

Base-Induced Cleavage of Oxo-Bridged Chromium(III) Dimers. Kinetic and Chromatographic Studies of $[\text{Cr}(\text{tmpa})(\text{NCS})_2]\text{O}^{2+}$, $[\text{Cr}(\text{tmpa})(\text{NCO})_2]\text{O}^{2+}$, and $[\text{Cr}(\text{tmpa})(\text{CN})_2]\text{O}^{2+}$ Hydrolysis Reactions in Alkaline Media

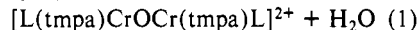
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The reactivities of $[\text{Cr}(\text{tmpa})(\text{NCS})_2]\text{O}^{2+}$, $[\text{Cr}(\text{tmpa})(\text{NCO})_2]\text{O}^{2+}$, $[\text{Cr}(\text{tmpa})(\text{CN})_2]\text{O}^{2+}$, and $[\text{Cr}(\text{tmpa})(\text{NCS})_2]^+$ toward base hydrolysis have been examined through kinetic and cation-exchange chromatographic determinations. The dimers undergo base-assisted oxo-bridge cleavage accompanied by loss of the pseudohalide ligand according to the overall stoichiometry: $[\text{L}(\text{tmpa})\text{CrO}(\text{tmpa})\text{L}]^{2+} + \text{H}_2\text{O} + 2\text{OH}^- \rightarrow 2[\text{Cr}(\text{tmpa})(\text{OH})_2]^+ + 2\text{L}^-$. Chromatographic investigations of product mixtures from the quenching of $[\text{Cr}(\text{tmpa})(\text{NCS})_2]\text{O}^{2+}$ in 0.1 M NaOH after 1 half-life of the base hydrolysis process at 45 °C demonstrated that both $[(\text{tmpa})(\text{SCN})\text{CrO}(\text{OH})(\text{tmpa})]^{2+}$ and $[\text{Cr}(\text{tmpa})(\text{OH})_2]\text{O}^{2+}$ are formed as intermediates prior to cleavage of the CrOcr bridge. Rapid conversions of both intermediates to $[\text{Cr}(\text{tmpa})(\text{OH})_2]^{4+}$ in acidic solution suggest that oxo-bridge migration to a cis coordination position accompanies the displacement of the first thiocyanate ligand from $[\text{Cr}(\text{tmpa})(\text{NCS})_2]\text{O}^{2+}$. The base hydrolysis rate law ($k_{\text{obsd}} = k_0 + k_{\text{OH}}[\text{OH}^-]$) for dimers with $\text{L}^- = \text{NCO}^-$ ($k_0 = 4.1 \times 10^{-5} \text{ s}^{-1}$; $k_{\text{OH}} = 1.07 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$; 40 °C; $I = 1.0 \text{ M}$ (NaNO_3)) and CN^- ($k_0 = 6.8 \times 10^{-5} \text{ s}^{-1}$; $k_{\text{OH}} = 4.17 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$; 40 °C; $I = 1.0 \text{ M}$ (NaNO_3)) differs from that characteristic of $[\text{Cr}(\text{tmpa})(\text{NCS})_2]\text{O}^{2+}$ ($k_{\text{obsd}} = (k_0 + k_2 Q_p [\text{OH}^-] / (1 + Q_p [\text{OH}^-]))$), where k_2 and Q_p represent the decay rate and preequilibrium formation constants of an intermediate complex between the dimer and OH^- ($k_0(40 \text{ °C}) = 5.3 \times 10^{-5} \text{ s}^{-1}$; $k_2(40 \text{ °C}) = 7.7 \times 10^{-4} \text{ s}^{-1}$ ($\Delta H^\ddagger = 21.5 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = -4 \text{ eu}$); $Q_p(40 \text{ °C}) = 20.9 \text{ M}^{-1}$ ($\Delta H^\circ = +5.8 \text{ kcal mol}^{-1}$; $\Delta S^\circ = +25 \text{ eu}$; $I = 1.0 \text{ M}$ (NaNO_3))). The proposed base hydrolysis mechanism features rate-limiting displacement of L^- by the migrating oxo function, induced by nucleophilic attack of OH^- on chromium within a 1:1 precursor complex. On this basis, it is concluded that $Q_p(\text{NCS}^-) \gg Q_p(\text{NCO}^- \text{ or } \text{CN}^-)$. The sensitivity of base hydrolysis rates to the L^- leaving group is reflected in the ranking of $k_{\text{OH}}/k_0(40 \text{ °C})$ ratios: NCS^- (300) \gg NCO^- (26) $>$ CN^- (6).

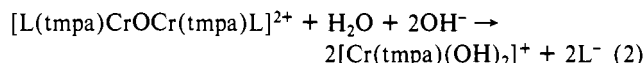
Introduction

Mechanistic studies of ammonia loss from the (μ -oxo)bis(pentaamminechromium(III)) ion¹ and cleavage of the (μ -oxo)bis(pentaquachromium(III)) dimer^{2,3} revealed patterns of substitutional and redox reactivity that are unprecedented in related monomeric Cr(III) species. Our recent discovery of a synthetic route (eq 1; tmpa = tris(2-pyridylmethyl)amine) to an extensive $[(\text{tmpa})\text{Cr}(\text{OH})_2\text{Cr}(\text{tmpa})]^{4+} + 2\text{L}^- \rightarrow$



class ($\text{L}^- = \text{NCS}^-, \text{NCO}^-, \text{CN}^-, \text{N}_3^-, \text{Cl}^-$) of linear, oxo-bridged chromium(III) dimers with aromatic amine ligands^{4,5} provided the opportunity to correlate electronic structures with the rates of redox and ligand-substitution reactions. A mechanistic study of the dimer-cleavage reactions of $[\text{Cr}(\text{tmpa})(\text{NCS})_2]\text{O}^{2+}$, $[\text{Cr}(\text{tmpa})(\text{NCO})_2]\text{O}^{2+}$, and $[\text{Cr}(\text{tmpa})(\text{CN})_2]\text{O}^{2+}$ in basic solution is presented in this paper. Since the base hydrolysis of $[\text{Cr}(\text{tmpa})(\text{NCS})_2]\text{O}^{2+}$ is accompanied by loss of thiocyanate ligands, chromatographic studies have been performed to determine whether Cr–NCS bond cleavage is a prerequisite to or a consequence of Cr–O–Cr fragmentation. For comparison, the base hydrolysis reactivity of $[\text{Cr}(\text{tmpa})(\text{NCS})_2]^+$ has also been examined.

