J. Am. Chem. Soc. 1992, 114, 4605-4610

Characterization of [*N*,*N*′-(Mercaptoethyl)(sulfinatoethyl)diazacyclooctane]nickel(II), (MESE-DACO)Ni (2). Single crystals suitable for X-ray crystal structure analysis were grown by slow diffusion of Et_2O into concentrated CH_3CN solutions. FTIR peaks were assigned to ν(SO) absorptions (KBr pellet): ^{16}O 1182 and 1053 cm^{-1}; ^{18}O 1146 and 1018 cm^{-1}. UV–vis absorptions were in EtOH solution: λ_{max} (ϵ, cm^{-1} M^{-1}) 430 (202) and 550 (51) nm. Anal. Calcd (Found) for $C_{10}H_{20}N_2S_2O_2Ni$: C, 37.17 (37.06); H, 6.24 (6.22); O, 9.90 (8.02).

Characterization of [*N*,*N*′-Bis(sulfinatoethyl)diazacyclooctane]nickel(II), (BSE-DACO)Ni (3). The yellow fraction eluted only with > 40% H_2O/EtOH eluant solutions, and the solutions were sensitive to decomposition while heating under vacuum. UV–vis absorptions were in EtOH solution: λ_{max} as obtained off the column, 365 and 440 nm; recrystallized from H_2O/acetone, 380 and 420 nm. Both forms have similar FTIR peaks assigned to ν(SO) absorptions (KBr pellet): ^{16}O 1192, 1180, 1071, and 1032 cm^{-1}; ^{18}O 1163, 1146, 1044, and 991 cm^{-1}. Anal. Calcd (Found) for $C_{10}H_{20}N_2S_2O_4Ni$: C, 33.80 (32.53); H, 5.63 (5.84); N, 7.88 (7.51).

Synthesis and Characterization of Bis[[*N*,*N*′-Bis(mercaptoethyl)-1,5-diazacyclooctane]nickel(II)] Nickelate Dibromide, $[(BME\text{-}DACO)_2Ni_3]Br_2$ (4). As $NiBr_2{\cdot}3H_2O$ (0.0927 g, 0.34 mM) was added to a solution of **1** (0.200 g, 0.687 mM) in 50 mL of MeOH, the color changed immediately from purple to dark brown/red. Concentration under vacuum and subsequent slow evaporation yielded 0.25 g (92%) of microcrystalline **4**. Single crystals suitable for X-ray crystal structure analysis were grown by slow diffusion of Et_2O into concentrated MeOH solutions. UV–vis absorptions were in EtOH solution: λ_{max} (ϵ, cm^{-1} M^{-1}) 408 (3033), 486 (1316), and 564 (851) nm. Anal. Calcd (Found) for $C_{20}H_{40}N_4S_4Ni_3Br_2$: C, 29.97 (29.98); H, 4.99 (5.03).

Reaction of 1 with a Deficiency of $NOBF_4$. **1** (0.100 g, 0.3435 mM) was dissolved in 30 mL of dry, degassed MeOH and treated with $NOBF_4$ (0.020 g, 0.171 mM) dissolved in 30 mL of MeOH. The solution color immediately changed from purple to dark red/brown. UV–vis of the resulting solution showed the major product to be **4**. Chromatography of the product mixture lead to recovery of 24% **1** (0.024 g, 0.082 mM); theoretical recovery, 25%.

Mixed-Labeling Reaction of $(BME\text{-}DACO)Ni^{II}$ (1) with $^{16}O_2$, $^{18}O_2$, and $^{16}O_2/^{18}O_2$ Mixtures. Three 100-mL flasks were loaded with samples of **1** (0.100 g, 3435 mM) and 30 mL of triply dried, degassed CH_3CN, evacuated, and backfilled 3 times with Ar and then left under a vacuum. Flask A was charged with natural abundance O_2 and flask B with 99% $^{18}O_2$ in 50-mL (2.23 mM) quantities. The third, flask C, was charged with 25 mL of $^{18}O_2$ and 25 mL of natural abundance O_2. All flasks were then slightly overpressured with Ar. By GC/MS, the isotopic purity for flask B was ~98% $^{18}O_2$ (reflecting minor contamination during transfer). By GC/MS, the isotopic ratio in flask C was 56:44 $^{16}O_2$:$^{18}O_2$, with less than 0.1% ^{16}O:^{18}O, and was unchanged after the workup. The reaction mixtures were stirred for 3 days, after which the reaction solutions were evaporated and chromatographically separated as above and submitted for FT-ICR/MS.

Reaction of Isolated and Purified 2 with O_2 and H_2O_2. A solution of chromatographically pure **2** (30 mg, 0.09 mmol) in 25 mL of dry, degassed CH_3CN was purged with O_2 for 30 min and then stirred under an O_2 atmosphere for 48 h without reaction (monitored by UV–vis). The O_2 was evacuated and replaced with N_2, and two 10-μL portions of 30% H_2O_2 (aqueous) (2 equiv) were injected into the solution. The resulting yellow product was identified as **3** by UV–vis and checked further by chromatography.

Acknowledgment. We thank our TAMU colleagues Professors D. H. R. Barton and D. T. Sawyer for their comments and interest in this work and W. Schenk for access to his unpublished work. Financial support from the National Science Foundation (CHE 91-09579 to M.Y.D., CHE 88-21780 to D.H.R., and CHE-85-13273 for the X-ray diffractometer and crystallographic computing system), the R. A. Welch Foundation, and the Texas Advanced Research Program is gratefully acknowledged. T. Soma is a R. A. Welch Foundation Undergraduate Fellow.

Supplementary Material Available: Statistical analysis of mass spectral data, including predicted and experimental ion abundance ratios and a mathematical fit of predicted-to-experimental data, tables of atomic coordinates, positional and displacement parameters, and bond lengths and angles, and a packing diagram and additional views of $C_{10}H_{20}N_2O_2S_2Ni$, a packing diagram of $C_{10}H_{20}N_2S_2Ni_{1.5}Br$, and numbering schemes for $(MESE\text{-}DACO)Ni^{II}$ and $\{[(BME\text{-}DACO)Ni]_2Ni\}Br_2$ (11 pages). Ordering information is given on any current masthead page.

