

12-23-2015

## A Stable Coordination Complex of Rh(IV) in an N,O-Donor Environment

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### Recommended Citation

Sinha, S., Shopov, D., Sharninghausen, L., Vinyard, D., Mercado, B., Brudvig, G., & Crabtree, R. (2015). A Stable Coordination Complex of Rh(IV) in an N,O-Donor Environment. *Journal of the American Chemical Society*, 137 (50), 15692-15695. <https://doi.org/10.1021/jacs.5b12148>

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Communication

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*J. Am. Chem. Soc.*, **Just Accepted Manuscript** • DOI: 10.1021/jacs.5b12148 • Publication Date (Web): 07 Dec 2015

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# A Stable Coordination Complex of Rh(IV) in an N,O-donor Environment.

Shashi B. Sinha<sup>†</sup>, Dimitar Y. Shopov<sup>†</sup>, Liam S. Sharninghausen<sup>†</sup>, David J. Vinyard, Brandon Q. Mercado, Gary W. Brudvig<sup>\*</sup>, Robert H. Crabtree<sup>\*</sup>.

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## Supporting Information Placeholder

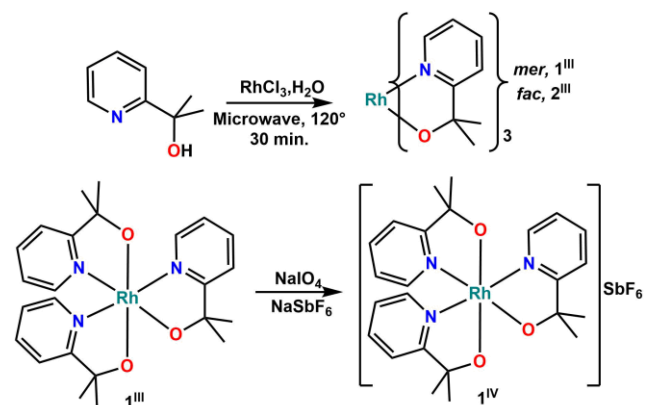
**ABSTRACT:** We describe facial and meridional isomers of  $[\text{Rh}^{\text{III}}(\text{pyalk})_3]$ , as well as meridional  $[\text{Rh}^{\text{IV}}(\text{pyalk})_3]^+$  {pyalk = 2-(2-pyridyl)-2-propanoate}, the first coordination complex in an N,O-donor environment to show a clean, reversible  $\text{Rh}^{\text{III/IV}}$  redox couple and to have a stable Rh(IV) form, which we characterize by EPR and UV-visible spectroscopy as well as X-ray crystallography. The unprecedented stability of the Rh(IV) species is ascribed to the exceptional donor strength of the ligands, their oxidation-resistance and the meridional coordination geometry.

Interest in high oxidation state transition metal complexes has grown considerably in recent years in connection with oxidation catalysis.<sup>1</sup> While there are a number of well-established Ir(IV) complexes, the highest oxidation state commonly encountered for rhodium is Rh(III).<sup>2,3</sup> Among the very few Rh(IV) species known,  $[\text{RhX}_6]^{2-}$  (X = Cl, F) are unstable in water, which has limited their characterization.<sup>4</sup> There are also a number of poorly characterized solid-state Rh(IV) oxide species,<sup>5</sup> as well as several formally Rh(IV) dinuclear organometallic compounds.<sup>6</sup> Several other complexes, such as Claus' Blue, originally thought to feature Rh(IV), are in fact superoxides of Rh(III).<sup>7</sup> Rh(IV) species have been postulated as intermediates in chemical transformations,<sup>8</sup> and characterization of a stable Rh(IV) complex is, therefore, of interest. However, there do not seem to be any examples of well characterized stable coordination compounds of Rh(IV) with organic ligands; a few reports of metastable Rh(IV) species present only very limited characterization.<sup>9</sup> A common problem with these and other highly oxidized complexes is oxidative instability of the organic ligands, which limits the formation of stable species.<sup>10</sup>

