ from the meri-quinones (\textit{vide supra}) in that each fragment retains its radical character;
FIGURE 39. The Electronic Spectrum of \( \text{PH}_2\text{Cl} \) In the \( \gamma, 500-20,000 \text{ cm}^{-1} \) Region In Methanol At (a) Ambient Temperature and (b) \( \gamma/\degree K \).
the complex is stabilized only by π-interactions, and the radicals lie one above the other in parallel planes.\textsuperscript{225} Although no evidence for the formation of these complexes in the solid state was found,\textsuperscript{225} there are indications of the existence of such species in solid PH\textsubscript{2}Cl. The Kel-F mull spectrum of PH\textsubscript{2}Cl at ambient temperature exhibits an extremely broad, nondescript band at \( \sim 8500 \) cm\textsuperscript{-1} similar to the bands mentioned above. This evidence is extremely tenuous, however; light scatter was very severe because of the highly reflective (almost metallic) surface of the crystalline solid, and the accuracy of this spectral data may be questionable. The magnetic moment of solid PH\textsubscript{2}Cl was determined to be 1.0 B.M. at ambient temperature by the Gouy method. This value, considerably less than the spin-only value of 1.73 B.M., may be evidence for spin-pairing in the solid. As in the case of determinations on other compounds (\textit{vide supra}), however, only one significant figure was obtainable, so that this evidence must also be considered to be quite tentative.

In the 20,000-50,000 cm\textsuperscript{-1} range, electronic spectra of Kel-F mulls and of solutions in methanol and EPA both at ambient temperature and at 77\textdegree{} K were recorded. Representative spectra are displayed in Figure 30. In all the spectra two characteristic bands were observed at \( \sim 2470 \) and 3630 Å (40,500 and 27,000 cm\textsuperscript{-1}), respectively, at ambient temperature. These bands are also present in the spectrum of phenazine, at the same positions. The molar absorptivity (\( \varepsilon \)) of the 3630 Å band of PH\textsubscript{2}Cl in EPA solution was estimated to be about 10,000, approximately equal to that of phenazine. At 77\textdegree{} K both bands become more intense and experience a slight red shift (ca. 10 Å); the shoulders on these
FIGURE 50. The Electronic Spectrum of \( \text{PH}_2\text{Cl} \) In the 20,000-50,000 cm\(^{-1} \) Region In (a) Kel-F Mull at 77°K and (b), (c) Methanol at Ambient Temperature. The Concentration in (c) is One-Fourth That in (b).
peaks are also more prominent, and several shoulders are resolved. Although the positions of the principal peaks (and their shoulders) of \( \text{PH}_2\text{Cl} \) are the same as those of phenazine, the relative intensities of the components of the band group at \( 2470 \text{ \AA} \) are not the same in the case of the two compounds.

In addition to the aforementioned bands, peaks were observed in some spectra at \( \sim 2570, 3000, \) and \( 4500 \text{ \AA}, (38,900, 33,300, \) and \( 22,200 \text{ cm}^{-1} \) respectively. The last two bands were always observed to occur simultaneously and appear to be due to the same species. The band at \( 2570 \text{ \AA} \) was not always present when the other two bands appeared, but the \( 2570 \text{ \AA} \) band never appeared when the other two bands were not present. Since the \( \text{UO}_2^{2+} \) entity is a byproduct of the synthesis of \( \text{PH}_2\text{Cl} \) (vide supra), it was first thought that the \( 4500 \text{ \AA} \) band is that of \( \text{UO}_2^{2+} \), which has a band in this region. Similar bands have been observed in the spectra of solutions of phenazine undergoing reduction. These bands were attributed to the neutral semiquinone radical, \( \text{Ph} \), to the cation radical, to a dimeric form of the cation radical, or to phenazhydrin. The fact that, in the present work, these bands were not observed in some mull spectra indicates that they are not due to the simple cation radical. They must, then, be due to some other species which forms in some samples of \( \text{PH}_2\text{Cl} \). The identity of this species is not known, but it may be the neutral semiquinone radical or the dimeric cation radical that were postulated by other investigators.

