

bond, the magnitude of the QS should be reduced compared to that of other compounds in its class.⁴⁷ However, both the IS and QS of **21** are typical for phosphine-coordinated gold(I) thiolates and differ little from those of **20**. Therefore, within the sensitivity of the Mössbauer experiment no evidence for Au-Au bonding is observed.

Summary and Conclusion

The ¹⁹⁷Au Mössbauer fitting parameters derived from the spectra of the PAuS compounds (**12-23**) are unique to this type and are not explained totally by an average-environment rule although their magnitude appears to be influenced by contiguous electron-withdrawing groups. The values for IS and QS for the simple gold(I) thiolates, besides being of lower magnitude compared to those of their phosphine-coordinated counterparts, appear to be affected by the ratio of sulfur ligand to gold; that is, as the ratio of ligand to gold increases, so also do the values of IS and QS, reflecting increased electron density around the gold nucleus.

The ¹⁹⁷Au Mössbauer data obtained from the injectable gold drugs **1** and **6** are compatible with a two-coordinate, nearly linear SAuS linkage. Therefore, these gold drugs (**1** and **6**), as well as other 1:1 gold(I) thiol derivatives, must, in the solid phase, be polymeric, i.e., $[-(R)S-Au(R)S-Au-]_n$. This conclusion, based on the ¹⁹⁷Au Mössbauer data, is supported by recent EXAFS measurements⁴³ and is consistent with what is known about the stoichiometry, coordination number, and stereochemistry of gold(I) complexes. Further, studies using a variety of physical methods have invariably determined that **1** behaves as an oligomer in solution. Thus, the overwhelming body of evidence indicates that gold sodium thiomalate (**1**) and therefore **6** and other 1:1 gold(I) thiolates are polymers. The degree of polymerization has not been determined, but most likely, on the basis of solution measurements of **1**, it is low. **1** and **6**, which are polymeric, contrast with auranofin (**15**), which ¹⁹⁷Au Mössbauer suggests and X-ray crystallography confirms is monomeric. Though speculative, these differences, polymer vs. monomer, may be invoked to explain, at least in part, the cited biological variances (see Introduction).

For example, it is reasonable to suppose that large molecules, even though water soluble, would be less likely to penetrate membranes and be absorbed compared to smaller lipophilic molecules. This might account partly for the oral absorption

(47) Reference 12, p 82.

of **15** vs. the nonabsorption of **1** and **6**. Walz et al., in a pharmacokinetic study of **1** vs. **15**, observed that **15** associates readily with the cellular elements of the blood whereas **1** is found mainly in the serum.⁴⁸ Similar findings were reported by Herrlinger, who noted that 40% of the gold in blood from **15** was localized within the erythrocytes compared to none for **1**.⁴⁹ These observations are compatible with the notion that large molecular species are less likely to penetrate membranes than smaller molecules although **1** may have a higher protein-binding affinity than **15**.

Conversely, high molecular weight metal species are more likely to be engulfed by macrophages and therefore effect lysosomal enzyme activity, as seen with **1**.⁶ It is also reasonable to suppose that thiol-exchange reactions, which may play a key role in the biology of gold, would be affected differently by a polymeric gold thiolate than by a monomeric species and would explain the differences in pharmacokinetics between **1** and **15**. Additionally, a comparison of blood gold levels revealed that gold from **15** was approximately 4 times more effective in stimulating cell-mediated immunity than was gold from **1**,⁵⁰ again suggesting that the physical form in which gold is presented to a biological system has a major effect on that system's response. These points deserve further attention and should be the subject of future investigations.

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Registry No. **1**, 12244-57-4; **6**, 74610-70-1; **8**, 65286-35-3; **9**, 86421-40-1; **10**, 86421-41-2; **11**, 10233-88-2; **12**, 52621-55-3; **13**, 14243-46-0; **14**, 54720-68-2; **15**, 34031-32-8; **16**, 34031-29-3; **17**, 85528-72-9; **18**, 41581-85-5; **19**, 86421-42-3; **20**, 15685-02-6; **21**, 51365-22-1; **22**, 86421-43-4; **23**, 55927-98-5; 2,2'-thiobis(ethanol), 111-48-8; *N*-acetylcysteine, 616-91-1; sodium tetrachloroaurate, 15189-51-2; chloro(triethylphosphine)gold, 15529-90-5; thiourea, 62-56-6; chloro(triphenylphosphine)gold, 14243-64-2; β -D-thioglucose, 19879-84-6; thiomalic acid, 70-49-5; 6-mercaptopurine, 50-44-2; 2-mercaptopbenzoxazole, 2382-96-9.

- (48) Walz, D. T.; Griswold, D. E.; DiMartino, M. J.; Bumbier, E. E. *J. Rheumatol., Suppl.* **5** 1979, 6, 56.
 (49) (a) Herrlinger, J. D.; Alsen, C.; Beress, R.; Heckser, U.; Weikert, W. *J. Rheumatol., Suppl.* **8**, 1982, 9, 81. (b) Herrlinger, J. D.; Beress, R.; Weikert, W. *Verh. Dtsch. Ges. Rheumatol.* **1981**, 7, 338; *Chem. Abstr.* **1982**, 96, 190u.
 (50) Walz, D. T.; Griswold, D. E. *Inflammation (N.Y.)* **1978**, 3, 117.

