the $[B_2H_7]^-$ impurity. Refinement of the populations corresponding to these four weak negative peaks resulted in an average H occupancy of 12 (3)%, a result (88% $[BH_3Cl]^-$/12% $[B_2H_7]^-$) consistent with the (81% $[BH_3Cl]^-$/19% $[B_2H_7]^-$) ratio obtained from the X-ray work (vide supra). Since the structure of the $[B_2H_7]^-$ anion subsequently has been solved on a pure sample of $[PPN]^+[B_2H_7]^-\cdot CH_2Cl_2$,[10,15] any discussion of the geometry of this minor $[B_2H_7]^-$ impurity would be superfluous here.

The structure of $[PPN]^+[BH_3Cl]^-\cdot CH_2Cl_2$ (ignoring the $[B_2H_7]^-$ impurity) initially was refined with a block-diagonal least-squares technique. The quantity minimized in the refinement was $\sum w^2(F_o - |F_c|)^2$, weights being chosen as $w = 1/\sigma^2(F_o)$, where $\sigma^2(F_o) = 4[\sigma_{count}{}^2(F_o{}^2) + (0.03F_o{}^2)^2]F_o{}^2$. In the later stages of full-matrix least-squares refinement, all reflections with $F_o{}^2 > 3\sigma_{count}(F_o{}^2)$ (2917 reflections) were included in the analysis. The six phenyl rings were treated as rigid groups with atoms placed in idealized positions (C–C = 1.397 Å; C–H = 1.089 Å) and individual isotropic thermal parameters; the rest of the atoms were refined with anisotropic thermal parameters. A final cycle (varying all positional and thermal parameters and scale and extinction[22] factors) resulted in $R_F = 0.071$ and $R_{wF} = 0.069$, with all shifts being less than 5% of their estimated standard deviations. The largest (negative) peak in the final difference Fourier synthesis was -0.16×10^{-12} cm/Å^3, corresponding to the bridging hydrogen of the $[B_2H_7]^-$ impurity. Neutron scattering factors used were (all $\times 10^{-12}$ cm) $b_B = 0.540$, $b_C = 0.665$, $b_N = 0.936$, $b_P = 0.513$, $b_{Cl} = 0.958$, and $b_H = -0.372$. An anomalous dispersion correction, $\Delta b'' = 0.021 \times 10^{-12}$ cm, was applied to boron.

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Registry No. $[PPN]^+[H_3BCl]^-$, 97391-09-8; $[Bu_4N]^+[H_3BCl]^-$, 69969-99-9; $[Et_4N]^+[H_3BCl]^-$, 97391-10-1; B_2H_6, 19287-45-7; $[PPN]^+Cl^-$, 21050-13-5; $[Bu_4N]^+Cl^-$, 1112-67-0; $[Et_4N]^+Cl^-$, 56-34-8; $[H_3BCl]^-$, 68011-52-9; $[BH_2Cl_2]^-$, 68011-51-8; $[B_2H_7]^-$, 27380-11-6.

Supplementary Material Available: Complete listings of anisotropic thermal parameters, bond distances, and bond angles from the X-ray analysis and anisotropic temperature factors from the neutron diffraction analysis of $[PPN]^+[BH_3Cl]^-\cdot CH_2Cl_2$ (9 pages). Ordering information is given on any current masthead page.

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Electrochemistry and Reductant-Catalyzed Acid Hydrolysis of the (μ-Oxo)bis(pentaaquochromium(III)) Ion

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Reductant-catalyzed acid hydrolysis of the (μ-oxo)bis(pentaaquochromium(III)) ion (aquo dimer), giving $Cr(H_2O)_6{}^{3+}$ as the sole product, has been examined through cyclic voltammetric and stopped-flow kinetic approaches. The aquo dimer exhibits an irreversible one-electron cathodic wave with [acid]-independent (0.025–1.00 M $HClO_4$) $E_{pc} = +0.40$ V and $E_{1/2} = +0.52$ V vs. SHE (25 °C). This cathodic process, shifted by +0.93 V relative to that of the parent $Cr(H_2O)_6{}^{3+/2+}$ couple, may be understood as electron acceptance into the essentially nonbonding e_g (π) molecular orbital of the linear, oxo-bridged reactant, followed by a rapid C_{2v} Jahn–Teller distortion, which lifts the orbital degeneracy of the resultant ^2E_g (D_{4h}) ground state, disrupts $2p\pi(O)$–$3d\pi(Cr)$ overlap, and leads ultimately to bridge cleavage. Consistent with the electrochemical observations, $((H_2O)_5Cr)_2O^{4+}$ is susceptible to rapid reductant-catalyzed acid hydrolysis with Cr^{2+}(aq), $Ru(NH_3)_6{}^{2+}$, and even ascorbic acid (H_2A) as the electron donor. Rate-limiting outer-sphere one-electron transfer to $((H_2O)_5Cr)_2O^{4+}$ from Cr^{2+}(aq) (k(25 °C) = 2.50×10^4 M^{-1} s^{-1}, $\Delta H^* = 6.0$ kcal/mol, $\Delta S^* = -17$ eu), $Ru(NH_3)_6{}^{2+}$ (k(25 °C) = 4×10^5 M^{-1} s^{-1}), H_2A (k(25 °C) = 6 M^{-1} s^{-1}) and HA^- (k(25 °C) = 7.2×10^5 M^{-1} s^{-1}, $\Delta H^* = 7.7$ kcal/mol, $\Delta S^* = -6$ eu) is implied by the kinetic results at $I = 1.0$ M ($HClO_4$/$LiClO_4$). The apparent $((H_2O)_5Cr)_2O^{4+/3+}$ self-exchange electron-transfer rate constant calculated from these data on the basis of Marcus theory (ca. 10 M^{-1} s^{-1}, 25 °C) is 6 orders of magnitude larger than that of the analogous $Cr(H_2O)_6{}^{3+/2+}$ couple, confirming the π^n character (comparatively small Franck–Condon inner-sphere reorganizational barrier) of the aquo dimer redox orbital.