2. The Mechanism of Radical Formation

Perhaps the most intriguing aspect of this current free radical research is the mechanism which produces the dihydrophenazine cation
radical. Several experiments were performed (they are described in Chapter II) to ascertain the source of the protons on the cation radical. First, the reaction was not retarded when (Ph₄As)₂UOCl₅ was substituted for (Et₄N)₂UOCl₅; this phenomenon indicated that the protons do not come from the Et₄N⁺ cation. Second, the reaction proceeded even when nitrobenzene replaced nitromethane as solvent; thus the solvent was not the proton source. Third, when the reaction was carried out under rigorously anhydrous conditions (e.g., dry box), it did not proceed to completion. Exposure of this reactant solution to the moist laboratory atmosphere caused the reaction to proceed at once to form an anhydrous product. When the solvent was saturated with water, the reaction occurred almost instantaneously. These results strongly suggest that water is the proton source. Since TGA studies and elemental analyses did not reveal the presence of water in either the (Et₄N)₂UOCl₅ or phenazine reactants, it is apparently readily absorbed from the atmosphere during the course of the reaction.

When (Et₄N)₂UOBr₅ was the starting material, the product was PH₂Br·H₂O. Substitution of Et₄NUCl₆ as starting material resulted in formation of the UCl₅P₂ complex; addition of undried acetone to the yellow filtrate caused the development of an emerald green color and precipitation of a dark solid that was presumed to be PH₂Cl.

In view of the above results and the isolation of (Et₄N)₂UOCl₄ as the other product of the reaction, the complete reaction can be written:

\[ P + (\text{Et}_4\text{N})_2\text{UOCl}_5 + \text{H}_2\text{O} \rightarrow \text{PH}_2\text{Cl} + (\text{Et}_4\text{N})_2\text{UO}_2\text{Cl}_4 \]  \( (53) \)
The fact that all coefficients in equation (33) are unity suggests the following course for the reaction:

\[ P + (\text{Et}_4\text{N})_2\text{UOCl}_5 \rightarrow \text{U} \cdots P \]  

\[ \text{III} \quad \text{H}_2\text{O} \quad \text{OH}_2 \]

\[ \text{Products} \leftarrow \text{U} \cdots \text{P} \]

\[ \text{IV} \]

In this scheme (III) is a complex of the \( \text{UOCl}_5^{2-} \) with phenazine; in (IV) water is also associated with the complex. The postulation of the existence of these species is based on the following evidence. When \( (\text{Et}_4\text{N})_2\text{UOCl}_5 \) was dissolved in a nitromethane solution of phenazine under rigorously anhydrous conditions, an emerald green solution resulted. This color is presumably that of the intermediate (III). Upon exposure to water the solution color darkened rapidly; this dark green color is attributed to the intermediate (IV). The solid chloride salt then began to form within several minutes, and the color of the solution gradually became lighter.

The fact that the stable cation radical is formed in a system to which no acid is added is a unique feature of this reaction. The phenazine cation radical has previously been produced as a stable species only in strongly acid solution;\textsuperscript{203-214,216-220,223,227,228} neutral media are more pertinent biologically. This point takes on added significance when it is considered that phenazine has been used as a model system for the isoalloxazine ring system of the flavoproteins, a class of enzymes that participate in biological oxidations.\textsuperscript{229,230}
The reaction was found to proceed readily in the dark (vide supra).

C. Other Radicals Formed by U(V)

In addition to \( \text{PH}_2\text{Cl} \), several other free radical compounds resulted from the direct reaction of \((\text{Et}_4\text{N})_2\text{UOCl}_5\) with various organic ligands. Some of the properties of these compounds are summarized in Table XII, where they are compared with the properties of \( \text{PH}_2\text{Cl} \) and \( \text{PH}_2\text{Br} \). The free radical bromide, \( \text{PH}_2\text{Br} \), is more soluble than \( \text{PH}_2\text{Cl} \) in methanol and nitromethanes, but \( \text{PH}_2\text{Br} \) is less stable than \( \text{PH}_2\text{Cl} \) in solution. The \( g \)-value of \( \text{PH}_2\text{Br} \) is slightly greater than that of \( \text{PH}_2\text{Cl} \). The ESR spectrum of a mixture of polycrystalline \( \text{PH}_2\text{Cl} \) and \( \text{PH}_2\text{Br} \cdot \text{H}_2\text{O} \) was obtained, but the signals were in such close proximity that the difference in their \( g \)-values could not be accurately determined.

None of the compounds in Table XII possess a U(V) ESR signal \((g \sim 1.1)\).

