Table IV. Second-Order Rate Constants, k_{BrBr}, at 25 °C (μ = 0.055 M)

pH	k_{BrBr}, M^{-1} s^{-1}	pH	k_{BrBr}, M^{-1} s^{-1}
2.0	0.31 (2)	5.5	0.90 (3)
2.6	0.32 (2)	5.8	1.07 (5)
3.4	0.37 (2)	6.2	1.20 (5)
3.9	0.40 (2)	6.7	1.52 (5)
4.2	0.46 (2)	7.1	1.86 (10)
4.7	0.47 (2)	7.3	2.10 (10)
5.2	0.67 (3)	7.6	2.84 (10)

Table V. Pseudo-First-Order Rate Constants, k_{obs}, for $[Pt_2(SO_4)_4ClOH_2]^{3-} + Cl^- \rightarrow [Pt_2(SO_4)_4Cl_2]^{4-}$ at 25 °C (μ = 0.5 M, Adjusted with $HClO_4$)

$[Cl^-]$, M	10^4k_{obs}, s^{-1}	$[Cl^-]$, M	10^4k_{obs}, s^{-1}
0.02	3.5	0.15	24.0
0.05	7.3	0.20	33.0
0.10	15.0		

with the large negative ΔS^* values suggest an interchange mechanism[12] for these anation reactions, and the relatively small activation enthalpies indicate that the axial water molecule is not strongly attached to the Pt–Pt unit for either X = Cl or X = Br.

The reactions studied above are not accelerated by the presence of added $[Pt_2(pop)_4]^{4-}$, as shown by the experimental data set out in Table III. This suggests that a two-electron atom-transfer pathway involving a bridged intermediate, Pt_2–X–Pt_2, is unlikely in the present case. This finding is in contrast with most work on monomeric Pt(II) and Pt(IV) complexes.[13] Presumably, the large Coulombic repulsion between the $[Pt_2(pop)_4X(OH_2)]^{3-}$ and $[Pt_2(pop)_4]^{4-}$ complexes prevents their association in solution even though one-dimensional Pt_2–X–Pt_2 species, $\{K_4[Pt_2(pop)_4X]\}_n$, exist in the solid state.[7] However, studies of the replacement of Cl^- in $[Pt_2(pop)_4Cl_2]^{4-}$ by Br^- have been interpreted[14] in terms of a bridged Pt_2–Cl–Pt_2 intermediate.

The bromide substitution of $[Pt_2(pop)_4Br(OH_2)]^{3-}$ was studied over a wider range of pH. Over the pH range 1–4, the observed rate constant varies only slightly; but as the pH becomes greater than 4.5, it gradually increases with increasing basicity of the solution (Table IV). Roundhill and co-workers found[14] that $[Pt_2(pop)_4]^{4-}$ and $[Pt_2(pop)_4Cl_2]^{4-}$ are dibasic acids with pK_1 of 3.10 and 4.95 and pK_2 of 6.75 and 7.55, respectively. The $[Pt_2(pop)_4Br(OH_2)]^{3-}$ ion would be expected to have smaller pK_a values than $[Pt_2(pop)_4Cl_2]^{4-}$, because of its lower negative charge. Thus at pH >4.5, deprotonation of the bridging pyrophosphite group(s) would occur. The rise in substitution rate therefore suggests that the deprotonated species are somewhat more labile than the parent complex.[14]

Substitution Reactions of $[Pt_2(SO_4)(OH_2)_2]^{2-}$. The reaction of $[Pt_2(SO_4)_4(OH_2)_2]^{2-}$ with Cl^- was studied in an aqueous perchloric acid medium. When a solution of $[Pt_2(SO_4)_4(OH_2)_2]^{2-}$ is treated with Cl^-, it rapidly changes to $[Pt_2(SO_4)_4Cl(OH_2)]^{3-}$,[15] which slowly reacts with Cl^- to give $[Pt_2(SO_4)_4Cl_2]^{4-}$. The final spectrum is identical with that of an authentic sample[13] of $[Pt_2(SO_4)_4Cl_2]^{4-}$. The chloride substitutions can thus be represented by (4) and (5), with reaction 4 much faster than reaction 5.

