Inorg. Chem. **1993,** *32,* 3196–3198

Kinetic Studies of Chloride Displacement from $[Cr(tmpa)Cl]_2O^{2+}$ in Aqueous Solution

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Received February 11, 1993

Introduction

The displacement of water from dihydroxo-bridged chromium(III) dimers affords a convenient synthetic route to $[LN_4CrON_4L]^{2+}$ dimers, where N_4 designates an aromatic amine or imine nitrogen-donor set and L^- is a pseudohalide or chloride ligand.[1-3] Our previous mechanistic investigations of oxo-bridged dimers with N-donor ligands focused on the base hydrolyses of $[(tmpa)Cr(O)_2Cr(tmpa)]^{2+}$ [4] and $[Cr(tmpa)L]_2O^{2+}$ [5] (tmpa = tris(2-pyridylmethyl)amine; L^- = NCS^-, NCO^-, CN^-) to yield a monomeric product, $[Cr(tmpa)(OH)_2]^+$, and the exceptional lability of NH_3 in the basic rhodo cation, $[Cr(NH_3)_5]_2O^{4+}$.[6] In addition, we recently described aliphatic and aromatic substituent effects on the bridging carboxylate hydrolysis rate in dinuclear complexes of the type $[(tmpa)Cr(\mu\text{-}RCO_2)Cr(tmpa)]^{3+}$.[7]

Of the $[Cr(tmpa)L]_2O^{2+}$ dimers studied to date, $[Cr(tmpa)Cl]_2O^{2+}$ is by far the most labile, readily losing chloride to form $[Cr(tmpa)(OH)]_2^{4+}$ in aqueous solution. We report here a kinetic investigation of this reaction (eq 1) and the analogous aquation of $[(tmpa)Cr(O)(F)Cr(tmpa)]^{3+}$ [8] (eq 2).

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

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

Experimental Section

Reagent grade chemicals and triply-distilled water were used to prepare solutions for kinetic runs. The complexes $[Cr(tmpa)Cl]_2O(ClO_4)_2\cdot 2H_2O$ and $[(tmpa)Cr(O)(F)Cr(tmpa)](ClO_4)_3\cdot H_2O$ were available from laboratory stock.[1,8] Ionic strength was maintained at 0.1 M for solutions buffered in the pH ranges 5.5–6.5 (0.10 M NaOH adjusted to the desired pH with MES), 6.5–7.5 (0.10 M NaOH adjusted to the desired pH with BES), and 7.5–8.5 (5 mM $NaHCO_3$ plus 0.10 M $NaNO_3$ adjusted to the desired pH with NaOH). Dilute $HClO_4$ was mixed with 0.10 M $NaNO_3$ to prepare solutions having a pH below 5.5. Hydrogen ion concentrations were calculated from pH readings (Brinkmann pH-104 meter) corrected for the activity of the medium.[9] Aquation reactions were monitored on Shimadzu UV-260 and Perkin-Elmer Lambda 5 spectrophotometers (360 nm), with cell compartments thermostated at 25.0 ± 0.1 °C. Kinetic runs were initiated by rapidly mixing 0.1 mL of 4 mM dimer (CH_3CN solution) with 2.9 mL of the aqueous solution in a 1-cm cell. Pseudo-first-order rate constants of fast (k_{fast}) and slow (k_{slow}) components in the consecutive first-order $[Cr(tmpa)Cl]_2O^{2+}$ aquation reaction were obtained by fitting absorbance–time traces to the appropriate integrated rate expression.[4] Simple first-order observed rate constants were derived from the least-squares slopes of $\ln(A_t - A_\infty)$ vs time plots that were linear over ≥90% of the total absorbance change. Reported values are the mean of at least two determinations. Aquation product mixtures were subjected to cation-exchange chromatography at 5 °C on SP Sephadex C-25-120 resin, with $LiClO_4$ eluants.

