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Preparation, Characterization, Substitution, and Redox Studies of Bidentate Thiol, Alkoxy, and Related Ligands on Aquochromium(III) Centers

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Monodentate alcohol, thiolate, or carboxylate Cr(III) products of inner-sphere redox reactions undergo hydrolysis or chelate ring closure, depending on conditions. The spontaneous in situ carboxylate ring closures appear anomalously fast and subject to acid catalysis, e.g., $d \ln [Cr^{III}]/dt = (5.9 + 13[H^+]) \times 10^{-3}$ (M and s) with mercaptoacetate. Excess Cr(II) appears to catalyze these in situ closures rapidly. Equilibrium constants and rates pertaining to cleavage and re-formation of the chromium(III)–sulfur bond, $Cr(H_2O)_4(chelate)^{n+} + H_3O^+ = Cr(H_2O)_5(chelate{-}H)^{(n+1)+}$, were determined with chromatographically isolated 2-mercaptoethylamine, mercaptoacetate, and 2-mercaptopropionate chelates. Predominantly featured in the cleavage is a first-order acid pathway ($10^6 k_a$ = 7.6, 70, and 77 $M^{-2} s^{-1}$, respectively) which probably involves protonation of the coordinated thiolate function. Additional evidence is presented in support of a real acid-independent cleavage pathway ($10^6 k_0$ = 1.9, 0.8 $M^{-1} s^{-1}$) for the first two ligands. Consideration is given to two mechanistic possibilities for this path, one involving intramolecular protonation of the coordinated sulfur and the other direct cleavage. The rate of chromium(III)–sulfur bond re-formation along the microscopic reverse of the latter mechanism, seemingly the only acceptable one for certain systems, is considerably more rapid than "normal" and consistent with significant bond making to Cr(III). Less extensive studies of related alcohol cleavages are also reported.

Introduction

The inner-sphere reactions described in the preceding article[1] produced chromium(III) complexes that were subject to subsequent change in the first coordination sphere. In several instances these changes appear to be redox catalyzed by chromium(II) whereas in others direct substitution processes are evident. For both categories the observations illuminate differences that can arise with chelate ligands compared to monodentate ligands. In this extension of a preliminary report[2] on one such system, we consider these complexes and their substitution processes in detail, making comparisons where possible with related studies[3,4] that have recently appeared.

Experimental Section

Materials. A representative preparation involved anaerobic reaction at $[H^+] = (5\text{–}20) \times 10^{-3}$ M of the cobalt complex at $(1\text{–}5) \times 10^{-3}$ M with equimolar (or slight excess) $Cr(H_2O)_6^{2+}$,[1] exposure to air, and charging onto a (20–30) × 1.2 cm column of Dowex or Bio-Rad 50W-X2, 200–400 mesh resin in the sodium or lithium form. Appropriate $HClO_4$–$LiClO_4$ (or $NaClO_4$) solutions eluted the dominant chromium(III) species with typically 90–98% recovery based on the initial amount of cobalt(III) complex. Following chromate analyses and spectral measurements, the pH and ionic strength of eluent solutions were adjusted for subsequent kinetic studies. Alternatively, equilibration of these solutions over 3–7 days, depending on the species and acidity, yielded mixtures of monodentate and bidentate complexes which could be separated by ion exchange.

Kinetic Determinations. Absorbancy data obtained on the Durrum or Cary instruments under pseudo-first-order, irreversible conditions yielded linear $\ln (A_t - A_\infty)$ vs. t plots over at least 75–90% reaction. Where it was desired to determine the forward and reverse rate constants for a reversible reaction, e.g.