Introduction

Since the discovery of $Cl_5RuORuCl_5{}^{4-}$, many other binuclear complexes with nearly linear M–O–M units have been structurally characterized.[1-7] The distinctive spectroscopic and magnetic properties of these linear μ-oxo-bridged species have been interpreted from both spin–spin-coupling and molecular orbital standpoints.[6,7] While linear M–O–M structures generally are attributed to $p\pi(O)$–$d\pi(M)$ overlap,[8] the strength of such π bonding is not easily assessed. Mechanistic studies of oxo-bridge cleavage should be revealing in this regard. This class of polynuclear complexes is susceptible to a variety of substitution reactions,[9] including exchange of nonbridging ligands and rearrangement to bis(μ-oxo) or hydroxo species, as well as rupture of the binuclear unit to give monomer fragments. The mechanistic characterization of these reactions has not advanced appreciably since Schwarzenbach and Magyar's pioneering study[10] of rearrangement coupled with substitution in the basic rhodo ($(NH_3)_5CrOCr(NH_3)_5{}^{4+}$) and related erythro chromium(III) ions (eq 1).

$$H_2O + (NH_3)_5CrOCr(NH_3)_4X^{(4-n)+} \rightarrow (NH_3)_5Cr(OH)Cr(NH_3)_4OH^{4+} + X^{n-} \quad (1)$$

$$X = NH_3,\ NCS^-,\ Cl^-,\ F^-$$

Although $(H_2O)_5CrOCr(H_2O)_5{}^{4+}$ (aquo dimer) has not been isolated in the solid state, this binuclear complex is readily obtained from the reaction of chromous ion with 1,4-benzoquinone in acidic

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solution.[11] Unlike $(NH_3)_5CrOCr(NH_3)_5^{4+}$, the aquo dimer is not highly susceptible to protonation but readily cleaves to give monomer fragments (eq 2).[11,12] Our initial kinetic observations

$$(H_2O)_5CrOCr(H_2O)_5^{4+} + 2H^+ + H_2O \rightarrow 2Cr(H_2O)_6^{3+} \quad (2)$$

showed that the rate of this reaction is strongly accelerated by hydrogen ion, according to eq 3; $k_0 = 5 \times 10^{-5}$ s^{-1}, $k_1 = 1.61 \times$

$$-d[((H_2O)_5Cr)_2O^{4+}]/dt = (k_0 + k_1[H^+])[((H_2O)_5Cr)_2O^{4+}] \quad (3)$$

10^{-3} M^{-1} s^{-1} (25 °C, $I = 1.0$ M ($HClO_4/LiClO_4$)).[12] Thus, the half-life of the acid hydrolysis reaction is 7.0 min in 1.0 M $HClO_4$ at 25 °C.

We report here unexpectedly potent catalysis of the aquo dimer acid hydrolysis reaction by both strong and weak reductants, including $Cr(H_2O)_6^{2+}$, $Ru(NH_3)_6^{2+}$, and ascorbic acid (H_2A). Such catalysis by weak reductants implies that the electronic structure of Cr(III) in the binuclear reactant is strongly perturbed, as compared with that of the weakly-oxidizing $Cr(H_2O)_6^{3+}$ monomer product ($E°(Cr(H_2O)_6^{3+/2+}) = -0.41$ V).[13] Electrochemical studies of oxo-bridged ruthenium[6,7] and osmium[4,14] dimers have shown that the relative thermodynamic stabilities of adjacent oxidation states (III, IV) are markedly different from those of the corresponding monomer units. These changes in oxidizing and reducing strength potentially may be important in catalytic applications of binuclear, oxo-bridged complexes involving multielectron transfer. Accordingly, we have also measured the cyclic voltammograms of $(H_2O)_5CrOCr(H_2O)_5^{4+}$ and $(H_2O)_4Cr(OH)(OC_6H_4OH)Cr(H_2O)_4^{4+}$, from which the aquo dimer may be generated through oxidative elimination of the bridging hydroquinone moiety.[11] In order to understand the mechanistic basis for reductant-catalyzed hydrolysis, the potential, reversibility, and number of electrons involved in aquo dimer cathodic processes are of particular importance.

Experimental Section

Materials and Solution Preparation. Ascorbic acid (Sigma) and $Ru(NH_3)_6Cl_3$ (Johnson Matthey) were used as received, solutions were prepared with triply distilled water, and other reagent grade chemicals were acquired and analyzed as before.[12] SP-Sephadex C-25 resin (Na^+ form) was used in all cation-exchange experiments. Anaerobic (N_2-purged) acidic stock solutions of Cr^{2+}(aq) and $Ru(NH_3)_6^{2+}$ [15] were freshly prepared by reduction of $Cr(ClO_4)_3$ and $Ru(NH_3)_6Cl_3$ over 2% zinc amalgam. For kinetic measurements, $(H_2O)_5CrOCr(H_2O)_5^{4+}$ was generated in situ from the reaction of $(H_2O)_4Cr(OH)(OC_6H_4OH)Cr(H_2O)_4^{4+}$ with stoichiometric Br_2 in $HClO_4/LiClO_4$ media.[12]

Kinetic Measurements. Kinetic measurements were made on a Durrum D-110 stopped-flow apparatus, with inlet of anaerobic reductant and aquo dimer solutions through Teflon needles. Decay of $(H_2O)_5CrOCr(H_2O)_5^{4+}$ (initial concentration 0.50 mM) was followed at 443 nm (ϵ 3.0 × 10^3 M^{-1} cm^{-1}).[11] Rate data were transmitted to an Apple II Plus computer through ADALAB/AI 13 interface A/D converter/clock cards controlled by program QUICKERSAMPLE, all supplied by Interactive Microware, Inc. At least 256 absorbance–time points were collected in each kinetic determination and stored on a floppy disk. Graphical display of the kinetic data on the Apple II Plus computer and subsequent quantitative interpretation were accomplished through a modification of the VIDICHART program (Interactive Microware, Inc.). Observed pseudo-first-order rate constants (k_{obsd}) were derived from the linear least-squares slopes of ln ($A_t - A_\infty$) vs. time graphs, which exhibited correlation coefficients of ≥0.99 over at least 90% of ΔA_{443}. Reported rate constants are the mean of at least three trials.

Electrochemical Measurements. Cyclic voltammograms were generated with a Bioanalytical Systems CV-1B apparatus, and output was obtained from a Hewlett-Packard Model 7004B recorder. The three-electrode configuration consisted of carbon-paste working, platinum-wire auxiliary, and aqueous saturated calomel reference electrodes. Frequent resurfacing and polishing of the carbon-paste working electrode was necessary in order to obtain reproducible cyclic voltammograms. Hydroxyethylferrocene ($E°$ = 402 mV vs. SHE)[16] was used as an internal calibrant, so that potentials could be expressed relative to the standard hydrogen electrode (aqueous $HClO_4/LiClO_4$ media). Voltammograms of $(H_2O)_4Cr(OH)(OC_6H_4OH)Cr(H_2O)_4^{4+}$, prepared by the method of Holwerda and Petersen,[11] were carried out on samples freshly eluted from a SP-Sephadex C-25 cation-exchange column. Some difficulty was initially encountered in voltammetric studies of $(H_2O)_5CrOCr(H_2O)_5^{4+}$, as material derived from cation-exchange chromatography of Cr^{2+}(aq)–benzoquinone or $(H_2O)_4Cr(OH)(OC_6H_4OH)Cr(H_2O)_4^{4+}$–$Br_2$ product mixtures invariably contained electroactive impurities, particularly benzoquinone and $(H_2O)_4Cr(OH)(OC_6H_4OH)Cr(H_2O)_4^{4+}$, which elutes barely ahead of the aquo dimer fraction. Small concentrations of both $Cr(H_2O)_6^{3+}$ and Ce^{3+}(aq) induce the rapid conversion of $(H_2O)_4Cr(OH)(OC_6H_4OH)Cr(H_2O)_4^{4+}$ to $(H_2O)_5CrOCr(H_2O)_5^{4+}$ and free hydroquinone in acidic solution,[11,12] offering a convenient method to prepare the aquo dimer in the absence of other species that may be reducible in the interval 100–650 mV vs. SHE. Thus, solutions containing ca. 0.2 mM aquo dimer were fully generated from the precursor within 5 min after mixing with $Cr(ClO_4)_3$ or $Ce(ClO_4)_3$ (0.01–0.10 M) in 0.025–0.10 M $HClO_4$ (25.0 °C). Voltammograms of the aquo dimer, with initial cathodic sweep, were confined to potentials smaller than 0.64 V vs. SHE in order to avoid the oxidation of free hydroquinone.