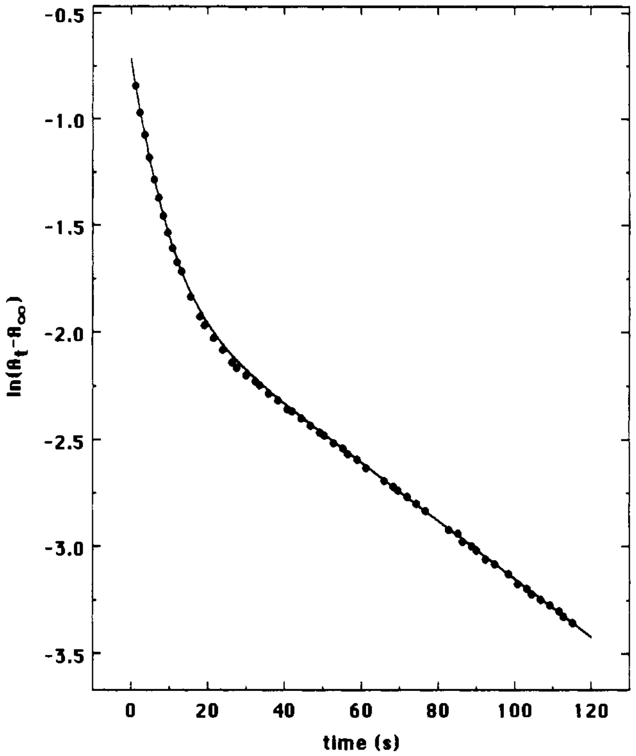

Figure 1. Typical biphasic kinetic trace for the aquation of $[Cr(tmpa)Cl]_2O^{2+}$ (0.133 mM) monitored at 360 nm in a 1-cm path length cell (25.0 °C, pH 5.48, I = 0.1 M). The solid curve is the least-squares fit to the integrated rate expression for consecutive first-order reactions.

Results and Discussion

Biphasic traces were observed for the aquation of $[Cr(tmpa)Cl]_2O^{2+}$ at pH's below 7.0, while straightforward first-order decay curves pertain in the pH range 7.0–8.5. Biphasic $\ln(A_t - A_\infty)$ plots were successfully fit to the integrated rate expression for consecutive first-order reactions (Figure 1). The first phase accounted for approximately 90% of the 360-nm absorbance change at pH 5.48. Kinetic measurements were not made on solutions having a pH greater than 8.5 in view of the competition between reaction 1 and base hydrolysis accompanied by dimer cleavage. Cation-exchange chromatography and product spectra showed that $[Cr(tmpa)(OH)]_2^{4+}$ is the sole Cr product when $[Cr(tmpa)Cl]_2O^{2+}$ and $[(tmpa)Cr(O)(F)Cr(tmpa)]^{3+}$ aquate at pH 7.0. The finding of $[(tmpa)Cr(O)(OH)Cr(tmpa)]^{3+}$ in alkaline product mixtures is not surprising, considering that $[Cr(tmpa)(OH)]_2^{4+}$ ionizes with a pK_a of 7.50.[4] Unfortunately, the intermediate generated in the biphasic aquation reaction is not sufficiently long-lived to be isolated and characterized subsequent to cation-exchange chromatography, even at 5 °C.

Observed rate constants for the aquation of $[Cr(tmpa)Cl]_2O^{2+}$ are presented in Table I. The rate constant characteristic of the fast phase (0.18 ± 0.03 s^{-1}) is essentially pH-independent over the narrow interval (pH 4.16–5.48) in which it could be quantitatively evaluated. In contrast, a k_{slow} vs pH plot is sigmoidal (Figure 2), following the pattern expected from a mechanism in which both protonated and singly-ionized reactant species contribute to the second phase of the aquation process. We propose the pathway of eq 3 to account for these findings. On this basis, a nonlinear least-squares fit of k_{slow}–$[H^+]$ points to eq 4 was performed, yielding the following parameters: pK_a = 6.43