We recently reported that the oxidatively robust, bidentate pyridine-alkoxide ligand pyalk (2-(2-pyridyl)-2-propanoate) strongly stabilizes high oxidation states.<sup>3</sup> Both the facial and meridional isomers of  $\text{Ir}(\text{pyalk})_3^{0/+}$  had easily accessible III/IV couples, with the meridional isomer having what may be the lowest  $\text{Ir}^{\text{III/IV}}$  reduction potential ever reported. In water-oxidation catalysis,<sup>11</sup> pyalk displays extremely high stability even under harsh catalytic conditions. We now report an extension of these observations to the stabilization of the more challenging Rh(IV) oxidation state. The meridional (**1<sup>III</sup>**) and facial (**2<sup>III</sup>**) isomers of  $[\text{Rh}^{\text{III}}(\text{pyalk})_3]$  (Scheme 1) can be synthesized, separated and characterized. The *mer* isomer shows a reversible electrochemical redox couple, and can be cleanly chemically oxidized to the corresponding  $[\text{Rh}^{\text{IV}}(\text{pyalk})_3]^+$  species, which proves to be kinetically stable in a range of solvents including water. Full

characterization, including the first clear and well-simulated Rh(IV) EPR spectrum as well as the first crystal structure of a Rh(IV) coordination complex with organic ligands, establishes the identity of this complex.

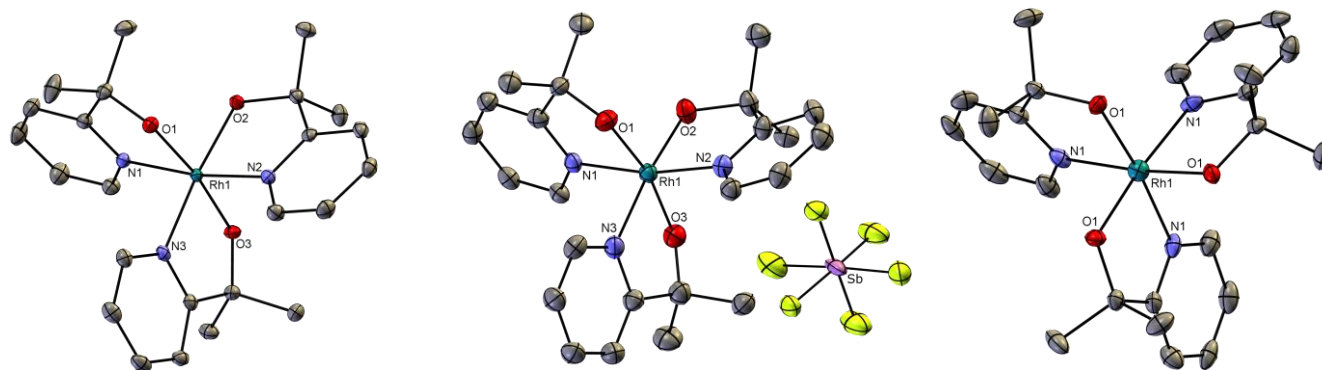
## Scheme 1. Preparation of complexes **1<sup>III</sup>**, **2<sup>III</sup>** and $[\text{1<sup>IV</sup>}] \text{SbF}_6$ .



Compounds **1<sup>III</sup>** and **2<sup>III</sup>** were prepared by microwave heating an aqueous solution of  $\text{RhCl}_3$  with an excess of Hpyalk (Scheme 1). With excess ligand as the base, clean conversion occurs without formation of metal oxides. Separation of **1<sup>III</sup>** and **2<sup>III</sup>** is possible due to their disparate polarities (see SI). Both **1<sup>III</sup>** and **2<sup>III</sup>** were isolated as air-stable yellow powders exhibiting a remarkably broad solubility range and were fully characterized. **1<sup>III</sup>** is the major product of the reaction (9:1 ratio *vs* **2<sup>III</sup>** based on <sup>1</sup>H NMR of the crude mixture; 60% isolated yield), while **2<sup>III</sup>** is the minor product (2% isolated yield). The complexes display the <sup>1</sup>H and <sup>13</sup>C NMR signals (See SI, Page S5) expected from their symmetry, with three sets of ligand signals for **1<sup>III</sup>** and only one for **2<sup>III</sup>**. The methyl groups of the ligands are inequivalent in both <sup>1</sup>H and <sup>13</sup>C NMR, as expected.