Preparation and Reactivity of a Cationic Dichromium–Semiquinone Complex

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Received October 28, 1991

Abstract: The complex described in the literature as the μ-oxo complex $(H_2O)_5CrOCr(H_2O)_5{}^{4+}$ is shown to be a dichromium(III)–semiquinone complex, $(H_2O)_5CrOC_6H_4OCr(H_2O)_5{}^{5+}$. It is prepared by the reaction of 1,4-benzoquinone with Cr^{2+} in acidic, aqueous solution. The reaction also yields $Cr(H_2O)_6{}^{3+}$ and a dichromium(III)–hydroquinone complex of 4+ charge. The semiquinone complex is reversibly reduced by outer-sphere electron transfer to the dichromium(III)–hydroquinone complex, $(H_2O)_5CrOC_6H_4OCr(H_2O)_5{}^{4+}$. This reduction is accomplished by any of Cr^{2+}, $Ru(NH_3)_6{}^{2+}$, or V^{2+}. The hydroquinone complex is reoxidized by Fe^{3+}, 1,4-benzoquinone, Br_2, or Ce(IV) to the semiquinone complex. Cyclic voltammograms obtained with either the hydroquinone complex or the semiquinone complex are identical and correspond to a reversible, one-electron process. The standard reduction potential of the semiquinone complex is +0.61 V (NHE). The semiquinone complex decomposes, over a period of hours, by aquation of Cr(III) followed by disproportionation of the organic ligand, yielding hydroquinone, benzoquinone, and $Cr(H_2O)_6{}^{3+}$. A literature report of the quinone oxidation of ethanol catalyzed by Cr^{3+} is reinterpreted as the reversible formation of a dichromium(III)–semiquinone radical complex.

Introduction

Our interest in the various intermediates in the reaction of Cr^{2+} with O_2 led us to consider the possible involvement of $(H_2O)_5CrOCr(H_2O)_5{}^{4+}$, hereafter $CrOCr^{4+}$. In particular, we asked whether this species might be produced in the reaction between the recently-prepared[1] oxochromium(IV) or chromyl ion, CrO^{2+}, and Cr^{2+}, or in another[2] stage of the Cr^{2+}–O_2 reaction. Our search was initially guided by reports that $CrOCr^{4+}$ is one of several major products of the reaction between Cr^{2+} and 1,4-benzoquinone in aqueous perchloric acid.[3] The product identified

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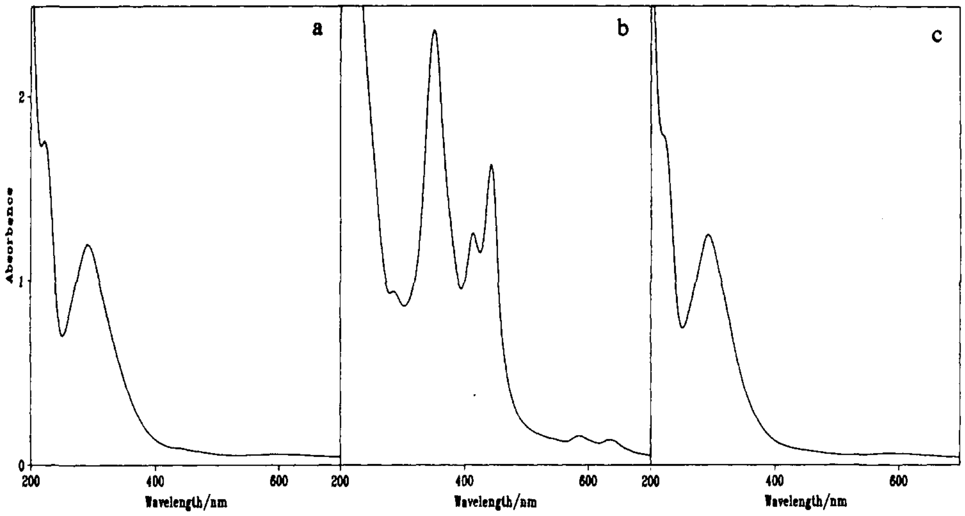

Figure 1. Reversible spectral changes upon oxidation of complex I and reduction of complex II. (a) Spectrum of 0.19 mM complex I in 0.10 M $HClO_4$/0.90 M $LiClO_4$, 1-cm cell; (b) spectrum of complex II obtained by adding Fe^{3+} to the solution of complex I; (c) spectrum of complex I obtained by adding Cr^{2+} to the deaerated solution of complex II.

as the $CrOCr^{4+}$ ion is unusual in that it has an intense visible spectrum with several narrow peaks. Moreover, it is a good oxidizing agent, with $E°$ given as 0.54 V (NHE).[4] Neither of these properties is characteristic of inorganic Cr(III) species, and thus special electronic interactions within a linear Cr–O–Cr unit were invoked. The so-called $CrOCr^{4+}$ ion was also claimed to decompose irreversibly to Cr^{3+} in a reaction catalyzed by H^+ or by reductants such as Cr^{2+}.[4,5]

In this work, we show that the intense and narrow visible bands actually belong to a complex containing a coordinated semiquinone radical, whose correct formula is $CrOC_6H_4OCr^{5+}$ (water molecules are presumed to occupy the remaining coordination positions). Reduction of the semiquinone complex yields a dichromium(III)–hydroquinone complex. This process is fully reversible. Coordination of semiquinone to two Cr(III) ions greatly stabilizes the semiquinone radical, which would otherwise disproportionate very rapidly in acidic solution. We propose a sequence by which the eventual disproportionation is limited by the low rate of aquation of bound Cr^{3+}.