In our previous study of $[(\text{tmpa})\text{Cr}(\text{O})_2\text{Cr}(\text{tmpa})]^{2+}$ base hydrolysis,⁶ biphasic decay of the dioxo-bridged dimer was observed, with both fast and slow processes exhibiting kinetic terms zeroth and first order in hydroxide ion. In the first phase, H_2O - and OH^- -assisted oxo-bridge openings generate an intermediate, $[(\text{tmpa})(\text{OH})\text{CrO}(\text{OH})(\text{tmpa})]^{2+}$, which undergoes water- and hydroxide-promoted bridge cleavage to give $[\text{Cr}(\text{tmpa})(\text{OH})_2]^+$. Since 90° oxo-bridge migration accompanies the conversion of $[(\text{tmpa})\text{Cr}(\text{OH})_2\text{Cr}(\text{tmpa})]^{4+}$ to $[\text{L}(\text{tmpa})\text{CrO}(\text{tmpa})\text{L}]^{2+}$ according to eq 1,⁵ it is of interest to determine whether a reverse μ -O migratory process governs the base hydrolysis of the latter species when the pseudohalide L^- group is lost (eq 2). The demonstration of common $[\text{Cr}(\text{tmpa})(\text{OH})_2]\text{O}^{2+}$ intermediacy in the base hydrolyses of $[(\text{tmpa})\text{Cr}(\text{O})_2]^{2+}$ and $[\text{Cr}(\text{tmpa})\text{L}_2]\text{O}^{2+}$



would point to μ -O migration prior to or concurrent with the rate-determining step, since this dinuclear complex is rapidly converted to $[(\text{tmpa})\text{Cr}(\text{OH})_2\text{Cr}(\text{tmpa})]^{4+}$ in acidic solution.⁶

Experimental Section

Materials. Reagent grade chemicals were used throughout. Solutions for kinetic determinations were prepared with triply distilled H_2O . Cation-exchange separations were performed on SP-Sephadex C-25-120 resin (Na^+ form) with eluants prepared from doubly distilled H_2O . The compounds $[\{\text{Cr}(\text{tmpa})(\text{NCS})_2\text{O}\}(\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ (**1**), $[\{\text{Cr}(\text{tmpa})(\text{CN})_2\text{O}\}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (**2**), $[\{\text{Cr}(\text{tmpa})(\text{OCN})_2\text{O}\}(\text{ClO}_4)_2$ (**3**), and $[\text{Cr}(\text{tmpa})(\text{NCS})_2](\text{ClO}_4)$ (**4**) were prepared as before.^{4,6}

In order to increase the aqueous solubility of $[\text{Cr}(\text{tmpa})(\text{NCS})_2]\text{O}^{2+}$ and to eliminate perchlorate interference in potentiometric $[\text{NCS}^-]$ determinations, bromide and nitrate salts were prepared. The bromide salt **5** was prepared from **1** by simple ion metathesis using KBr and NaBr. **1** (1.00 g) was stirred rapidly in 500 mL of doubly distilled H_2O containing 5.0 g of KBr for 30 min at ambient temperature. The colorless supernatant was removed by filtration. Crude **5** was separated from the less soluble KClO_4 by washing with small aliquots of H_2O until the remaining solid showed no brown color. The golden-brown product was precipitated by slow addition of solid NaBr to the stirred solution until cloudiness was observed, followed by cooling to 5 °C and digestion for 2 h. The solid was reprecipitated twice in this manner. Microcrystalline **5** was filtered, washed with cold triply distilled H_2O , and air-dried. The absence of perchlorate was confirmed by loss of the characteristic strong infrared feature near 1100 cm^{-1} . Anal. Calcd for $[\{\text{Cr}(\text{tmpa})(\text{NCS})_2\text{O}\}(\text{Br})_2 \cdot 3\text{H}_2\text{O}$ (**5**): Cr, 10.09. Found: Cr, 10.1. The nitrate salt was prepared similarly by using KNO_3 and NaNO_3 . Anal. Calcd for $[\{\text{Cr}(\text{tmpa})(\text{NCS})_2\text{O}\}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (**6**): Cr, 10.64. Found: Cr, 10.6.

Instrumentation and Analyses. Kinetic determinations were performed on a Perkin-Elmer Lambda 5 spectrophotometer. UV-visible spectra of base hydrolysis products and intermediates obtained from cation-exchange experiments were obtained with a Shimadzu UV-260 spectrophotometer. Infrared spectra were acquired on a Perkin-Elmer Model 1600 instrument. Thiocyanate ion concentrations were determined potentiometrically (Brinkmann pH 104 meter) with an Orion thiocyanate-sensitive electrode referenced to Ag/AgCl . Chromium was assayed by the basic peroxide method.⁷

$[\text{NCS}^-]$ Determinations. The time course of NCS^- release from the first coordination sphere of chromium in **6** was monitored at 35.0 °C. A stock KSCN solution was standardized through a Volhard titration (0.100 M HNO_3 /0.01 M Fe^{3+} medium) to a $\text{Fe}(\text{NCS})_2^{2+}$ end point. A working curve for $[\text{NCS}^-]$ was prepared from thiocyanate-sensitive

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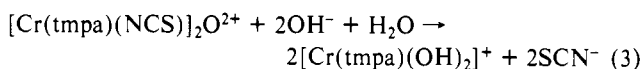
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electrode responses to standard solutions covering the 0.1–100 mM range; in each case, the solution pH was adjusted to 3 with HNO₃ and a constant ionic strength of 0.100 M was maintained by using NaNO₃. On consideration of the typical electrode response time (30 s), potentiometric readings were taken after 1 min. In order to evaluate [NCS⁻] during the base hydrolysis of **6**, 0.1954 g (0.2000 mmol) was dissolved in 190 mL of triply distilled H₂O and thermostated at 35.0 °C. After the addition of 4.92 mL of 4.057 M NaOH (20.0 mmol), the solution volume was quickly brought to 200 mL. Aliquots (10 mL) were withdrawn periodically and quenched by the addition of HNO₃ (to pH 3) prior to the determination of thiocyanate concentrations under the same conditions employed in preparing the standard curve.

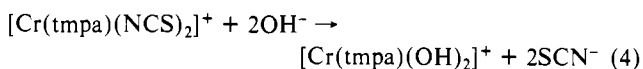
Kinetics. Spectrophotometric measurements of [Cr(tmpa)(NCS)₂O₂]²⁺, [Cr(tmpa)(NCO)₂O₂]²⁺, [Cr(tmpa)(CN)₂O₂]²⁺, and [Cr(tmpa)(NCS)₂]⁺ base hydrolysis rates were performed at 352, 347, 352, and 336 nm, respectively, on thermostated solutions in 1.00-cm quartz cells. The hydroxide ion concentration was varied with NaOH or KOH, and appropriate amounts of NaNO₃, KNO₃, NaSCN, or NaCl were added to maintain a constant ionic strength of 1.00 M. In all cases, pseudo-first-order rate constants (*k*_{obsd}) were obtained from the least-squares slopes of ln (*A*_{*t*} - *A*_∞) vs time plots that were linear over greater than 95% of the overall absorbance change. Reported values are the mean of at least three independent determinations.