Addition of sodium periodate to a solution of **1<sup>III</sup>** causes a color change from pale yellow to dark purple over approximately 20 minutes. This new species can be extracted into dichloromethane and crystallized, after addition of  $\text{SbF}_6^-$ , to give  $[\text{1<sup>IV</sup>}] \text{SbF}_6$  as a dark violet solid. This rare Rh(IV) complex shows much greater stability in both aqueous and oxidation-resistant organic solvents than previous Rh(IV) coordination compounds.<sup>9</sup> At room temperature, degradation proceeds over the course of several days and primarily involves the reversible reduction to **1<sup>III</sup>**, a process also achieved with chemical reductants like sodium ascorbate. In contrast, attempts to oxidize **2<sup>III</sup>** did not result in

an isolable species. This difference in redox properties is consistent with our findings for the Ir analogues.



**Figure 1.** Thermal ellipsoid diagrams of the crystal structures of **1<sup>III</sup>** (left, at 50% probability level), [**1<sup>IV</sup>**]SbF<sub>6</sub> (center) and **2<sup>III</sup>** (left) at 30% probability level. Hydrogen atoms have been omitted for clarity.

Crystal structures were obtained for **1<sup>III</sup>**, [**1<sup>IV</sup>**]SbF<sub>6</sub> and **2<sup>III</sup>** (Figure 1). The Rh-O bonds contract noticeably (by ca. 0.08 Å on average) upon oxidation (Table 1), consistent with a metal-centered process, while the Rh-N bonds undergo a slight extension, trends that are in line with the analogous Ir complexes.<sup>3</sup> To our knowledge, the structure of [**1<sup>IV</sup>**]SbF<sub>6</sub> represents the first example of a crystal structure of a molecular Rh(IV) coordination complex with organic ligands. Complex **1<sup>III</sup>** crystallizes as a well-ordered monohydrate. Complex **2<sup>III</sup>**, demonstrates high cation affinity by coordinating to Na<sup>+</sup> ions with its facial alkoxide groups; chloride counterions and disordered dichloromethane molecules are also present (See SI).

**Table 1. Comparison of selected crystallographic bond distances in 1<sup>III</sup> and [1<sup>IV</sup>]SbF<sub>6</sub>.**

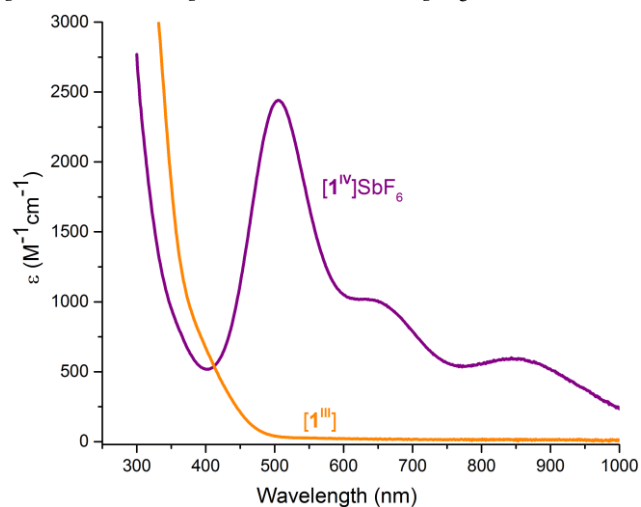
Bond	<b>1<sup>III</sup></b>	[ <b>1<sup>IV</sup></b> ]SbF <sub>6</sub> <sup>a</sup>
Rh1-N1	2.019(1)	2.025(5)
Rh1-N2	2.015(1)	2.027(6)
Rh1-N3	2.029(1)	2.063(5)
Rh1-O1	2.022(1)	1.920(5)
Rh1-O2	1.990(1)	1.923(6)
Rh1-O3	2.044(1)	1.965(5)

<sup>a</sup>Bond lengths calculated as average of lengths in the two molecules in the asymmetric unit.