Our understanding of the spectra and redox properties of the hydroquinone- and semiquinone-bridged dichromium complexes now permits a reinterpretation of an earlier report on the Cr^{3+}-catalyzed quinone oxidation of ethanol.[6] Despite their favorable potentials, quinones by themselves do not react with ethanol at appreciable rates. However, the reaction takes place readily in the presence of Cr^{3+}. Reversible formation of a semiquinone radical complex is clearly indicated by the spectral changes observed during the reaction. In the presence of O_2, the semiquinone complex is reoxidized to the quinone complex, thereby accomplishing catalyzed autoxidation of ethanol.

Experimental Section

Because we dispute the literature assignments of the two chromium complexes in this study, we will use the original labels to describe their preparation and reactivity. Complex I is the species described by Holwerda and Petersen[3] as a dichromium(III)–hydroquinone complex, although with a structure different from the one we propose. Complex II is identical to the proposed $CrOCr^{4+}$ ion, for which we have found an entirely different composition. Both complex I and complex II were prepared by the literature procedure;[3] however, yields of both complexes were found to be much higher when a 2:1 rather than a 1:1 mole ratio of Cr^{2+}:1,4-benzoquinone was used. (Note: The products obtained using either the 1:1 or the 2:1 ratio of Cr^{2+}:benzoquinone showed identical behavior in all the experiments described below. The ratio of the reactants therefore influences only the product distribution and not the nature of the products.) 1,4-Benzoquinone (65 mg; 0.6 mmol) was dissolved in 2 mL of CH_3CN and diluted to 100 mL with 0.1 M aqueous $HClO_4$. This solution was thoroughly deaerated with argon, and then 1.2 mmol of Cr^{2+} was added dropwise by syringe. The solution containing the products was loaded onto a column of ice-cooled Sephadex SP C-25 cation-exchange resin. The column was rinsed repeatedly with 0.1 M $HClO_4$ to remove uncoordinated benzoquinone and hydroquinone, which were retained by the resin more strongly than expected for uncharged species. Because this procedure took approximately 2 h complexes I and II decomposed slightly on the column, liberating more free hydroquinone as well as Cr^{3+}. Therefore, to obtain samples of highest purity, both complexes were eluted with 0.10 M $HClO_4$/0.90 M $LiClO_4$ and then re-ion-exchanged. Complex I eluted as a dense dark green band followed by a diffuse yellow-green band of complex II. Complex II was used immediately, since it decomposes completely within a few hours. Complex I was frozen and used over the course of the next 3 days. To obtain fresh samples of complex II, complex I was oxidized with Br_2 and then ion-exchanged again to remove any uncoordinated quinone species and Cr^{3+}.

Solutions of $Ru(NH_3)_6^{2+}$, Cr^{2+}, and V^{2+} were prepared by reducing air-free, acidic aqueous $[Ru(NH_3)_6]Cl_3$, $Cr(ClO_4)_3$, and $VO(ClO_4)_2$, respectively, over Zn/Hg. $Fe(ClO_4)_3$ was prepared by dissolving $FeCl_3 \cdot 6H_2O$ in concentrated $HClO_4$ and evaporating HCl until the solution gave a negative test for Cl^- with $AgNO_3$. Total chromium was analyzed by the basic H_2O_2 method.[7] Hydroquinone and benzoquinone were quantified spectrophotometrically (λ = 290 nm, $\epsilon = 2.3 \times 10^3$ M^{-1} cm^{-1}, and λ = 248 nm, $\epsilon = 2.14 \times 10^4$ M^{-1} cm^{-1}, respectively).[8,9] Br_2 was standardized spectrophotometrically (λ = 392 nm, ϵ = 175 M^{-1} cm^{-1}).[10]

Electronic spectral measurements, spectrophotometric titrations, and kinetic runs were performed on a Shimadzu UV-3101PC scanning spectrophotometer equipped with a thermostated cell holder. Cyclic voltammetry was performed on a BAS-100 electrochemical analyzer with a freshly-polished glassy carbon working electrode and a Ag/AgCl reference electrode containing saturated NaCl.

Results

Composition. The composition of complex I was established by analysis of a decomposed sample for hydroquinone and total Cr. The solution contained 3.6 mM hydroquinone and 7.6 mM total Cr, confirming the original assignment of a 1:2 hydroquinone–chromium complex.[3] Extinction coefficients were determined from the spectrum of the solution, Figure 1a, immediately after ion-exchange and are given in Table I. The values are slightly higher than those given in the previous work, but differ significantly only for the weak band in the visible region.[3] Doubly-ion-exchanged complex II was analyzed for total Cr, and the resulting extinction coefficients are also shown in Table I.

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Table I. Spectral Bands and Extinction Coefficients for Free Quinones and Quinone Complexes, $CrQCr^{4+}$ and $CrQCr^{5+}$

chromophore	λ_{max}/nm	$\epsilon/M^{-1}\ cm^{-1}$ [a]	ref
1,4-benzoquinone	248	2.14×10^4	9
hydroquinone	290	2.3×10^3	8
	221	4.4×10^3	
semiquinone radical anion	458	9.4×10^3	12
	428	7.5×10^3	
	406	4.7×10^3	
	325	2.5×10^4	
$CrQCr^{4+}$ (complex I)	599	2.4×10^2	this work
	292	6.50×10^3	
	224	1.00×10^4	
$CrQCr^{5+}$ (complex II)	634	4.6×10^2	this work
	585	5.5×10^2	
	443	7.52×10^3	
	413	5.84×10^3	
	350	1.19×10^4	
	226	9.32×10^3	

[a] For complexes I and II, extinction coefficients are given per mole of complex, i.e., per 2 mol of chromium. Standard errors are approximately 1.5%.

These values are also slightly higher than those previously reported; however, the earlier determinations were based on lowest obtained Cr analysis. Decomposition of the metastable complex II to $Cr(H_2O)_6^{3+}$ causes overestimation of the Cr content of complex II and therefore gives low values for the extinction coefficients. Our determinations are based on freshly-ion-exchanged samples which contained as little $Cr(H_2O)_6^{3+}$ as possible. The very high extinction coefficients in the visible region and the sharpness of the bands (Figure 1b) are unique. They set complex II apart from almost every other reported chromium(III) complex.