Table I. Effect of Chromium(II) on the Aquo Dimer Hydrolysis Rate[a]

temp, °C	[H$^+$], M	[Cr^{2+}], mM	k_{obsd}, s^{-1}
25.0	0.100	9.3	230 (7)
		5.3	136 (1)
		2.3	60.6 (0.1)
		1.5	36.6 (0.3)
		0.90	24.4 (0.1)
		0.30	7.4 (0.3)
25.0	0.550	9.3	230 (6)
		5.3	131 (1)
		2.3	57.9 (0.6)
		1.5	36.2 (0.9)
		0.90	18.4 (0.3)
		0.30	6.6 (0.4)
25.0	1.00	9.3	236 (4)
		5.3	141 (1)
		2.3	62.8 (0.5)
		1.5	42.3 (0.4)
		0.90	20.5 (0.4)
36.7	0.550	0.90	35 (1)
31.0		0.90	31.4 (0.1)
22.4		0.90	21 (1)
16.0		0.90	6.5 (0.7)

[a] I = 1.0 M ($HClO_4/LiClO_4$). Average deviations from the mean are given in parentheses.

Results

Kinetics and Stoichiometry of Reductant-Catalyzed Acid Hydrolysis of $(H_2O)_5CrOCr(H_2O)_5^{4+}$. Although both cations ($Cr(H_2O)_6^{3+}$, H^+(aq)) and anions (Cl^-, Br^-, SO_4^{2-}, ClO_4^-) accelerate the aquo dimer acid hydrolysis reaction,[12,17] the catalytic effectiveness of reducing agents is far greater. For example, the half-life for aquo dimer decay decreases from 7.0 min to only 34 ms in the presence of 0.90 mM Cr^{2+} (25 °C, 1.0 M $HClO_4$). As a result, the separate contribution of $HClO_4$ alone to the rate law[12,17] may be neglected when the effects of Cr^{2+}(aq), $Ru(NH_3)_6^{2+}$, and ascorbic acid on the aquo dimer hydrolysis rate are considered. Pseudo-first-order analyses of A_{443}–time curves were successful in the reactions of $((H_2O)_5Cr)_2O^{4+}$ with excesses of all reductants considered.

A chromatographic experiment was carried out at 25 °C to determine the products of the Cr^{2+}–aquo dimer reaction. A 2-fold excess of Cr(II) was mixed anaerobically with 25 mL of 0.75 mM aquo dimer in 0.10 M $HClO_4$. After 5 min the solution was diluted 3-fold aerobically and applied to a 10 × 1.5 cm cation-

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exchange column. Two bands were observed upon elution with 0.5 M $LiClO_4$/0.1 M $HClO_4$. Chromium present initially as $(H_2O)_5CrOCr(H_2O)_5^{4+}$ was quantitatively accounted for in the leading blue-violet band, identified as $Cr(H_2O)_6^{3+}$ from its UV-visible spectrum.[11] The green trailing component contained $(H_2O)_4Cr(OH)_2Cr(H_2O)_4^{4+}$, generated from the aerobic oxidation of chromous ion.[18]

Kinetic results on the Cr^{2+}(aq)-catalyzed hydrolysis reaction are given in Table I. Plots of k_{obsd} vs. $[Cr^{2+}(aq)]$ are linear for studies carried out at 25.0 °C, $I = 1.0$ M ($LiClO_4/HClO_4$), $[H^+] = 0.100$, 0.550, and 1.00 M, and $0.30 \leq [Cr^{2+}(aq)] \leq 9.3$ mM. The identical slopes and zero intercepts of these plots, within experimental error, support the rate law of eq 4, where k(25 °C)

$$-d[((H_2O)_5Cr)_2O^{4+}]/dt = k[Cr^{2+}][((H_2O)_5Cr)_2O^{4+}] \quad (4)$$

= $(2.50 \pm 0.03) \times 10^4$ M^{-1} s^{-1}. The temperature dependence of k_{obsd}, in the 16.0–36.7 °C range, is also shown in Table I at $[Cr^{2+}] = 0.90$ mM. Activation parameters derived from the least-squares analysis of the Eyring plot ($\ln (k\ (=k_{obsd}/[Cr^{2+}]))/T$ vs. $1/T$) are $\Delta H^{\ddagger} = 6.0 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger} = -17 \pm 6$ eu.

In contrast to Cr^{2+} (d^4, high-spin), which transfers an electron from a σ-symmetry (e_g) d orbital, $Ru(NH_3)_6^{2+}$ (d^6, low spin) is a π (t_{2g}) electron donor.[19] Although the thermodynamic reducing strength of $Ru(NH_3)_6^{2+}$ ($E° = +0.050$ V)[20] is considerably smaller than that of chromous ion, $Ru(NH_3)_6^{2+}$ is more reactive, by more than an order of magnitude, in the catalyzed hydrolysis of $(H_2O)_5CrOCr(H_2O)_5^{4+}$. The $Ru(NH_3)_6^{2+}$-catalyzed reaction was immeasurably fast at reductant concentrations greater than 1.0 mM, but k_{obsd} values of $(2.0 \pm 0.3) \times 10^2$ s^{-1} and $(4.0 \pm 0.5) \times 10^2$ s^{-1} were obtained at $[Ru(NH_3)_6^{2+}] = 0.50$ and 1.0 mM, respectively (25.0 °C, $[H^+] = 0.550$ M, $I = 1.0$ M ($HClO_4/LiClO_4$)). A first-order $Ru(NH_3)_6^{2+}$ dependence is apparent from this very limited data set, and an overall second-order rate constant of $(4 \pm 1) \times 10^5$ M^{-1} s^{-1} may be reported. The effect of H^+, if any, on the $Ru(NH_3)_6^{2+}$-catalyzed hydrolysis pathway was not investigated.