The compound denoted as \((\text{BPH}_2)_2\text{UO}_2\text{Cl}_4\) was obtained by bubbling HCl gas into a nitromethane solution of \((\text{Et}_4\text{N})_2\text{UOCl}_5\) plus benzo[a]-phenazine. The ESR spectrum of the polycrystalline powder of this species was obtained and is shown in Figure 31. The five line pattern is probable due to hyperfine coupling of the electron with the two nitrogen nuclei of the BP center ring. The fact that hyperfine coupling is observed in the case of this material is indicative of lack of electron exchange; this phenomenon is typical of the case of a radical in a dilute solution or host lattice.\(^{176}\) This spectrum indicates that the species in question may actually be a small amount of \((\text{BPH}_2)_2\text{UO}_2\text{Cl}_4\) trapped in a (polycrystalline) host of \((\text{BPH})_2\text{UO}_2\text{Cl}_4\). Attempts to obtain a solution ESR spectrum were unsuccessful.
<table>
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<tr>
<th>Compound</th>
<th>Color</th>
<th>$g$-value$^a$</th>
<th>ESR Signal Width (Gauss)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{PH}_2\text{Cl}$</td>
<td>Dk. green</td>
<td>2.005</td>
<td>0.9</td>
</tr>
<tr>
<td>$\text{PH}_2\text{Br} \cdot \text{H}_2\text{O}$</td>
<td>Dk. green</td>
<td>2.006</td>
<td>3.2</td>
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<tr>
<td>($\text{DPH}_2$)$_2\text{UO}_2\text{Cl}_4$</td>
<td>Red-brown</td>
<td>2.005$^b$</td>
<td>---$^b$</td>
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<tr>
<td>($\text{DBPH}_2$)$_2\text{UO}_2\text{Cl}_4$</td>
<td>Yellow</td>
<td>2.006</td>
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<tr>
<td>($\text{MB}$)$_2\text{UOCl}_5$</td>
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<td>2.006</td>
<td>15</td>
</tr>
</tbody>
</table>

---

a. For the polycrystalline solid.
b. See text and Figure 31.
c. See text for the actual formulation of this compound.
FIGURE 51. The ESR Spectrum of Solid \((\text{BPH}_2)_2\text{UO}_2\text{Cl}_4\) at Ambient Temperature.
It was noted in Chapter II that the use of a larger UOCl$_5^{-}$:BP ratio resulted in the precipitation (the HCl treatment was not necessary) of a mixture of BPHCl and (BPH$_2$)$_2$UO$_2$Cl$_4$. The ESR spectrum of this material is more intense than that of the above species and consists of a single line that has a width of 4.4 gauss; these characteristics indicate that a higher concentration of radical is present in this material than in the substance above.

The compound formulated as (DBPH$_2$)$_2$UO$_2$Cl$_4$ was prepared by bubbling HCl gas into a MeNO$_2$-PhNO$_2$ solution of (Et$_4$N)$_2$UOCl$_5$ and dibenz[a,c]phenazine. The ESR spectrum of this material (polycrystalline sample) consists of a single line (Table XII). When the reaction was carried out in pure nitrobenzene (Chapter II), a red precipitate formed; this precipitate turned brown when it was dried in vacuo. The ESR spectrum was identical with that of (DBPH$_2$)$_2$UOCl$_4$, but it was weaker than that of the latter compound. It is reported$^{203}$ that DBPHCl (the monohydrochloride of DBP) is red and that it hydrolyzes readily. This evidence and the elemental analysis (vide supra) suggest that the original precipitate was a mixture of DBPH$_2$Cl and DBPHCl.

The above results indicate that both BP and DBP form free radicals with UOCl$_5^{-}$ much less readily than does unsubstituted phenazine. There have been relatively few reports of semiquinones of these compounds$^{203,231}$; this scarcity of semiquinones is probably caused by the weak basicities of the compounds and the difficulty of reduction to the corresponding N,N'-dihydro-(fully reduced) form.$^{203}$ In addition, steric consideration may be important in the present reaction.

The direct reaction of (Et$_4$N)$_2$UOCl$_5$ and 2,3-di(2-pyridyl)-quinoxaline resulted in the formation of (DPyQH$_2$)$_2$UO$_2$Cl$_4$ (Table XII).
Although there have been reports of the radical anions of quinoxaline\textsuperscript{110,215,232-235}, 2,3-dimethylquinoxaline\textsuperscript{234} and 2,3-diphenylquinoxaline\textsuperscript{236} and of the cation radicals of dihydroquinoxaline\textsuperscript{212,235} and dihydro-2,3-dimethylquinoxaline\textsuperscript{212} radical ions have not been reported for DPyQ.