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Acid Hydrolysis of the (μ -Oxo)bis(pentaaquochromium(III)) Ion

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In acid solution, the (μ -oxo)bis(pentaaquochromium(III)) ion decays to give $Cr(H_2O)_6^{3+}$ as the sole product: $(H_2O)_5CrOCr(H_2O)_5^{4+} + 2H^+ + H_2O \rightarrow 2Cr(H_2O)_6^{3+}$. The rate law for this reaction in a $HClO_4/LiClO_4$ medium, $I = 1.0$ M, is $-d[(H_2O)_5CrOCr(H_2O)_5^{4+}]/dt = (k_0 + k_1[H^+])[(H_2O)_5CrOCr(H_2O)_5^{4+}]$ where $k_0(25^\circ C) = 5 \times 10^{-5} s^{-1}$ ($\Delta H^\ddagger = 22$ kcal/mol, $\Delta S^\ddagger = -5$ eu) and $k_1(25^\circ C) = 1.61 \times 10^{-3} M^{-1} s^{-1}$ ($\Delta H^\ddagger = 12.9$ kcal/mol, $\Delta S^\ddagger = -28$ eu). The k_0 pathway corresponds to rate-limiting cleavage of a Cr-bridging oxygen bond, with probable associative assistance from the incoming H_2O ligand. Rapid preequilibrium protonation of the weakly basic bridging oxygen atom, followed by a rate-determining structural change, is proposed to account for the predominant k_1 hydrolysis pathway.

Introduction

The rhodo and erythro oxo- and hydroxo-bridged series of amminechromium(III) ions were reported in 1882.¹ In

contrast, the (μ -oxo)bis(pentaaquochromium(III)) ion, prepared through the oxidation of chromous ion by 1,4-benzoquinone, was reported only recently.² The "basic rhodo"

(1) Jorgensen, S. *J. Prakt. Chem.* **1882**, 25, 321.

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

chromium(III) ion, $(\text{NH}_3)_5\text{CrO}(\text{NH}_3)_5^{4+}$, has spectral³⁻⁵ and magnetic⁶ properties markedly different from those of mononuclear chromium(III) complexes. Three sharp, intense bands in the near-ultraviolet spectrum have been assigned as simultaneous pair excitations involving the 2E_g , 2E_g ; 2E_g , ${}^2T_{1g}$; and ${}^2T_{1g}$, ${}^2T_{1g}(O_h)$ ligand field states of the two Cr(III) centers.⁵ Analogous transitions occur in $(\text{H}_2\text{O})_5\text{CrO}(\text{H}_2\text{O})_5^{4+}$ at 443, 413, and 347 nm.² The magnetic susceptibility of $(\text{NH}_3)_5\text{CrO}(\text{NH}_3)_5\text{Cl}_4 \cdot \text{H}_2\text{O}$ shows moderately strong antiferromagnetic spin-spin coupling between the $S = 3/2$ chromium atoms, with the singlet-triplet separation being 450 cm^{-1} .⁶ Magnetic exchange^{4,5,7} and molecular orbital⁸ models of the bonding in $(\text{NH}_3)_5\text{CrO}(\text{NH}_3)_5^{4+}$ have been presented, but the quantitative relationships among the features in the electronic spectrum remain poorly understood.

In addition to its unusual physical properties, the basic rhodo ion exhibits a reactivity in solution quite unlike that of mononuclear Cr(III) analogues. Thus, $(\text{NH}_3)_5\text{Cr}_2\text{O}^{4+}$ undergoes hydrolysis of one NH_3 ligand with a half-life of 44 s (20 °C),⁹ whereas $\text{Cr}(\text{NH}_3)_6^{3+}$ is stable to loss of NH_3 over a period of several days.¹⁰ Strong π -bonding in the linear Cr-O-Cr unit may specifically labilize the NH_3 ligand trans to the bridging oxide ion.⁹

We report here a kinetic study of the acid hydrolysis reaction (eq 1) of the (μ -oxo)bis(pentaaquochromium(III)) ion, heretofore referred to as the "aquo dimer".

$$(\text{H}_2\text{O})_5\text{CrO}(\text{H}_2\text{O})_5^{4+} + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow 2\text{Cr}(\text{H}_2\text{O})_6^{3+} \quad (1)$$

Our interest in this reaction is based on several significant differences between the reactivities of the basic rhodo- and aquo-dimer ions. Although the basic rhodo ion reversibly protonates ($\text{p}K_a = 7.63$)⁹ to give $(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_5^{5+}$, the aquo dimer remains unprotonated even at pH 1.² Furthermore, the aquo dimer is susceptible to rapid, acid-catalyzed cleavage of the oxo bridge,² whereas the cleavage rate of the more robust acid rhodo ion is small ($t_{1/2} = 15 \text{ min}$) even at 55 °C¹¹ and is independent of $[\text{H}^+]$.