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(1) Gafford, B. G.; O'Rear, C. J.; Zhang, J. H.; O'Connor, C. J.; Holwerda, R. A. *Inorg. Chem.* **1989**, *28*, 1720.
(2) Holwerda, R. A.; Tekut, T. F.; Gafford, B. G.; Zhang, J. H.; O'Connor, C. J. *J. Chem. Soc., Dalton Trans.* **1991**, 1051.
(3) Tekut, T. F.; O'Connor, C. J.; Holwerda, R. A. *Inorg. Chem.* **1993**, *32*, 324.
(4) Gafford, B. G.; Holwerda, R. A. *Inorg. Chem.* **1989**, *28*, 60.
(5) Gafford, B. G.; Holwerda, R. A. *Inorg. Chem.* **1990**, *29*, 233.
(6) Gafford, B. G.; Holwerda, R. A. *Inorg. Chem.* **1988**, *27*, 210.
(7) Tekut, T. F.; Holwerda, R. A. Submitted for publication.
(8) Gafford, B. G.; Holwerda, R. A. *Inorg. Chem.* **1990**, *29*, 4353.
(9) Baek, H.; Holwerda, R. A. *Inorg. Chem.* **1983**, *22*, 3452.

0020-1669/93/1332-3196$04.00/0

Table I. Observed Rate Constants for the Biphasic Aquation of $[Cr(tmpa)Cl)]_2O^{2+}$ [a]

medium	pH	$10k_{fast}$, s^{-1}	10^2k_{slow}, s^{-1}
$HClO_4/NaNO_3$	4.16	1.6	0.696
	4.27	1.9	0.682
	5.16	2.1	0.834
MES/NaOH	5.48	1.6	1.39
	6.00		2.28
BES/NaOH	6.56		3.72
	7.01		5.75
	7.51		7.50
$NaHCO_3/NaNO_3$	8.31		8.01
	8.45		8.06

[a] 25.0 °C, $I = 0.1$ M. Uncertainties in k_{fast} and k_{slow} are estimated at ±10% and ±6%, respectively.

± 0.05, $k_a = (6.7 \pm 1.2) \times 10^{-3}$ s^{-1}, and $k_b = (8.11 \pm 0.15) \times 10^{-2}$ s^{-1} (25.0 °C, $I = 0.1$ M).

$$[Cl(tmpa)CrOCr(tmpa)Cl]^{2+} + H_2O \xrightarrow{k_{fast}} [Cl(tmpa)CrOCr(tmpa)(H_2O)]^{3+} + Cl^-$$

$$[Cl(tmpa)CrOCr(tmpa)(H_2O)]^{3+} \overset{K_a}{\rightleftarrows} [Cl(tmpa)CrOCr(tmpa)(OH)]^{2+} + H^+$$

$$H_2O + [Cl(tmpa)CrOCr(tmpa)(H_2O)]^{3+} \xrightarrow{k_a} [(H_2O)(tmpa)CrOCr(tmpa)(H_2O)]^{4+} + Cl^- \quad (3)$$

$$H_2O + [Cl(tmpa)CrOCr(tmpa)(OH)]^{2+} \xrightarrow{k_b} [(H_2O)(tmpa)CrOCr(tmpa)(OH)]^{3+} + Cl^-$$

$$[(H_2O)(tmpa)CrOCr(tmpa)(H_2O)]^{4+} \xrightarrow{fast} [(tmpa)Cr(OH)_2Cr(tmpa)]^{4+} + H_2O$$

$$[(H_2O)(tmpa)CrOCr(tmpa)(OH)]^{3+} \xrightarrow{fast} [(tmpa)Cr(O)(OH)Cr(tmpa)]^{3+} + H_2O$$