Reversible Redox Chemistry. A sample of 0.19 mM complex I, Figure 1a, was oxidized with 1 equiv of Fe^{3+}. The spectrum of complex II developed over several minutes, Figure 1b. Its concentration was also 0.19 mM, based on the independently-determined extinction coefficients. The solution of complex II was deaerated with argon, and an equal concentration of Cr^{2+} was added. The spectrum of 0.19 mM complex I was recovered quantitatively, Figure 1c. The addition of Fe^{3+} followed by Cr^{2+} was repeated several times, and the same reversible spectral changes were observed, eqs 1 and 2. The yield of complex II from a solution of complex I decreases as the time delay between addition of Cr^{2+} (to form complex I) and the addition of Fe^{3+} increases. After 2 h, only 73% recovery of complex II was obtained. On the basis of the rate constant for the decomposition of complex I (see below), a yield of 75% is predicted.

$$\text{complex I} + Fe^{3+} \rightarrow \text{complex II} + Fe^{2+} \qquad (1)$$

$$\text{complex II} + Cr^{2+} \rightarrow \text{complex I} + Cr^{3+} \qquad (2)$$

A sample of complex II was reduced with 1 equiv of Cr^{2+}, and the product solution was loaded onto a Sephadex cation-exchange column. A blue band, corresponding to $Cr(H_2O)_6^{3+}$, eluted easily with 0.25 M $HClO_4$. A green band which remained at the top of the column was eluted with 0.1 M $HClO_4$/0.9 M $LiClO_4$, at the same rate as an authentic sample of complex I. Thus the reduction of complex II by Cr^{2+} gives the products as shown in eq 2. A small amount of colored material was retained on the column. This minor product may be a trinuclear Cr–hydroquinone complex with 6+ charge; its identity was not pursued.

Qualitatively, the same spectral changes were observed using Br_2, Ce(IV), or 1,4-benzoquinone as the oxidant and either $Ru(NH_3)_6^{2+}$ or V^{2+} as the reductant. However, the Br_2 and Ce(IV) oxidations produce complex II quantitatively only when complex I is in excess, because of overoxidation (see below). Fe^{2+} does not reduce complex II.

To establish the stoichiometry of the reversible redox reaction, two spectrophotometric titrations were carried out. The addition of 0.036 mM Br_2 to a solution containing 0.236 mM complex I resulted in the formation of 0.068 mM complex II. Continued addition of Br_2 did not lead to a 100% yield of complex II, but did cause formation of a peak at 248 nm attributed to free benzoquinone. The stoichiometry of the reaction when Br_2 is not in excess is clearly 1 Br_2:2 complex I. Stoichiometric or excess amounts of Br_2 cause a slow decomposition of complex II. It is significant that the spectrum of complex II appears before benzoquinone is formed, implying that the production of benzoquinone is a subsequent process, not concurrent with complex II formation as previously reported.[3] Doubly-ion-exchanged complex II was titrated with Cr^{2+}, and a clean end point was observed at 0.90 Cr^{2+}:1 complex II, Figure 2. We believe this result to be identical within the experimental error to a 1:1 end point since complex II is not completely stable on the time scale required for these manipulations.

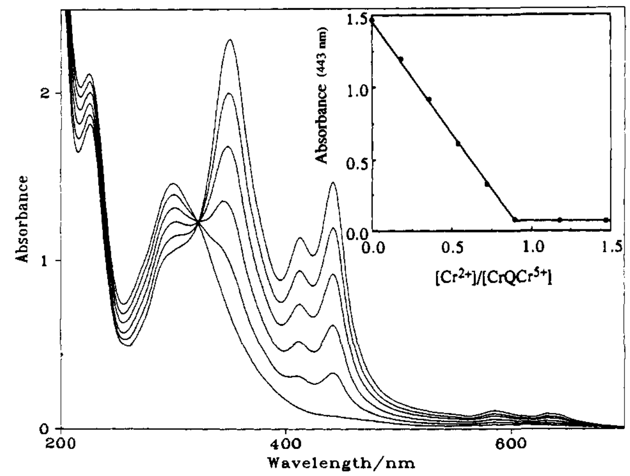


Figure 2. Spectrophotometric titration of air-free 0.195 mM complex II with Cr^{2+} in 0.10 M $HClO_4$/0.90 M $LiClO_4$. Path length = 1 cm.

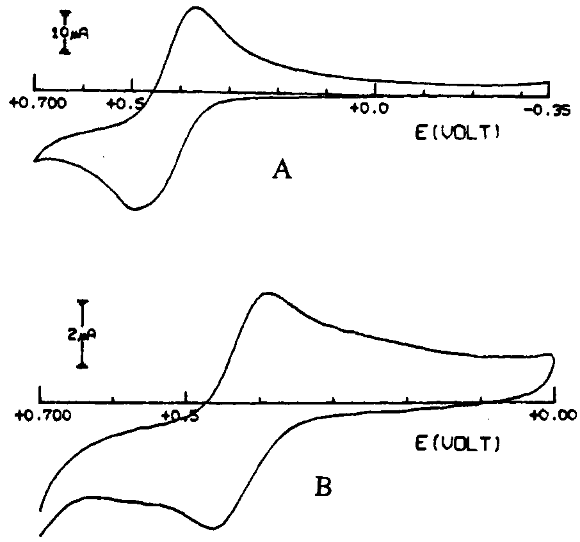


Figure 3. Cyclic voltammograms of (A) 5 mM complex I and (B) 0.5 mM complex II in 0.10 M $HClO_4$/0.90 M $LiClO_4$ at a glassy carbon working electrode and a Ag/AgCl reference electrode. Both complexes were purified by ion-exchange. Initial sweep directions were (A) anodic and (B) cathodic.