Experimental Section

Materials. Reagent grade chemicals were used throughout. Solutions for kinetic measurements were prepared with triply distilled water. $\text{Cr}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ and LiClO_4 (G. F. Smith) and NH_4ClO_4 (Fluka) were used as received. Practical grade 1,4-benzoquinone was purified through vacuum sublimation. SP-Sephadex C-25 resin (Na^+ form) was used in all cation-exchange experiments. A stock solution of chromium(II) perchlorate was prepared by reducing anaerobic $\text{Cr}(\text{ClO}_4)_3$ in 0.951 M HClO_4 over 2% zinc amalgam. Potassium tris(oxalato)chromate(III) trihydrate was prepared by the method of Brauer.¹²

In view of the limited stability of the aquo dimer in solution and the impracticality of crystallizing this species,² $(\text{H}_2\text{O})_5\text{CrO}(\text{H}_2\text{O})_5^{4+}$ was generated in situ immediately prior to a kinetic determination. The $(\text{H}_2\text{O})_4\text{Cr}(\text{OH})(\text{OC}_6\text{H}_4\text{OH})\text{Cr}(\text{H}_2\text{O})_4^{4+}$ ion (I) was synthesized by the method of Holwerda and Petersen,² purified through cation-exchange chromatography using LiClO_4 as the eluent,² and stored frozen in liquid nitrogen until needed. The aquo dimer was produced rapidly through the oxidation of the hydroquinone ligand in complex I by Br_2 .

Strong transition metal ion oxidants (i.e. Tl(III), Ce(IV), MnO_4^-) bring about the conversion of complex I to the aquo dimer more rapidly than does Br_2 . These oxidants were avoided in kinetic studies, however,

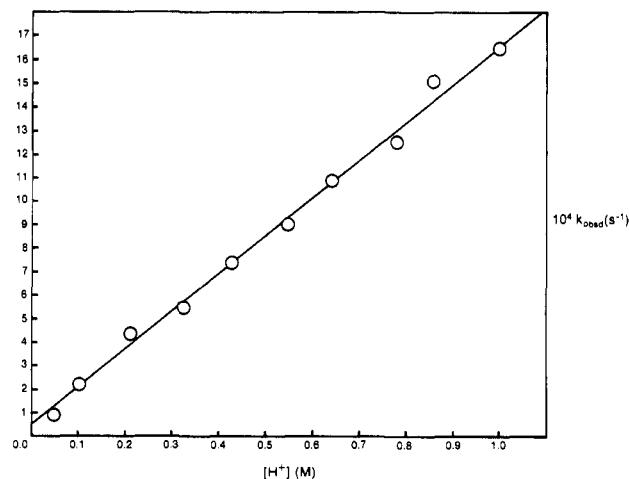


Figure 1. Acid dependence of the $(\text{H}_2\text{O})_5\text{CrO}(\text{H}_2\text{O})_5^{4+}$ hydrolysis rate (25.0 °C, $I = 1.0 \text{ M}$ (LiClO_4)).

because small concentrations of many transition metal cations strongly perturb the hydrolysis rate of the aquo dimer.¹³ In a typical kinetic run, complex I (0.50 mM) in a 1-cm quartz spectrophotometer cell was mixed with a slight excess of oxidant ($[\text{Br}_2]_0 = 0.52\text{--}1.3 \text{ mM}$). The distinctive absorption spectrum (Cary 17 spectrophotometer) of the aquo dimer was observed immediately after mixing.

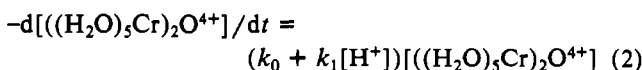
Kinetic Measurements. Decay of $(\text{H}_2\text{O})_5\text{CrO}(\text{H}_2\text{O})_5^{4+}$ was followed at 443 nm on a Bausch & Lomb Spectronic 100 spectrophotometer with a thermostated cell block. Absorbance-time traces were obtained from a Fisher Recordall Series 5000 recorder. Identical rate parameters for a given set of reaction conditions were derived from absorbance-time traces recorded at 347, 443, 480, and 632 nm. With the initial concentration of the aquo dimer fixed at 0.50 mM, rate parameters were found to be independent of bromine ($[\text{H}^+] = 1.0 \text{ M}$) concentration in the range 0.52–1.30 mM and $[\text{Br}^-]$ ($[\text{H}^+] = 0.55 \text{ M}$) in the interval 0.75–1.50 mM.

Observed pseudo-first-order rate constants (k_{obsd}) were derived from the least-squares slopes of $\ln(A_t - A_\infty)$ vs. time plots. All rate constants reported are the average of at least three trials. These first-order plots were found to be reproducibly linear over the final 30–70% of ΔA_{443} (0.45–1.0 absorbance unit), with points at early times falling below the extrapolated least-squares line. This induction period is not characteristic of the hydrolysis reaction of interest but rather may be attributed to the similar rates of formation (from complex I and Br_2) and decay of the aquo dimer at early reaction times. Thus, the induction period could be shortened by increasing $[\text{Br}_2]_0$ or abolished entirely by using MnO_4^- , a more reactive oxidant, in place of Br_2 . Excellent agreement was found between hydrolysis rate constants ($[\text{H}^+] = 1.0 \text{ M}$) obtained from runs with Br_2 and with MnO_4^- as the oxidant. The latter oxidant was not used routinely because of low aquo-dimer yields attained from the complex I– MnO_4^- reaction at low acidities.

