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Electrochemical Studies of a Series of Dirhodium(II) Complexes with Acetate and Acetamidate Bridging Ligands

Sir:

Recently, the synthesis of a new class of rhodium(II) complexes was reported.[1-3] These compounds, $Rh_2(RNOCR')_4$, have a structure similar to that of the well-studied[4,5] rhodium carboxylates $Rh_2(O_2CR)_4$ but have mixed oxygen and nitrogen donor atoms in place of the two oxygen donors of the carboxylato bridging ligands. In the first reported synthesis of these compounds, it was shown that $Rh_2(HNOCCF_3)_4$ could be electrochemically oxidized in a number of solvents to form $[Rh_2(HNOCCF_3)_4]^+$ at a potential between +0.90 and 1.08 V vs. SCE.[1,2] This is not the case for the corresponding trifluoroacetate-bridged complex $Rh_2(O_2CCF_3)_4$, which is not oxidized at potentials up to 1.8 V vs. SCE.[6] Thus, replacing four of the eight oxygens in $Rh_2(O_2CR)_4$ by NH groups lowers the oxidation potential of the dirhodium(II) complex by at least 700 mV.

It appears that the oxidation potential of the amidate-bridged complexes is quite sensitive to the substituents on the amide carbon and nitrogen atoms. For example, $Rh_2(C_6H_5NOCCH_3)_4$ has recently been isolated and electrochemically investigated.[3] This complex is oxidized to the radical cation at 0.54 ± 0.01 V vs. SCE and, unlike any other known dirhodium(II) complex, undergoes a second reversible one-electron oxidation at 1.64 ± 0.01 V vs. SCE in CH_2Cl_2.

The above two examples of how amidate bridging ligands shift dirhodium(II) oxidation potentials suggested to us the possibility of using mixed carboxylate and amidate bridging ligands in order to better "tune" the Rh(II,II)/Rh(II,III) and Rh(II,III)/Rh(III,III) redox potentials. We have now isolated these types of complexes, and their electrochemistry is presented here. The investigated series of compounds have the formula $Rh_2(ac)_n(acam)_{4-n}$ where ac = $[O_2CCH_3]^-$, acam = $[HNOCCH_3]^-$, and n = 0–4.

The synthesis of the mixed bridging ligand complexes is straightforward and involves separation of each $Rh_2(ac)_n(acam)_{4-n}$ species during the stepwise exchange reactions summarized by eq 1–4.

$$\underset{\text{I}}{Rh_2(ac)_4} + acam \rightarrow \underset{\text{II}}{Rh_2(ac)_3(acam)} + ac \tag{1}$$

$$\underset{\text{II}}{Rh_2(ac)_3(acam)} + acam \rightarrow \underset{\text{III}}{Rh_2(ac)_2(acam)_2} + ac \tag{2}$$

$$\underset{\text{III}}{Rh_2(ac)_2(acam)_2} + acam \rightarrow \underset{\text{IV}}{Rh_2(ac)(acam)_3} + ac \tag{3}$$

$$\underset{\text{IV}}{Rh_2(ac)(acam)_3} + acam \rightarrow \underset{\text{V}}{Rh_2(acam)_4} + ac \tag{4}$$

The exchange reactions were carried out for 48 h in a 300-fold excess of molten acetamide under vacuum at 120 °C. Excess acetamide was then removed by sublimation, and the five substitution products were separated by HPLC using a CN-bonded phase column with methanol eluant. Molecular weights of complexes I–V were determined by liquid chromatography/mass spectrometry operating in the negative-ion mode and showed parent masses of 442 (I), 441 (II), 440 (III), 439 (IV), and 438 (V). Carbon, hydrogen, nitrogen, and rhodium analysis were in good agreement for the new complexes II–V.