$$[Pt_2(SO_4)_4(OH_2)_2]^{2-} + Cl^- \rightarrow [Pt_2(SO_4)_4Cl(OH_2)]^{3-} \quad (4)$$

$$[Pt_2(SO_4)_4Cl(OH_2)]^{3-} + Cl^- \rightarrow [Pt_2(SO_4)_4Cl_2]^{4-} \quad (5)$$

The kinetics of reaction 5 were studied at 25 °C. As in the case of $[Pt_2(pop)_4X(OH_2)]^{3-}$, pseudo-first-order rate constants depend linearly on $[Cl^-]$ (Table V); the second-order rate constant k_{ClCl} = 0.016 M^{-1} s^{-1}. The observation that the axially coordinated water molecules in $[Pt_2(pop)_4X(OH_2)]^{3-}$ and $[Pt_2(SO_4)_4Cl(OH_2)]^{3-}$ are labile to substitution is readily interpreted in terms of a strong σ(Pt–Pt) trans effect.[7]

Acknowledgment. Financial support to C.-M.C. and C.-K.P. by the University of Hong Kong and the Croucher Foundation is gratefully acknowledged. Research at the California Institute of Technology was supported by National Science Foundation Grant CHE84-19828.

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Electrochemical Oxidation of the Ru(sar)$^{2+}$ (sar = Sarcophagine) Ion and Its Relation to the Disproportionation of Ru(sar)$^{3+}$ in Aqueous Solution

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Received January 30, 1989

Recently a kinetic study of the disproportionation of the Ru(sar)$^{3+}$ ion (sar (Figure 1): 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane) was presented.[1] The spectroscopic characterization of Ru(IV) intermediates[2] confirmed earlier indications[3] that the initial stage of the disproportionation of ruthenium amine complexes, which leads eventually to ligand oxidation, involves metal-centered electron-transfer chemistry accompanied by rapid deprotonation of the coordinated amines (eq 1–4). Chemical or electrochemical oxidation of Ru(sar)$^{2+}$ in D_2O was not accompanied by rapid H–D exchange on any of the methylene groups in the complex.[1] For this reason, the site of the deprotonation involved in equilibrium 3 is believed to be one of the coordinated nitrogen atoms in the complex. Experimental estimates of the rate and equilibrium constants for reactions 1–4 have been obtained:[1] $K_{III}k_d$ = 37 s^{-1}, k_{-d} = 6.2 × 10^3 M^{-1} s^{-1}, and k_e = 6 × 10^{-4} to 12 s^{-1}.[4] Furthermore, the kinetics of the reaction of Ru(sar)$^{2+}$ with dioxygen, which follows a complex pathway, provided an approximate value for pK_{III} of 6.2–6.4, from which a value of (6–9) × 10^7 M^{-1} s^{-1} was calculated for k_d.

$$\mathrm{Ru(sar)^{3+} = Ru^{III}(sar(-H^+))^{2+} + H^+} \quad K_{III} \quad (1)$$

$$\mathrm{Ru(sar)^{3+} + Ru^{III}(sar(-H^+))^{2+} = Ru(sar)^{2+} + Ru^{IV}(sar(-H^+))^{3+}} \quad k_d, k_{-d} \quad (2)$$

$$\mathrm{Ru^{IV}(sar(-H^+))^{3+} = Ru^{IV}(sar(-2H^+))^{2+} + H^+} \quad K_{IV} \quad (3)$$

$$\{\mathrm{Ru(IV)}\} \rightarrow \mathrm{Ru(imine\text{–}sar)^{2+}} \quad k_e \quad (4)$$

(The notation follows that utilized in ref 2.)

In order to probe the consistency of these results and to clarify a remaining uncertainty about pK_{IV}, we carried out an electrochemical investigation of the oxidation of Ru(sar)$^{2+}$ in aqueous solution. Earlier attempts to study the pH dependence with stationary platinum or glassy-carbon electrodes were thwarted by poor reproducibility above pH 4, where the results depended strongly upon the pretreatment of the electrode surfaces. Fortunately, the potentials of interest turned out to be accessible to measurement with mercury electrodes without serious interference from the limit set by the anodic oxidation of mercury. Hanging mercury drop electrodes provided the necessary surface reproducibility. The results of this study, presented in this paper, include a Pourbaix (E^f vs pH) diagram for the Ru$^{IV/III/II}$sar system and a comparison with some related complexes.