Analyses. Lithium perchlorate stock solutions were standardized either gravimetrically¹⁴ or potentiometrically by using an Orion perchlorate-sensitive electrode (Ag/AgCl reference) calibrated against known LiClO_4 solutions. The Cr content of the $\text{Cr}(\text{ClO}_4)_3$ stock solution was determined spectrophotometrically by the basic peroxide method.¹⁴

Results

Acid Dependence and Stoichiometry. The rate of hydrolysis of the aquo dimer is highly sensitive to the hydrogen ion concentration, as shown in Figure 1 for studies carried out at 25.0 °C, $0.05 \leq [\text{H}^+] \leq 1.0 \text{ M}$, and constant ionic strength of 1.0 M ($\text{HClO}_4/\text{LiClO}_4$). The data demonstrate the existence of both acid-dependent and -independent pathways for hydrolysis:



- Dubicki, L.; Martin, R. L. *Aust. J. Chem.* **1970**, *23*, 215.
- Glerup, J. *Acta Chem. Scand.* **1972**, *26*, 3775.
- Güdel, H. U.; Dubicki, L. *Chem. Phys.* **1974**, *6*, 272.
- Pedersen, E. *Acta Chem. Scand.* **1972**, *26*, 333.
- Kahn, O.; Briat, B. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 268.
- Schmidtke, H.-H. *Theor. Chim. Acta* **1971**, *20*, 92.
- Schwarzenbach, G.; Magyar, B. *Helv. Chim. Acta* **1962**, *45*, 1425.
- Earley, J. E.; Cannon, R. D. *Transition Met. Chem. (N.Y.)* **1965**, *1*, 33.
- Hoppenjans, D. W.; Hunt, J. B. *Inorg. Chem.* **1969**, *8*, 505.
- Brauer, G., Ed. "Handbook of Preparative Inorganic Chemistry"; Academic Press: New York, 1965; Vol. 2, p 1372.

- Johnston, R.; Holwerda, R., work in progress.
- Deutsch, E.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1532.

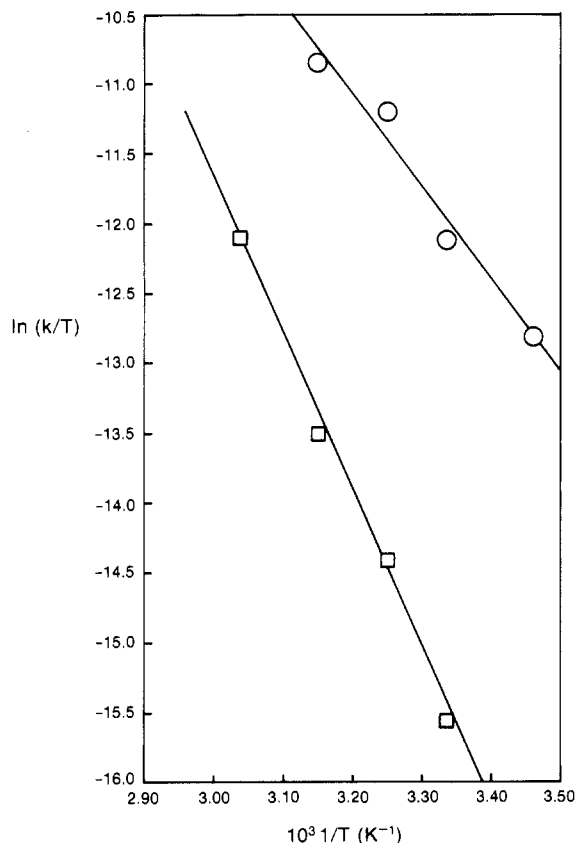


Figure 2. Eyring plots corresponding to the k_0 (\square) and k_1 (\circ) hydrolysis pathways of $(\text{H}_2\text{O})_5\text{CrO}(\text{H}_2\text{O})_5^{4+}$ ($I = 1.0$ M ($\text{HClO}_4/\text{LiClO}_4$)).

where $k_0 = (5 \pm 2) \times 10^{-5} \text{ s}^{-1}$ and $k_1 = (1.61 \pm 0.05) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. Thus, the predominant k_1 pathway carries 97% of the hydrolysis reaction at $[\text{H}^+] = 1.0$ M.

Activation parameters associated with k_0 ($\Delta H^\ddagger = 22 \pm 2$ kcal/mol, $\Delta S^\ddagger = -5 \pm 6$ eu) and k_1 ($\Delta H^\ddagger = 12.9 \pm 1.5$ kcal/mol, $\Delta S^\ddagger = -28 \pm 5$ eu) were calculated from the Eyring plots shown in Figure 2. The rate law of eq 2 was found to pertain over the temperature range 15.6–55.3 °C. The k_0 and k_1 values used in the activation parameter calculations were obtained from the linear least-squares analysis of $k_{\text{obsd}}-[\text{H}^+]$ profiles at 15.6, 25.0, 35.0, 44.4, and 55.3 °C (Table I).¹⁵ Nonlinear first-order analytical plots were observed in runs above 55.3 °C, preventing the extension of the Eyring plots in this direction.