Results

Base Hydrolysis Product Identification. In order to determine the [Cr(tmpa)(NCS)₂O₂]²⁺ base hydrolysis products, a 2.0 mM solution of **1** (0.0104 g in 50 mL of 0.050 M NaOH) was thermostated at 50.0 °C. The color of the solution changed from deep golden-brown to light blue within 1 h. A spectrum of this solution after reaction completion (2 h) exhibited the d-d bands (578, 400 nm) and strong 262-nm feature characteristic of [Cr(tmpa)(OH)₂]⁺.⁶ A single blue species identical with the [(tmpa)Cr(O)₂Cr(tmpa)]²⁺ base hydrolysis product⁶ eluted upon cation-exchange chromatography of the reaction mixture (pH 10, 0.10 M LiClO₄ eluant). Consistent with the [Cr(tmpa)(OH)₂]⁺ assignment, acidified product solutions exhibited the spectroscopic signature of [Cr(tmpa)(H₂O)₂]³⁺ (501- and 375-nm d-d bands).⁶ Thiocyanate loss therefore accompanies the base-induced cleavage of [Cr(tmpa)(NCS)₂O₂]²⁺ (eq 3). Similarly, repetitive 300–



700-nm scans of [Cr(tmpa)(NCS)₂]⁺ undergoing base hydrolysis in 0.100 M NaOH converged on the spectrum of [Cr(tmpa)(OH)₂]⁺, consistent with the stoichiometry of eq 4. Spectro-



photometric observations also showed that [Cr(tmpa)(OH)₂]⁺ is the sole chromium product of [Cr(tmpa)(CN)₂O₂]²⁺ and [Cr(tmpa)(NCO)₂O₂]²⁺ base hydrolyses in the range 0.01 ≤ [OH⁻] ≤ 1 M.

Chromatographic Intermediate Identification. A series of 5 °C cation-exchange separations was carried out to probe the existence of long-lived intermediates in the conversion of [Cr(tmpa)(NCS)₂O₂]²⁺ to [(tmpa)Cr(OH)₂]⁺. Duplicates of three chromatographic experiments were performed.

A. Separation of Monomeric and Dimeric Products. **5** (32.6 mg, 0.0316 mmol) was dissolved in 24 mL of triply distilled H₂O and thermostated to 45.0 °C. After 15 min, 0.32 mL of 3.92 M NaOH (1.25 mmol) was added, and the mixture was quantitatively diluted to 25 mL. Base hydrolysis was allowed to proceed for 14.4 min (*t*_{1/2}) at 45.0 °C, at which time the flask was placed in water/ice for quenching by rapid cooling. The reaction mixture was then adsorbed on a 15 × 2.5 cm column that had been equilibrated with 5.00 mM NaOH for 1 h at 5 °C. Upon elution with 5 mM NaOH/0.30 M NaBr, a leading blue band separated cleanly from a slowly moving brown-green component. The blue band was identified as [Cr(tmpa)(OH)₂]⁺ from its electronic spectrum and elution behavior. Subsequent elution with 5 mM NaOH/0.50 M NaBr brought about partial resolution of the trailing species, but the band was collected as one fraction because a clear separation could not be achieved. Unreacted **5** was

identified in this fraction from its distinctive near-ultraviolet absorption features. Both fractions and the recovered Sephadex resin were subjected to chromium analyses, which indicated a total chromium recovery of >98% (first fraction, 30%; second fraction, 70% of recovered Cr).

B. Isolation of a Dimeric Base Hydrolysis Intermediate. In order to resolve the second fraction (from experiment A) components, LiClO₄ eluants were used in another separation of the product mixture generated as in experiment A. Upon elution with 5 mM NaOH/0.10 M LiClO₄, unreacted [Cr(tmpa)(NCS)₂O₂]²⁺ precipitated on the column as the perchlorate salt while [Cr(tmpa)(OH)₂]⁺ separated cleanly as before. A slowly moving green species separated from precipitated **1** on elution with 5 mM NaOH/0.30 M LiClO₄. This green fraction, attributed to a base hydrolysis intermediate (**7**) because of its ultimate decomposition to [Cr(tmpa)(OH)₂]⁺ was collected with a 5 mM NaOH/0.50 M LiClO₄ eluant. Chromium analyses showed >98% recovery of Cr from the column, including [Cr(tmpa)(OH)₂]⁺ (30%), the green intermediate (10%; λ_{max} = 566 (ε = 85 M⁻¹ cm⁻¹) and 364 nm (ε = 450 M⁻¹ cm⁻¹)), and precipitated **1** (60%). Upon acidification with HNO₃, **7** rapidly converts to [(tmpa)Cr(OH)₂Cr(tmpa)]⁴⁺, which was identified from its d-d band maxima at 540 and 385 nm.⁶ The SCN⁻ content of **7** (<0.1 mol of NCS⁻/mol of dimer) was evaluated potentiometrically after conversion to [(tmpa)Cr(OH)₂Cr(tmpa)]⁴⁺ at pH 3 (HNO₃) and ionic strength adjustment to 0.10 M with NaNO₃. On this basis, it may be concluded that both thiocyanate ligands of [Cr(tmpa)(NCS)₂O₂]²⁺ are lost in the formation of **7**. The similarities between the chromatographic behaviors, compositions, reactivities with acid, and electronic spectra of **7** and [(tmpa)(OH)CrOCr(OH)(tmpa)]²⁺ (λ_{max} = 580 (ε = 85 M⁻¹ cm⁻¹) and 364 nm (ε = 415 M⁻¹ cm⁻¹)), a [(tmpa)Cr(O)₂Cr(tmpa)]²⁺ base hydrolysis intermediate,⁶ suggest that the two green species are identical.

C. Chromatography of an Acid-Quenched Base Hydrolysis Product Mixture. In a third separation of the product mixture generated as in experiment A, the cooled solution was immediately acidified to [H⁺] = 1 mM by the addition of 0.63 mL of 2.02 M HBr. This acid-quenched mixture was adsorbed onto a column that had been equilibrated with 1 mM HBr at 5 °C. Upon elution with 1 mM HBr/0.10 M NaBr, there was no movement of Cr-containing species. A sharp resolution of leading brown, middle red, and top purple bands was achieved over the course of 15 min during elution with 1 mM HBr/0.30 M NaBr. The first and second fractions were collected after changing the eluant to 1 mM HBr/0.50 M NaBr; fraction 3 was eluted with 1 mM HBr/1.0 M NaBr. Electronic spectra supported the assignments of fractions 1 (44% of total recovered chromium), 2 (24% of Cr), and 3 (32% of Cr) to [Cr(tmpa)(NCS)₂O₂]²⁺,⁴ [Cr(tmpa)(H₂O)₂]³⁺,⁶ and [Cr(tmpa)(OH)₂]⁴⁺,⁶ respectively. Over 99% of reactant Cr was accounted for in these three fractions.