$$k_{slow} = \frac{k_a[H^+] + k_bK_a}{[H^+] + K_a} \quad (4)$$

The formulation of $[Cl(tmpa)CrOCr(tmpa)(H_2O)]^{3+}$ as the aquation intermediate is supported by the pH dependence of k_{slow}, the absence of a pH dependence for k_{fast}, and the proximity of our kinetically-determined pK_a value to those of related cations.[10] An intermediate similar to that proposed here, $[Cr(tmpa)(OH)]_2O^{2+}$, was isolated by cation-exchange chromatography from the base hydrolyses of both $[(tmpa)Cr(O)_2Cr(tmpa)]^{2+}$ and $[Cr(tmpa)(NCS)]_2O^{2+}$.[4,5] Acidification of $[Cr(tmpa)(OH)]_2O^{2+}$ gives $[Cr(tmpa)(OH)]_2^{4+}$ in quantitative yield within the mixing time,[4] supporting the proposed fast processes which follow the k_a and k_b aquation steps. The rate constants k_{fast}, k_a, and k_b may be correlated with those for the displacement of chloride ion from the cis isomers of $[Cr(en)_2Cl_2]^+$ (3.3×10^{-4} s^{-1}),[11] $[Cr(en)_2(H_2O)Cl]^{2+}$ (2.4×10^{-5} s^{-1}),[12] and $[Cr(en)_2(OH)Cl]^+$ (3.3×10^{-3} s^{-1})[13] at 25 °C, respectively. When a comparison is made of the rate parameters for the aquation of two chloride ligands from mononuclear and dinuclear chromium(III) complexes, it should be noted that the charge per chromium ratios of corresponding reactant species are identical (1+ per Cr atom) except in the case of $[Cl(tmpa)CrOCr(tmpa)(H_2O)]^{3+}$ (1.5+ per Cr atom vs 2+ per Cr atom in $[Cr(en)_2(H_2O)Cl]^{2+}$). Chloride aquation rates in the $[Cr(tmpa)Cl]_2O^{2+}$ system are consistently higher than the corresponding *cis*-$[Cr(en)_2Cl_2]^+$ rates by more than 2 orders of magnitude. The ratios k_{fast}/k_a (13) and k_b/k_a (12) may be compared with *cis*-$[Cr(en)_2Cl_2]^+$ vs *cis*-$[Cr(en)_2(H_2O)Cl]^{2+}$ (7) and *cis*-$[Cr(en)_2(OH)Cl]^+$ vs *cis*-$[Cr(en)_2(H_2O)Cl]^{2+}$ (1.4×10^2) reactivity quotients, respectively.[14] Relative aquation rates of the first and second chloride ions are little different in the dinuclear and mononuclear systems, while rate sensitivity to ionization of an aqua ligand is much smaller in the former. Electrostatic promotion of anion aquation by charge reduction within a cationic reactant is expected to be smaller when the leaving group is not bound to the metal center whose charge is attenuated. In this regard, we note that the aquation rate of $[Cr(H_2O)_5Cl]^{2+}$ is strongly enhanced with decreasing $[H^+]$.[15] There is no basis for concluding that a modest k_b/k_a ratio reflects intracomplex nucleophilic attack by ligated OH^- on Cl^- in the intermediate, $[Cl(tmpa)CrOCr(tmpa)(OH)]^{2+}$.

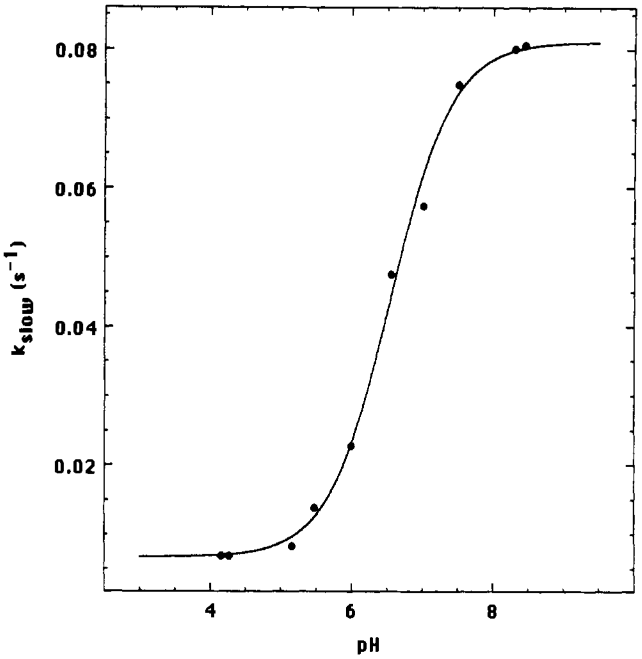

Figure 2. pH dependence of k_{slow} for the aquation of $[Cr(tmpa)Cl]_2O^{2+}$ (25.0 °C, $I = 0.1$ M). The solid curve is the nonlinear least-squares fit of rate data from Table I to eq 4.