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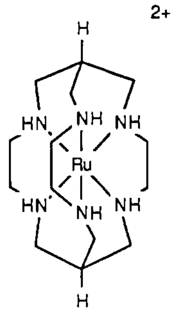

Figure 1. Structure of the Ru(sar)$^{2+}$ complex.

Experimental Section

[Ru(sar)](CF$_3$SO$_3$)$_2$ was synthesized as reported previously.[1] Water for the electrochemical measurements was passed through a Barnstead Nanopure train. Reagent grade chemicals and the buffers MES (2-morpholinoethanesulfonic acid) and HEPES (*N*-(2-hydroxyethyl)-piperazine-*N'*-ethanesulfonic acid) were used without further purification. Argon was passed through V$_{aq}{}^{2+}$ solutions.

Electrochemcial measurements were performed in aqueous solution at 22 °C under argon in a 5-mL cell by using a BAS 100 electrochemical analyzer interfaced to a PAR 303 Hg electrode. The rotating-disk voltammetry was conducted with a Pine Instrument Co. rotator and conventional PAR instrumentation. Solutions were 10^{-6} to 10^{-4} M in Ru(sar)$^{2+}$, and the ionic strength was adjusted to 0.1 M with NaClO$_4$. In the pH range between 5 and 10, solutions were buffered with 2 mM buffers. The pH was measured with an Orion pH meter and a combination glass electrode calibrated with commercial buffers at pH 4, 7, and 10.

The electrochemical techniques (normal-pulse polarography (NPP), differential-pulse polarography (DPP), square-wave voltammetry (SW-V), and cyclic voltammetry (CV)) were restricted to time scales such that reaction 4 proceeded to a negligible extent.[5] Formal potentials evaluated with the different techniques agreed to ±10 mV up to pH 4 and to ±30 mV at higher pH where adsorption phenomena were evident (vide infra). Potentials are quoted with respect to the normal hydrogen electrode.

Results and Discussion

In Figure 2A formal potentials evaluated in solutions containing Ru(sar)$^{2+}$ are plotted vs pH. Below pH 2 the formal potential is independent of pH and is in agreement with the previously reported value of 0.29 V.[1] At pH >2.5 the formal potential shifts to more negative values. The overall dependence on pH between pH 2.5 and 12 corresponds to a Nernstian slope of −59 mV/pH unit (dotted line), and the horizontal and sloping lines intersect at pH 2.5 ± 0.3. Except for the expected curvature in the pH range between 2 and 3, there seems to be no clearly discernible region of intermediate slope.

The formal potentials measured at pH >2.5 were rather close to the limit imposed by the anodic oxidation of the mercury electrode. However, careful measurements of the background currents in the supporting electrolytes at the same potential convinced us that the formal potentials could be determined reliably to ±10 mV.

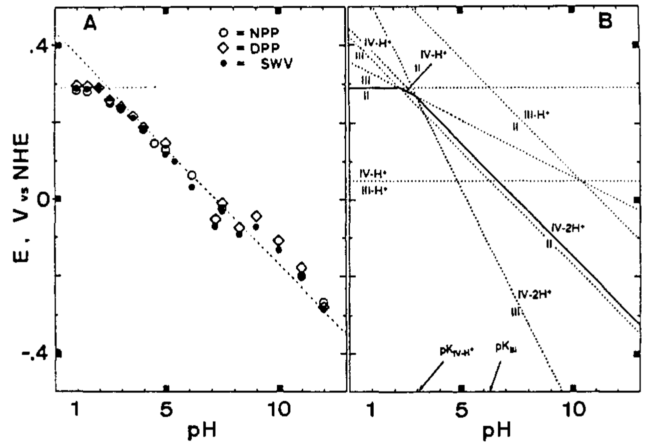

Figure 2. (A) pH dependence of the formal potentials of the reversible couples exhibited by Ru(sar)$^{2+}$ as measured by normal-pulse polarography (NPP), differential-pulse polarography (DPP), and square-wave voltammetry (SWV) at a hanging mercury drop electrode. (B) pH dependence of formal potentials calculated for redox couples of the Ru$^{II/III/IV}$sar system. II = Ru(sar)$^{2+}$, III = Ru(sar)$^{3+}$, III-H$^+$ = Ru^{III}(sar(−H$^+$))$^{2+}$, IV-H$^+$ = Ru^{IV}(sar(−H$^+$))$^{3+}$, IV-2H$^+$ = Ru^{IV}(sar(−2H$^+$))$^{2+}$.