Table II. Electrochemical Data for $CrQCr^{4+}$ and $CrQCr^{5+}$ [a]

complex	$E_{p,c}$/mV [b]	$E_{p,a}$/mV [b]	$I_{p,c}/I_{p,a}$
$CrQCr^{4+}$ (complex I)	678	791	0.961
$CrQCr^{5+}$ (complex II)	692	768	0.974

[a] Obtained at a glassy carbon working electrode versus a Ag/AgCl reference electrode. Solutions contained 0.10 M $HClO_4$/0.90 M $LiClO_4$ and air. Sweep rate 50 mV/s. [b] All potentials are given relative to the standard hydrogen electrode.

Electrochemistry. Cyclic voltammetry was performed separately on pure samples of complexes I and II. Both complexes show identical quasi-reversible cathodic and anodic waves, Figure 3.

The peak positions and intensity ratios are given in Table II. The average position of the cathodic and anodic peaks yields a reduction potential of 0.61 V (NHE) in 0.10 M $HClO_4$/0.90 M $LiClO_4$. The cylic voltammogram is not pH-dependent in acidic solution (0.01–1 M H^+). The number of electrons transferred, n, was determined using eq 3,[11] where $E_{p/2}$ is the potential at which the current is one-half of its peak value. For both the anodic and cathodic peaks in Figure 3B, the value of $|E_p - E_{p/2}|$ is 0.056 V, therefore, $n = 1$.

$$|E_p - E_{p/2}| = -0.0565/n \qquad (3)$$

Kinetics. The kinetics of reduction of complex II with Cr^{2+} and $Ru(NH_3)_6{}^{2+}$ have already been reported.[4] We repeated a few of these experiments and obtained essentially the same results: $k_{Cr} = 1.8 \times 10^4$ L mol^{-1} s^{-1} and k_{Ru} too fast to measure by the stopped-flow technique. The kinetics of oxidation of complex I have not been examined, so we undertook a study of the reaction between complex I and Fe^{3+}. In the presence of a pseudo-first-order excess of Fe^{3+}, an exponential increase in absorbance at 443 and 350 nm was recorded. When aged samples of complex I were used, a biphasic absorbance increase was observed. The rate constant for the slower phase, 28 L mol^{-1} s^{-1}, is similar to that observed for the oxidation of free hydroquinone by Fe^{3+}.[9] The rate constant for the faster phase, which is the direct reaction between Fe^{3+} and complex I, is linearly dependent on the concentration of excess Fe^{3+}, with a slope of 1.5×10^2 L mol^{-1} s^{-1} in 0.10 M $HClO_4$/0.90 M $LiCLO_4$ at 25.0 °C.

The kinetics of the decomposition of doubly-ion-exchanged complexes I and II were studied by following the loss of absorbance at 290 and 443 nm, respectively, in 0.10 M $HClO_4$/0.90 M $LiClO_4$ at 25 °C. Both processes were first-order. The rate constant for decomposition of complex I is 3.9×10^{-5} s^{-1} and for complex II is 2.4×10^{-4} s^{-1}. The latter agrees with the previously-determined value for complex II at this pH.[5] The acid dependence found in previous work was therefore not investigated further.

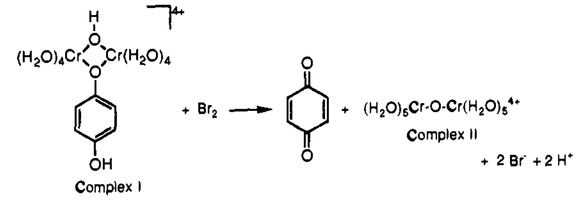
Decomposition Products. The spectrum of a solution of decomposed complex I contains two very weak bands in the visible region at 574 and 406 nm and two intense peaks in the UV region at 288 and 221 nm. The positions and intensities of the visible peaks are consistent with $Cr(H_2O)_6{}^{3+}$ as the sole inorganic product. The positions and intensities of the UV peaks match exactly those for hydroquinone.

The spectrum of a solution containing decomposed complex II in 0.1 M $HClO_4$/0.9 M $LiClO_4$ has all the peaks described above and an additional peak at 248 nm, the maximum for 1,4-benzoquinone. Evidence that this peak is actually due to 1,4-benzoquinone was obtained by addition of Cr^{2+} to the nearly colorless decomposed solution. The yellow-green color and the characteristic intense spectrum of complex II reappeared immediately, as in the reaction of Cr^{2+} with authentic 1,4-benzoquinone. The total amount of quinone (0.20 mM hydroquinone + 0.10 mM benzoquinone) found in the decomposed solution 1 day later is essentially equal to the initial amount of complex II, 0.29 mM. Because the amount of complex II was calculated from extinction coefficients which are based on analysis of total chromium, the analysis of the decomposed solution serves to confirm the stoichiometry of complex II as a 2:1 complex of chromium and a quinone species. A slightly higher proportion of the total quinone appeared as benzoquinone when the medium contained 1.0 M $HClO_4$. Under these conditions, decomposition of complex II was complete in 1 h. A blank experiment revealed that aqueous solutions of benzoquinone are unstable, with 30% loss of the 248-nm peak in 24 h in 0.1 M $HClO_4$. Concurrent formation of peaks at 221 and 290 nm was also observed.

