are extremely small. The situation might be different for viscous solutions and/or for macromolecular systems.

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Doubly Bridged μ-Fluoro–μ-Oxo and μ-Fluoro–μ-Hydroxo Chromium(III) Dimers

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Introduction

Dihydroxo-bridged chromium(III) dimers with aromatic amine ligands are susceptible to nucleophilic attack by halide and pseudohalide ions, resulting in the displacement of a single μ-OH$^-$ group.[1,2] Thus, linear oxo-bridged dimers of the type $[L(tmpa)CrOCr(tmpa)L]^{2+}$ (tmpa = tris(2-pyridylmethyl)amine; L^- = NCS^-, NCO^-, CN^-, N_3^-, Cl^-) are formed from the reactions of L^- with $[(tmpa)Cr(OH)_2Cr(tmpa)]^{4+}$ (eq 1).[2] This reaction

$$[(tmpa)Cr(OH)_2Cr(tmpa)]^{4+} + 2L^- \rightarrow [L(tmpa)CrOCr(tmpa)L]^{2+} + H_2O \quad (1)$$

is not completely general, however, in that Br^-, I^-, and neutral nucleophiles fail to react with the chromium diol (i.e. *N*,*N*-dimethylformamide, urea) or only deprotonate a bridging hydroxo substituent (i.e. ammonia, pyridine). In the course of these studies, it was found that F^- reacts with $[Cr(tmpa)(OH)]_2^{4+}$ to give products other than the anticipated $[Cr(tmpa)F]_2O^{2+}$ cation.[2] We report here the synthesis of $[(tmpa)Cr(O)(F)Cr(tmpa)](ClO_4)_3 \cdot H_2O$ and $[(tmpa)Cr(OH)(F)Cr(tmpa)](ClO_4)_4$, the first well-characterized examples of μ-fluoro–μ-oxo and μ-fluoro–μ-hydroxo doubly-bridged chromium(III) dimers.

Experimental Section

The preparations of $[Cr(tmpa)(OH)]_2(ClO_4)_4 \cdot 4H_2O$ and $[(tmpa)Cr(O)(OH)Cr(tmpa)](ClO_4)_3 \cdot H_2O$ have already been described.[3] Reagent grade chemicals were used throughout. Microanalyses were performed by Desert Analytics (C,H,N; Tucson, AZ) and Galbraith Laboratories (F; Knoxville, TN). Chromium was assayed by the basic peroxide method.[4] Cation-exchange chromatography was carried out at 5 °C on SP-Sephadex C-25-120 resin (Na^+ form), and eluting solutions were prepared from doubly distilled water. Ultraviolet–visible and infrared measurements were acquired on Shimadzu UV-260 and Perkin-Elmer 1600 spectrophotometers, respectively. Cyclic voltammograms of 0.5 mM electroactive solute solutions were acquired with a Bioanalytical Systems CV-1B triangular wave generator and a Hewlett-Packard 7004 B X-Y recorder.[1,5] Working electrodes were referenced to an aqueous saturated calomel electrode in 0.1 M $NaNO_3$; a Pt wire was the auxiliary electrode in all experiments. Reported potentials were converted to the SHE scale as before[5] by using (hydroxyethyl)ferrocene as an internal calibrant. Half-wave potentials were calculated as the mean of anodic and cathodic peak potentials when the $E_{1/2}$ value exhibited no sweep rate dependence from 50 to 300 mV/s.

$[(tmpa)Cr(O)(F)Cr(tmpa)](ClO_4)_3 \cdot H_2O$ was prepared by refluxing 2.00 g (1.68 mmol) of $[Cr(tmpa)(OH)]_2(ClO_4)_4 \cdot 4H_2O$ with NaF (0.7065 g, 16.8 mmol) in CH_3CN (200 mL) for 1 h. The deep green reaction mixture was then evaporated to 100 mL following the removal of excess NaF from the hot solution by filtration. This filtrate was combined with 400 mL of water to which 1 mL of 4.0 M NaOH had been added to ensure that all of the complex would be present in the μ-oxo–μ-fluoro form. Precipitation of the product was induced by the addition of solid $LiClO_4$, after which digestion of the stirred solid was allowed to proceed for 1 h at 5 °C. The dark brown microcrystalline product was collected by filtration, washed with triply distilled water, and air-dried (1.05 g, 60%). Anal. Calcd for $Cr_2C_{36}H_{38}N_8Cl_3FO_{14}$: Cr, 10.04; C, 41.73; H, 3.70; N, 10.81; F, 1.83. Found: Cr, 9.98; C, 42.01; H, 3.82; N, 10.88; F, 1.48. UV–vis (CH_3CN; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 256 (21 500), 298 (4650), 330 (4620), 386 (2940), 418 (2520). IR (KBr pellet; cm^{-1}): 3422 vs, 1609 s, 1484 w, 1438 m, 1400 w, 1290 w, 1158 m, 1090 vs, 1031 m, 906 w, 881 m, 766 s, 736 w, 723 w, 669 m, 655 m, 623 s.