The reaction of (Et\textsubscript{4}N\textsubscript{2})\textsubscript{2}UOCl\textsubscript{5} with methylene blue chloride produced the compound designated in Table XII as (MB)\textsubscript{2}UOCl\textsubscript{5}. The ESR spectrum, which reveals that the lone electron of the U(V) is delocalized in the methylene blue system, suggests that the compound should be formulated as (MB\textsuperscript{+})UOCl\textsubscript{5}(MB) in which one of the methylene blue units is a neutral radical. There have been numerous reports of the neutral MB radical (e.g., refs. 237 and 238) and various protonated forms of the radical (e.g., ref. 239), and the isolation of the solid neutral radical has been reported\textsuperscript{238}. The relation between biological activity and semiquinone formation has also been discussed\textsuperscript{240-242} in the case of methylene blue and related systems.

Although the compound precipitated from nitromethane, (MB\textsuperscript{+})-UOCl\textsubscript{5}(MB) is soluble in excess nitromethane in which it forms a blue solution; addition of excess UOCl\textsubscript{5}\textsuperscript{2-} decolorizes the solution, probably by formation of leucomethylene blue, MBH (fully reduced form).

D. Reactions of (Et\textsubscript{4}N\textsubscript{2})\textsubscript{2}UOCl\textsubscript{5} With Other Ligands

It was noted in Chapter II that reactions were carried out between (Et\textsubscript{4}N\textsubscript{2})\textsubscript{2}UOCl\textsubscript{5} and a variety of organic ligands other than those which produced free radical products. The reactions with triphenylphosphine, o-phenanthroline, and riboflavin (Vitamin B\textsubscript{2}) apparently
resulted in disproportionation of the $U(V)$. This disproportionation is not surprising in view of the inherent instability of the $UOCl_3^{2-}$ species in solution.\textsuperscript{22} The hydroxylated side chain of riboflavin was probably particularly instrumental in the decomposition.

In the reactions with pyridine, pyrazine, and phthalazine, spectral data indicate that the uranium($V$) was oxidized to $U(VI)$. In addition, there was isolated from the phthalazine reaction a product the analysis of which is consistent with the formula $UOCl_3\cdot(\text{phthalazine})$. This product may be an adduct of $U(VI)$ with the phthalazine radical anion, which is known (\textit{vide supra}). It is possible that radicals of phthalazine, pyrazine, and pyridine were produced and that the pyridine and pyrazine radicals did not precipitate. Since this work was done prior to the discovery of the phenazine radical, the production of radicals was not suspected, and no attempt was made to detect their presence.

\textbf{E. Reactions of Phenazine With Mo($V$) Compounds}

Molybdenum is known to be important in at least five enzymes: xanthine oxidase, aldehyde oxidase, nitrate reductase, nitrogenase, and sulfite oxidase.\textsuperscript{243} Furthermore, it seems to be generally accepted that the molybdenum alternates between the +5 and +6 oxidation states during electron transport by the enzyme and that flavosemiquinones are also involved.\textsuperscript{243} Thus, it seemed important to investigate the reactions of Mo($V$) compounds with phenazine to determine if free radicals would be formed by this biologically important metal.

Reactions were carried out between phenazine and three Mo($V$) compounds: $Et_4NMoOCl_4 \cdot H_2O$, $(NH_4)_2MoOCl_5$, and $MoO_2Cl(oxine H)_2$. In
the reaction with $(\text{NH}_4)_2\text{MoOCl}_5$ no radical signal was found by means of ESR (Chapter II). The very low solubility of $(\text{NH}_4)_2\text{MoOCl}_5$ in nitromethane presumably prevented reaction with the phenazine.

In the reaction with $\text{Et}_4\text{NMoOCl}_4\cdot\text{H}_2\text{O}$, there were obtained several different products that depended on the reaction conditions. Although several of these compounds contain phenazine, a radical was produced only when oxygen and moisture were excluded from the system; this behavior contrasts with that of the phenazine-UOCl$_5^{2-}$ system. This behavior may be due to the greater affinity of molybdenum(V) for oxygen donors than that for nitrogen ligands.$^{142,243}$ One of the compounds isolated by this procedure possesses both Mo(V) and free radical ESR signals (Figure 32a) but contains only a trace of Mo(V). The analysis of the material is almost identical with that of $\text{PH}_2\text{Cl}$, but the compounds are vastly different in appearance; $\text{PH}_2\text{Cl}$ is dark green (almost black), and the compound in question has a gold color. The idea that this compound might be phenazine monohydrochloride (PHCl) was also considered, but the latter species is reported$^{203}$ to form dark blue-green needles. This reaction was carried out twice under anhydrous, anaerobic conditions, and both reactions resulted in the formation of crystalline substances that have both Mo(V) and free radical ESR signals. The appearance of the free-radical signal was different in the case of the two preparations (Figure 32), however, and a formula could not be fit to the analysis of one of the isolated solids (vide supra, Chapter II). At present, there is no satisfactory explanation for the apparently anomalous properties of these compounds; further study is obviously required.
FIGURE 32. The ESR Spectra of the Solid Free-Radical-Mo(V) Compounds. Curves (a) and (b) Illustrate the Variation of the Free-Radical Signal in the Case of Two Different Preparations.
The reaction of phenazine with a Mo(V)-oxine complex was undertaken because of the similarity of the Mo-oxine system to enzyme systems. The complex MoOCl(oxine H)_{2} was selected as reactant because it was thought that the reaction