The magnitude of the current responses obtained during the evaluation of the formal potentials in Figure 2A was also pH dependent. The currents were approximately twice as large in the pH range where the formal potentials exhibited a pH dependence. Thus, the electrode reaction appeared to shift from a one-electron to a two-electron process as it became pH-dependent. Above pH 5 the situation was complicated by adsorption of the cationic reactants on the surface of the mercury electrode, which increased as the pH increased and the electrochemical responses shifted to more negative potentials. In addition, the measured formal potentials exhibited a greater scatter between pH 6 and 9, where buffering agents were added to the supporting electrolytes. These factors reduced the precision and accuracy of the measurements of formal potentials and allowed only estimates for the potentials to be obtained. Our confidence in the values given in Figure 2A was strengthened by the agreement between the values obtained from the variety of techniques employed. Also, steady-state current–potential curves recorded at a rotating graphite-disk electrode at pH 12 yielded a value of $E_{1/2}$ of −0.24 V, which is in reasonable agreement with the values in Figure 2A that were obtained from the transient, pulse polarographic methods. If the adsorption were extensive enough to affect significantly the measured formal potentials, larger differences between the two types of techniques would be expected.[6] A Levich plot of the plateau currents at the rotating disk electrode vs (rotating rate)$^{1/2}$ was quite linear with a slope that was consistent with a simple two-electron oxidation.

To accommodate the observed pH dependences of both the formal potentials and the magnitude of the current responses, the following half-reactions are proposed:

pH <2

$$\mathrm{Ru(sar)^{3+} + e^- = Ru(sar)^{2+}} \tag{5}$$

$$E^{f}{}_{\mathrm{III/II}} = 0.29\ \mathrm{V}$$

pH >3

$$\mathrm{Ru^{IV}(sar(-2H^+))^{2+} + 2e^- + 2H^+ = Ru(sar)^{2+}} \tag{6}$$

$$E^{f}{}_{\mathrm{IV\text{-}2H^+/II}} = (0.44 \pm 0.03) - 0.059\mathrm{pH\ V}$$

On the basis of half-reactions 5 and 6, the equilibrium constant governing the disproportionation of Ru(sar)$^{3+}$ to Ru(sar)$^{2+}$ and the doubly deprotonated Ru(IV) complex (eq 7) can be calculated.

$$\mathrm{2Ru(sar)^{3+} = Ru(sar)^{2+} + Ru^{IV}(sar(-2H^+))^{2+} + 2H^+} \quad K_{\mathrm{disp}} \tag{7}$$

$$\log K_{\mathrm{disp}} = 2(0.29 - (0.44 \pm 0.03))/0.059 = -5.2 \pm 0.6 \tag{8}$$

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[4] For 1 < pH < 3.5, $k_e \approx 17(1 + 0.01/[\mathrm{H^+}])\ \mathrm{s^{-1}}$.[1] At higher pH the rate decreases further and reaches a limiting value at pH ≥9 of $6 \times 10^{-4}\ \mathrm{s^{-1}}$.

[5] Experimental parameters were as follows. NPP: scan rate (SR) = 4 mV s^{-1}, pulse width (PW) = 50 ms, sampling time (ST) = 25 ms, drop time (DT) = 1 s. DPP: SR = 4 mV s^{-1}, PW = 50 ms, amplitude (AM) = 50 mV, ST = 25 ms, DT = 1 s. OSWV: AM = 25 mV, frequency = 15 Hz, step = 4 mV, ST = 16 ms. Mercury drop sizes were 0.023 or 0.014 cm^2. For description of the techniques see: Bard, A. J.; Faulkner, L. *Electrochemical Methods*; Wiley: New York, 1980.