$$Cr(H_2O)_4(chelate)^{n+} + H^+ \underset{k_r}{\overset{k_f}{\rightleftarrows}} Cr(H_2O)_5(chelate\ H)^{(n+1)+}$$

$$K_{eq} = k_f/k_r$$

With hydrogen ion in large excess, the appropriate equation[5,6] is

$$\log (A_t - A_{eq}) = -\frac{k_{obsd}t}{2.303} + \log (A_0 - A_{eq})$$

where $k_{obsd} = k_f + k_r$, $k_f = k_{obsd}/(1 + 1/K_{eq}[H^+])$, and $k_r = k_{obsd}/(1 + K_{eq}[H^+])$. Subsequent absorbancy changes due to the slower, irreversible hydrolyses of the monodentate complexes

$$Cr(H_2O)_5(chelate{-}H)^{(n+1)+} + H_3O^+ \xrightarrow{k_{hyd}} Cr(H_2O)_6^{3+} + chelate{-}H_2^{(n-1)+}$$

were approximately corrected for as described under Results to obtain A_{eq}.

Since this research was concluded, a detailed investigation of a kinetically analogous system has been reported.[5b] The less comprehensive procedures employed here should not result in significant kinetic error since, except in one experiment, the equilibrations were initiated with chromatographically isolated *chelate* complexes and $k_{obsd} \gtrsim 10k_{hyd}$. Ion-exchange separation or A_{eq} estimations of mixtures after $\gtrsim$5 half-lives (based on k_{obsd}) yielded estimates of K_{eq} which, due to the subsequent hydrolysis reaction, are steady-state rather than true equilibrium values. As found elsewhere,[5b] the discrepancies should not be large since $k_f + k_r >> k_{hyd}$ and $k_f >> k_{hyd}[H^+]$ for these systems. The sensitivity of our kinetic results to variations in K_{eq} is illustrated for one example below. Rate constants reported herein at 25 °C, with standard deviations from least-squares kinetic plots, are in appropriate units of M and s at I = 1.00 M ($LiClO_4$), unless stated otherwise.

Results

Characterization of the Complexes. The formulation of the species listed in Table I is based on the identity of the bridging ligand captured in the chromium(III) product of the redox reaction, the charge as ascertained by calibrated ion-exchange elution, and the spectral characteristics. Of note are (a) the higher extinction coefficients characteristic of bidentate vs. monodentate ligation, (b) the high-intensity ultraviolet transition (at higher energies than with the more oxidizing cobalt(III) centers[1]) which arises whenever divalent sulfur is coordinated and which we attribute, along with others,[3] to a sulfur-to-metal charge-transfer transition, and (c) the marked similarity between analogous thiolate and alcoholate complexes in the energies of their d–d transitions.

Our spectral results are in agreement with those available elsewhere[3a,4,7–11a] with two exceptions. First, observations with $Cr(H_2O)_4(OOCCH_2O)^+$ and $Cr(H_2O)_4(OOCCH(CH_3)O)^+$ at pH $\gtrsim$2.8, where the complexes elute as 1+ ions, differ from those reported at an unspecified acidity.[7] The close spectral correspondence between the two ions and, in the d–d energetics, with their thiolate analogues (as with related cobalt(III) complexes[1]) supports the data reported here. Second, our extinction coefficients for $Cr(H_2O)_5SCH_2CH_2NH_3^{3+}$ are nonuniformly lower than those reported under colder, less acidic elution conditions.[3a] Our A_{437}/A_{580} ratio of 1.56

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Table I. Spectral Parameters of Various Chromium(III) Complexes[a]