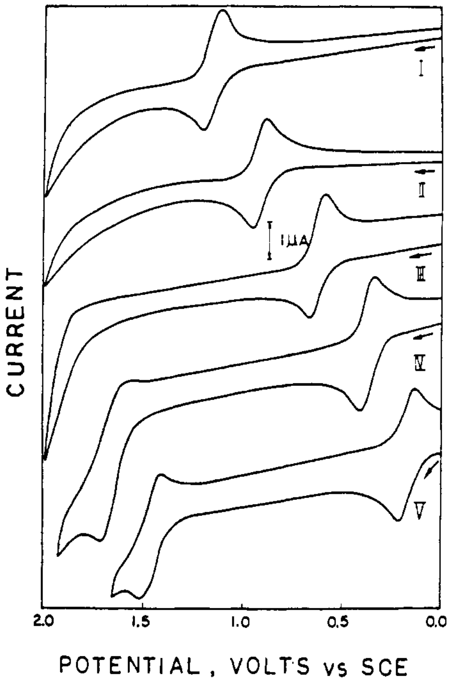

Figure 1. Cyclic voltammograms of compounds I–V at a Pt electrode in acetonitrile–0.1 M TBAP (scan rate 0.10 V/s).

An examination of structures for compounds II–V reveals that compounds III and V may each have four geometric isomers, while compound IV may have three such isomers. No geometric isomers are possible for compound II. The HPLC results indicate only one geometric isomer of IV and V is produced in the reaction.[7] In contrast, analytical-scale HPLC of compound III gave three overlapping peaks at very slow flow rates, suggesting that three geometric isomers are produced. This mixture was used in the present study because of difficulty involved in the preparative-scale separation of the isomers. However, the shape of the current–voltage curves for compound III suggests that all isomers are oxidized at approximately the same potential, indicating a minimal isomer effect on half-wave potentials.[8]

Cyclic voltammograms of compounds I–V are illustrated in Figure 1, and a summary of half-wave potentials is listed in Table I. All of the reactions are reversible to quasi-reversible ($E_{pa} - E_{pc}$ = 60–80 mV). As seen in this table, the potentials for Rh(II,II) ⇄ Rh(II,III) vary linearly with the number of amidate bridging ligands, up to a value of 3. A smaller shift in $E_{1/2}$ is observed upon addition of the fourth acetamidate group. At the same time, a second oxidation wave appears for $Rh_2(ac)(acam)_3$ (at 1.65 V vs. SCE) and $Rh_2(acam)_4$ (at 1.41 V vs. SCE).

Linear shifts of electronic absorption spectra also occur with an increasing number of acetamidate bridging ligands, but in this case deviations in the trend are opposite that observed for the shifts of $E_{1/2}$. This is shown in Table I, which lists λ_{max} of each major peak. As seen in this table, λ_{max} for the lower energy peak shifts to shorter wavelengths by approximately 14 nm for each exchange of acetamide ligand after the first. In contrast, only a 9.2-nm shift is observed on going from $Rh_2(ac)_4$ to $Rh_2(ac)_3(acam)$. Also, a second shoulder is observed in the absorption spectrum of compound III that is not

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(7) Unpublished X-ray data of $Rh_2(acam)_4$ (compound V) show that the two nitrogen and two oxygen atoms of each rhodium(II) are cis to their own kind.

(8) Studies with $Rh_2(C_6H_5NOCCH_3)_4$[3] and $Rh_2(HNOCCF_3)_4$ also indicate that half-wave potentials are relatively insensitive to isomer effects.

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Table I. Half-Wave Potentials (V vs. SCE) and Spectral Characteristics of Investigated Compounds in Acetonitrile[a]

compd	$E_{1/2}(1)$	$\Delta E_{1/2}$, V	$E_{1/2}(2)$	$\Delta E_{1/2}$, V	λ_{max}, nm ($10^{-2}\epsilon$, M^{-1})	
$Rh_2(ac)_4$ (I)	1.17	0.26			551 (2.7)	437 (1.9)
$Rh_2(ac)_3(acam)$ (II)	0.91	0.29			542 (2.2)	416 (1.7)
$Rh_2(ac)_2(acam)_2$ (III)	0.62	0.25			528 (2.0)	398 (sh), 359 (sh)
$Rh_2(ac)(acam)_3$ (IV)	0.37	0.22	1.65	0.24	514 (2.0)	356 (sh)
$Rh_2(acam)_4$ (V)	0.15		1.41		500 (2.2)	345 (sh)

[a] Half-wave potentials are measured in the presence of 0.1 M TBAP. sh = shoulder.

present with any of the other four complexes. This extra shoulder may be due to one of the three unresolved isomers, or it may be that compound III is spectrally more complex than any of the other complexes.