$[(tmpa)Cr(OH)(F)Cr(tmpa)](ClO_4)_4$ was prepared as above, except that a crude product from evaporation of the reaction mixture in CH_3CN was recrystallized quickly by addition of $LiClO_4$ to a *neutral* aqueous solution. The red-brown solid was filtered off and air-dried. Anal. Calcd for $Cr_2C_{36}H_{37}N_8Cl_4FO_{17}$: Cr, 9.30; C, 38.66; H, 3.33; N, 10.02. Found: Cr, 9.28; C, 38.66; H, 3.60; N, 9.79. UV–vis (H_2O, 0.01 M HBr; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 261 (15 800), 387 (222), 537 (281).

Results and Discussion

Fluoride ion combines readily with the tmpa chromium(III) diol in refluxing acetonitrile according to eq 2, leaving no trace of either unreacted starting material or the expected product,

$$[(tmpa)Cr(OH)_2Cr(tmpa)]^{4+} + F^- \rightarrow [(tmpa)Cr(O)(F)Cr(tmpa)]^{3+} + H_2O \quad (2)$$

$[Cr(tmpa)F]_2O^{2+}$. The corresponding μ-fluoro–μ-hydroxo complex is easily isolated following the protonation of $[(tmpa)Cr(O)(F)Cr(tmpa)]^{3+}$ by water. An attempt to grow large crystals of $[(tmpa)Cr(OH)(F)Cr(tmpa)](ClO_4)_4$ by digestion in 0.02 M $HClO_4$ for 6 h at 5 °C resulted in the recovery of a decomposition product, $[Cr(tmpa)(OH)]_2(ClO_4)_4 \cdot 4H_2O$, identified from its spectroscopic and acid–base properties.[3] In a similar fashion, $[(tmpa)Cr(O)(F)Cr(tmpa)]^{3+}$ is highly susceptible to base-induced hydrolysis even in weakly alkaline solutions. Although detailed kinetic studies have not been performed, repetitive spectra of aqueous $[(tmpa)Cr(O)(F)Cr(tmpa)]^{3+}$ show that the intense, near-ultraviolet bands decay over a period of 2 h at ambient temperature. In contrast, $[(tmpa)Cr(O)(OH)Cr(tmpa)]^{3+}$ strongly resists base hydrolysis in the pH 8–11 interval.[3] This sensitivity to water and the tendency of both complexes to precipitate as fine powders from non-aqueous solvents has prevented us from obtaining crystals of sufficient quality for X-ray crystallographic structural analysis.

The identities of both complexes may be inferred from elemental analyses, electronic and infrared spectra, and reactivity studies of aqueous solutions. Thus, the possibility that the complex with empirical formula $Cr_2C_{36}H_{38}N_8Cl_3FO_{14}$ contains $[(H_2O)(tmpa)CrOCr(tmpa)(F)]^{3+}$ or $[(OH)(tmpa)Cr(OH)Cr(tmpa)(F)]^{3+}$ rather than $[(tmpa)Cr(O)(F)Cr(tmpa)]^{3+}$ cations is ruled out by the failure of this material to exhibit neutralization of the putative H_2O or μ-OH$^-$ ligands in strongly alkaline media, affording a diperchlorate salt. Furthermore, the rapid and reversible protonation of this complex to $[(tmpa)Cr(OH)(F)Cr(tmpa)]^{4+}$, monitored spectrophotometrically in aqueous solution, is most easily understood in terms of a bridging hydroxide ligand with pK_a near 7, analogous to those of $[Cr(tmpa)(OH)]_2^{4+}$ (pK_{a1} = 7.50, pK_{a2} = 12.4; 25 °C, I = 0.1 M).[3] The facile conversion of the complex with empirical formula $Cr_2C_{36}H_{37}N_8Cl_4FO_{17}$ to $[(Cr(tmpa)(OH)]_2(ClO_4)_4 \cdot 4H_2O$ in acidic solution implicates a dinuclear precursor, and absorption peaks at 387 and 537 nm correspond closely in both position and intensity to the d–d bands of $[Cr(tmpa)(OH)]_2^{4+}$ at 385 (ϵ = 226 M^{-1} cm^{-1}) and 540 nm (ϵ = 262).[3] The electronic spectrum of $[(tmpa)Cr(O)(OH)Cr(tmpa)]^{3+}$ is not well-resolved, showing only a single near-ultraviolet peak at 370 nm (ϵ = 900 M^{-1} cm^{-1}) superimposed on a rapidly rising absorption envelope.[3] A striking similarity may be noted, however, between the spectra of $[(tmpa)Cr(O)(F)Cr(tmpa)]^{3+}$ and $[(tmpa)Cr(O)(CH_3CO_2)Cr(tmpa)]^{3+}$, for which