Entry	Species	λ_1 (ϵ)	λ_2 (ϵ)	λ_3 (ϵ)
1	$Cr(H_2O)_4(OOCCH_2S)^+$	548 (68.3)	437 (53.4)	264 (5070)
2	$Cr(H_2O)_5(OOCCH_2SH)^{2+}$	568 (26.0)	411 (25.1)	...
3	$Cr(H_2O)_4(OOCCH_2O)^+$	548 (32.5)[b]	436 (38.5)[b]	...
4	$Cr(H_2O)_5(OOCCH_2OH)^{2+}$	568 (24.5)	411 (30.5)	...
5	$Cr(H_2O)_4(OOCCH(CH_3)S)^+$	545 (71.2)	440 (52.2)	265 (5050)
6	$Cr(H_2O)_5(OOCCH(CH_3)SH)^{2+}$	568 (25.0)	411 (24.3)	...
7	$Cr(H_2O)_4(OOCCH(CH_3)O)^+$	548 (31.0)[b]	437 (38.0)[b]	...
8	$Cr(H_2O)_5(OOCCH(CH_3)OH)^{2+}$	568 (26.8)	413 (33.2)	...
9	$Cr(H_2O)_4(SCH_2CH_2NH_2)^{2+}$	518 (69.3)	440 sh (46.9)	266 (5680)
10	$Cr(H_2O)_5(SCH_2CH_2NH_3)^{3+}$	580 (21.6)[b]	437 (33.8)[b]	273 (4640)[b]
11	$Cr(H_2O)_5(NH_2CH_2CH_2SH)^{3+}$ [c]	550 (23.4)	398 (23.8)	...
12	$Cr(H_2O)_5(HOCH_2CH_2NH_3)^{4+}$	573 (13.9)	408 (17.5)	...
13	$Cr(H_2O)_5(OOCCH_2SCH_3)^{2+}$	567 (26.7)	412 (25.9)	...
14	$Cr(H_2O)_5(OOCCH_2NH_3)^{3+}$	572 (22.0)	412 (23.0)	...
15	$Cr(H_2O)_4(OOCCH_2NH_2)^{2+}$	555 (38.0)	420 (41.0)	...

[a] Wavelengths, λ, of maxima or shoulders (sh) are in nm; molar extinction coefficients, ϵ, given in parentheses, are in M^{-1} cm^{-1}; "..." signifies no band observed. [b] Values conflict with other reports; see text. [c] Absorption at 669 nm (ϵ 1.8) was detected as similar to that at 666 nm (ϵ 1.4) in the analogous ethylenediamine complex.[11a]

(compared to 1.77[3a]) suggests that this eluent solution (pH 1) contained some $Cr(H_2O)_6^{3+}$ which would not affect the kinetic results.

Kinetic Results with the Thiolato Ligands. The major initially isolable product of chromous reaction with equimolar or 15-fold deficient $Co(en)_2(SCH_2CH_2NH_2)^{2+}$ at pH ≤ 1.7 was the green $Cr(H_2O)_5(SCH_2CH_2NH_3)^{3+}$ ion. Its hydrolysis to $Cr(H_2O)_6^{3+}$ was followed at 273 nm in six experiments over the range $0.050 \leq [H^+] \leq 0.50$ M at $I = 1.00$ M ($NaClO_4$) and conformed to the rate law

$$-d \ln [Cr(H_2O)_5(SCH_2CH_2NH_3)^{3+}]/dt = (2.8 \pm 0.2) \times 10^{-5} + (8.0 \pm 0.7) \times 10^{-5} [H^+]$$

Reasonable agreement is found with rate coefficients of $3.2 \times 10^{-5} + 6.0 \times 10^{-5}[H^+]$ reported with $LiClO_4$.[3a]

When the pH after the redox reaction was ~4, the initial product changed to the red-pink $Cr(H_2O)_4(SCH_2CH_2NH_2)^{2+}$ which was isolated by ion exchange. This chelate equilibrated with a second monodentate complex

$$Cr(H_2O)_4(SCH_2CH_2NH_2)^{2+} + H_3O^+ \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Cr(H_2O)_5(NH_2CH_2CH_2SH)^{3+} \quad K_{eq}$$