An interpretation of the chromatographic findings from experiments A–C is proposed in Table I. Two intermediates, [Cr(tmpa)(OH)₂O₂]²⁺ and [(tmpa)(SCN)CrOCr(OH)(tmpa)]²⁺ (**8**), are thought to be present after 1 half-life of the base hydrolysis reaction, along with unreacted [Cr(tmpa)(SCN)₂O₂]²⁺ and the [Cr(tmpa)(OH)₂]⁺ product. The recovery of 44% unreacted [Cr(tmpa)(SCN)₂O₂]²⁺ in experiment C is close to expectations from the choice of *t*_{1/2} as the reaction time. The slight discrepancy of 6% between monomer recoveries from separations in basic (A, B) and acidic (C) media reflects the continuation of slow base hydrolysis in the former two experiments. The 32% yield of [Cr(tmpa)(OH)₂]⁴⁺ in experiment C must be entirely derived from dinuclear base hydrolysis intermediates, since neither starting material nor the monomeric product (as [Cr(tmpa)(H₂O)₂]³⁺) is converted to the chromium diol under the acidic quenching conditions. Taking into account the 10% yield of [Cr(tmpa)(OH)₂]²⁺ in experiment B and presumed 6% conversion of this intermediate to [Cr(tmpa)(OH)₂]⁺ while adsorbed on the cation exchange column, it is apparent that 16% of another *dinuclear* chromium intermediate, most logically [(tmpa)(SCN)CrOCr(OH)(tmpa)]²⁺, is present at *t*_{1/2}. Although **8** was not isolated pure as a separate fraction in any of the chromatographic studies,

Table I. Chromium Product Distributions from Quenched [Cr(tmpa)(NCS)]₂O²⁺ Base Hydrolysis Reaction Mixtures at Time $t_{1/2}$ ^a

complex ^b	distribn, %			
	overall ^c	chromatographic experimental code (eluant) ^d		
		A (NaBr/NaOH)	B (NaClO ₄ /NaOH)	C (NaBr/HBr)
[Cr(tmpa)(NCS)] ₂ O ²⁺	44	44	44	44
7	16	10	10	
8	16	16	16	
[Cr(tmpa)(OH)] ₂ ⁺	24	30	30	
[Cr(tmpa)(H ₂ O)] ₂ ³⁺				24
[Cr(tmpa)(OH)] ₂ ⁴⁺				32

^aProduct percentages based on cation-exchange separations of [Cr(tmpa)(NCS)]₂O²⁺ solutions in 0.10 M NaOH at 45 °C, quenched at $t_{1/2}$ of the base hydrolysis reaction (14.4 min). See text for chromatographic details. Typical uncertainty: ±2%. ^bComplexes identified in quenched base hydrolysis mixtures. 7: [Cr(tmpa)(OH)]₂O²⁺; 8: [(tmpa)(SCN)-CrOCr(OH)(tmpa)]₂²⁺. ^cProposed distribution of chromium species in the [Cr(tmpa)(NCS)]₂O²⁺ base hydrolysis reaction mixture at time $t_{1/2}$, based on the analysis of chromatographic separation results from experiments A-C; see text. ^dChromium product distributions from chromatographic experiments A-C.

the stated 16% yield may be quantitatively reconciled with the chromium distribution results of all three experiments provided that (a) 8 is eluted together with [Cr(tmpa)(NCS)]₂O²⁺ and 7 in experiment A, (b) 8 and [Cr(tmpa)(NCS)]₂O²⁺ are both precipitated by ClO₄⁻ in experiment B, and (c) 8 is rapidly converted to [Cr(tmpa)(OH)]₂⁴⁺ in acidic solutions, with liberation of NCS⁻.

Base Hydrolysis Kinetics. The [Cr(tmpa)(L)]₂O²⁺ dimers with L⁻ = NCS⁻, CN⁻, and NCO⁻ exhibited linear (correlation coefficient = 0.999) first-order analytical plots over at least 95% of the absorbance change in kinetic studies of their base hydrolysis reactions. By contrast, biphasic traces characteristic of consecutive first-order kinetics were observed in studies of [Cr(tmpa)(O)]₂²⁺ base hydrolysis.⁶ Since the base hydrolyses of [Cr(tmpa)(NCS)]₂O²⁺ and [Cr(tmpa)(O)]₂²⁺ evidently proceed through a common intermediate (7), the considerably larger Δε associated with the first phase of the former reaction (1.4×10^4 vs 2.7×10^3 M⁻¹ cm⁻¹) accounts in part for the absence of a detectable second phase in kinetic studies of reaction 3. For this reason, the kinetically monitored 352-nm absorbance decrease measures the rate of OH⁻-induced NCS⁻ displacement rather than that of oxo-bridge cleavage.

Another point of contrast with [(tmpa)Cr(O)₂Cr(tmpa)]₂²⁺ decay,⁶ for which k_{obsd} takes the form ($k_0 + k_{\text{OH}}[\text{OH}^-]$), is the hydroxide ion dependence of the [Cr(tmpa)(NCS)]₂O²⁺ base hydrolysis rate. Thus, plots of k_{obsd} vs [OH⁻] approach a saturation limit at high hydroxide concentrations at all five temperatures examined, consistent with rate expression 5. The parameters k_2

$$k_{\text{obsd}} = k_0 + \frac{k_2 Q_p [\text{OH}^-]}{1 + Q_p [\text{OH}^-]} \quad (5)$$

$$k_{\text{obsd}} = k_0 + k_{\text{OH}} [\text{OH}^-] \quad (6)$$

and Q_p correspond to the decay rate and preequilibrium formation constants of an intermediate complex between the CrOCr dimer and OH⁻, respectively (vide infra). The dimers with L = CN⁻ and NCO⁻ follow the simpler two-term rate expression (eq 6), however, manifested by linear k_{obsd} vs [OH⁻] correlations. A summary of k_{obsd} values for L⁻ = NCS⁻, CN⁻, and NCO⁻ as a function of [OH⁻] and temperature at a constant ionic strength of 1.0 M (NaOH/NaNO₃) is presented in Table II. In order to probe the possibility that rate saturation in the case of L⁻ = NCS⁻ is an artifact of the electrolyte medium, the base hydrolyses of [Cr(tmpa)(NCS)]₂O²⁺ (NaOH/NaCl) and [Cr(tmpa)(CN)]₂O²⁺ (KOH/KNO₃) were examined at $I = 1.0$ M in media for which NO₃⁻ and Na⁺ were replaced by Cl⁻ and K⁺, respectively (Table II). Finally, a study of the free thiocyanate ion influence on the [Cr(tmpa)(NCS)]₂O²⁺ decay rate was performed to determine whether an activated base hydrolysis intermediate forms