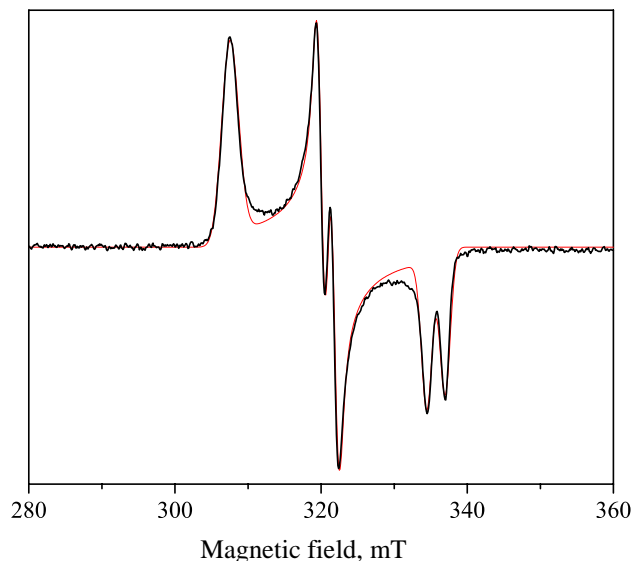
While the UV-visible spectrum (Figure 2) of **1<sup>III</sup>** only shows a weak absorption tail in the visible region, the oxidized state shows three peaks, the strongest at 520 nm having  $\epsilon = 2500 \text{ M}^{-1}\text{cm}^{-1}$ . These peaks are assigned to ligand-to-metal charge transfers by analogy with Ir(IV) species; the Rh(IV) spectrum closely resembles the Ir analog's, but is red-shifted by approximately 100-150 nm.<sup>3</sup>

Electron paramagnetic resonance spectroscopy on **1<sup>IV</sup>** (Figure 3) provides further evidence for the Rh(IV) state. Consistent with the proposed  $S = 1/2$  system, a rhombic signal is evident which displays hyperfine coupling to <sup>103</sup>Rh ( $I = 1/2$ ), resolved as doublets in the mid-field and high-field peaks. The magnitude of the <sup>103</sup>Rh hyperfine coupling and the breadth of the signal are strongly indicative of a metal-centered electron spin. Coupling to <sup>14</sup>N is not observed, consistent with calculations on the analogous Ir complex that showed essentially no frontier orbital occupancy on N.<sup>3</sup> The spectrum was successfully simulated by considering only the <sup>103</sup>Rh coupling and diffuse hyperfine

strain (Figure 3). This seems to be the first example of a clean, solution-phase Rh(IV) EPR spectrum for which Rh coupling is resolved.



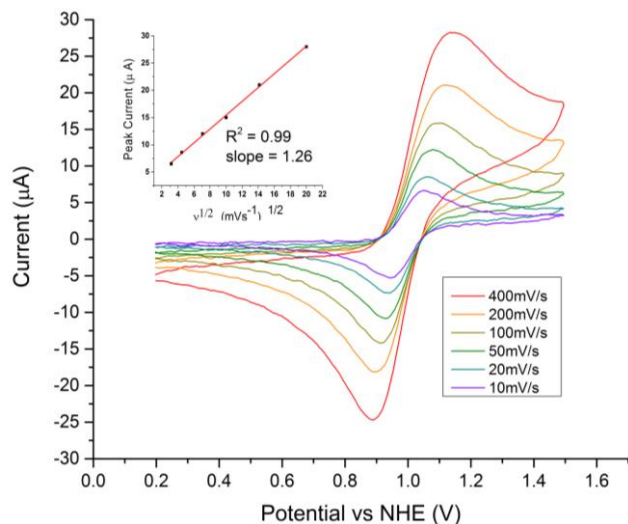
**Figure 2.** UV-visible absorption spectra of [**1<sup>III</sup>**] (orange) and [**1<sup>IV</sup>**]SbF<sub>6</sub> (purple) in dichloromethane.



**Figure 3.** X-band EPR spectrum of compound **1<sup>IV</sup>** measured at 8 K

(black) and simulation (red). Compound **1**<sup>IV</sup> has a rhombic EPR spectrum with  $g = [2.180, 2.089, 1.997]$  consistent with low-spin ( $S = \frac{1}{2}$ ) Rh(IV). Hyperfine interactions from the  $I = \frac{1}{2}$   $^{103}\text{Rh}$  nucleus (100%) were simulated using principal values of 31, 53, and 70 MHz. Anisotropic line broadening was simulated using the H-strain tensor [70, 33, 44] MHz to account for unresolved hyperfine interactions.