Absorbancy corrections at 518 nm due to the slower amine hydrolysis[11b] yielded linear plots for k_{obsd} (Table II) through 2–3 half-lives and, from the initial chelate concentration and the extinction coefficients of both chromium complexes at 518 nm (69.3 and 17.1, respectively), an estimate of $K_{eq} = 5.4 \pm 1.1$ ($[H^+] = 0.050$–0.50 M). Plots of the resultant k_f vs. $[H^+]$ and k_r vs. $[H^+]^{-1}$ (Table II) were linear leading to the rate expression

$$-d [Cr(H_2O)_4(SCH_2CH_2NH_2)^{2+}]/dt = k_f [Cr(H_2O)_4(SCH_2CH_2NH_2)^{2+}] - k_r [Cr(H_2O)_5(NH_2CH_2CH_2SH)^{3+}]$$

where $k_f = \{(1.93 \pm 0.09) + (7.57 \pm 0.26)[H^+]\} \times 10^{-6}$ and $k_r = \{(0.359 \pm 0.003)[H^+]^{-1} + (1.41 \pm 0.03)\} \times 10^{-6}$. Attempts to accommodate the data within single-term, media-dependent expressions for k_f and k_r yielded less satisfactory fits and larger Harned factors than those expected for Li^+–H^+ solutions.[3b,6c]

When mercaptoacetate and 2-mercaptopropionate transferred from cobalt to chromium(III) in the presence of excess chromium(II), the first species which could be spectrally observed or isolated by ion exchange (in nearly stoichiometric amounts) were the chelated ions $Cr(H_2O)_4(SCH_2COO)^+$ and $Cr(H_2O)_4(SCH(CH_3)COO)^+$. When either redox reaction occurred with a deficiency of $Cr(H_2O)_6^{2+}$, an intermediate was detected that transformed rapidly, with small absorbancy increases, to the corresponding chelate.

Table II. Equilibration Rate Results

$[H^+]$, M	$10^6 k_{obsd}$, s^{-1}	$10^6 k_f$, s^{-1}	$10^6 k_r$, s^{-1}
$I^a = 1.00$ M; $Cr(H_2O)_4(SCH_2CH_2NH_2)^{2+} + H_3O^+ = Cr(H_2O)_5(NH_2CH_2CH_2SH)^{3+}$; $K_{eq} = 5.4 \pm 1.1$			
0.500	7.86	5.74	2.12
0.400	7.09	4.85	2.24
0.300	6.96	4.30	2.66
0.200	6.71	3.48	3.28
0.050	10.9	2.27	8.58
$I^a = 1.00$ M; $Cr(H_2O)_4(SCH(CH_3)COO)^+ + H_3O^+ = Cr(H_2O)_5(OOCCH(CH_3)SH)^{2+}$; $K_{eq} = 10.5 \pm 1.0$			
0.650	58.5	51.2	7.45
0.500	42.6	35.7	6.83
0.300	29.5	22.4	7.12
0.180	20.4	13.4	7.07
0.100	14.7	7.5	7.16
$I^a = 0.25$ M; $Cr(H_2O)_4(SCH_2COO)^+ + H_3O^+ = Cr(H_2O)_5(OOCCH_2SH)^{2+}$; $K_{eq} = 10.3 \pm 1.4$			
0.0200	12.7	2.16	10.5
0.0400	13.1	3.81	9.25
0.0600	12.2	4.64	7.52
0.100	15.3	7.74	7.61
0.100[b]	15.8	8.11	7.71
0.110	15.8	8.39	7.42
0.0100[c]	16.6	1.55	15.0
0.200[c]	23.2	15.6	7.59

[a] $HClO_4$-$LiClO_4$. [b] Determination beginning with $Cr(H_2O)_5(OOCCH_2SH)^{2+}$ alone. [c] $I \approx 0.5$ M ($HClO_4$-$NaClO_4$).