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(1) Gafford, B. G.; Holwerda, R. A.; Schugar, H. J.; Potenza, J. A. *Inorg. Chem.* **1988**, *27*, 1126.
(2) Gafford, B. G.; O'Rear, C.; Zhang, J. H.; O'Connor, C. J.; Holwerda, R. A. *Inorg. Chem.* **1989**, *28*, 1720.
(3) Gafford, B. G.; Holwerda, R. A. *Inorg. Chem.* **1989**, *28*, 60.
(4) Holwerda, R. A.; Petersen, J. S. *Inorg. Chem.* **1980**, *19*, 1775.
(5) Johnston, R. F.; Holwerda, R. A. *Inorg. Chem.* **1985**, *24*, 3176.

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the Cr–O–Cr bond angle imposed by the carboxylate bridging group is 131.9°.[6] Thus, the latter dimer is characterized by closely spaced bands at 419 (ϵ = 1780 M^{-1} cm^{-1}), 388 (sh, ϵ = 2070), 372 (ϵ = 2890) and 336 nm (ϵ = 4090), assigned to transitions from metal-centered, nonbonding molecular orbitals to π^* levels resulting from Cr(dπ)–O(pπ)–Cr(dπ) orbital overlaps.[6]

The X-ray crystal structures of $[Cr(tmpa)(OH)]_2^{4+}$ and $[Cr(tmpa)(NCS)]_2O^{2+}$ reveal that one bridging oxygen atom undergoes a 90° migration when the former is converted to the latter in the presence of thiocyanate ion.[1-3]. Attack by the first thiocyanate incoming group is thought to generate an intermediate of the type $[(OH)(tmpa)Cr(OH)Cr(tmpa)(NCS)]^{3+}$, which subsequently undergoes oxo migration prior to or concurrent with addition of the second NCS^- ligand. The apparent preference of μ-F^- bridging over the uptake of two nonbridging F^- ligands is reasonable on consideration of the well-documented thermodynamic stability of fluoride-bridged Cr(III) coordination polymers,[7-9] the relative inertness of the Cr(III)–F^- linkage toward aquation,[10-12] and the fact that F^- is isoelectronic with OH^-.

A chromatographic experiment was carried out to ascertain whether dimer cleavage occurs in the course of the $[(tmpa)Cr(OH)(F)Cr(tmpa)]^{4+}$ acid hydrolysis reaction. A 25-mL volumetric flask containing 0.042 mmol of $[(tmpa)Cr(OH)(F)Cr(tmpa)]^{4+}$ in 0.1 M HBr was thermostated at 40.0 °C, and an identical reaction mixture was monitored spectrophotometrically. The original absorbance maxima at 387 and 537 nm shift to 384 and 527 nm with little change in ϵ_{max} over the course of the acid hydrolysis reaction. After a 20-min incubation period, the entire 25-mL reaction mixture was adsorbed onto a cation-exchange column equilibrated with 1 mM HBr at 5 °C. A pale pink fraction emerged from the top purple band upon elution with 0.1 M NaBr/1 mM HBr. Subsequent elution with 0.2, 0.5, and 1.0 M NaBr/1 mM HBr resolved leading pink, red, light purple, and dark purple components, listed consecutively. Spectra taken immediately following quantitative fraction collection revealed that the third (15% of eluted Cr) and fourth (64% of eluted Cr) components are $[(tmpa)Cr(OH)(F)Cr(tmpa)]^{4+}$ and $[(tmpa)Cr(OH)_2Cr(tmpa)]^{4+}$, respectively. The elution behaviors of the first (7% of eluted Cr; λ_{max} = 526 and 375 nm) and second (14% of eluted Cr; λ_{max} = 519 and 390 nm) fractions are consistent with ionic charges of 2+ and 3+, respectively; total chromium recovery from the cation-exchange column was 97%. Since solid complexes could not be isolated from the first two fractions, they are tentatively assigned to $[Cr(tmpa)(H_2O)F]^{2+}$ and a mixture of $[Cr(tmpa)(H_2O)_2]^{3+}$ (λ_{max} = 501 and 375 nm)[3] with $[Cr(tmpa)(H_2O)(HF)]^{3+}$. The major $[(tmpa)Cr(OH)(F)Cr(tmpa)]^{4+}$ acid hydrolysis pathway clearly leads to a dinuclear product, $[Cr(tmpa)(OH)]_2^{4+}$, although some dimer to monomer conversion was observed.