Surprisingly, even ascorbic acid, a very weak one-electron organic reductant ($E°(H_2A^{+\cdot}/H_2A) = +1.31$ V, $E°(HA\cdot/HA^-) = +0.93$ V; $H_2A^{+\cdot}$ and $HA\cdot$ represent the free radical one-electron oxidation products of unionized and singly ionized ascorbic acid, respectively),[21] strongly accelerates the aquo dimer acid hydrolysis reaction. Considering the structural similarities among ascorbic acid, oxalic acid, and catechol (*cis*-1,2-$(OH)_2$ donor groups), both reducing and chelating roles could be attributed to ascorbic acid in the catalytic mechanism. A comparison was made, therefore, of the catalytic reactivities of these three organic reagents (1 mM) at 25.0 °C, $[H^+] = 0.550$ M, and $I = 1.0$ M ($HClO_4/LiClO_4$). Observed hydrolysis rate constants of $(1.9 \pm 0.1) \times 10^{-1}$ s^{-1} (ascorbic acid), $(1.28 \pm 0.02) \times 10^{-3}$ s^{-1} (catechol), and $(7.2 \pm 0.2) \times 10^{-4}$ s^{-1} (oxalic acid) may be compared with that of 9.1×10^{-4} s^{-1} [12] determined in the absence of these compounds. Clearly, only ascorbic acid influences the aquo dimer hydrolysis rate appreciably under these conditions.

Table II presents a study of the ascorbic acid-catalyzed aquo dimer hydrolysis rate, as a function of $[H_2A]$, $[H^+]$, and temperature. A first-order reductant dependence is apparent from the variation of k_{obsd} with $[H_2A]$ (0.001–0.100 M) at 25.0 °C, $[H^+] = 0.550$ M, and $I = 1.0$ M ($HClO_4/LiClO_4$). The $[H^+]$ variation results show that the H_2A-catalyzed hydrolysis rate is inhibited with increasing acidity, as described by the rate law of eq 5. Least-squares rate parameters derived from a fit of the

$$\begin{aligned}-d[((H_2O)_5Cr)_2O^{4+}]/dt &= (k_1 + k_2/[H^+])[H_2A] \times [((H_2O)_5Cr)_2O^{4+}] \\ &= k_{obsd}[((H_2O)_5Cr)_2O^{4+}]\end{aligned} \quad (5)$$

Table II. Effect of Ascorbic Acid on the Aquo Dimer Hydrolysis Rate[a]

temp, °C	$[H^+]$, M	$[H_2A]$, mM	k_{obsd}, s^{-1}
25.0	0.550	100	14.2 (0.2)
		60	8.64 (0.08)
		30	4.44 (0.06)
		10	1.49 (0.02)
		10	1.57 (0.08)[b]
		6	0.97 (0.01)
		3	0.50 (0.01)
		1	0.19 (0.01)
25.0	1.00	10	0.84 (0.01)
	0.800	10	1.00 (0.01)
	0.700	10	1.19 (0.01)
	0.400	10	1.97 (0.09)
	0.250	10	3.29 (0.07)
	0.100	10	7.9 (0.1)
15.4	0.550	10	0.75 (0.03)
19.7	0.550	10	1.16 (0.01)
31.3	0.550	10	2.38 (0.01)
35.9	0.550	10	3.28 (0.02)

[a] $I = 1.0$ M ($HClO_4/LiClO_4$). Average deviations from the mean are given in parentheses. Measurements made anaerobically, unless otherwise noted. [b] Aerobic measurement.

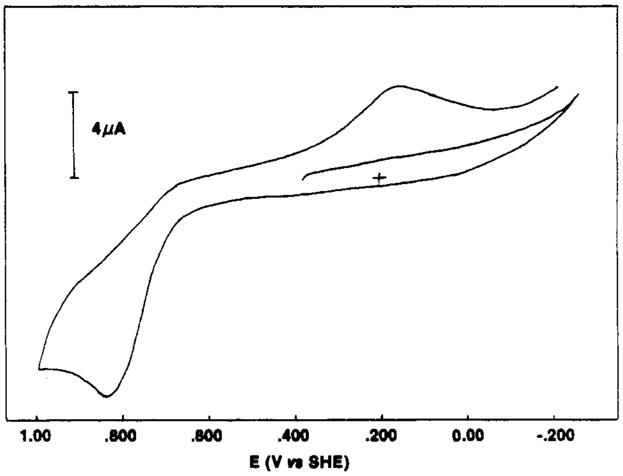

Figure 1. Cyclic voltammogram of 1.0 mM $(H_2O)_4Cr(OH)(OC_6H_4OH)Cr(H_2O)_4^{4+}$ in 0.01 M $HClO_4$–0.10 M $LiClO_4$: 25.0 °C, carbon-paste working electrode, SCE reference, 50 mV/s sweep rate.

25.0 °C rate data to eq 5 are $k_1 = 6 \pm 1$ M^{-1} s^{-1} and $k_2 = (7.8 \pm 0.1) \times 10^1$ s^{-1}. Since the k_1 pathway carries only 4% of the hydrolysis reaction at 25.0 °C, $[H^+] = 0.550$ M, it is assumed that the temperature dependence of k_{obsd} (15.4–35.9 °C) measured at constant $[H_2A] = 0.01$ M and $[H^+] = 0.550$ M primarily reflects k_2 activation requirements. This assumption is further justified by the linearity of an Eyring plot constructed as $\ln (k_{obsd}[H^+]/[H_2A]T)$ vs. $1/T$. Apparent k_2 activation parameters obtained from this analysis are $\Delta H^{\ddagger} = 12.1 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger} = -9 \pm 1$ eu.

Electrochemistry of $(H_2O)_5CrOCr(H_2O)_5^{4+}$ and $(H_2O)_4Cr(OH)(OC_6H_4OH)Cr(H_2O)_4^{4+}$. Since $(H_2O)_4Cr(OH)(OC_6H_4OH)Cr(H_2O)^{4+}$ is readily converted to the aquo dimer through oxidative elimination of the hydroquinone bridging group,[11] the cyclic voltammogram of this species could, in principle, exhibit waves due to both complexes. Voltammetric results on 1 mM $(H_2O)_4Cr(OH)(OC_6H_4OH)Cr(H_2O)_4^{4+}$ in 0.01 M $HClO_4$ and 0.10 M $LiClO_4$ are displayed in Figure 1. No electroactive species was detected in the 0.6–0.0-V interval during the initial cathodic sweep, but a strong, quasireversible anodic wave with $E_{pa} = 0.81 \pm 0.01$ V was observed upon reversing the scan direction. A broad, poorly defined wave with $E_{pc} = 0.19 \pm 0.01$ V was found in the second and subsequent cathodic sweeps, indicative of an oxidant not present initially. This voltammogram

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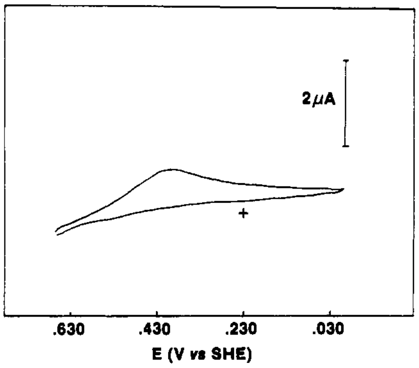

Figure 2. Cyclic voltammogram of 0.2 mM $(H_2O)_5CrOCr(H_2O)_5^{4+}$ in 0.01 M $Ce(ClO_4)_3$–0.10 M $HClO_4$: 25.0 °C, carbon-paste working electrode, SCE reference, 50 mV/s sweep rate.