These observations and the steric improbability of chromium(II) binding mercaptide and carboxylate when both functions are coordinated to cobalt(III) support formulating the immediate redox products as $Cr(H_2O)_5(SCH_2COOH)^{2+}$ and $Cr(H_2O)_5(SCH(CH_3)COOH)^{2+}$. The failure to detect the monodentate intermediates in the presence of chromium(II) is most reasonably attributed to a catalysis of chelate ring closure by $Cr(H_2O)_6^{2+}$ analogous to that reported with the less reactive chromium(III)–maleate system.[5a] Assuming first-order dependences on $[Cr(H_2O)_6^{2+}]$ and $[Cr(H_2O)_5(SCH_2COOH)^{2+}]$, the most restrictive conditions under which ring closure was not observed (excess $[Cr^{2+}] = 7 \times 10^{-3}$ M, $t_{1/2} < 5$ ms) lead to an estimate of $k \gtrsim 2 \times 10^4$ M^{-1} s^{-1} for the catalyzed closure at $[H^+] = 0.10$ M, $I = 1.0$ M ($LiClO_4$).

Table III. Apparent Rate Dependence of Carboxylate Chelate Ring Closure[a]

$[H^+]$, M	10^3k_{obsd},[b] s^{-1}	$[H^+]$, M	10^3k_{obsd},[b] s^{-1}
$Cr(H_2O)_5(SCHCOOH)^{2+} \rightarrow Cr(H_2O)_4(SCH_2COO)^+ + H_3O^+$			
0.019	5.85	0.23	9.10
0.098	7.29	0.58	13.4
$Cr(H_2O)_5(SCH(CH_3)COOH)^{2+} \rightarrow Cr(H_2O)_4(SCH(CH_3)COO)^+ + H_3O^+$			
0.093	12.4	0.65	27.1
0.31	17.3	0.90	33.2

[a] I = 1.00 M ($LiClO_4$-$HClO_4$), 25 °C. [b] Rate of absorbancy increase at low-energy chelate maxima for in situ systems following redox process; see Results and Discussion.

With deficient $Cr(H_2O)_6^{2+}$ the spontaneous chelate closures appeared detectable as pseudo-first-order absorbancy increases at the low-energy chelate maxima with slopes that increased linearly with acidity

$$d[Cr(H_2O)_4(SCH_2COO)^+]/dt = (5.9 + 13[H^+]) \times 10^{-3}[Cr(H_2O)_5(SCH_2COOH)^{2+}]$$

$$d[Cr(H_2O)_4(SCH(CH_3)COO)^+]/dt = (9.7 + 26[H^+]) \times 10^{-3}[Cr(H_2O)_5(SCH(CH_3)COOH)^{2+}]$$

from four experiments each over $[H^+]$ = 0.020–0.58 and 0.090–0.90 M, respectively (Table III).

The ion-exchange-isolated chelates equilibrated with the monodentate carboxylate-bound ions

$$H_3O^+ + Cr(H_2O)_4(SCH(R)COO)^+ \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Cr(H_2O)_5(OOCCH(R)SH)^{2+} \quad K_{eq}$$

at rates (Table II) which, at the acidities studied, were sufficiently faster than the subsequent carboxylate hydrolyses (see ref 5b and 10 for related results) to expect only small errors in K_{eq}, k_f, and k_r.

With mercaptoacetate K_{eq} was estimated as 10.3 ± 1.4 ($[H^+]$ = 0.055–0.12 M, I = 0.25 M ($LiClO_4$)) by chromium analyses of the two fractions eluted from an exchange column charged with equilibrium mixtures generated from either complex at a given acidity. Values of A_{eq} were calculated from K_{eq}, $[H^+]$, and $[Cr^{III}]_{tot}$ for each kinetic run.

With 2-mercaptopropionate absorbance corrections due to $Cr(H_2O)_6^{3+}$ production were made, as with 2-mercaptoethylamine, by extrapolation of the gradually decreasing terminal portion of the equilibration plot. From the known acidity and molar absorptivities of the chromium complexes at 545 nm, K_{eq} was estimated as 10.5 ± 1.0 ($[H^+]$ = 0.30–1.0 M). For two kinetic runs at $[H^+]$ < 0.30 M, A_{eq} was calculated as with mercaptoacetate providing an internal overlap of the two approaches within one system.