In summary, the experimental fact that $Rh_2(ac)_n(acam)_{4-n}$ has spectral and electrochemical properties between those of $Rh_2(ac)_4$ and $Rh_2(acam)_4$ should provide a basis for systematically examining the Rh_2^{4+}, Rh_2^{5+}, and Rh_2^{6+} units as a function of controlled changes in the bridging ligand. Literally hundreds of different combinations of R, R′, and R″ may be utilized in the synthesis of novel $Rh_2(RONCR')_n(O_2CR'')_{4-n}$ complexes. Thus, a carefully designed synthetic series of dirhodium(II) compounds can be used to systematically probe the electronic levels of the metal–metal bond in the oxidized and reduced species. This degree of structural control has never been available before and should provide the basis for a much better understanding of structure–reactivity relationships with these type compounds.

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Registry No. I, 15956-28-2; II, 87985-37-3; II (monooxidized), 87985-41-9; III, 87985-38-4; III (monooxidized), 87985-42-0; IV, 87985-39-5; IV (monooxidized), 87985-43-1; IV (dioxidized), 87985-45-3; V, 87985-40-8; V (monooxidized), 87985-44-2; V (dioxidized), 87985-46-4.

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Electrochemistry in Liquid Sulfur Dioxide. 5. Oxidation of Bipyridine and Phenanthroline Complexes of Osmium, Ruthenium, and Iron

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The electrochemical oxidation of bipyridine and phenanthroline complexes of Fe, Ru, and Os in liquid sulfur dioxide was investigated by cyclic voltammetry and coulometry. $Os(bpy)_3^{2+}$ and $Os(phen)_3^{2+}$ undergo two successive one-electron oxidations to form stable 3+ and 4+ species. In contrast $Fe(phen)_3^{2+}$ and $Ru(phen)_3^{2+}$, when oxidized to the 4+ form, produce an electroactive layer on the electrode surface. Electrochemical, magnetic susceptibility, and ^1H NMR data suggest that the oxidation to the 4+ form is metal centered in the Os complexes but ligand centered in the Fe and Ru complexes. Resonance Raman spectra of $Os(bpy)_3^{4+}$ exhibit unusual complexity that suggests either static inequivalency of the bpy ligands on the vibrational time scale or a multiple-minimum electronic potential.

Introduction

We showed in a previous study from our laboratory[1] that highly oxidized transition-metal complexes could be produced electrochemically in liquid sulfur dioxide. $Ru(bpy)_3^{2+}$ and $Fe(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) were oxidized in two successive one-electron oxidations to the 3+ and 4+ forms. The 3+ species were stable for hours while the 4+ species reacted with SO_2 in a catalytic cycle to regenerate the 3+ form. The 3+ → 4+ oxidation for $Ru(bpy)_3^{3+}$ and $Fe(bpy)_3^{3+}$ is believed to be ligand centered, on the basis of spectroscopic and electrochemical data.[1] We describe here the electrochemical oxidation of $Os(bpy)_3^{2+}$, $Fe(phen)_3^{2+}$, $Ru(phen)_3^{2+}$, and $Os(phen)_3^{2+}$ (phen = 1,10-phenanthroline) in liquid SO_2 along with information concerning the site of oxidation of the 3+ species. Both Os complexes form stable 3+ and 4+ forms while $Fe(phen)_3^{2+}$ and $Ru(phen)_3^{2+}$ undergo polymerization when oxidized to the 4+ species.

Magnetic susceptibility and ^1H NMR data are presented for the $Os(bpy)_3^{3+}$ and $Os(bpy)_3^{4+}$ species suggesting metal-centered oxidation. Resonance Raman (RR) spectroscopy of the series Os^{II}-, Os^{III}-, and $Os^{IV}(bpy)_3$ is also reported. The RR results are consistent with metal-centered oxidation in $Os(bpy)_3^{4+}$, if significant splitting of the ligand vibrational states occurs due to a dynamic Jahn–Teller effect or static ligand inequivalency.

Experimental Section

Measurements. Electrochemical measurements were made with a PAR Model 173 potentiostat, a Model 175 universal programmer, and a Model 179 digital coulometer (Princeton Applied Research

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