Table II. Observed Base Hydrolysis Rate Constants for (tmpa)Cr^{III} Complexes^a

complex	medium	temp, °C	[OH ⁻], M	10 ⁴ k_{obsd} , s ⁻¹			
[Cr(tmpa)(NCS)] ₂ O ²⁺	NaOH/NaNO ₃	35.0	0.010	0.813			
			0.020	1.36			
			0.050	2.32			
			0.100	2.97			
			0.500	3.89			
			1.00	4.53			
			40.0	0.010	1.83		
				0.050	4.43		
				0.075	5.19		
				0.100	5.97		
	0.200	6.70					
	0.300	7.04					
	0.400	7.36					
	0.500	7.49					
	0.600	7.61					
	0.700	7.80					
	45.0	0.010	3.11				
		0.020	4.82				
		0.050	8.02				
		0.100	9.78				
0.500		12.3					
1.00		14.1					
50.0		0.010	6.34				
		0.020	9.65				
		0.050	16.1				
		0.100	18.4				
	0.500	21.1					
	1.00	24.3					
	55.3	0.010	11.1				
		0.020	16.6				
		0.050	25.8				
		0.100	32.5				
0.500		37.6					
1.00		41.5					
[Cr(tmpa)(NCO)] ₂ O ²⁺		NaOH/NaNO ₃	40.0	0.020	0.410		
				0.050	0.897		
				0.100	1.53		
				0.150	2.14		
	0.200			2.66			
	0.300			3.68			
	0.500			5.70			
	1.00			11.1			
	[Cr(tmpa)(CN)] ₂ O ²⁺			NaOH/NaNO ₃	40.0	0.150	1.14
						0.200	1.45
0.300		2.07					
0.500		2.98					
1.00		4.75					
[Cr(tmpa)(NCS)] ₂ O ²⁺		NaOH/NaCl	40.0			0.010	2.12
						0.020	3.23
						0.050	5.24
						0.100	6.65
						0.500	7.93
	1.000			8.33			
	[Cr(tmpa)(CN)] ₂ O ²⁺			KOH/KNO ₃	40.0	0.100	0.906
						0.200	1.71
						0.300	2.33
						0.400	2.79
0.500		3.15					
0.600		3.46					
0.700		3.67					
0.800		3.91					
0.900		4.12					
1.00		4.41					
[Cr(tmpa)(NCS)] ₂ ⁺		40.0	0.005	5.2			
			0.025	5.3			
			0.050	5.9			
			0.100	5.7			
			0.500	5.6			
			0.800	6.0			
			1.00	6.5			

^a $I = 1.00$ M. Uncertainty in k_{obsd} is estimated at ±3%.

through reversible loss of NCS⁻ from the Cr first-coordination sphere. Measurements carried out at $I = 1.0$ M with [NCS⁻] = 0.025–0.500 M showed only very slight rate retardation (9%) over the 20-fold concentration interval examined (average $k_{\text{obsd}} = 5.6$

Table III. Comparison of $[\text{Cr}(\text{tmpa})(\text{L})_2\text{O}^{2+}]$ Base Hydrolysis Rate Parameters^a

L^-	medium	temp, °C	$10^5 k_0, \text{s}^{-1}$	$10^4 k_{\text{OH}}, \text{M}^{-1} \text{s}^{-1}$	$10^3 k_2, \text{s}^{-1}$	Q_p, M^{-1}
NCS^-	NaOH/NaNO ₃	35.0		79	0.44 (0.03)	18.0 (4.9)
		40.0	5.3 (2.1)	160	0.77 (0.02)	20.9 (1.7)
		45.0		290	1.33 (0.10)	22.1 (6.2)
		50.0		710	2.40 (0.06)	29.6 (2.4)
		55.3		1300	4.02 (0.28)	31.4 (7.2)
NCO^-	NaOH/NaCl	40.0	5 (3)	220	0.81 (0.02)	27.2 (1.7)
		40.0	4.1 (0.6)	10.7 (0.2)		
CN^-	NaOH/NaNO ₃	40.0	6.8 (1.4)	4.17 (0.27)		
		40.0	13.9 (1.5)	3.16 (0.23)		

^a $I = 1.00 \text{ M}$. Rate parameters are defined by eq 5 and 6 and were extracted from k_{obsd} vs $[\text{OH}^-]$ profiles by least-squares procedures described in the text. Standard deviations are shown in parentheses. For $\text{L}^- = \text{NCS}^-$, k_{OH} was calculated as $k_2 Q_p$.

$\pm 0.2) \times 10^{-4} \text{ s}^{-1}$; 40 °C). It is concluded that this very small kinetic thiocyanate influence does not justify the inclusion of a $[\text{NCS}^-]$ term in the rate law.

Linear least-squares analyses of k_{obsd} and $[\text{OH}^-]$ data sets yielded k_0 and k_{OH} values for the base hydrolysis reactions of dimers with $\text{L}^- = \text{CN}^-$ and NCO^- (Table III). A nonlinear least-squares routine (method of steepest descent)³ verified the appropriateness of eq 5 and afforded the k_0 , k_2 , and Q_p parameters that govern the base hydrolysis of $[\text{Cr}(\text{tmpa})(\text{NCS})_2\text{O}^{2+}]$ (Table III). This three-parameter fit typically gave uncertainties in k_0 on the same order as the rate constant, such that a quantitatively reliable value may only be derived from the largest (40 °C) data set. Comparisons of $\text{L}^- = \text{NCS}^-$ or CN^- rate parameters determined in two ionic media at 40 °C show that the choice of electrolyte used to maintain constant ionic strength has little influence on either the absolute rates or the form of the rate law. It follows, therefore, that rate saturation in OH^- carries genuine mechanistic significance in the case of $\text{L}^- = \text{NCS}^-$. Activation parameters corresponding to k_0 ($\Delta H^\ddagger = 18 \pm 4 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = -22 \pm 11 \text{ eu}$) and k_2 ($\Delta H^\ddagger = 21.5 \pm 0.3 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = -4 \pm 1 \text{ eu}$) were computed from Eyring plots (35.0–55.3 °C) for $[\text{Cr}(\text{tmpa})(\text{NCS})_2\text{O}^{2+}]$ base hydrolysis. A van't Hoff plot of the Q_p temperature dependence gave the associated standard enthalpy ($+5.8 \pm 0.8 \text{ kcal mol}^{-1}$) and entropy ($+25 \pm 2 \text{ eu}$) changes.

Potentiometric determinations of $[\text{NCS}^-]$ in acid-quenched $[\text{Cr}(\text{tmpa})(\text{NCS})_2\text{O}^{2+}]$ base hydrolysis reaction mixtures were performed under the same conditions as a 35 °C kinetic run ($[\text{OH}^-] = 0.100 \text{ M}$) in order to correlate loss of the CrOCr chromophore with the release of NCS^- from the chromium coordination sphere. Figure 1 exhibits a 352-nm spectrophotometric decay curve overlaid on the free NCS^- formation curve, normalized as the ratio $[\text{NCS}^-]_{\text{free}}/[\text{dimer}]_0$. Although the quantitative quality of the $[\text{NCS}^-]$ vs time data is not sufficient to support a rate calculation, it is clear that the free thiocyanate concentration tends to zero at time 0, as expected. Considering that the $[\text{NCS}^-]_{\text{free}}/[\text{dimer}]_0$ ratio approaches 2 concurrent with the convergence of A_{352} on A_∞ , we conclude that both $[\text{Cr}(\text{tmpa})(\text{NCS})_2\text{O}^{2+}]$ thiocyanate ligands are liberated on the time scale of the spectrophotometric rate determinations, consistent with the stoichiometry of eq 3. Since the acidification to pH 3 required to obtain accurate thiocyanate-sensitive electrode responses apparently induces the rapid liberation of NCS^- from **8**, the data shown in Figure 1 overstate somewhat the actual $[\text{NCS}^-]$ in the reaction mixture immediately prior to quenching.