For both systems plots for k_{obsd} were linear over at least 2 half-lives. Linear plots of the resultant k_f vs. $[H^+]$ and k_r vs. $[H^+]^{-1}$ yielded the rate expression

$$-d[Cr(H_2O)_4(SCH(R)COO)^+]/dt = k_f[Cr(H_2O)_4(SCH(R)COO)^+] - k_r[Cr(H_2O)_5(OOCCH(R)SH)^{2+}]$$

where, for R = H, $[H^+]$ = 0.020–0.11 M (six runs), and I = 0.25 M ($LiClO_4$), $k_f = \{(0.8 \pm 0.3) + (70 \pm 3)[H^+]\} \times 10^{-6}$ and $k_r = \{(0.8 \pm 0.1)[H^+]^{-1} + (68 \pm 3)\} \times 10^{-7}$.

One kinetic equilibration beginning with $Cr(H_2O)_5(OOCCH_2SH)^{2+}$ gave results in agreement with the k_f and k_r plots as did two experiments at $[H^+]$ = 0.010 and 0.20 M and $I \approx 0.5$ M ($NaClO_4$) using K_{eq} = 10.3. The sensitivity to our apparent uncertainties in estimating K_{eq} is indicated by the expressions $k_f = \{(1.0 \pm 0.2) + (73 \pm 3)[H^+]\} \times 10^{-6}$, $k_r = \{(0.8 \pm 0.1)[H^+]^{-1} + (62 \pm 3)\} \times 10^{-7}$ and $k_f = \{(0.6 \pm 0.2) + (66 \pm 3)[H^+]\} \times 10^{-6}$, $k_r = \{(0.8 \pm 0.1)[H^+]^{-1} + (62 \pm 3)\} \times 10^{-7}$ obtained using K_{eq} = 11.7 and 8.9, respectively.

With R = CH_3 and $[H^+]$ = 0.10–0.65 M (five runs), $k_f = \{(-0.7 \pm 1.4) + (77 \pm 4)[H^+]\} \times 10^{-6}$ and $k_r = \{(0.02 \pm 0.4)[H^+]^{-1} + (71 \pm 2)\} \times 10^{-7}$. The uncertainties in the first terms at these acidities leave open the possibility that such a pathway exists.

Results with Alkoxy and Related Ligands. Our principal interest in the behavior of bidentate thiol ligands resulted in less emphasis being placed on the Cr(III) substitution reactions with alkoxy and related ligands included in the redox studies[1] primarily for comparative purposes. Nevertheless, certain observations are of interest.

The generation of $Cr(H_2O)_5(HOCH_2CH_2NH_3)^{4+}$ via an alkoxide-bridged redox reaction seems assured by the nature of the cobalt reactant and the rate law.[1] Moreover, when reaction mixtures were charged onto a column, some $Cr(H_2O)_6^{3+}$ (assumed to be a hydrolysis product) was eluted with 3 M $HClO_4$ followed by a second fraction with spectral characteristics (Table I) very similar to those of $Cr(H_2O)_6^{3+}$ as expected for a 4+ monoalcohol complex. No attempt was made to convert this species to $Cr(H_2O)_4(OCH_2CH_2NH_2)^{2+}$ by equilibration at higher pH although related results suggest this to be feasible.