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It follows that at pH = $^1/_2$pK_{disp} = 2.6, the oxidation of $\mathrm{Ru(sar)^{2+}}$ to $\mathrm{Ru^{III}(sar)^{3+}}$ and to $\mathrm{Ru^{IV}(sar(-2H^+))^{2+}}$ will be equally favorable thermodynamically. At higher pH values the two-electron oxidation will be increasingly favored. At lower pH values the disproportionation of $\mathrm{Ru(sar)^{2+}}$ may result in the formation of the singly deprotonated Ru(IV) complex (eq 9). The value of

$$2\mathrm{Ru(sar)^{3+}} = \mathrm{Ru(sar)^{2+}} + \mathrm{Ru^{IV}(sar(-H^+))^{3+}} + \mathrm{H^+} \quad K'_{\mathrm{disp}} \tag{9}$$

K'_{disp} can be calculated from the equilibrium and kinetic parameters evaluated previously[1] for reactions 1 and 2.

$$\log K'_{\mathrm{disp}} = \log (K_{\mathrm{III}}k_{\mathrm{d}}/k_{-\mathrm{d}}) = -2.2 \pm 0.1 \tag{10}$$

It follows that $\mathrm{Ru^{III}(sar)^{3+}}$ and $\mathrm{Ru^{IV}(sar(-H^+))^{3+}}$ are equally favored as the product of the oxidation of $\mathrm{Ru(sar)^{2+}}$ at pH 2.2, with the two-electron-oxidation product (Ru(IV)) becoming increasingly favored at higher pH.

The equilibrium constant for the reaction

$$\mathrm{Ru^{IV}(sar(-H^+))^{3+}} = \mathrm{Ru^{IV}(sar(-2H^+))^{2+}} + \mathrm{H^+} \quad K_{\mathrm{IV}} \tag{11}$$

can be calculated from

$$\mathrm{p}K_{\mathrm{IV}} = \mathrm{p}K_{\mathrm{disp}} - \mathrm{p}K'_{\mathrm{disp}} = 3.0 \pm 0.6 \tag{12}$$

Thus, on the basis of the thermodynamic parameters, one expects the oxidation of $\mathrm{Ru(sar)^{2+}}$ to yield $\mathrm{Ru^{III}(sar)^{3+}}$ at pH <2, $\mathrm{Ru^{IV}(sar(-2H^+))^{2+}}$ at pH >3, and $\mathrm{Ru^{IV}(sar(-H^+))^{3+}}$ at 2 < pH < 3. The oxidation to $\mathrm{Ru^{IV}(sar(-H^+))^{3+}}$ should yield a segment of the formal potential vs pH plot with a slope of 30 mV/pH unit. This behavior is indistinct in the data of Figure 2 because of the narrow pH range over which the slope changes from 0 to 60 mV per pH unit. Previously,[1] on the basis of kinetic evidence, it was only possible to provide a lower limit of 3 for pK_{IV}. The additional electrochemical data obtained in this study allow the more quantitative estimate that pK_{IV} = 3.0 ± 0.6.

By employing the formal potentials and equilibrium constants quoted above, it is possible to construct the set of Pourbaix diagrams shown in Figure 2B for the Ru(sar) complexes in oxidation states II, III, and IV. The solid line gives the reversible potentials at which the oxidation of $\mathrm{Ru(sar)^{2+}}$ to the various products is expected to occur. The dotted lines depict the theoretical behavior for the other redox couples that would be encountered if the system did not equilibrate rapidly.

It is important to mention that a further reaction of $\mathrm{Ru^{IV}(sar)}$ complexes, not contemplated in the construction of Figure 2B, is ligand dehydrogenation to produce a Ru(II) imine complex (reaction 4).[1,4] Our experiments were conducted at pH values and on time scales where reaction 4 could be neglected, but it should be noted that the instability of $\mathrm{Ru(sar)^{3+}}$ in acidic solution is attributable to its continuous disproportionation (reaction 2) followed by acid-catalyzed removal of the resulting $\mathrm{Ru^{IV}(sar)}$ complexes via reaction 4.

It may be of interest to compare our results for the $\mathrm{Ru(sar)^{3+}}$ complex with the behavior of related systems for which estimates of the relevant kinetic and thermodynamic parameters are at least partially available. (We will adopt the same notation utilized with the Ru(sar) system.) The disproportionation-dehydrogenation of $\mathrm{[Ru(bpy)_2(ampy)]^{3+}}$ (bpy = 2,2′-bipyridine; ampy = 2-(aminomethyl)pyridine) proceeds much faster than that for $\mathrm{Ru(sar)^{3+}}$ and leads to a singly deprotonated Ru(IV) product.[3] This behavior is understandable as the result of a more favorable disproportionation constant, log K'_{disp} = −0.08 (eq 8), that originates from a much lower value of pK_{III} (2.4), coupled with a more rapid conversion of the Ru(IV)–amine to Ru(II)–imine complex ($k_{\mathrm{e}} \sim 100\ \mathrm{s^{-1}}$).[3] The formation of a planar five-membered ring that accompanies the oxidation of the ligand undoubtedly facilitates the dehydrogenation reaction.