\[ \text{MoOCl(oxine H)}_{2} + \text{P} \rightarrow \text{MoO}_{2}($\text{oxine}$)_{2} + \text{PH}_{2}\text{Cl} \] (35)

might be favorable because the very stable $^{1/2}\text{MoO}_{2}($oxine$)_{2}$ might be produced. Two compounds, MoOCl(oxine)$_{2}$ and (PH)$_{2}$MoO$_{2}$Cl, were isolated as products of the reaction; both products exhibit very weak free radical ESR signals in addition to the Mo(V) signal. The starting material did not possess a free radical signal.

The results obtained from these reactions demonstrate the ability of Mo(V) to form free radicals with phenazine. However, this tendency is not as pronounced as that of the UOCl$_{5}^{2-}$ case, and the results in the case of Mo(V) are not amenable to a simple interpretation. This behavior on the part of Mo(V) is probably due to a combination of factors: (1) Mo(V) is much more stable relative to Mo(VI) than is U(V) relative to U(VI), (2) Mo(V) has a greater affinity for O- than for N-donors, and (3) Mo(V) tends to form a variety of complex species in solution via hydrolysis and dimerization.$^{138,140,142}$
CHAPTER V

SOME ADDITIONAL ASPECTS OF THE CHEMISTRY
OF U(IV), U(V) AND Mo(V)

It was previously noted (Chapter II) that the starting compound \(\text{UC}_{15}^\cdot\text{TCAC}\) was prepared by a modification of the original procedure. The modification consists specifically of a filtration step which enhances the purity of the product and renders it essentially free of \(\text{U(IV)}\) and \(\text{U(VI)}\). The utility of \(\text{UC}_{15}^\cdot\text{TCAC}\) as a starting material for the preparation of \(\text{U(V)}\) compounds was expanded as a result of the present research. The complex \((\text{Et}_4\text{N})_2\text{UOCl}_5\) was prepared from \(\text{UC}_{15}^\cdot\text{TCAC}\), and it is possible that it may be used to prepare other salts of the \(\text{UOCl}_5^\cdot\) species. In addition, while checking Ryan's preparative methods for \(\text{UC}_{15}^\cdot\) complexes, it was found that the preparation of these compounds from \(\text{UC}_{15}^\cdot\text{TCAC}\) is superior to Ryan's method in terms of flexibility, purity, and yield.

There were carried out preliminary studies of the utility of uranium complexes as NMR chemical shift reagents. The \(\text{U(V)}\) complexes \((\text{Et}_4\text{N})_2\text{UOCl}_5\) and \(\text{Pr}_4\text{NUC}_{15}^\cdot\) and the \(\text{U(IV)}\) complex \(\text{U(dpm)}_4\) did not produce measurable shifts in the spectra of \(n\)-hexanol, anisole, and ethanol, respectively. Decomposition of the \(\text{U(V)}\) complexes by the added reagents may have been involved.

The complex \((\text{Et}_4\text{N})_2\text{MoOCl}_5\) was previously reported, but all attempts to prepare it were unsuccessful. The previously unreported \(\text{Et}_4\text{NMoOCl}_4\cdot\text{H}_2\text{O}\) was prepared by several methods, however. It now appears that the reports of \((\text{Et}_4\text{N})_2\text{MoOCl}_5\) are in error. The
MoOCl$_5^{2-}$ species forms salts with NH$_4^+$, K$^+$, Rb$^+$, Cs$^+$, PyH$^+$, QiH$^+$, MeNH$_3^+$, Me$_2$NH$_2^+$, Me$_3$NH$^+$, and Me$_4$N$^+$. All of these cations except PyH$^+$ and QiH$^+$ are smaller than Et$_4$N$^+$. The PyH$^+$ and QiH$^+$ cations are planar, and thus a comparison with the others in the above list is not valid. It thus appears that the Et$_4$N$^+$ cation is simply too large to form a salt of MoOCl$_5^{2-}$. It is interesting to note that the large dipyH$^+$, Ph$_4$As$^+$, and Ph$_4$P$^+$ cations are also reported to form MoOCl$_4^-$ salts.
CHAPTER VI

SUGGESTIONS FOR FURTHER WORK

As a result of the present research, numerous possibilities for further work on U(V) and Mo(V) chemistry have arisen.