Definitive results with the chromium(III) glycolate and lactate complexes were limited by their rapid interconvertibility as a function of acidity which we summarize together due to qualitative similarities. Only $Cr(H_2O)_5(OOCCH(R)OH)^{2+}$ (in ~95% yield) could be isolated from reaction of $Co(en)_2(OOCCH(R)OH)^{2+}$ with an excess or deficiency of chromium(II) in 0.10 M $HClO_4$. Reaction with a deficiency of chromium(II) at an initial pH $\gtrsim$3 (rising to ~4 during reaction) yielded $Cr(H_2O)_4(OOCCH_2O)^+$ as the major (90%) product which discharged as a pink 1+ species with unacidified eluent. Reaction of $Co(en)_2(OOCCH(R)O(H))^{+(2+)}$ with excess Cr(II) at an initial acidity of (4–8) × 10^{-4} M yielded two elutable species, $Cr(H_2O)_4(OOCCH(R)O)^+$ and $Cr(H_2O)_5(OOCCH(R)OH)^{2+}$, in molar ratios of ~(2–3):1.

Adjustment of solutions containing $Cr(H_2O)_5(OOCCH(R)OH)^{2+}$ or $Cr(H_2O)_4(OOCCH(R)O)^+$ to pH ~3 or 1, respectively, resulted in their interconversion being observable within minutes. For example, when solutions of $Cr(H_2O)_4(OOCCH(R)O)^+$ at pH ≃3 are quickly brought to $[H^+]$ = 0.050–0.10 M (I = 0.25 M) on the stopped-flow or Cary instruments, linear decreases of log $(A_t - A_\infty)$ at ~437 nm with time appear to reflect a first-order conversion

$$H_2O + Cr(H_2O)_4(OOCCH(R)OH)^{2+} \xrightarrow{k} Cr(H_2O)_5(OOCCH(R)OH)^{2+}$$

with $k = 3.2 \times 10^{-2}$ s^{-1} independent of $[H^+]$ over the range described with lactate and $k = (3 \pm 1) \times 10^{-2}$ s^{-1} with glycolate.

The monoalkoxy-bonded species $Cr(H_2O)_5(HOCH(R)COOH)^{3+}$, previously argued[1] to be the initial redox product via the inverse acid path and, therefore, the major initial product at high pH, could not be identified in the times required for ion exchange. Presumably, they transform to the chelate species by pathways similar to those described above for the monothiolate analogues.

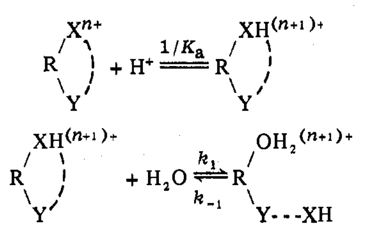
Entires 13 and 14 of Table I are for isolated products of carboxylate-bridged redox reactions. Chelated $Cr(H_2O)_4(OOCCH_2NH_2)^{2+}$ was obtained in low yield on equilibration of a solution of $Cr(H_2O)_5(OOCCH_2NH_3)^{3+}$ at pH 4.5 for several days as judged by spectral characteristics and ion-exchange behavior.

Table IV. Rate Parameters for Cr^{III}–X Bond Breaking–Making (Scheme I)

Complex	I, M	k_1/K_a, $M^{-1}\ s^{-1}$	k_1, s^{-1}	k_{-2}, s^{-1}	Ref
$(H_2O)_5Cr(SCH_2CH_2NH_3)^{3+}$	1.0[b]	8.0×10^{-5}			*a*
	1.0	6.0×10^{-5}			3a
$(H_2O)_4Cr(SCH_2CHNH_2)^{2+}$	1.0	7.6×10^{-6}		1.4×10^{-6}	*a*
$(en)_2Cr(SCH_2CH_2NH_2)^{2+}$	1.0	7.6×10^{-6}			3b
	4.0	3.4×10^{-5}			3b
$(H_2O)_4Cr(SCH_2COO)^{+}$	0.25	7.0×10^{-5}		6.8×10^{-6}	*a*
$(H_2O)_4Cr(SCH_2COO)^{+}$	2.0	$\sim 2.6 \times 10^{-4}$			*c*
$(H_2O)_4Cr(SCH(CH_3)COO)^{+}$	1.0	7.7×10^{-5}		7.1×10^{-6}	*a*
$(en)_2Cr(SCH_2COO)^{+}$	1.0	1.1×10^{-3}		(2.8×10^{-5})[d]	3b
$(en)_2Cr(SCH_2COO)^{+}$	4.0	9.3×10^{-3}	1.1×10^{-2}		3b
$(H_2O)_4Cr(HOCH(CH_3)COO)^{2+}$	0.25		(3.2×10^{-2})		*a*
$(H_2O)_4Cr(HOCH_2COO)^{2+}$	0.25		$((3 \pm 1) \times 10^{-2})$		*a*
$(H_2O)_4Cr(HOCH_2CH_2OH)^{3+}$	0.18?		4.8×10^{-3}	9.5×10^{-4}	12
$(H_2O_5Cr(SC_6H_4NH_3)^{3+}$	2.0	1.1×10^{-5}			3c
$(H_2O)_5CrN_3^{2+}$	1.0	8.2×10^{-7}		2.8×10^{-8}	3c, 13, 14
$(H_2O)_5CrF^{2+}$	1.0	1.3×10^{-8}		2.2×10^{-7}	3c, 13, 15