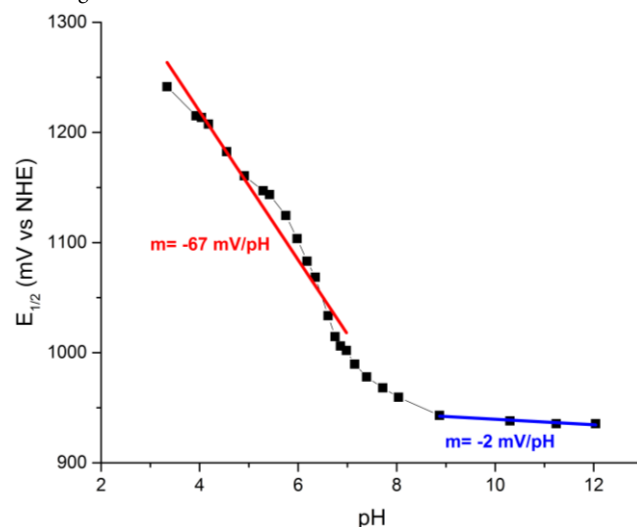
In cyclic voltammetry, each isomer shows only one redox feature in the range studied, but at significantly different potentials. For **1**, a fully reversible feature at 0.98 V vs. NHE (pH 7, phosphate buffer) is observed with cathodic and anodic currents essentially equal at all scan rates (Figure 4) and with the expected square-root relationship between peak current and scan rate. The symmetry between anodic and cathodic waves supports the reversible nature of this feature, which we assign as the Rh<sup>III/IV</sup> couple. While there is a noticeable rise in the peak-to-peak separation at higher scan rates, this is likely due to slow electron transfer at the working electrode, boron-doped diamond (BDD). Although BDD is known to have substantially slower electron transfer kinetics than more common electrodes,<sup>12</sup> it is better adapted for aqueous work at these high potentials, having much lower background current. In contrast to **1**, the redox feature for **2** is only quasi-reversible (See SI, Page S9). Due to its very high potential (1.38 V vs. NHE), as well as an underlying catalytic wave (presumably degradation), the oxidized state is most likely short-lived under these conditions. While no characterization has been attempted so far, we tentatively attribute this feature to a Rh<sup>III/IV</sup> couple as well.



**Figure 4.** Cyclic voltammograms of **1** in 0.1 M phosphate buffer at pH 7.0 at different scan rates from 10 mV s<sup>-1</sup> to 400 mV s<sup>-1</sup>. Insert: plot of peak current versus (scan rate)<sup>1/2</sup>.

The Rh<sup>III/IV</sup> couples are pH dependent, suggesting that the alkoxide groups in the Rh(III) state are sufficiently basic to be partially protonated even at neutral pH. The Pourbaix curve for the Rh<sup>III/IV</sup> couple of **1** (Figure 5) indicates a proton-dependent ( $1 \text{ H}^+ / e^-$ ) electron-transfer regime below pH 7 and a proton-independent regime above pH 8. Based on the basicity of the alkoxide, we assign the Rh(III) species in acid as monoprotonated [**1**<sup>IIIH</sup>]<sup>+</sup>, in base as **1**<sup>III</sup>, and in the oxidized state as the pH-invariant [**1**<sup>IV</sup>]<sup>+</sup>. Because basic conditions provide a stable regime involving two well-defined species, we can compare the aqueous Rh<sup>III/IV</sup> potential for **1**<sup>III</sup> at 0.935 V vs. NHE with that for **2**<sup>III</sup> with  $E_{1/2} = 1.28 \text{ V}$  at pH 11, their separation being 0.345 V. We will use these as the formal aqueous Rh<sup>III/IV</sup> potentials. Both the *mer*/*fac* isomer separation and the features of the Pourbaix curve very closely mirror those for the Ir(pyalk)<sub>3</sub> complexes,<sup>3</sup> the primary difference being the Rh/Ir offset, of ca. 0.5 V. The lack of perfect linearity in the pH = 3–7 range is attributed to the highly basic character of the alkoxide ligands that promotes pH-

dependent hydrogen bonding and ion binding, as also observed for the Ir analog.<sup>3</sup>



**Figure 5.** pH dependence of the Rh<sup>III/IV</sup> electrochemical redox couple for **1**. Linear regression fits and their slopes are given for data points pH < 7 (red) and pH > 8 (blue).