A chromatographic experiment was carried out at 5 °C to verify that $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ is the product of the aquo-dimer hydrolysis reaction and also to detect, if possible, any long-lived reaction intermediates. Two separate product solutions from 25 °C runs were diluted and applied to cation-exchange columns immediately following completion of the reaction. A single blue-violet band was observed upon elution of these columns with 0.5 M $\text{LiClO}_4/0.1$ M HClO_4 . The product was identified as $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ on the basis of its elution behavior and visible absorption maxima at 574 and 408 nm.² No

(15) Supplementary material. An attempt was made to better define k_0 values through the extension of $k_{\text{obsd}}-[\text{H}^+]$ profiles to acidities lower than 0.05 M. However, two complications were apparent in runs at $[\text{H}^+] \leq 0.01$ M. First, significant differences in band positions and intensities were noted between spectra of $(\text{Cr}(\text{H}_2\text{O})_5)_2\text{O}^{4+}$ and the product of the complex I- Br_2 reaction under these conditions. Thus, 443-nm absorbance changes would reflect, in part, the decay of some new reactant species (presumably derived from the aquo dimer by ionization of H_2O ligands). Also, the induction period attributable to the complex I- Br_2 reaction was so long at low acidities that first-order plots were nonlinear over more than 80% of ΔA_{443} .

Table II. Salt Effects on the Hydrolysis of the $(\mu\text{-Oxo})\text{bis}(\text{pentaquo}(\text{chromium}(\text{III})))$ Ion^a

salt	[salt], M	$[\text{H}^+]$, M	$10^3 k_{\text{obsd}}$, ^b s^{-1}
NH_4ClO_4	0.000	0.275	0.520
	0.120	0.275	0.555
	0.370	0.275	0.654
	0.620	0.275	0.733
	0.840	0.275	0.754
$\text{Cr}(\text{ClO}_4)_3$	0.000 ^c	0.100	0.226
	0.200	0.100	0.359
	0.350	0.100	0.887
	0.500	0.100	1.36
	0.000 ^c	0.300	0.534
	0.200	0.300	1.05
	0.350	0.300	2.45
	0.500	0.300	4.07
	0.000 ^c	0.550	0.905
	0.100	0.550	0.986
	0.200	0.550	2.33
	0.300	0.550	3.99
	0.400	0.550	5.69
	0.500	0.550	9.28
	0.000 ^c	0.840	1.40
0.200	0.840	4.61	
0.350	0.840	10.2	
0.500	0.840	19.3	
0.000 ^c	1.00	1.65	
0.200	1.00	4.89	
0.350	1.00	14.2	
0.500	1.00	26.8	
$\text{K}_3\text{Cr}(\text{ox})_3$	0.125	0.550	1.13
	0.250	0.550	1.37

^a 25.0 ± 0.1 °C; all solutions contained 0.08 M LiClO_4 , introduced from the complex I stock solution. ^b The uncertainty in k_{obsd} typically was $\pm 5\%$. ^c $I = 1.0$ M (LiClO_4).

chromium remained on the column after the elution of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$.

Salt Effects. The hydrolysis rate of the aquo dimer is strongly perturbed by many salts, including alkali-metal, alkaline-earth, and transition-metal perchlorates.¹³ As a result, it is difficult to separately evaluate ionic strength and specific-cation effects on the rate. NH_4ClO_4 was chosen to determine the effect of a nonmetal salt on the aquo dimer hydrolysis rate. With $[\text{H}^+] = 0.275$ M at 25 °C, a 50% increase in k_{obsd} was found when $[\text{NH}_4\text{ClO}_4]$ was varied from 0 to 0.84 M (Table II).

The product $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ is a moderately effective catalyst¹⁶ for the hydrolysis of $(\text{H}_2\text{O})_5\text{Cr}_2\text{O}^{4+}$; this cation, like $\text{Ce}^{3+}(\text{aq})$,² also accelerates the conversion of complex I to the aquo dimer, even in the absence of an oxidant. Rate studies of the $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ -catalyzed decay of the aquo dimer were not carried out at constant ionic strength, as LiClO_4 and other traditionally inert salts also accelerate the hydrolysis rate at high salt concentrations.¹³ For example, at constant $[\text{H}^+] = 0.55$ M, 25 °C, and $I = 2.95$ M, $k_{\text{obsd}}(\text{LiClO}_4)$ ($2.3 \times 10^{-3} \text{ s}^{-1}$)¹³ is comparable to $k_{\text{obsd}}(\text{Cr}(\text{ClO}_4)_3)$ ($5.7 \times 10^{-3} \text{ s}^{-1}$).

The dependence of k_{obsd} on $[\text{Cr}(\text{H}_2\text{O})_6^{3+}]$ (0.10–0.50 M) was studied at constant $[\text{H}^+]$ and 25.0 °C, with $[\text{H}^+] = 0.10, 0.30, 0.55, 0.84,$ and 1.00 M (Table II). The high background absorbance of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ required the use of 480 nm as the monitoring wavelength in some runs. Also included in Table II are data showing the effect of $\text{K}_3\text{Cr}(\text{ox})_3$ on k_{obsd} . This salt clearly has a much smaller influence on the aquo-dimer hydrolysis rate than does $[\text{Cr}(\text{H}_2\text{O})_6^{3+}](\text{ClO}_4)_3$.

It is tempting to include $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ in the rate law for decay of the aquo dimer, as the rate enhancement due to this

(16) Autocatalytic behavior was not detected in any runs where the initial concentration of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ was zero, and the effect of the product on k_{obsd} was shown to be negligible under these conditions.