Discussion

The Nature of Complexes I and II. We have confirmed the previous finding that complex I is a 2:1 complex of Cr and hydroquinone, and its ion-exchange behavior indicates that its charge is 4+. However, in that work, the oxidation of complex I to II was reported to be irreversible with liberation of free p-benzoquinone into solution.[3] The authors also claimed that complex II contains no coordinated quinone. On the basis of a similarity with the spectrum of the basic rhodo ion, $(NH_3)_5CrOCr(NH_3)_5{}^{4+}$, the formula $(H_2O)_5CrOCr(H_2O)_5{}^{4+}$ was assigned to complex II. The latter was claimed to decompose to Cr^{3+} in a reaction catalyzed by Cr^{2+} and $Ru(NH_3)_6{}^{2+}$. The proposed reactions are shown in Scheme I, eqs 4–7.[3,4]

Scheme I



(4)

$$(H_2O)_5CrOCr(H_2O)_5{}^{4+} + C_{red} \rightarrow (H_2O)_5CrOCr(H_2O)_5{}^{3+} + C_{ox} \qquad (5)$$

$$(H_2O)_5CrOCr(H_2O)_5{}^{3+} + H_2O + 2\,H^+ \rightarrow Cr(H_2O)_6{}^{2+} + Cr(H_2O)_6{}^{3+} \qquad (6)$$

$$Cr(H_2O)_6{}^{2+} + C_{ox} \rightarrow Cr(H_2O)_6{}^{3+} + C_{red} \qquad (7)$$

In Scheme I, C_{red} and C_{ox} are the reduced and oxidized forms of the catalyst, which is supposed to catalyze the hydrolysis of complex II to Cr^{3+}. For example, C_{red} may be either Cr^{2+} or $Ru(NH_3)_6{}^{2+}$. The products of the reaction of Cr^{2+} with complex II were subjected to ion-exchange. A blue 3+ species was identified as Cr^{3+} and a green 4+ species was presumed to be $Cr(OH)_2Cr^{4+}$ resulting from aerobic oxidation of the Cr^{2+} catalyst during workup. As reported above and discussed later, we have shown that this green 4+ species is actually complex I, and the reaction of complex II with C_{red} is actually a stoichiometric (not catalytic) reduction to complex I. The latter is more stable toward hydrolysis than complex II and is not further reduced by Cr^{2+}.

Our results indicate that complex II is an intact one-electron-oxidized product from the hydroquinone complex I, as demonstrated by the complete reversibility of the chemical reactions, by the peak-to-peak separations, and by $|E_p - E_{p/2}|$ values observed in the cyclic voltammograms. The quinone ligand must still be coordinated, and the spectrum of complex II resembles that of the unbound semiquinone radical anion, whose spectral characteristics are given in Table I.[12] Only three intense visible bands are seen in the spectrum of complex II whereas the spectrum of semiquinone contains four bands. The difference is probably due to broadening upon coordination to Cr(III). The intensities of the peaks of complex II, Table I, are comparable to those of the semiquinone radical anion.

In contrast, the visible spectrum of the basic rhodo ion, $(NH_3)_5CrOCr(NH_3)_5{}^{4+}$, while intense, is considerably weaker, with an extinction coefficient of 650 L (mol of Cr)$^{-1}$ cm^{-1} at 325 nm.[13] Analogues of the basic rhodo ion with the ammine ligands replaced by aromatic ligands such as tris(2-pyridylmethyl)amine or bipyridyl have higher extinction coefficients, but none of these complexes can be reduced.[14] The only electrochemical features they possess are reversible oxidation waves. In addition, these complexes are not susceptible to acid-catalyzed hydrolysis. Therefore complex II is quite unlike known μ-oxo bridged dichromium(III) species. A different orbital ordering was invoked to explain the different reactivity and electrochemical properties of the purported $CrOCr^{4+}$ ion relative to the known μ-oxo ions. If this explanation were true, then the difference in electronic configuration would be inconsistent with a close spectral resemblance.

The mechanism of reduction of complex II by Cr^{2+} and $Ru(NH_3)_6{}^{2+}$ was convincingly argued to be outer-sphere.[4] Although

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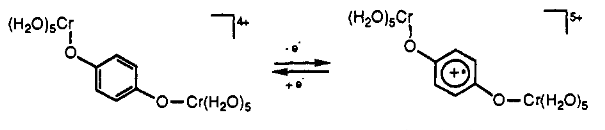
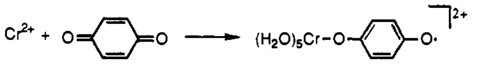
Scheme II



Complex I Complex II (8)

Cr^{2+} ($E°_{3+/2+}$ = −0.41 V) is a much stronger reductant than $Ru(NH_3)_6^{2+}$ ($E°_{3+/2+}$ = +0.06 V), $k_{Cr(II)}$ is 1 order of magnitude smaller than $k_{Ru(II)}$. This reactivity order is not observed when Cr^{2+} can react by an inner-sphere mechanism, but it is quite common when the reaction is perforce outer-sphere, because the self-exchange rate constant for the Cr^{2+}/Cr^{3+} couple is so low, $\leq 2 \times 10^{-5}$ L mol^{-1} s^{-1}.[15] Were we to accept the proposed structure for complex I, eq 3, then reversibly-formed complex II would also have to have both Cr(III) ions coordinated to the same oxygen atom of semiquinone, leaving most of the radical character of the semiquinone on the uncoordinated oxygen. Cr^{2+} is most unlikely to utilize an outer-sphere pathway if a donor site permitting inner-sphere attack is readily available. Instead, we propose that complexes I and II contain quinone coordinated at both oxygens, as in Scheme II. This structural type was previously proposed for the product of the reaction between $Co(CN)_5^{3-}$ and 1,4-benzoquinone, $(NC)_5CoOC_6H_4OCo(CN)_5^{6-}$,[16] as well as for the product of reaction of Cr^{2+} with various substituted quinones.[6] Moreover, if we consider the stepwise process by which complex I is formed, starting with a 1:1 reaction of Cr^{2+} and 1,4-benzoquinone,[2b] the first intermediate would be the mononuclear semiquinone radical complex shown in eq 9. The rate constant for this reaction was determined by pulse radiolysis to be 3.2 × 10^8 L mol^{-1} s^{-1}.[17] The product of eq 9 seems more likely to react with a second Cr^{2+} at the uncoordinated oxygen radical to yield the complex I shown in Scheme II than at the oxygen coordinated to Cr to yield the structure in Scheme I. Finally, complex II is formed in the reaction between Cr^{2+} and 1,4-benzoquinone by the *in situ* oxidation of complex I by benzoquinone. We have tested this independently, showing that an ion-exchanged sample of complex I yields complex II when benzoquinone is added.