is essentially identical with that of free hydroquinone under the same conditions, formed quantitatively from the slow acid hydrolysis of $(H_2O)_4Cr(OH)(OC_6H_4OH)Cr(H_2O)_4^{4+}$.[11] Thus, the waves at 0.81 and 0.19 V correspond to the two-electron oxidation of coordinated hydroquinone and the subsequent reduction of free benzoquinone, respectively. A distinct cathodic component due to $((H_2O)_5Cr)_2O^{4+}$ was therefore not resolved in this experiment. An apparent half-wave potential ($E_{1/2}$) of 0.75 ± 0.01 V was calculated from an excellent fit of the anodic current–potential profile to eq 6,[22] where i, i_d, and n represent the current at potential

$$E = E_{1/2} + (RT/nF)\ \ln\ [(i_d - i)/i] \tag{6}$$

E, the diffusion current, and the number of electrons involved in the anodic process, respectively. This value may be compared with the standard reduction potential of free 1,4-benzoquinone, +0.70 V.[13] The slope of the linear E vs. ln $[(i_d - i)/i]$ plot (26 ± 1 mV) is in reasonable agreement with that expected for a two-electron oxidation (30 mV).

A cathodic wave clearly assignable to $((H_2O)_5Cr)_2O^{4+}$ was successfully resolved in cyclic voltammograms of solutions generated through the addition of $Cr(H_2O)_6^{3+}$ or Ce^{3+}(aq) to $(H_2O)_4Cr(OH)(OC_6H_4OH)Cr(H_2O)_4^{4+}$, as described in the Experimental Section. Although $Cr(H_2O)_6^{3+}$ catalyzes both formation of the aquo dimer from this precursor and subsequent hydrolytic decay,[11,17] the latter reaction was sufficiently slow to permit partial electrochemical characterization of the aquo dimer within 5 min after mixing. Since Ce^{3+}(aq) actually retards aquo dimer hydrolysis,[17] somewhat better voltammetric reproducibility was attained through the use of this reagent. The cyclic voltammogram of $Ce(ClO_4)_3$ (0.01 M)-generated aquo dimer (0.2 mM) in 0.1 M $HClO_4$ is shown in Figure 2. When the initial cathodic sweep (50 mV/s)) started at 0.64 V, a totally irreversible response with E_{pc} = 0.40 ± 0.02 V was found. No corresponding anodic wave was detected even upon doubling the sweep rate.

Table III offers a comparison of aquo dimer cathodic peak potentials observed at various $Cr(H_2O)_6^{3+}$, Ce^{3+}(aq), and H^+ concentrations. It should be noted that none of these supporting electrolytes contributed appreciably to current drawn within the 0.64–0.03-V potential interval examined. Several observations support the assignment of the irreversible cathodic wave to a one-electron reduction of the aquo dimer, followed by rapid chemical decay of the product. First, essentially identical voltammograms and E_{pc} values pertain for aquo dimer solutions generated with $Cr(H_2O)_6^{3+}$ and Ce^{3+}(aq), indicating that the redox reactivity of the electroactive species is not a function of its point of origin. Excellent linear E vs. ln $[(i_d - i)/i]$ graphs with slope of 59 ± 6 mV, consistent with an $n = 1$ reduction, and intercept ($E_{1/2}$) of 0.52 ± 0.01 V were constructed from cathodic potential and current points ($[HClO_4]$ = 0.10 M; $[Cr(ClO_4)_3]$ or $[Ce(ClO_4)_3]$ = 0.010 M). This n value, the independence of E_{pc} on $[H^+]$ (0.025–1.0 M), and the large discrepancy between the observed E_{pc} values and those characteristic of 1,4-benzoquinone at each acidity examined definitively rule out the possibility that benzoquinone or some other organic impurity is responsible for the observed electrochemistry. Additionally, we note that i_{pc}, the cathodic current maximum, decreased with time in the $Cr(H_2O)_6^{3+}$ experiments at a rate consistent with that of chromic ion-catalyzed aquo dimer hydrolysis.[12] Finally, the irreversibility of the cathodic wave is as expected for $((H_2O)_5Cr)_2O^{4+}$ from the chemical reductant-catalyzed hydrolysis results, which imply rapid cleavage of the aquo dimer into monomer $Cr(H_2O)_6^{2+/3+}$ ions subsequent to the electron-transfer step.

Table III. Electrochemical Results on the Reduction of the Aquo Dimer[a]

metal ion,[b] M^{3+}	$[M^{3+}]$, M	$[H^+]$, M	E_{pc}, V[c]
Ce^{3+}	0.010	0.10	0.40
Cr^{3+}	0.010	0.10	0.42
	0.10	0.10	0.39
	0.10	1.0	0.40
	0.10	0.025	0.42

[a] 25.0 ± 0.1 °C, carbon-paste working electrode, sweep rate = 50 mV/s. [b] Metal ion used to generate $((H_2O)_5Cr)_2O^{4+}$ from $(H_2O)_4Cr(OH)(OC_6H_4OH)Cr(H_2O)_4^{4+}$; see text. [c] Potential corresponding to cathodic current maximum, relative to SHE. Uncertainty estimated at ±0.02 V.

Discussion

By far the most significant aspect of our results is the remarkable positive shift in the one-electron reduction potential of $(H_2O)_5CrOCr(H_2O)_5^{4+}$ (+ 0.52 V vs. SHE), as compared with that of $Cr(H_2O)_6^{3+}$ (–0.41 V vs. SHE).[13] This unexpectedly high oxidizing strength, coupled with the total irreversibility of the aquo dimer cathodic cyclic voltammetric wave, accounts for the potent activity of even weak reductants as catalysts for cleavage of the Cr–O–Cr unit. The acceptor redox orbital of the aquo dimer clearly must be at much lower energy than that of $Cr(H_2O)_6^{3+}$ ($3d\text{–}e_g{}^*$); the 0.93-V positive shift in $E°$ corresponds to a free-energy stabilization of 21.4 kcal/mol.