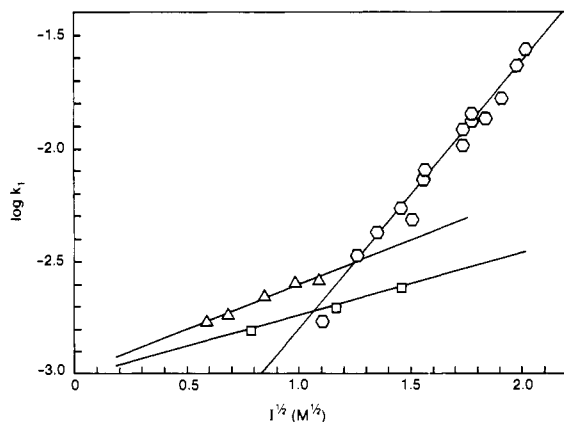


Figure 3. Salt effects on the hydrolysis of $(\text{H}_2\text{O})_5\text{CrOCr}(\text{H}_2\text{O})_5^{4+}$: $\text{Cr}(\text{ClO}_4)_3$ (O); NH_4ClO_4 (Δ); $\text{K}_3\text{Cr}(\text{ox})_3$ (\square). Conditions are as given in Table II. Apparent k_1 values are calculated as described in the text.

species ($k_{\text{obsd}}' = k_{\text{obsd}} - (k_0 + k_1[\text{H}^+])$) may be quantitatively described by the relationship

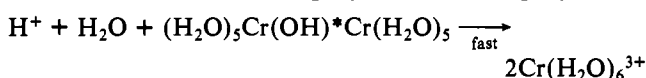
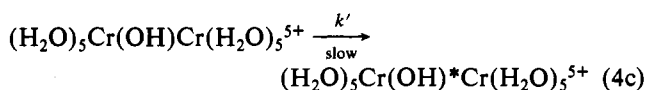
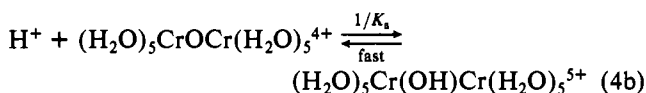
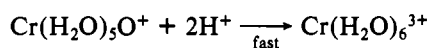
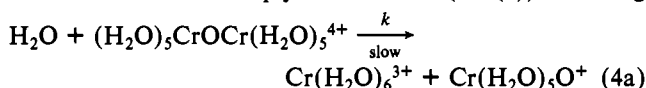
$$k_{\text{obsd}}' = [\text{Cr}(\text{H}_2\text{O})_6^{3+}]^2(k_2 + k_3[\text{H}^+]^2) \quad (3)$$

where $k_2 = (5 \pm 1) \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$ and $k_3 = (9.7 \pm 0.2) \times 10^{-2} \text{ M}^{-4} \text{ s}^{-1}$ at 25 °C. The validity of this treatment is highly questionable, however, in view of the variable ionic strength and high sensitivity of k_{obsd} to the nature of the electrolyte in the reaction mixture.

The large chromic perchlorate induced enhancements in the aquo-dimer hydrolysis rate may reflect a specific-cation effect on the k_1 pathway. Apparent k_1 values at various salt and hydrogen ion concentrations may be calculated ($k_1 = (k_{\text{obsd}} - k_0)/[\text{H}^+]$), by assuming that the small k_0 term ($5 \times 10^{-5} \text{ s}^{-1}$) is unaffected by changes in ionic strength. A linear correlation between $\log k$ and $I^{1/2}$ is anticipated in a second-order reaction between ions A and B at very low ionic strength, with slope $\approx 2AZ_A Z_B$ (Z = ionic charge, $A = 0.509$ in water at 25 °C).¹⁷ Linear plots of $\log k_1$ vs. $I^{1/2}$ may in fact be derived from the data in Table II (Figure 3), but the slopes for $\text{Cr}(\text{ClO}_4)_3$ (1.23 ± 0.04), NH_4ClO_4 (0.39 ± 0.04), and $\text{K}_3\text{Cr}(\text{ox})_3$ (0.28 ± 0.01) are widely different and fall far below the theoretical value of 4.1. While the linearity of these empirical correlations cannot be justified theoretically, the substantially larger slope of the $\text{Cr}(\text{ClO}_4)_3$ line implies that specific-cation catalysis, rather than a simple secondary salt effect, is involved in the $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ -assisted hydrolysis reaction.

Discussion

Our kinetic results imply a mechanism (see (4)) consisting



of two parallel pathways for the hydrolysis of the (μ -oxo)-

bis(pentaaquochromium(III)) ion. The relationship between experimental rate parameters and those in the proposed mechanism is $k_0 = k$ and $k_1 = k'/K_a$. Rapid preequilibrium protonation of the bridging oxygen atom in the k_1 pathway is not demanded by the rate law but is preferred over attack by H^+ concurrent with bond rearrangements within the coordination sphere of $\text{Cr}(\text{III})$. The unusual spectroscopic characteristics of the aquo dimer are associated specifically with a linear Cr–O–Cr linkage.² It may be concluded, therefore, that this linear unit is not disrupted by the protonation equilibrium (eq 4b). The rate-limiting process governing k_1 is proposed to be a structural change (eq 4c), yielding a highly reactive second protonated intermediate $((\text{H}_2\text{O})_5\text{Cr}(\text{OH})^*\text{Cr}(\text{H}_2\text{O})_5^{5+})$ analogous to the acid rhodo ion, $(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_5^{5+}$ (Cr–OH–Cr bond angle of 154°, visible absorption spectrum dominated by weak d–d bands).¹⁸