(9)

Reduction of complex II does not lead to rapid aquation to $Cr(H_2O)_6^{3+}$, as previously suggested. The Cr^{3+} product is formed directly from the Cr^{2+} reactant, and the green 4+ product is complex I, eq 2. Although the colors and ion-exchange properties of complex I and the $Cr(OH)_2Cr^{4+}$ ion are very similar, the product spectrum is clearly not that of $Cr(OH)_2Cr^{4+}$. We conclude that complex I must have the formula $CrOC_6H_4OCr^{4+}$, or simply $CrQCr^{4+}$, and complex II must be $CrOC_6H_4OCr^{5+}$, or $CrQCr^{5+}$. The reversible oxidation of aqua[6] and azamacrocyclic[18] chromium–hydroquinone complexes has been previously noted.

Several mononuclear metal–semiquinone complexes are known as products of the reactions of reduced metal ions with *o*-quinones or by oxidation of metal–catecholate complexes.[19] In many cases, the assignment of oxidation states to the metal and ligands is ambiguous.[20] However, the substitutional inertness of Cr(III) relative to either Cr(II) or Cr(IV) is consistent with the low rate of aquation of the $CrQCr^{5+}$ complex; therefore, we conclude that $CrQCr^{5+}$ is accurately described as a semiquinone radical coordinated to two Cr(III) ions.

It is possible that two different compounds, $CrOCr^{4+}$ and $CrOC_6H_4OCr^{5+}$, would possess similar ion-exchange properties, and both could in principle be products of the complex reaction between Cr^{2+} and benzoquinone. However, it is extremely unlikely that both complexes would have nearly identical UV–vis spectra as well as identical rate constants for reduction by Cr^{2+} and $Ru(NH_3)_6^{2+}$ and for spontaneous decomposition. In light of the evidence presented here, we conclude that the formulation of complex II as $CrOCr^{4+}$ is incorrect.

The failure of earlier workers to identify the organic component in complex II may have been caused by the unusual retention of benzoquinone and hydroquinone on the Sephadex cation-exchange resin. When decomposed samples of complex II are loaded onto a chromatographic column, the quinones do not appear quantitatively in the eluent. They are observed only after much rinsing of the column with 0.10 M $HClO_4$. In the same way, when reaction mixtures containing complexes I and II, benzoquinone, and hydroquinone are loaded onto the column, the quinones are retained and elute with complexes I and II unless the column is rinsed thoroughly. The previously-reported cyclic voltammogram of complex I is identical to that of free hydroquinone, and we believe that this sample was probably contaminated by hydroquinone which was not completely removed from the column during the preparation of complex I.

The conversion of complex I to complex II was previously reported to occur by hydrolysis, catalyzed by H^+, Cr^{3+}, and Ce^{3+}. A hydrolysis reaction is inconsistent with the revised formulations of complexes I and II, which require electron transfer for interconversion. Hydrolysis is also inconsistent with the original study of the decomposition reactions, because it is kinetically impossible to observe complex II as a product of the hydrolysis of complex I when II is much less stable than I. In the previous reports, as well as in our own experience, conversion of complex I to II in the absence of added oxidants occurs only when the solutions are stored in the freezer. We propose that this conversion is caused by dissolved O_2, which is not normally excluded from the ion-exchanged samples. If oxidation by O_2 and decomposition (hydrolysis) of complex I have different activation parameters, then it is possible that oxidation by O_2 dominates at low temperature, whereas hydrolysis to $Cr(H_2O)_6^{3+}$ and hydroquinone is the major pathway at room temperature.

Redox Properties. The one-electron reduction potential of free hydroquinone $E°(HQ^•/H_2Q)$ is 1.04 V at pH 0.[21] This potential is strongly pH-dependent because of the difference in protonation levels between reactants and products (pK_1 = 9.85 and pK_2 = 11.4 for H_2Q and pK = 4.1 for $HQ^•$).[9,21] At pH 14, where both hydroquinone and semiquinone are fully deprotonated, the lower potential $E(Q^-/Q^{2-})$ = 0.023 V[22] reflects the increased ease of oxidation of hydroquinone once the proton barrier is removed. Then by comparison, hydroquinone coordinated to Cr(III) as Q^{2-} is much more difficult to oxidize than free Q^{2-}, given that ($CrQCr^{5+}/CrQCr^{4+}$) = 0.61 V. This is also true for $(NC)_5CoOC_6H_4OCo(CN)_5^{6-}$, where no oxidation wave for the hydroquinone complex was observed at potentials up to +1.1 V.[16] The increased stability of $(NC)_5CoOC_6H_4OCo(CN)_5^{6-}$ compared to free hydroquinone toward oxidation was attributed to both a coordination effect, since binding to cobalt(III) increases the electronegativity of the oxygen atoms, and interaction of the π levels of the ligand with the π^* levels of the $Co(CN)_5$ groups, which effectively stabilizes the ligand HOMO.

The failure of complex II to react rapidly with oxidants, including benzoquinone, Br_2, and MnO_4^-, contrasts with the high reactivity of the semiquinone radical toward many oxidants. Coordination of both oxygen atoms of semiquinone to Cr(III) precludes an inner-sphere pathway for oxidation. Outer-sphere electron transfer from coordinated semiquinone probably involves

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considerable reorganization, due to the large changes required in the Cr–O bond lengths.

The self-exchange rate constant for $CrQCr^{5+/4+}$ was calculated from the Marcus cross-relation,[23] using the rate constant for eq 2, $k_2 = 1.8 \times 10^4$ M^{-1} s^{-1}, the potential for eq 2, $E = (0.61 + 0.41)$ V = 1.02 V, and the self-exchange rate constant for the $Cr^{3+/2+}$ couple, $\leq 2 \times 10^{-5}$ M^{-1} s^{-1}. The derived value for $CrQCr^{5+/4+}$ self-exchange is 0.04 M^{-1} s^{-1}, compared to 1.3 M^{-1} s^{-1} calculated previously.[5] This value is several orders of magnitude lower than self-exchange rate constants for many uncoordinated organic radicals.[24] However, the accuracy of the Marcus equation declines rapidly as the driving force becomes very large. The reversibility of the cyclic voltammograms implies that the true self-exchange rate constant is larger than 0.04 M^{-1} s^{-1}.