A qualitative molecular orbital treatment of linear $L_5M\text{–}O\text{–}ML_5$ complexes (approximate D_{4h} symmetry), first offered by Dunitz and Orgel,[8] has proved to be useful in understanding their structural,[3] spectroscopic,[4,6,7,9] magnetic,[2,6,7] and electrochemical properties.[4,6,7] Considering only π bonding of the $Cr(d\pi)\text{–}O(p\pi)\text{–}Cr(d\pi)$ type, the electronic configuration expected for the aquo dimer is $(e_u{}^b)^4[(b_{2g})(b_{1u})(e_g)]^6(e_u{}^*)^0$, where $e_u{}^b$ and $e_u{}^*$ represent the strongly bonding and antibonding molecular orbitals, respectively, derived from the p_x, p_y (O), and d_{xz}, d_{yz} (Cr) atomic orbitals; Cr–O–Cr is the z axis. The ordering of the approximately nonbonding b_{2g}, b_{1u} (derived from d_{xy}), and e_g levels is uncertain, being dependent on the contributions of Cr–Cr δ and π bonding from the nonbridging ligands.[2,8,23,24]

Although acceptance of an electron into the antibonding $e_u{}^*$ level would provide a straightforward explanation of reduction-linked instability, this hypothesis cannot be reconciled with spectroscopic and electrochemical observations. The 479 (ϵ 5.2 × 10^3 M^{-1} cm^{-1}) and 492 nm (ϵ 4.9 × 10^3 M^{-1} cm^{-1}) bands of $[Ru_2OCl_{10}]^{4-}$ and $[Ru_2OBr_{10}]^{4-}$, respectively, have been definitively assigned as the fully allowed $e_g\text{–}e_u{}^*$ ($^1A_{2u} \leftarrow {}^1A_{1g}$) electronic transition of the Ru(IV)–O–Ru(IV) chromophore from the resonance Raman coupling of these bands to the totally symmetric M–O–M stretching vibration.[9,25] Similar intense bands in the visible and near-ultraviolet regions typically dominate the spectra of linear, oxo-bridged complexes ($d^2\text{–}d^4$ monomer) in which the e_g level is populated.[4-7,9,26] One of the intense aquo dimer bands at 22.6 (ϵ 3.0 × 10^3 M^{-1} cm^{-1}), 24.2 (ϵ 2.3 × 10^3 M^{-1} cm^{-1}), and 28.8 × 10^3 cm^{-1} (ϵ 5.0 × 10^3 M^{-1} cm^{-1})[11] reasonably should

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correspond to the e_g–e_u^* transition. If the maximum electron pairing energy in one-electron-reduced aquo dimer is approximated as that of $Cr^{2+}(g)$ (20.4×10^3 cm^{-1}),[27] spin pairing in the approximately nonbonding levels should be preferred over population of e_u^*. Indeed, the energies of the aquo dimer d–d bands at 15.8 and 17.0×10^3 cm^{-1} [11,12] suggest that both d_{z^2} and $d_{x^2-y^2}$ would be populated before e_u^*. Clearly, then, the differential in electrode potential between $Cr(H_2O)_6^{3+}$ and the aquo dimer also is inconsistent with electron acceptance into e_u^*.

The aquo dimer $E°$ value and susceptibility to reductant-catalyzed hydrolysis imply that the MO electronic configuration of the one-electron reduction product is $(e_u^b)^4(b_{2g})^2(b_{1g})^2(e_g)^3$ (^2E_g ground state). By comparison with other transition-metal ions having the orbitally degenerate E_g ground state, this product should undergo a strong Jahn–Teller distortion, which removes the orbital degeneracy.[28] Such distortion necessarily would involve bending of the Cr–O–Cr unit (C_{2v} symmetry component), with accompanying loss of $d\pi(Cr)$–$p\pi(O)$ overlap, as axial perturbations which preserve the 180° bond angle (and C_4 symmetry axis) cannot lift the degeneracy of an E_g state. The conceivable aquo dimer reduction products with an electron hole in the b_{2g} ($^2B_{2g}$ ground state) or b_{1u} ($^2B_{1u}$ ground state) levels would not be subject to Jahn–Teller configurational instability.

Considering both Coulomb and exchange contributions,[27,28] the electron-pairing energy required to form the reduced aquo dimer with ^2E_g ground state should be smallest of the three alternatives. Thus, an electron accepted into the e_g level ($d_{xz}(1) + d_{xz}(2)$, $d_{yz}(1) + d_{yz}(2)$ combinations) is delocalized over both Cr atoms and between two degenerate molecular orbitals. Since $E°$ values are primarily responsive to the energy of the redox electron in the reduction product, including the pairing energy,[29] this delocalization will be reflected in $\Delta E°$ between the aquo dimer and $Cr(H_2O)_6^{3+}$. The proposed redox orbital of the aquo dimer (e_g–D_{4h}, from t_{2g}–O_h) is stabilized by approximately $10Dq$ (O_h) relative to that of $Cr(H_2O)_6^{3+}$ (e_g–O_h), providing an ample basis (17.4×10^3 cm^{-1} [12] or 50 kcal/mol) to support the enhancement in thermodynamic driving force for reduction of the binuclear complex. The pairing energy of the $((H_2O)_5Cr)_2O^{4+} + e^- \rightarrow ((H_2O)_5Cr)_2O^{3+}$ half-reaction implied by this approximate treatment (29 kcal/mol) is only 50% of that required in $Cr^{2+}(g)$ (58.4 kcal/mol),[27] underscoring the essential role of electron delocalization in promoting aquo dimer oxidizing strength.

A recently reported oxo- and bis(diphenylphosphino)methane-(dppm-) bridged binuclear Os(IV) complex, $Os_2(\mu\text{-}O)(\mu\text{-}dppm)_2Cl_6 \cdot 2CHCl_3$, exhibits a quasireversible oxidation wave at +1.62 V vs. SCE in CH_2Cl_2 (0.1 M TBAP) to give a relatively stable Os(IV)–O–Os(V) species with the same d electronic configuration (d^3,d^4) as the reduced aquo dimer.[4] The apparent absence of Jahn–Teller configurational instability in the former species is understandable in terms of the effective D_{2h} symmetry of the $Os_2OP_4Cl_6$ skeleton,[4] which would lift the degeneracy of the e_g molecular orbital (b_{2g}, b_{3g} components) even before oxidation of the parent complex. Unlike $((H_2O)_5Cr)_2O^{4+}$, $((NH_3)_5Ru)_2O^{4+}$ and related Ru(III) dimers are poor one-electron oxidants but strong one-electron reductants when compared with monomer analogues having the same nonbridging ligands.[6,7] This is consistent with the expected change in HOMO/LUMO from π^n (Cr) to π^* (Ru). The magnetic properties of $((NH_3)_5Ru)_2O^{4+}$ suggest some lowering of symmetry from D_{4h}, possibly involving slight bending of the M–O–M axis.[7] Thus, the degeneracy of the e_u^* level would be lifted, accounting for the considerable stability[7] of the Ru(III)–O–Ru(IV) (formal $(e_u^*)^1$ electronic configuration) analogue. Once π bonding within the Cr(III)–O–Cr(III) unit is disrupted by bending, the rate of substitution at Cr(III), including bridge cleavage, will be governed by crystal field activation requirements and the electrostatic interaction between the metal centers. The distinctively high susceptibility of $((H_2O)_5Cr)_2O^{4+}$ to oxo-bridge cleavage, as compared with that of $((NH_3)_5Cr)_2O^{4+}$ [30] and analogous binuclear complexes of second- and third-row transition metals,[31] can be related[32] to the low rank of H_2O in the spectrochemical series and increases in $10Dq$ with increasing principal quantum number of the valence d electrons.