Water exchange in $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ ($k(25 \text{ °C}) = 4.3 \times 10^{-7} \text{ s}^{-1}$; $\Delta H^\ddagger = 26 \text{ kcal/mol}$, $\Delta S^\ddagger = 0 \text{ eu}$)¹⁹ is 2 orders of magnitude slower than hydrolysis of the aquo dimer through the unassisted (k_0) pathway. The activation volume of $-9.3 \text{ cm}^3/\text{mol}$ is strong evidence for associative character in the former reaction,¹⁹ and similar evidence supports the I_a mechanism in other $\text{Cr}(\text{III})$ solvent-exchange reactions.²⁰ The activation parameters associated with the k_0 pathway strongly resemble those characteristic of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ water exchange. Indeed, the ΔS^\ddagger values are identical within experimental error, leaving a 4 kcal/mol advantage in ΔH^\ddagger as the factor responsible for the larger rate of the aquo-dimer hydrolysis reaction. This modest difference in ΔH^\ddagger values may be understood on Coulombic grounds, considering the different charges of the leaving groups (H_2O vs. $\text{OCr}(\text{H}_2\text{O})_5^+$). The above-mentioned similarity in ΔS^\ddagger values suggests that nucleophilic attack by water on $\text{Cr}(\text{III})$ stabilizes the activated complex in the k_0 pathway. Associative character is expected to be even more important in this reaction than in $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ water exchange, as $\text{Cr}(\text{III})$ –OH₂ bond making would partially offset the substantial enthalpic barrier posed by π -bonding within the Cr–O–Cr linkage.

Very weak basicity of the aquo dimer bridging oxygen atom is evident from both spectroscopic and kinetic observations. Thus, the first-order hydrogen ion dependence of the k_1 pathway can be reconciled with the proposed mechanism (eq 4b,c) only if $[\text{H}^+]/K_a \ll 1$, i.e. $[(\text{H}_2\text{O})_5\text{Cr}(\text{OH})\text{Cr}(\text{H}_2\text{O})_5^{5+}] \ll [(\text{H}_2\text{O})_5\text{CrOCr}(\text{H}_2\text{O})_5^{4+}]$. The $\text{p}K_a$ value of $\text{Cr}(\text{H}_2\text{O})_6^{3+}(\text{aq})$ is 3.82 ($\Delta H^\circ = 9.4 \text{ kcal/mol}$, $\Delta S^\circ = +14.1 \text{ eu}$) at 25 °C and $I = 0 \text{ M}$.²¹ Considering $((\text{H}_2\text{O})_5\text{Cr})_2\text{OH}^{5+}$ to be a derivative of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ (replacement of one H atom by a $\text{Cr}(\text{H}_2\text{O})_5^{3+}$ unit), the $\text{p}K_a$ of the bridging OH group may be estimated at ca. 0.6 through a simple Coulomb law calculation, neglecting stabilization of the conjugate base owing to π -bonding and assuming invariance of the ΔS° term. The actual $\text{p}K_a$ value may be 2–4 units more negative than this estimate, considering the strong attenuation in bridging oxygen atom basicity associated with π -bonding in ions of the form $\text{trans}-(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4\text{X}$, where $\text{X} = \text{NCS}^-$, Cl^- , F^- , OH^- , and NH_3 .⁹ Thus, the $\text{p}K_a$ values⁹ of the unsymmetrical (weaker π -bonding) rhodo erythro ions with $\text{X} = \text{NCS}^-$ (10.62), Cl^- (11.37), F^- (13.4), and OH^- (>16) increase uniformly, as expected,²⁰ with increasing basicity of the substituent. Considered in this perspective, the $\text{p}K_a$ of the symmetrical (strong π -bonding) acid rhodo ion (7.63) clearly lies far below that expected from the basicity of the NH_3 substituent.

(18) Ferguson, J.; Güdel, H. U. *Aust. J. Chem.* **1973**, *26*, 505.

(19) Stranks, D. R.; Swaddle, T. W. *J. Am. Chem. Soc.* **1971**, *93*, 2783.

(20) Burgess, J. "Metal Ions in Solution"; Wiley: New York, 1978; p 324.

(21) Postmus, C.; King, E. L. *J. Phys. Chem.* **1955**, *59*, 1208.

(17) Espenson, J. H. "Chemical Kinetics and Reaction Mechanisms"; McGraw-Hill: New York, 1981; p 172.

The predominance of the k_1 pathway for hydrolysis of the (μ -oxo)bis(pentaaquochromium(III)) ion may be attributed to its substantially lower enthalpic activation barrier. Bond making (O-H) presumably provides energetic compensation for the loss of π -bonding and Cr-O bond stretching required to form the activated complex. The ΔS^\ddagger value of -28 eu may be attributed to a loss of translational entropy suffered by H^+ in equilibrium 4b and to the ordering of water molecules required to accommodate an activated complex bearing a 5+ charge.