Since rate saturation in OH^- is not typical of Cr(III) base hydrolysis processes,⁶ it is important to know whether this effect is a distinctive reactivity characteristic of the CrOCr bridging unit or rather is a consequence of hydroxide interaction with the tmpa ligand, which could appear in the base hydrolyses of both $(\text{tmpa})\text{Cr}^{\text{III}}$ dimers and monomers. This question was addressed through kinetic studies of NCS^- release from $[\text{Cr}(\text{tmpa})(\text{NCS})_2]^+$. Time-dependent 300–600-nm spectra of **4** in alkaline solution revealed that loss of the first thiocyanate ligand, associated with 348-nm absorbance bleaching, is followed by slower conversion of $[\text{Cr}(\text{tmpa})(\text{NCS})(\text{OH})]^+$ to $[\text{Cr}(\text{tmpa})(\text{OH})_2]^+$, monitored by the decay of a 313-nm spectral feature. Pseudo-first-order rate constants for release of the first thiocyanate ligand from **4** (Table II) are independent of $[\text{OH}^-]$ ($(5.8 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$; 40 °C, I

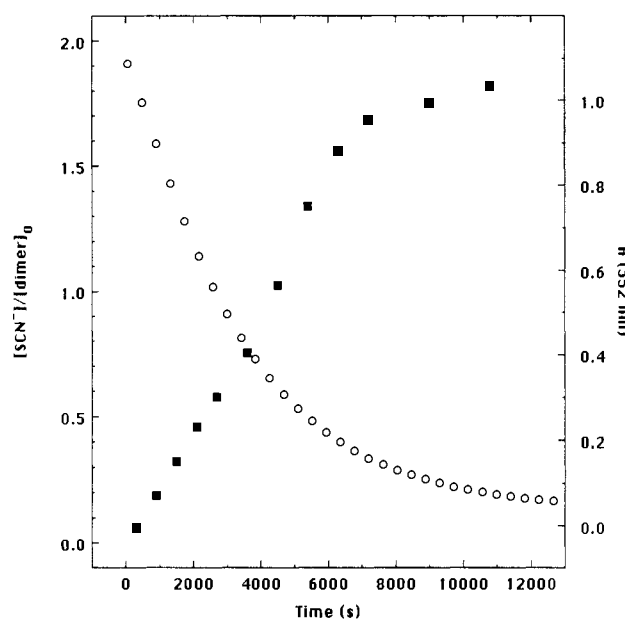


Figure 1. Time course of 352.0-nm absorbance decay (O points, right-hand coordinate axis) and free NCS^- formation (■ points, left hand coordinate axis) during the base hydrolysis reaction of $[(\text{tmpa})(\text{SCN})\text{CrOCr}(\text{NCS})(\text{tmpa})]^{2+}$ at 35.0 °C in 0.10 M NaOH.

$= 1.0 \text{ M}$) over the interval 0.050–0.800 M. The absence of a kinetic hydroxide dependence for monomer **4** confirms that the saturation behavior observed in the dimer base hydrolysis studies does not originate solely from tmpa ligand reactivity.

Discussion

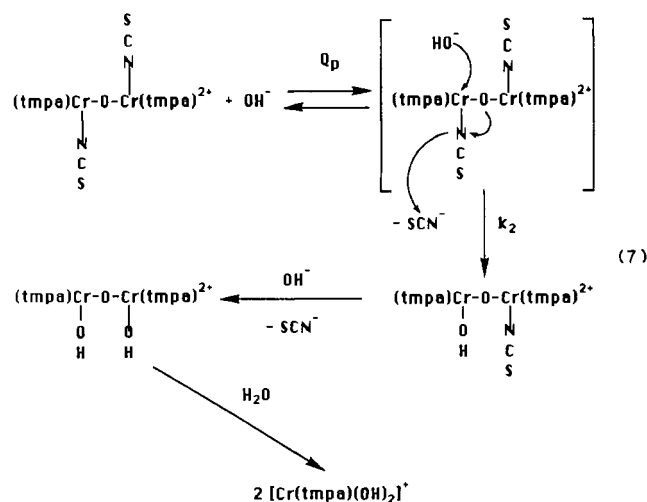
The isolation of $[\text{Cr}(\text{tmpa})(\text{OH})_2]^{4+}$ from acid-quenched solutions of partially base-hydrolyzed $[\text{Cr}(\text{tmpa})(\text{NCS})_2\text{O}^{2+}]$ carries significant mechanistic implications. The excellent agreement between electronic spectra of authentic $[(\text{tmpa})\text{Cr}(\text{OH})_2\text{Cr}(\text{tmpa})](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$ ⁵ and the dimeric product isolated from the base hydrolysis reaction mixture quenched with acid at time $t_{1/2}$ leaves no doubt that the species are identical in both composition and geometry. Coupled with chromatographic evidence for $[(\text{tmpa})(\text{SCN})\text{CrOCr}(\text{OH})(\text{tmpa})]^{2+}$ and $[\text{Cr}(\text{tmpa})(\text{OH})_2\text{O}^{2+}]$ precursors to the ultimate $[\text{Cr}(\text{tmpa})(\text{OH})_2]^{4+}$ base hydrolysis product, the finding of $[\text{Cr}(\text{tmpa})(\text{OH})_2]^{4+}$ in the acid-quenched reaction mixture demonstrates that (1) both $[\text{Cr}(\text{tmpa})(\text{NCS})_2\text{O}^{2+}]$ NCS^- ligands are lost prior to oxo-bridge cleavage and (2) migration of the oxo bridge to a cis coordination position accompanies or precedes generation of the $[\text{Cr}(\text{tmpa})(\text{OH})_2\text{O}^{2+}]$ intermediate. The latter conclusion is based on the same reasoning as was advanced in favor of oxo migration during $[\text{Cr}(\text{tmpa})(\text{NCS})_2\text{O}^{2+}]$ synthesis from the diol; i.e., both tmpa apical N atoms are trans to thiocyanate ligands in the CrOCr dimer, having started trans to bridging oxygen atoms in the $\text{Cr}(\text{OH})_2\text{Cr}$ complex.^{5,6} In the present circumstance, it is assumed that oxo migration is *not* initiated by the acidification of intermediates **7** or **8**. Such a presumption is supported by the very rapid acid-induced conversion of **7** to the diol, within the time of mixing, similar to the well-documented transformations of $[(\text{en})_2(\text{OH})\text{Cr}(\text{OH})\text{Cr}(\text{OH})-$

(en)₂]⁴⁺ and related dinuclear chromium complexes with aliphatic amine ligands to dihydroxo-bridged dimers.^{8,9} Microscopic reversibility does *not* demand that oxo-bridge migration occur in both the formation of [Cr(tmpa)(NCS)]₂O²⁺ from [Cr(tmpa)(OH)]₂⁴⁺ and its base hydrolysis to [Cr(tmpa)(OH)₂]⁺, since these are not the forward and reverse processes constituting a single overall reaction.