By contrast, the $\mathrm{Ru(tacn)_2^{3+}}$ complex (tacn = 1,4,7-triazacyclonane), which is similar in many respects to $\mathrm{Ru(sar)^{3+}}$, dehydrogenates 10^5–10^6 times more slowly[7] than the latter complex, most likely because of the greater difficulty faced by the tacn ligand in providing a planar geometry at the nitrogen atom, which would tend to make K'_{disp} smaller.

Some formal potentials have been quoted for the IV/III/II couples of the ethylenediamine (en) complexes of osmium in a study of the (slow) conversion of the structurally characterized, deprotonated Os(IV) complex to the corresponding Os(II) imine complex.[8] The values quoted were −0.52 V vs NHE for the $\mathrm{Os(en)_3^{3+/2+}}$ couple and 0.29 V vs Ag/AgCl (saturated LiCl in acetone) for the $\mathrm{Os(en)_2(en(-H^+))^{3+/2+}}$ couple. The latter potential would be approximately 0.2 V more positive vs NHE. Using these potentials to calculate a value for the equilibrium constant governing the disproportionation of $\mathrm{Os(en)_3^{3+}}$ to $\mathrm{Os(en)_3^{2+}}$ and $\mathrm{Os^{IV}(en)_2(en(-H^+))^{3+}}$ yields log $K'_{\mathrm{disp}} = -(17 + \mathrm{p}K_{\mathrm{III}})$ where pK_{III}, the acid dissociation constant of $\mathrm{Os(en)_3^{3+}}$, is ≫1. Thus, the disproportionation of $\mathrm{Os(en)_3^{3+}}$ to $\mathrm{Os(en)_3^{2+}}$ and $\mathrm{Os^{IV}(en)_2(en(-H^+))^{3+}}$ is thermodynamically highly unfavorable. The fact that the formation of Os(IV) complexes is nevertheless observed in basic solutions of $\mathrm{Os(en)_3^{3+}}$[8] suggests that the further deprotonation of $\mathrm{Os^{IV}(en)_2(en(-H^+))^{3+}}$ may serve to drive the dispropotionation reaction. Alternatively, it is possible that $\mathrm{Os^{III}(en)_2(en(-H^+))^{2+}}$ might be oxidized to $\mathrm{Os^{IV}(en)_2(en(-H^+))^{3+}}$ by trace quantities of an oxidant (such as $\mathrm{O_2}$) so that a disproportionation reaction is not involved.

While the existence of N-deprotonated M(IV) species is well documented for the cases M = Ru, Os, the situation for M = Fe is still unresolved. In cases where dehydrogenation of aliphatic amine ligands bound to Fe(III) has been studied,[8-10] an (unobserved) intermediate species has been formulated as an $\mathrm{Fe^{III}(^{\bullet}NR)^{3+}}$ radical rather than as an $\mathrm{Fe^{IV}(^{-}NR)^{3+}}$ species. Unfortunately, the presently available data do not allow a separation of the thermodynamic and kinetic factors (i.e., K'_{disp} and k_{e}) that might permit one to choose between these possibilities.

Conclusions

It was our original intention to use electrochemical measurements to evaluate pK_{III} for $\mathrm{Ru(sar)^{3+}}$ to compare with an earlier value estimated from kinetic data.[1] However, it quickly became evident that the thermodynamic properties of the Ru(IV, III, II)–sarcophagine complexes were incompatible with our objective. We therefore utilized measurements of the pH dependence of the formal potentials for the couples to obtain values for the equilibrium constant for disproportionation of $\mathrm{Ru^{III}(sar)^{3+}}$ that were consistent with a previous estimate from kinetic data and led to a value for pK_{IV} for $\mathrm{Ru^{IV}(sar(-H^+))^{3+}}$. The approach adopted in this study could prove useful in investigations of other metal complexes for which oxidative dehydrogenation of coordinated ligands has been reported.[12,13]

Acknowledgment. This work was supported by the National Science Foundation.

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