Table IV. Comparison of Rate Parameters for the Reductant-Catalyzed Hydrolysis of the Aquo Dimer[a]

reductant	k(25 °C), M^{-1} s^{-1}	ΔH^*, kcal/mol	ΔS^*, eu
H_2A	6 (1)		
HA^- [b]	$7.2\ (0.2) \times 10^5$	7.7 (0.8)	−6 (2)
$Cr^{2+}(aq)$	$2.50\ (0.03) \times 10^4$	6.0 (0.5)	−17 (6)
$Ru(NH_3)_6^{2+}$	$4\ (1) \times 10^5$		

[a] $I = 1.0$ M ($HClO_4/LiClO_4$). Error estimates are shown in parentheses. [b] Rate parameters calculated from k_2 (eq 5) as described in footnote 34.

A common mechanism involving one-electron transfer in the rate-determining step agrees with rate laws for the $Cr^{2+}(aq)$-, $Ru(NH_3)_6^{2+}$-, and ascorbic acid-catalyzed hydrolysis of the aquo dimer (eq 7; C_{red} and C_{ox} represent reduced and oxidized catalyst species). The failure of oxalic acid and catechol to strongly catalyze aquo dimer hydrolysis rules out a purely chelating role for H_2A in the ascorbic acid-catalyzed pathway. Furthermore, the rate law defining this pathway (eq 5) agrees exactly with that for the ascorbic acid reduction of $IrCl_6^{2-}$ and other transition-metal oxidants.[21,33] The two-term rate law is readily interpreted through the parallel reduction of the aquo dimer by H_2A (rate constant $k = k_1$) and the ascorbate anion HA^- (rate constant $k = k_2/K_{a1}$; K_{a1} is the first acid ionization constant of H_2A). The rate constant and corresponding activation parameters of the predominant HA^-–aquo dimer redox pathway may therefore be calculated[34] and compared with other $((H_2O)_5Cr)_2O^{4+}$ reduction rate parameters (Table IV). The $k(HA^-)/k(H_2A)$ ratio of 1.2×10^5 is somewhat larger than that characteristic of $IrCl_6^{2-}$ (1.9×10^4),[21] as expected from the influence of oxidant charge on precursor complex formation in the reaction of HA^-. The similarity of electron-transfer rate constants from $Cr^{2+}(aq)$, $Ru(NH_3)_6^{2+}$, and HA^- to that of the aquo dimer is remarkable, considering the wide range in thermodynamic one-electron-reducing strengths represented.

$$C_{red} + (H_2O)_5CrOCr(H_2O)_5^{4+} \xrightarrow[\text{slow}]{k} C_{ox} + (H_2O)_5CrOCr(H_2O)_5^{3+}$$

$$H_2O + 2H^+ + (H_2O)_5CrOCr(H_2O)_5^{3+} \xrightarrow[\text{fast}]{} Cr^{2+}(aq) + Cr(H_2O)_6^{3+} \quad (7)$$

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

$$\text{net:}\quad (H_2O)_5CrOCr(H_2O)_5^{4+} + 2H^+ + H_2O \rightarrow 2Cr(H_2O)_6^{3+}$$

Considering the very different nature of the aquo dimer (π^n) and $Cr(H_2O)_6^{3+}$ (σ^*) electron-acceptor orbitals, a comparison of the intrinsic electron-transfer reactivities of these close relatives, as expressed by the $(H_2O)_5CrOCr(H_2O)_5^{4+/3+}$ and $Cr(H_2O)_6^{3+/2+}$ self-exchange rate constants, is of interest. Relative Marcus theory could be useful in this regard provided, of course, that all redox reactions considered are outer sphere. Given the well-known inner-sphere preference of $Cr^{2+}(aq)$,[19] this point can hardly be

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taken for granted. The ratio of cross-reaction rate constants, $R = k(\mathrm{Ru(NH_3)_6^{2+}})/k(\mathrm{Cr^{2+}})$, offers one criterion for distinguishing between oxidants attacked by $\mathrm{Cr^{2+}(aq)}$ through inner- and outer-sphere pathways. If electrostatic work terms are neglected, the relationship of eq 8[35] (for 25 °C) is predicted for outer-sphere

$$R = \left[\frac{k_{22}(\mathrm{Ru(NH_3)_6^{3+/2+}})}{k_{22}(\mathrm{Cr(H_2O)_6^{3+/2+}})}\exp(38.94(\Delta E'))\right]^{1/2} \quad (8)$$

reactions, where the k_{22}'s are self-exchange electron-transfer rate constants and $\Delta E'$ is the difference between $\mathrm{Cr(H_2O)_6^{3+}}$ and $\mathrm{Ru(NH_3)_6^{3+}}$ standard reduction potentials (−0.46 V). Since direct measurements of the $\mathrm{Cr(H_2O)_6^{3+/2+}}$ ($\leq 2 \times 10^{-5}$ $\mathrm{M^{-1}\ s^{-1}}$)[36] and $\mathrm{Ru(NH_3)_6^{3+/2+}}$ (8.2×10^{2} $\mathrm{M^{-1}\ s^{-1}}$)[15] k_{22} values are available, an outer-sphere R on the order of ≥ 1, independent of oxidant, may be predicted. It should be noted that $R <<< 1$ may be anticipated in cases where the reactivity of $\mathrm{Cr^{2+}}$ is promoted by an effective bridging ligand.[37] The experimental R (aquo dimer) (16) is in reasonable agreement with this estimation and analogous ratios from unambiguously outer-sphere oxidants such as $\mathrm{Co(NH_3)_6^{3+}}$ (11)[37] and $\mathrm{Ru(NH_3)_6^{3+}}$ (4),[37] supporting the assignment of the $\mathrm{Cr^{2+}}$–aquo dimer reaction to the outer-sphere class. Indeed, the absence of an $[\mathrm{H^+}]^{-1}$-dependent term in the rate law rules out a hydroxo-bridged inner-sphere intermediate in this reaction. Outer-sphere reactivity appears likely in the ascorbic acid–aquo dimer reaction as well, considering that $\mathrm{(Cr(H_2O)_5)_2O^{4+}}$ water exchange is not known to occur on the fast time scale of the catalyzed cleavage reaction.[17]

From the rate constant and standard cell potential of an outer-sphere cross-reaction, the Marcus relationship may be used to calculate an apparent self-exchange electron-transfer rate constant for one redox partner (k_{11}) given that of the other (k_{22}).[38] This calculation yields $\mathrm{((H_2O)_5Cr)_2O^{4+/3+}}$ k_{11} estimates of ≥ 1.3 and 15 $\mathrm{M^{-1}\ s^{-1}}$ from aquo dimer reductions by $\mathrm{Cr^{2+}}$ [13,36] and $\mathrm{Ru(NH_3)_6^{2+}}$,[15,20] respectively, including the f term but neglecting small electrostatic work corrections. Although this k_{11} calculation is only approximate at best, an impressive 10^6-fold increase in intrinsic electron-transfer reactivity (8 kcal/mol decrease in ΔG^*) is apparent upon comparison with the parent $\mathrm{Cr(H_2O)_6^{3+/2+}}$ couple ($k_{11} \leq 2 \times 10^{-5}$ $\mathrm{M^{-1}\ s^{-1}}$, $\Delta H^* = 21$ kcal/mol, $\Delta S^* = -8$ eu).[36] This increase confirms the π^n character of the aquo dimer redox orbital, which should be reflected in a much smaller Franck–Condon inner-sphere reorganization barrier than is required for electron transfer involving the e_g (σ^*) orbital of $\mathrm{Cr(H_2O)_6^{3+/2+}}$.[38] Such benefit of electron acceptance into an essentially nonbonding orbital is also seen in ΔH^* of the $\mathrm{Cr^{2+}}$–$\mathrm{((H_2O)_5Cr)_2O^{4+}}$ reaction, smaller by 15 kcal/mol than that of the analogous $\mathrm{Cr(H_2O)_6^{2+/3+}}$ self-exchange electron-transfer process.