The empirical dependence of k_{obsd} on [OH⁻] expressed by eq 5 has been encountered rarely in D_{cb} processes for which a substantial fraction of an aminocobalt(III) complex is converted to a conjugate base form prior to base hydrolysis, but the simpler $k_{\text{obsd}} = (k_0 + k_{\text{OH}}[\text{OH}^-])$ relationship is typical of chromium(III) base hydrolyses.¹⁰ Such behavior could also arise from a "covalent hydration" mechanism in which OH⁻ attacks a carbon atom adjacent to pyridine N, forming an amido trans-labilizing group.¹⁰ We find no direct evidence for such attack on tmpa pyridyl groups, and discount the "covalent hydration" alternative also because kinetic saturation behavior was not found in the case of [Cr(tmpa)(NCS)₂]⁺, for which the base hydrolysis rate is independent of [OH⁻] throughout the concentration interval used in the [Cr(tmpa)(NCS)]₂O²⁺ studies. Considering that both fast and slow phases of [(tmpa)Cr(OH)]₂²⁺ hydrolysis follow the $k_{\text{obsd}} = (k_0 + k_{\text{OH}}[\text{OH}^-])$ rate expression, we conclude that eq 5 reflects a distinctive substitutional reactivity of the linear CrOCr structural unit.

Three mechanistic types give rise to saturation kinetics of the type reported here: activated-intermediate, intermediate-complex, and dead-end-complex pathways.¹¹ The distinction among these alternatives is particularly challenging in the present circumstance. Nevertheless, it is clear that dead-end complexation is seldom invoked by coordination chemists.¹² In the activated-intermediate mechanism, [Cr(tmpa)L]₂O²⁺ would undergo structural or electronic activation in a reversible first step to give a steady-state transient, which would then be irreversibly scavenged by OH⁻ to form products. This alternative suffers from the lack of a plausible activation step, however. In particular, the activation process most consistent with the intermediate identification studies would involve L⁻ displacement induced by oxo-bridge migration. The failure of free NCS⁻ to markedly influence the rate of [Cr(tmpa)(NCS)]₂O²⁺ base hydrolysis is not consistent with such an activation step, however, since the uptake of NCS⁻ in the reverse reaction would result in the appearance of a [NCS⁻]-dependent term in the denominator of the rate law. Alternative potential activation processes in which the Cr-L bond is left intact, such as rotation about or bending of the CrOCr linkage, are speculative and unproductive toward the end result of achieving oxo-bridge cleavage through an intermediate (7) that has lost both L⁻ ligands. In addition, the failure of k_{obsd} to approach a saturation limit for all three CrOCr reactants (at 40 °C) is difficult to reconcile with an activated-intermediate mechanism, leaving a pathway requiring intermediate complexation between [Cr(tmpa)L]₂O²⁺ and OH⁻ as the only viable alternative.

The base hydrolysis mechanism considered to be most likely (eq 7) features rate-limiting displacement of NCS⁻ by the migrating oxo function, induced by nucleophilic attack of OH⁻ on chromium within a 1:1 precursor complex. Such a mechanism agrees well with both kinetic and chromatographic findings provided that (a) the Q_p equilibrium is established rapidly as compared with the rate of the k_2 step, (b) the near-ultraviolet absorbance decrease monitored in kinetic experiments is essentially complete at the conclusion of the k_2 step, and (c) $Q_p(\text{NCS}^-) \gg Q_p(\text{NCO}^- \text{ or } \text{CN}^-)$. The k_2 activation parameters for L⁻ = NCS⁻



are consistent with an intracomplex rate-limiting step ($\Delta S^\ddagger \approx 0$) in which the activation barrier predominantly reflects the energetics of Cr-NCS bond-breaking.

Although I_d mechanisms have been proposed frequently for Cr(III) anation and base hydrolysis processes,¹⁴⁻²³ intramolecular displacement of NCS⁻ by bridging O²⁻ triggered by an incoming nucleophile is unprecedented. Indeed, hindered formation of trigonal-bipyramidal base hydrolysis intermediates could *attenuate* the stereomobility of octahedral Cr(III) complexes relative to their Co(III) analogues.¹⁴ This view is contested, however, by evidence that kinetic differences between Cr(III) and Co(III) species derive primarily from ground-state π -bonding and ionic radius characteristics, such that the D_{cb} mechanism applies equally well to both metal centers.²⁴ In any case, the feasibility of mechanism 7 cannot be adequately judged on the basis of existing literature, which does not speak to the issue of base hydrolysis in Cr(III) complexes for which a conjugate base mechanism is precluded by the absence of an ionizable amine proton. A complete proof that loss of the first thiocyanate ligand from [Cr(tmpa)(NCS)]₂O²⁺ is accompanied by μ -O migration would include the solid-state structure of **8**, which has proved to be unattainable thus far. The crystallographic demonstration⁴⁶ of nucleophile-induced μ -O migration in the conversion of [(tmpa)Cr(OH)₂Cr(tmpa)]⁴⁺ to [Cr(tmpa)(NCS)]₂O²⁺ provides an adequate precedent, however, that such a step is not unreasonable at least within the [Cr(tmpa)L]₂O²⁺ class of ions.

The ΔH° and ΔS° values associated with Q_p demonstrate that the proposed ion-pairing between [Cr(tmpa)(NCS)]₂O²⁺ and OH⁻ is driven by a highly favorable entropy term that offsets an endothermic enthalpic contribution. While such an unfavorable ΔH° term is difficult to understand in terms of simple ion pairing between the reactants, a donor-acceptor interaction of a hydroxide lone pair with the slightly antibonding⁵ b_{1u} CrOCr dimer LUMO should be considered. A significant energy gap between b_{2g} HOMO and b_{1u} LUMO levels, formally δ nonbonding and near-degenerate in the *absence* of π -acceptance from the aromatic amine ligands, is implied by the large singlet-triplet gaps of 509 ($L^- = \text{NCS}^-$) and 580 cm^{-1} ($L^- = \text{CN}^-$) characteristic of the [Cr(tmpa)L]₂O²⁺ dimers.⁵ Release of solvating water molecules from both [Cr(tmpa)L]₂O²⁺ and OH⁻ resulting from charge neutralization in their intermediate complex could partly account

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for the exceptional entropic driving force of the Q_p equilibrium. Unfortunately, there is no obvious explanation of the apparent attenuation of Q_p values for the $L^- = \text{NCO}^-$ and CN^- dimers, which presumably underlies their failures to exhibit saturation base hydrolysis kinetics. As a point for further examination, we note that increases in b_{1u} MO energy (and antibonding character) should destabilize a $b_{1u}\text{-OH}^-$ interaction by forcing the ΔH° term to become even more endothermic.