The first area in which further work could be done is the theoretical model presented in Chapter III. In the calculation, the spin-orbit coupling constant ($\zeta$) for UOCl$_5^{2-}$ was assumed to be identical with that of UC$_6^{2-}$. This assumption is probably not the case, however, since nephelauxetic effects in the two complexes would be expected to be different. Different values of $\zeta$ should be used in the calculation. It would also be interesting to conduct theoretical and spectral studies of UOF$_5^{2-}$ and UOBr$_5^{2-}$ in a manner analogous to the UOCl$_5^{2-}$ studies given in Chapter III.

In connection with these theoretical studies, it would be interesting to attempt to prepare complexes of general formula M$_x$UC$_5A$ in which M is a univalent cation and A is an inorganic anion that has a charge of ($-x$). Anions such as F$^-$, CN$^-$, and S$^{2-}$ would be interesting. These complexes might conceivably be prepared from UC$_5$·TCAC and the appropriate salt, M$_x$A, in an inert, dry, oxygen-free solvent and atmosphere. It should be noted that an attempt was made to prepare (Et$_4$N)$_2$USCl$_5$, but disproportionation of the U(V) occurred. This disproportionation was probably due to the use of a large excess of H$_2$S in the reaction; use of a stoichiometric quantity of M$_x$S might prevent disproportionation. The complexes thus prepared would be analogs of the UOCl$_5^{2-}$ salts in which A replaces O as the sixth ligand. Electronic
spectral studies of these complexes would be useful in testing the theory proposed in Chapter III because changing the identity of A would result in a corresponding change in the value of the perturbation parameter \( \tau \). It might then be possible to arrange these ligands in a "spectrochemical series" for U(V).

If these \( M_x UCl_9 A \) complexes could be prepared, their hydrolysis behavior would be worthy of study. If A were a stronger ligand than \( Cl^- \) for uranium(V), the hydrolysis could conceivably produce \( M_{2+x} UOCl_4 A \).

In the present research, hydrolysis of \( UCl_5 \cdot Me_2 \) and \( UCl_5(\text{phthalazine}) \) produced \( UOCl_5^{2-} \) and indicated that \( Me_2 O \) and phthalazine are held less tightly than is chloride. It would be interesting to observe which chloride (cis or trans), if any, would be preferentially removed in the hydrolysis.

Jorgensen\(^{246}\) has noted the formation in solution of the U(IV) mixed halide complexes \( UBr_x Cl_{8-x} \). In addition to the proposed \( UFCl_5^- \), it might be possible to prepare mixed halide complexes of U(V) by addition of fluoride to \( UCl_6^- \) or \( UBr_6^- \) solutions or by addition of chloride to \( UBr_6^- \) solutions. Since the strength of the U-X bond varies in the order \( F^- > Cl^- > Br^- \), fluoride would presumably displace both chloride and bromide from the U(V) coordination sphere, and chloride would displace bromide.

An attempt was made to prepare the U(IV) complex \( (Et_4 N)_3 UOCl_5 \) in order to compare its electronic spectrum with that of \( (Et_4 N)_2 UCl_6 \) in the manner done in the case of the analogous U(V) complexes. The procedure was similar to that for the preparation of the \( UOCl_5^{2-} \) salts. The preparation of this compound might be possible by treatment of \( (Et_4 N)_2 UCl_6 \) with \( Ag_2 O \) in a non-aqueous system.
In Chapter I it was mentioned that complexes of general formula $\text{UCl}_5 \cdot L_x$ were prepared by Selbin, et al.,$^{45}$ from $\text{UCl}_5 \cdot \text{TCAC}$ in benzene by adding the appropriate ligand. A similar series was prepared by Paul, et al.,$^{25}$ from $\text{U}^{(v)}$ in thionyl chloride. In the former series of compounds, $g$-values are near the free electron value, but they are all approximately 1.1 for the latter series. A study should be undertaken to try to determine the reasons for the differences in the properties of these compounds.