A comparison of the electrochemical behaviors of $[(tmpa)Cr(O)(OH)Cr(tmpa)]^{3+}$ and $[(tmpa)Cr(O)(F)Cr(tmpa)]^{3+}$ is instructive and offers a distinctive point of contrast with the $[Cr(tmpa)L]_2O^{2+}$ class of dimers. In CH_3CN (25 °C, 0.1 M $N(n\text{-}Bu)_4ClO_4$, with a Pt working electrode), $[(tmpa)Cr(O)(OH)Cr(tmpa)]^{3+}$ exhibits two irreversible oxidation waves within the 0 to +2.0 V potential window (E_{pa} = 0.93 and 1.28 V vs SHE; 50 mV/s sweep rate). When the switching potential was changed to 1.1 V, a quasi-reversible wave with $E_{1/2}$ = 0.62 ± 0.01 V (25–300 mV/s sweep rate) and very large peak-to-peak separation of 590 mV (50 mV/s sweep rate) emerged. Under the same conditions, $[(tmpa)Cr(O)(F)Cr(tmpa)]^{3+}$ undergoes a more reversible oxidation with $E_{1/2}$ = 0.74 ± 0.01 V vs SHE (ΔE_p = 95 mV at 50 mV/s; i_{pa}/i_{pc} = 0.9) when both short (0–0.8 V) and long (0–1.5 V) scanning intervals are employed. In addition, an irreversible anodic wave with E_{pa} = 1.27 V was found. For comparison, we note that the cyclic voltammograms of $[Cr(tmpa)L]_2O^{2+}$ dimers typically feature a single, fully reversible oxidation wave with more positive $E_{1/2}$ in the range 0.96–1.17 V vs SHE.[2]

Although $[(tmpa)Cr(OH)_2Cr(tmpa)]^{4+}$ is not reactive toward electrochemical oxidation in either CH_3CN or H_2O, both its first and second ionization products gave distinct anodic waves in aqueous solutions. The cyclic voltammogram of aqueous $[(tmpa)Cr(O)(OH)Cr(tmpa)]^{3+}$ (25 °C, pH 10.0 (5 mM carbonate buffer), 0.1 M $NaNO_3$, carbon paste working electrode) features a quasi-reversible oxidation with $E_{1/2}$ = 0.71 ± 0.01 V vs SHE (50–300 mV/s sweep rate; ΔE_p = 200 mV at 50 mV/s; i_{pa}/i_{pc} = 0.9). No new anodic or cathodic features were observed in steady-state voltammograms. Only an irreversible anodic peak with E_{pa} = 0.63 V vs SHE was found in the cyclic voltammogram of a pH 12.82 solution (0.1 M NaOH/0.1 M $NaNO_3$) in which $[(tmpa)Cr(O)_2Cr(tmpa)]^{2+}$ was the major dimeric species present. Previously reported studies showed that this dioxo-bridged dimer undergoes base hydrolysis through parallel pathways characterized by both zero-order and first-order hydroxide dependences.[3]

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[6] Gafford, B. G.; Marsh, R. E.; Schaefer, W. P.; Zhang, J. H.; O'Connor, C. J.; Holwerda, R. A. *Inorg. Chem.*, in press.

[7] Schwartz, M.; Hatfield, W. E.; Joesten, M. D.; Hanack, M.; Datz, A. *Inorg. Chem.* **1985**, *24*, 4198.

[8] Knoke, G.; Babel, D. *Z. Naturforsch., B: Anorg Chem., Org. Chem.* **1975**, *30B*, 454.

[9] Holler, H.; Kurtz, W.; Babel, D.; Knop, W. *Z. Naturforsch., B: Anorg Chem., Org. Chem.* **1982**, *37B*, 54.

[10] Swaddle, T. W.; King, E. L. *Inorg. Chem.* **1965**, *4*, 532.

[11] Vaughn, J. W.; King, E. L. *Inorg. Chem.* **1985**, *24*, 4221.

[12] Herbert, B.; Reinhard, D.; Saliby, M. J.; Sheridan, P. S. *Inorg. Chem.* **1987**, *26*, 4024.