According to the proposed mechanism, k_{OH} in rate expression 6 is equivalent to the product $k_2 Q_p$. In order to facilitate a comparison of overall base hydrolysis reactivities among the three CrOCr dimers, k_2 values calculated in this fashion for $L^- = \text{NCS}^-$ are included in Table III. On this basis, 40 °C k_{OH}/k_0 ratios may be ranked according to NCS^- (300) \gg NCO^- (26) $>$ CN^- (6). The substantial variation in this ratio throughout the series supports our hypothesis of rate-limiting Cr–L dissociation induced by oxo-bridge migration. In this respect, the CrOCr dimer base hydrolyses are typical of chromium(III) complexes as a whole, for which kinetic leaving group sensitivities are larger in base hydrolysis processes than in related acid hydrolysis or simple aquation reactions.¹⁰ Indeed, composite k_{OH} ($L^- = \text{NCS}^-$) activation parameters calculated from the temperature dependences of k_2 and Q_p ($\Delta H^\ddagger = 27.3 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = +21 \text{ eu}$) are strongly reminiscent of those reported for a variety of Cr(III) and Co(III) species.¹⁰ It should also be noted that the trend in CrOCr dimer k_{OH}/k_0 ratios results almost entirely from variations in k_{OH} . Thus,

the k_0 (40 °C) values characteristic of $L^- = \text{NCS}^-$, NCO^- , and CN^- are essentially identical at $(5 \pm 2) \times 10^{-5} \text{ s}^{-1}$, suggesting that Cr–O rather than Cr–L bond-breaking dominates the activation process corresponding to the minor hydroxide-independent term.

Finally, a comparison of rate parameters for $[\text{Cr}(\text{tmpa})\text{L}]_2\text{O}^{2+}$ and $[\text{Cr}(\text{tmpa})(\text{O})]_2^{2+}$ base hydrolysis reactions is instructive. Most noteworthy are the small k_{OH}/k_0 ratios that characterize both fast (1.9) and slow (0.6) phases of dioxo dimer base hydrolysis.⁶ The importance of OH^- as an attacking nucleophile therefore is dramatically muted in Cr(O)₂Cr dimer cleavage, for which the second bridging oxo function occupies the position thought to be filled by the incoming OH^- ligand in the analogous LCrOCrL reactions. Nevertheless, there is an unexpectedly close resemblance between the $[\text{Cr}(\text{tmpa})(\text{NCS})]_2\text{O}^{2+}$ k_{OH} activation parameters and those reported previously for $[\text{Cr}(\text{tmpa})(\text{OH})]_2\text{O}^{2+}$ ($\Delta H^\ddagger = 28 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = +14 \text{ eu}$)⁶ cleavage. The overall base hydrolysis reactivities of the two families are not greatly different at 40 °C, considering the k_{OH} ($\text{M}^{-1} \text{ s}^{-1}$) ranking: $[\text{Cr}(\text{tmpa})(\text{NCS})]_2\text{O}^{2+}$ (1.6×10^{-2}) $>$ $[\text{Cr}(\text{tmpa})(\text{O})]_2^{2+}$ (4.6×10^{-3})⁶ $>$ $[\text{Cr}(\text{tmpa})(\text{NCO})]_2\text{O}^{2+}$ (1.1×10^{-3}) $>$ $[\text{Cr}(\text{tmpa})(\text{CN})]_2\text{O}^{2+}$ (4.2×10^{-4}) $>$ $[\text{Cr}(\text{tmpa})(\text{OH})]_2\text{O}^{2+}$ (1.5×10^{-4}).⁶

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Synthesis and Electrochemistry of 2,2'-Bipyridyl Complexes of Dioxorhenium(V)

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The rhenium(V) bipyridyl (bpy) complexes $[(\text{bpy})(\text{py})_2\text{Re}(\text{O})_2](\text{ClO}_4)$ and $[(\text{bpy})(3\text{-pySO}_3)_2\text{Re}(\text{O})_2](\text{Na})\cdot 2\text{H}_2\text{O}$ have been prepared by reaction of 2,2'-bipyridine with *trans*- $[(\text{py})_4\text{Re}(\text{O})_2](\text{Cl})$ and *trans*- $[(3\text{-pySO}_3)_4\text{Re}(\text{O})_2](\text{Na})_3$ in methanol or methanol/water solutions (py = pyridine, 3-pySO₃ = 3-pyridinesulfonate). Despite the seemingly trivial change in coordination environment, the bpy-containing complexes were found to behave very differently from the corresponding tetrapyridyl complexes. For example, the pH-independent formal potential for reduction of Re(VI) to Re(V) was lowered by some 600 mV. On the other hand, the pH-dependent potential for the Re(V/III) couple increased by ca. 200 mV upon bpy coordination. The V/III couple also became considerably more reversible (kinetically) in its electrochemical response. The Re(III/II) potential was also shifted in the positive direction. At high pH's, the V/III and III/II couples coalesced to yield the first example of three-electron redox behavior in rhenium chemistry. By analogy with known dioxoosmium complexes, both the thermodynamic and kinetic electrochemical effects were attributed to a relative stabilization of the inaccessible Re(IV) oxidation state following bpy coordination. It was proposed that the destabilization is induced by *trans* to *cis* isomerization. The *cis*-dioxo configuration has only rarely been seen in d² coordination chemistry, and never for hexacoordinate rhenium. Nevertheless, circumstantial evidence from IR, NMR, and Raman experiments supported the assignment. Unfortunately, proof was not possible by these methods since both *cis*- and *trans*- $(\text{bpy})(\text{py})_2\text{Re}(\text{O})_2^{2+}$ would possess C_{2v} symmetry. Very recent X-ray investigations (to be reported elsewhere) have now confirmed the *cis* assignment.

Introduction

We and many others have had a long-standing interest in the kinetics and dynamics of single-electron-transfer (ET) reactions involving metal complexes.¹ Recently that interest has turned toward multielectron processes. In particular, we have been interested in multi-ET kinetics at electrochemical interfaces. Among the most prominent multielectron reagents are the many oxo and dioxo complexes of transition metals.² Typically these feature a very rich, yet chemically reversible, redox chemistry.³

Furthermore, they often figure importantly in both artificial and naturally occurring catalytic systems.²

For our purposes the *trans*-dioxo complexes of rhenium(V) were deemed nearly ideal for initial studies.^{4–6} While not yet par-

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