The interpretation of chloride aquation rates is complicated by the need to take cation charge, the Cr–Cl bond length, steric effects, and the influence of Cr–Cl π-bonding into account.[16,17] In kinetic studies of chloride-assisted cleavage of $[(H_2O)(en)_2Cr]_2OH^{5+}$ in 12 M HCl, Springborg and co-workers noted that the displacement of water by chloride is approximately 10 times faster in the dinuclear diaqua species than in *cis*-

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[10] For example, the pK_a values of *cis*-$[Cr(en)_2(OH)(H_2O)]^{2+}$ (7.17 at 25 °C, $I = 1.0$ M) and $[(OH)(en)_2Cr(\mu\text{-}OH)Cr(en)_2(H_2O)]^{4+}$ (7.94 at 0.8 °C, $I = 1.0$ M) may be cited: Couldwell, M. C.; House, D. A.; Powell, H. K. J. *Aust. J. Chem.* **1973**, *26*, 425. Woldbye, F. *Acta Chem. Scand.* **1958**, *12*, 1079. Springborg, J.; Toftlund, H. *Acta Chem. Scand., Ser. A* **1976**, *30*, 171.

[11] Selbin, J.; Bailar, J. C. *J. Am. Chem. Soc.* **1957**, *79*, 4285.

[12] Chang, J. C. *Inorg. Chem.* **1982**, *21*, 837.

[13] Olson, D. C.; Garner, C. S. *Inorg. Chem.* **1963**, *2*, 558.

[14] When rate parameters for dichloro and monochloro species are compared, the k_{fast}/k_a ratios must be divided by a statistical factor of 2 to account for the fact that either of two equivalent chloride ligands may aquate in the former.

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

[16] Lay, P. *Inorg. Chem.* **1987**, *26*, 2144.

[17] Lawrance, G. A.; Schneider, K.; van Eldik, R. *Inorg. Chem.* **1984**, *23*, 3922.

$[Cr(en)_2(H_2O)_2]^{3+}$.[18] This reactivity enhancement was attributed to a cis-labilizing influence of the hydroxo bridge.[18,19] Although the crystal structure of $[Cr(tmpa)(NCS)]_2O^{2+}$ reveals a much larger trans than cis influence of the bridging oxo group on Cr–N bond lengths,[20] we are exploring the hypothesis that a μ-O^{2-} cis-labilizing effect contributes to the substitutional reactivity of $[Cr(tmpa)L]_2O^{2+}$ dimers. In this regard, we note that both cis thiocyanate ligands are displaced prior to oxo-bridge cleavage in the base hydrolysis reaction of $[Cr(tmpa)(NCS)]_2O^{2+}$.[5]

For the purpose of comparison, a brief kinetic investigation of $[(tmpa)Cr(O)(F)Cr(tmpa)]^{3+}$ hydrolysis was carried out under the same conditions as the $[Cr(tmpa)Cl]_2O^{2+}$ aquation studies. A rate constant of $(4.0 \pm 0.4) \times 10^{-3}$ s^{-1} pertains over the narrow pH interval of 6.90–7.59 in which $[(tmpa)Cr(O)(F)Cr(tmpa)]^{3+}$ is predominantly unprotonated ($pK_a = 6.25$)[3] and not susceptible to base-assisted hydrolysis. Thus, the loss of a nonbridging Cl^- ligand from $[Cr(tmpa)Cl]_2O^{2+}$ is faster than aquation of the bridging F^- substituent in $[(tmpa)Cr(O)(F)Cr(tmpa)]^{3+}$ by 1 order of magnitude.

Acknowledgment. We thank the Welch Foundation for support of this research (Grant D-735).

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(18) Kaas, K.; Nielsen, B.; Springborg, J. *Acta Chem. Scand.* **1989**, *43*, 233.
(19) Springborg, J. *Adv. Inorg. Chem.* **1988**, *32*, 55.
(20) Gafford, B. G.; Holwerda, R. A.; Schugar, H. J.; Potenza, J. A. *Inorg. Chem.* **1988**, *27*, 1126.