When the present research was initiated, one of the objectives was the preparation of complexes of the $\text{UO}_3^{3+}$ entity by three preparative methods (vide supra, Chapter I). As a result of certain findings in the course of this research, the research objectives were modified somewhat; the original project was not carried out to the extent which was planned. This facet of $\text{UO}_3^{3+}$ research should be extended. In particular, the same series of ligands should be used in each of the three reactions. In addition, other methods could be used to attempt to prepare complexes of the $\text{UO}_3^{3+}$ species. For instance, the hydrolysis of $\text{UF}_5^{2-}$, $\text{UCl}_5^{2-}$, and $\text{UBr}_5^{2-}$ could be carried out in the presence of certain ligands, as in the case of the analogous reaction of $\text{UCl}_5 \cdot \text{TCAC}$. The direct reactions of $\text{UOF}_5^{2-}$ and $\text{UOBr}_5^{2-}$ with certain ligands would also be interesting for comparison with the case of $\text{UOCl}_5^{2-}$; these reactions have already been carried out with phenazine.$^{247}$ The results of the present research suggest that certain $\text{U}^{(v)}$ compounds may undergo reactions similar to those which occur in enzymatic systems and that these reactions may be useful as models for enzymatic processes. Accordingly, there should be carried out reactions of $\text{UOX}_5^{2-}$ with a variety of compounds that have ring systems similar to those of the flavins. Some work in this area is now in progress.$^{247}$ Finally, no complexes of the $\text{UO}_3^{+}$ species have yet been prepared by displacement of chloride from
the uranium coordination sphere. These complexes might be prepared by a reaction such as:

$$L + \text{MUC}_6 + \text{Ag}_2\text{O} \rightarrow \text{MUOCl}_4 \cdot L + 2\text{AgCl}$$

(36)

It was previously postulated that, in the direct reactions of \((\text{Et}_4\text{N})_2\text{UOCl}_5\) with pyridine, pyrazine, and phthalazine, the organic ligands may have remained in solution as radicals. It might be possible to precipitate such radicals by bubbling dry \(\text{HCl}\) gas into these solutions or by adding the chloride salt of a large cation.

It was observed in Chapter IV that the radical \(\text{BPHe}_2\text{Cl}\) showed a greater tendency to form when a larger ratio of \(\text{UOCl}_5^{2-}:\text{BP}\) was used in this reaction. This reaction should be carried out again when, for example, a \(\text{UOCl}_5^{2-}:\text{BP}\) ratio of 4:1 is used. The pure chloride salt would probably precipitate from such a solution.

Additional studies of the very interesting \(\text{PH}_2\text{Cl}\) would be worthwhile. Data from similar compounds\(^{222}\) suggest that \(\text{PH}_2\text{Cl}\) may have a very high electrical conductivity. Because of the reflective, almost metallic appearance of this compound, a diffuse reflectance spectrum may yield valuable new information concerning the electronic structure of the solid state. (A diffuse reflectance attachment was not available for use in this research.) It would also be interesting to attempt to exchange the chloride anion. This exchange might be done, for instance, by dissolving the compound in ethanol or methanol and adding fluoboric acid, \(\text{HBF}_4\), which is available as a 50\% aqueous solution. In addition, thermal studies suggest that \(\text{PH}_2\text{Cl}\) may sublime; vacuum sublimation and analysis of the product should be done. Thermal studies also suggest that hydrated \(\text{PH}_2\text{Cl}\) can be dried by heating in
this drying could be attempted. It would also be interesting to
determine whether or not the NMR spectrum of \( \cdot \text{PH}_2\text{Cl} \) can be observed.

While it is thought that the unique reaction which produces
\( \cdot \text{PH}_2\text{Cl} \) is now understood, some further research could be done in this
area. For instance, the intermediate(III) in equation (34) could be
studied by means of its solution ESR spectrum and other physical data.
It might also be possible to isolate this compound by chilling the
solution or by adding a cosolvent to induce its precipitation. This
compound would, no doubt, be a very reactive species. It should be
possible to produce the deutero compound, \( \cdot \text{PD}_2\text{Cl} \), by adding \( \text{D}_2\text{O} \) to a
solution containing the intermediate(III). Infrared and solution ESR
spectra would verify the presence of the deuterium ions. This work
would provide additional confirmation of the reaction pathway postulated
in Chapter IV. Work is also in progress in this area.\(^{247}\)