Quinone Oxidation of Ethanol Catalyzed by Chromic Ion. The spectral changes reported[6] during the Cr^{3+}-catalyzed quinone oxidation of ethanol are now understandable in terms of the complexes described here. A green species, G, was observed but not correctly identified in the reaction of Cr^{2+} with 2,5-dihydroxy-1,4-benzoquinone, H_2Q'. G has the distinctive spectrum of a semiquinone radical complex, with intense, narrow bands in the visible spectrum.

$$2Cr^{2+} + (Q')^{2-} \rightarrow CrQ'Cr^{2+} \xrightarrow{(Q')^{2-}} \underset{G}{CrQ'Cr^{3+}} \qquad (10)$$

G is also formed when Cr^{3+} and H_2Q' are combined in ethanol solvent. (The rate of substitution on Cr(III) is apparently much higher in anhydrous ethanol than in aqueous solutions, possibly because ethanol is a weaker ligand than H_2O.) In this reaction, ethanol is simultaneously oxidized to acetaldehyde, eqs 11 and 12. In the presence of oxygen, eq 13, G is slowly oxidized to a red species, R, which is probably a dichromium quinone complex. R then reacts with more ethanol, creating a catalytic cycle for the autoxidation of alcohols.

$$2Cr^{3+} + (Q')^{2-} \rightarrow CrQ'Cr^{4+} \qquad (11)$$

$$2CrQ'Cr^{4+} + CH_3CH_2OH \rightarrow 2CrQ'Cr^{3+} + CH_3CHO + 2H^+ \qquad (12)$$

$$4\underset{G}{CrQ'Cr^{3+}} + O_2 + 4H^+ \rightarrow 4\underset{R}{CrQ'Cr^{4+}} + 2H_2O \qquad (13)$$

The intermediacy of a dichromium–semiquinone complex was proposed[25] in the oxidation of ethanol by chloranilate, catalyzed by Cr(III). An intensely-absorbing species was assigned the formula Cr(III)–bridging hydroquinone–Cr(III) with an electronic structure described as Cr(II)–bridging semiquinone–Cr(III). In view of the high substitutional lability of Cr(II) and the possibility demonstrated here of a stable Cr(III)–bridging semiquinone–Cr(III) complex, we suggest that the species observed in the chloranilate reactions may have a formula containing two Cr(III) ions bridged by a semiquinone radical.

Coordinative Stabilization of Radicals. Coordination of radicals to metal ions sometimes leads to impressive stabilization of the radical species. The reaction of Cr^{2+} with various substituted pyrazines leads to long-lived complexes of Cr(III) with the pyrazine radical anion, whose reducing ability is much lower than that of the unbound radical anion.[26] Reaction of O_2 with Cr^{2+} gives a stable superoxochromium(III) ion whose UV spectrum resembles that of the free superoxide radical.[2] The coordination of the semiquinone radical to two Cr(III) ions greatly enhances the stability of the radical toward disproportionation. Whereas free semiquinone disproportionates by a second-order process at nearly the diffusion-controlled rate ($k_d = 1.1 \times 10^9$ L mol^{-1} s^{-1} for $HQ^{\bullet} + HQ^{\bullet}$; $k_d = 1 \times 10^8$ L mol^{-1} s^{-1} for $Q^{\bullet-} + Q^{\bullet-}$),[27] the dichromium(III)–semiquinone complex, $CrQCr^{5+}$, decomposes in a slow first-order process which is acid-catalyzed.[5] Rate-limiting acidolysis, a common process in substitutionally-inert Cr(III) complexes with organic ligands, was suggested as the first step. The products of acidolysis would be Cr^{3+} and a mononuclear semiquinone–Cr(III) complex. The latter was not observed, probably because it is less stable than the dinuclear complex. The mononuclear complex may disproportionate, eq 14, or release quinone by internal electron transfer, eq 15. The latter reaction is analogous to the decomposition reactions of the Cr(III)–pyrazine radical complexes.[26] The Cr^{2+} product of eq 15 may react with quinone by an inner-sphere mechanism, regenerating the mononuclear semiquinone complex prior to its disproportionation, or by an outer-sphere electron transfer, yielding Cr^{3+} and the semiquinone radical anion. In either case, a product ratio of hydroquinone:benzoquinone of 1:1 is expected. Benzoquinone is known to decompose in aqueous solution to 1,2,4-trihydroxybenzene,[28] which likely has spectral characteristics very similar to those of hydroquinone. The spontaneous decomposition of benzoquinone can account for most, but not all, of the "missing" benzoquinone among the products of decomposition of $CrQCr^{5+}$. Coordination of benzoquinone to Cr(III) apparently enhances its rate of decomposition in water.

$$2CrQH^{3+} \rightarrow CrQ^{3+} + CrQH^{2+} + H^+ \rightarrow 2Cr^{3+} + Q + H_2Q \qquad (14)$$

$$CrQH^{3+} \rightleftarrows Cr^{2+} + Q + H^+ \qquad (15)$$

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-9007283). Some of the results were obtained with the use of the facilities of the Ames Laboratory. S.L.S. acknowledges the Natural Sciences and Engineering Research Council of Canada for a 1967 Science and Engineering Scholarship.

Registry No. $CrOCr^{4+}$, 73347-70-3; $CrQCr^{4+}$, 141018-07-7; $CrQCr^{5+}$, 141018-08-8; $Ru(NH_3)_6{}^{2+}$, 19052-44-9; Cr, 7440-47-3; V, 7440-62-2; Br_2, 7726-95-6; Ce, 7440-45-1; Fe, 7439-89-6; $[(H_2O)_4Cr(\mu\text{-}OH)(\mu\text{-}OC_6H_4OH)Cr(H_2O)_4]^{4+}$, 73360-43-7; 1,4-benzoquinone, 106-51-4.

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