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Registry No. $\mathrm{(H_2O)_5CrOCr(H_2O)_5^{4+}}$, 73347-70-3; $\mathrm{(H_2O)_4Cr(OH)(OC_6H_4OH)Cr(H_2O)_4^{4+}}$, 73360-43-7; $\mathrm{(H_2O)_5CrOCr(H_2O)_5^{3+}}$, 97644-50-3; $\mathrm{Cr(H_2O)_6^{3+}}$, 14873-01-9; $\mathrm{Cr(H_2O)_6^{2+}}$, 20574-26-9; $\mathrm{Ru(NH_3)_6^{2+}}$, 19052-44-9; $\mathrm{H_2A}$, 50-81-7; $\mathrm{HA^-}$, 299-36-5; Ce, 7440-45-1; carbon, 7440-44-0.

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Anion and Cation Effects on the Acid Hydrolysis Rate of the (μ-Oxo)bis(pentaaquochromium(III)) Ion

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Anion ($\mathrm{ClO_4^-}$, $\mathrm{Cl^-}$, $\mathrm{Br^-}$) and cation ($\mathrm{Cr(H_2O)_6^{3+}}$) catalysis of oxo-bridge cleavage in the (μ-oxo)bis(pentaaquochromium(III)) ion (aquo dimer) has been examined. Increases in pseudo-first-order acid hydrolysis rate constants (k_{obsd}) caused by $\mathrm{LiClO_4}$, $\mathrm{NaClO_4}$, $\mathrm{Mg(ClO_4)_2}$, $\mathrm{Zn(ClO_4)_2}$, $\mathrm{Al(ClO_4)_3}$, and $\mathrm{Fe(ClO_4)_2}$ in $\mathrm{HClO_4}$ media at 25 °C are entirely attributable to perchlorate ion, according to $k_{\mathrm{obsd}} = k_0 + k'_1[\mathrm{H^+}] + ab[\mathrm{H^+}][\mathrm{ClO_4^-}]/(1 + b[\mathrm{H^+}])$, where $k_0 = 5 \times 10^{-5}$ $\mathrm{s^{-1}}$, $k'_1 = 1 \times 10^{-4}$ $\mathrm{M^{-1}\ s^{-1}}$, $a = 2.0 \times 10^{-3}$ $\mathrm{M^{-1}\ s^{-1}}$, and $b = 1.6$ $\mathrm{M^{-1}}$. The rate expressions pertaining to $\mathrm{Cl^-}$ (parameters c and d analogous to a and b, respectively) and $\mathrm{Br^-}$ (parameters e and f) exactly parallel that of $\mathrm{ClO_4^-}$; $c = 2.4 \times 10^{-3}$ $\mathrm{M^{-1}\ s^{-1}}$, $d = 1.2$ $\mathrm{M^{-1}}$, $e = 3.0 \times 10^{-3}$ $\mathrm{M^{-1}\ s^{-1}}$, and $f = 2.0$ $\mathrm{M^{-1}}$. Anation of Cr(III) is not responsible for oxo-bridge cleavage, as $\mathrm{Cr(H_2O)_6^{3+}}$ was the sole hydrolysis product under conditions where the chloride-assisted pathway contributed 83% of the overall reaction. Since catalytic activity appears to be governed by anion charge, the proposed mechanism involves bending of the initially linear Cr–O–Cr unit within an ion pair, providing electrostatic anion-incipient dipole stabilization to compensate for the loss of π bonding. Further lowering of the transition-state energy would then be achieved by protonation of an emergent lone pair on oxygen. This improved understanding of anion-assisted aquo dimer hydrolysis now permits the incorporation of $\mathrm{Cr(H_2O)_6^{3+}}$ into the rate law: $k_{\mathrm{obsd}} = k_0 + k'_1[\mathrm{H^+}] + ab[\mathrm{H^+}][\mathrm{ClO_4^-}]/(1 + b[\mathrm{H^+}]) + [\mathrm{Cr(H_2O)_6^{3+}}]^2(k_2 + k_3[\mathrm{H^+}]^2)$, where $k_2 = 1 \times 10^{-3}$ $\mathrm{M^{-2}\ s^{-1}}$ and $k_3 = 9.0 \times 10^{-2}$ $\mathrm{M^{-4}\ s^{-1}}$ (25 °C, $\mathrm{HClO_4/Cr(ClO_4)_3}$ medium). A bonding interaction between the $\mathrm{Cr(H_2O)_6^{3+}}$ t_{2g} (π^n) and approximately nonbonding e_g $\mathrm{((H_2O)_5Cr)_2O^{4+}}$ orbitals, accompanied by protonation of the oxo bridge, is proposed to account for the distinctive catalytic activity of the chromic ion. Unexpectedly greater resistance of the oxo bridge to acid hydrolysis in the presence of $\mathrm{Fe(H_2O)_6^{3+}}$ and especially $\mathrm{Ce(H_2O)_6^{3+}}$ also is reported.

Introduction

The acid hydrolysis reaction (eq 1) of the (μ-oxo)bis(pentaaquochromium(III)) ion (aquo dimer) is accelerated by $\mathrm{H^+}$ and many salts, including alkali-metal, alkaline-earth-metal, and transition-metal perchlorates.[1,2] The rate law of eq 2 was established for this reaction in our initial study[1] at constant ionic strength of 1.0 M ($\mathrm{HClO_4/LiClO_4}$); $k_0 = 5 \times 10^{-5}$ $\mathrm{s^{-1}}$ and $k_1 = 1.61 \times 10^{-3}$ $\mathrm{M^{-1}\ s^{-1}}$ at 25 °C. Protonation of the weakly basic bridging oxygen atom before or during the rate-limiting step was

$$\mathrm{(H_2O)_5CrOCr(H_2O)_5^{4+} + 2H^+ + H_2O \rightarrow 2Cr(H_2O)_6^{3+}} \quad (1)$$

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(1) Johnston, R. F.; Holwerda, R. A. *Inorg. Chem.* **1983**, *22*, 2942.

(2) Holwerda, R. A.; Petersen, J. S. *Inorg. Chem.* **1980**, *19*, 1775.

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