Our assignment of the bent $(H_2O)_5Cr(OH)Cr(H_2O)_5^{5+}$ ion as a highly reactive transient conflicts with a recent report²² that this species is formed as a relatively stable intermediate during the hydrolysis of $(H_2O)_4Cr(OH)_2Cr(H_2O)_4^{4+}$ in 6 N $HClO_4$. Unfortunately, our hypothesis cannot be strongly supported, as it rests entirely on negative evidence, i.e. no 5+ cation was detected in the chromatographic separation of product mixtures from the hydrolysis of $((H_2O)_5Cr)_2O^{4+}$ or the oxidation of $(H_2O)_4Cr(OH)(OC_6H_4OH)Cr(H_2O)_4^{4+}$.² We must allow the possibility, therefore, that Cr-O bond cleavage occurs in the slow step of the k_1 pathway. Conflicting reports exist concerning the stability of singly hydroxo-bridged binuclear intermediates formed in the hydrolysis of various bis(μ -hydroxo)chromium(III) dimers.²²⁻²⁴

Salt effects on the hydrolysis rate of the aquo dimer are a particularly intriguing aspect of this study and are the focus of continuing research.¹³ The autocatalytic behavior of the $Cr(H_2O)_6^{3+}$ ion is especially surprising, as loss of water from the first coordination sphere of Cr(III) is far too slow¹⁹ for this to be a requirement in the $Cr(H_2O)_6^{3+}$ -assisted hydrolysis of $((H_2O)_5Cr)_2O^{4+}$. Stabilization of the activated complex in reaction 4c through a cation-incipient dipole interaction is one of several possible explanations of the $Cr(H_2O)_6^{3+}$ catalysis. A more detailed account of this interesting behavior must be postponed until a wider range of cation and anion effects have been examined.

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(22) Thompson, M.; Connick, R. E. *Inorg. Chem.* **1981**, *20*, 2279.

(23) Grant, D. M.; Hamm, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 4166.

(24) Wolcott, D.; Hunt, J. B. *Inorg. Chem.* **1968**, *7*, 755.

Appendix

Effect of π Bonding on the Visible Spectrum of $(H_2O)_5CrOCr(H_2O)_5^{4+}$. The ${}^4T_{2g} \leftarrow {}^4A_{2g}$ d-d band of an octahedral Cr(III) complex (CrX_6) will split as the symmetry is lowered from O_h to C_{4v} (CrX_5Y), with no change in the energy ($= 10Dq$) of the ${}^4B_2 \leftarrow {}^4B_1$ component and a shift to lower frequency in the ${}^4E \leftarrow {}^4B_1$ transition if the perturbing ligand Y falls lower in the spectrochemical series than X.²⁵ This analysis provides a reasonable assignment for the comparatively weak visible transitions of $(H_2O)_5CrOCr(H_2O)_5^{4+}$ at 587 (4B_2) and 632 (4E) nm, as the broad ${}^4T_{2g} \leftarrow {}^4A_{2g}$ transition of $Cr(H_2O)_6^{3+}$ has λ_{max} at 574 nm. If the configuration interaction among the 4E excited states is neglected, the tetragonal splitting parameter Dt may be related to transition energies and octahedral crystal field parameters through the equation²⁵

$$Dt = \frac{1}{35}(E({}^4B_2) - E({}^4E)) = \frac{2}{7}(Dq_x - Dq_y) \quad (5)$$

On this basis, crystal field parameters for $((H_2O)_5Cr)_2O^{4+}$ are $Dt = +139$ cm^{-1} and $Dq(OCr(H_2O)_5^+) = 1200$ cm^{-1} , with $Dq(H_2O) = 1740$ cm^{-1} . With $Dt = +139$ cm^{-1} , two spin-forbidden transitions are predicted²⁶ in the vicinity of 15 000 cm^{-1} , in agreement with our previous report² of shoulders at 665 (2E , ${}^2A_2 \leftarrow {}^4B_1$) and 685 (2A_1 , ${}^2B_1 \leftarrow {}^4B_1$) nm. The assignment of the strongest near-ultraviolet band at 347 nm as a simultaneous pair excitation appears reasonable, as its energy is almost exactly twice that of the 685-nm spin-forbidden transition. The considerable attenuation in Dq - $((H_2O)_5CrO^+)$ compared with $Dq(H_2O)$ reflects strong π -donation from the bridging oxygen atom (p_x, p_y) into the d_{xz} and d_{yz} orbitals of chromium.

Registry No. $(H_2O)_5CrOCr(H_2O)_5^{4+}$, 73347-70-3.

Supplementary Material Available: Table I, showing the temperature dependence of k_{obsd} , used to construct Figure 2 (1 page). Ordering information is given on any current masthead page.

(25) Krishnamurthy, R.; Schaap, W. B.; Perumareddi, J. R. *Inorg. Chem.* **1967**, *6*, 1338. To be consistent with current usage (Donini, J. C.; Hollebene, B. R.; Lever, A. B. P. *Prog. Inorg. Chem.* **1977**, *22*, 225), the equalities involving Dt given in the original reference were multiplied by -1 .

(26) König, E.; Kremer, S. "Ligand Field Energy Diagrams"; Plenum Press: New York, 1977; p 139.