It has recently been found\(^{247}\) that compounds such as pheno-
thiazine (PT), which form free radicals by undergoing a one-electron
oxidation, will react with \( \text{Et}_4\text{NUCl}_6 \) to form compounds of the type \( (\cdot \text{PT}^+) \text{UCl}_6 \).
Thus, dihydrophenazine may react with \( \text{Et}_4\text{NUCl}_6 \) in the following
manner.

\[
2\text{PH}_2 + 2\text{Et}_4\text{NUCl}_6 \rightarrow (\cdot \text{PH}_2)_2\text{UCl}_6 + (\text{Et}_4\text{N})_2\text{UCl}_6
\]

(37)

In the reaction of phenazine with \( (\text{Et}_4\text{N})_2\text{UOCl}_5 \), the very stable \( (\text{Et}_4\text{N})_2\text{UO}_2\text{Cl}_4 \) was one of the products; the formation of this very stable com-
 pound may be one of the driving forces for this reaction. It would be
interesting to determine if, in the presence of excess dry HCl, the
reaction

\[
P + 2\text{HCl} + \text{Et}_4\text{NUCl}_6 \rightarrow \text{UCl}_6 + \cdot \text{PH}_2\text{Cl} + \text{Et}_4\text{NCl}
\]

(38)
would proceed. If reactions (37) and (38) both occur as written, then Et₄NUCl₄ could be used to form radical ions with both oxidizable and reducible organic species.

It was noted in Chapter IV that treatment of the complex Et₄NMoOCl₄·P with water produced a dark product that has a color reminiscent of PH₂Cl. The investigation of this reaction would be a worthwhile project.

Several other reactions could be carried out with a view toward production of free radicals by molybdenum. It was observed (Chapter IV) that MoOCl(oxine)₂ is not appreciably soluble in nitromethane. If, however, a suitable solvent could be found, the reaction

\[
\text{MoOCl}(\text{oxine})_2 + \text{P} + \text{H}_2\text{O} \rightarrow \text{PH}_2\text{Cl} + \text{MoO}_2(\text{oxine})_2
\]

might occur because the Mo(VI) product has been reported to be very stable. It might also be possible to prepare a MoOCl₅²⁻ salt which is sufficiently soluble in nitromethane to permit reaction with phenazine. In addition, it would be worthwhile to investigate reactions of Mo(VI) compounds with oxidizable species such as dihydrophenazine, to determine if the tendency toward free radical formation would be greater than that of Mo(V). Finally, the great affinity of Mo(V) and Mo(VI) for O-donor ligands may cause these species to form radicals more readily with O-donor ligands than with nitrogen donors such as phenazine.

The study of U(IV) and U(V) compounds as NMR chemical shift reagents should be continued. It would be interesting to determine if proton resonances of ligands such as ethyl ether would be shifted in compounds such as UCl₅·2OEt₂, in which the ligand is within the U(V) coordination sphere.
Due to the unexpected discovery of free-radical formation by U(V), some of the present research, particularly in the case of that of Mo(V), consisted in the main of a rapid search for free radical formation. As a result, several compounds were isolated for which little characterizing data was obtained. The characterization of these compounds would be a useful project. Some of this work would require considerable effort in the development of techniques. For example, measurements of spin concentrations of some compounds containing radicals might be carried out. This measurement is not presently done at Louisiana State University. Also, the Gouy method is not adequate for the determination of magnetic moments of many of the compounds in this study because their magnetic moments and densities are quite low. The Faraday method would be useful for these measurements, but a Faraday apparatus is not presently available. The magnetic moments of some of the compounds could, however, be measured by means of the NMR concentric tube method.248
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VITA

David Glen Durrett was graduated with valedictory honors from Bunkie High School in Bunkie, Louisiana, in 1960. That year he entered the University of Southwestern Louisiana as a recipient of a four-year academic scholarship that was awarded on the basis of competitive examinations. While attending that University, he was elected to membership in Phi Eta Sigma and Tau Beta Pi and was vice-president of the Student Chapter of the American Institute of Chemical Engineers, from which he received the 1962 Annual Chapter Scholarship Award. He was graduated "With Highest Distinction" and earned the B.S. degree in Chemical Engineering. In 1964 he married the former Dianne Zimmerman.

Having been employed during two summer vacations as an engineering assistant by Allied Chemical Corporation in Baton Rouge, Louisiana, he joined that company upon graduation as a Process Engineer.

In 1965 he enrolled in the New Orleans Baptist Theological Seminary, from which he received the degree of Master of Theology (Th.M.), Honors Program in 1968. He was part-time instructor in Chemistry and Physics at Delgado (Junior) College in New Orleans from 1966 to 1968.

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Date of Examination: July 10, 1972