The reasons our *mer* complex avoids the typical instability of the Rh(IV) state are the strong donor and oxidation-resistant tertiary alkoxide ligands, as well as the meridional geometry itself. For iridium, alkoxides can be extremely potent donors, surpassing even phenyl ligands;<sup>3,13</sup> this has been ascribed to their dual  $\sigma$ - and  $\pi$ -donating character. Furthermore, we and others<sup>3,11</sup> have shown the importance of ligand orientation on redox properties. The ease of oxidation depends not only on the sum of the donor effects of the ligand groups, following Lever,<sup>14</sup> but also on the electronic splitting of the otherwise degenerate  $t_{2g}$   $d$ -orbitals. A  $d^6 \rightarrow d^5$  oxidation of a pseudo octahedral complex is facilitated when one orbital energy is raised via this splitting. Because the  $t_{2g}$  orbitals are planar in shape, the greatest effect occurs when the most electron-donating ligands all lie in one plane. In our case, all three alkoxides occupy one plane in the *mer* complex **1**, whereas for the symmetric *fac* complex **2**, all planes, and thus all  $t_{2g}$  orbitals, are equivalent. The net result is that **1** experiences this anisotropic oxidation enhancement effect that splits the  $t_{2g}$   $d$ -orbitals, while **2** does not. Although the magnitude of the effect is essentially the same for Rh and Ir, the practical implications for Rh(pyalk)<sub>3</sub> are far more impressive: one isomer (**1**<sup>III</sup>) forms an unprecedentedly stable and long-lived Rh(IV) species, while the other (**2**<sup>III</sup>) forms one only transiently.

In conclusion, we have prepared and characterized *mer*-[Rh<sup>III</sup>(pyalk)<sub>3</sub>], a rhodium coordination complex capable of accessing the rare Rh(IV) oxidation state through both chemical and electrochemical oxidation. In contrast to the previously known Rh(IV) coordination complexes, *mer*-[Rh<sup>IV</sup>(pyalk)<sub>3</sub>] is stable for long periods in a range of solvents. This facilitates characterization by several methods including unprecedented X-ray crystallography and EPR spectroscopy for the Rh(IV) state. The remarkable stability of this complex arises from the strongly donating ligand set, the oxidation-resistant nature of the ligand and the meridional ligand arrangement. The importance of this last aspect is illustrated by the inability of the compositionally equivalent facial isomer, *fac*-[Rh<sup>III</sup>(pyalk)<sub>3</sub>], to form a stable Rh(IV) state, showing that coordination geometry can be a critical factor in oxidation state stability.

## ASSOCIATED CONTENT

### Supporting Information

Crystal structure files, additional figures, as well as detailed synthetic procedures and physical methods are available free of charge via the Internet at <http://pubs.acs.org>.

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### Author Contributions

<sup>†</sup>These authors contributed equally.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENT

This work was supported the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences under Award Number DE-SC0001059 as part of the Argonne-Northwestern Solar Energy Research (ANSER) Energy Frontier Research Center (spectroscopy and characterization) and under Award Number DEFG02-07ER15909 (synthesis).

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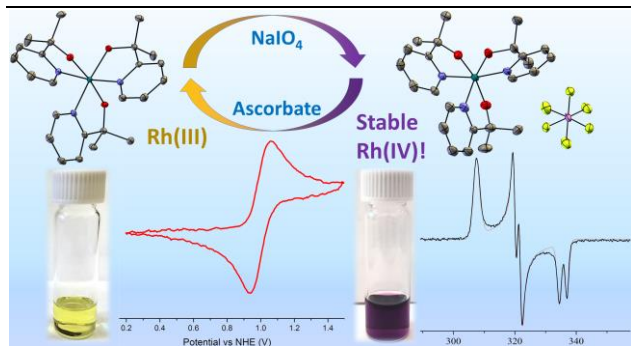
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