[a] This work. [b] $NaClO_4$; all others with $LiClO_4$. [c] Calculated from an initial rate study at $[H^+] = 0.80$ M.[4] [d] Calculated from $k_1/K_a k_{-1} = 40$.[3b] The calculation of $k_{-1} = 1 \times 10^{-5}\ s^{-1}$ [3b] was intended to be an order of magnitude estimate: E. Deutsch, personal communication.

Scheme I



Discussion

Since this research was concluded, several closely related reports have appeared.[3–5,12] For the reaction $H_3O^+ + Cr(en)_2(SCH_2COO)^+ = Cr(en)_2(H_2O)(OOCCH_2SH)^{2+}$ an estimate of $K_{eq} \approx 40$ ($I = 1.00$ M) has been made, permitting substantial conversion to the monodentate form and a different kinetic approach.[3b] Correspondence is found with our estimates of $K_{eq} \approx 10$ for the mercaptoacetate– and mercaptopropionate–aquo systems on division of their value by a statistical factor of 4. Values for the reactions $Cr(H_2O)_4(HOCH_2CH_2OH)^{3+} + H_2O = Cr(H_2O)_5(HOCH_2CH_2OH)^{3+}$ and $Cr(H_2O)_4(OOCCH_2COO)^+ + H_3O^+ = Cr(H_2O)_5(OOCCH_2COOH)^{2+}$ of $K_{eq} = 5.9$[12] and 0.13 ($I = 1.00$ M)[5b] have been reported. The smaller value in the malonate system undoubtedly reflects a pendent carboxylate function which is less basic than pendent thiolates.

Major Pathway for Chromium(III)–Chalcogen Bond Breaking and Making. All available results regarding first-order acid paths for cleavage of chromium(III)–thiolate bonds and their re-formation are in accord with Scheme I using Deutsch's designations.[3] In the scheme R = $Cr(H_2O)_4^{3+}$ or $Cr(en)_2^{3+}$, X is usually the sulfur or oxygen of a thiolate or alkoxy function, Y is another donor function, e.g., H_2O, amine, or carboxylate, and the dashed line represents a chelate link, where present. When Y is carboxylate, its protonation would be kinetically indistinguishable, but the comparisons now available with amine or H_2O donors as Y render this much less likely. Our results are summarized in Table IV with related observations.

The rates of cleavage, k_1/K_a, with mercaptoacetate are in reasonable correspondence after allowance is made for an increase in rate with ionic strength.[3b] As with R = $Cr(en)_2^{3+}$,[3b] our k_1/K_a values with carboxylate as the cochelating function are higher than with amine (but by a factor of ~10 rather than ~150). Labilizations of other ligands, most probably in cis positions for many cases, by coordinated carboxylate and other oxy anions are well-known; e.g., see ref 16–19 and 45. However, steric restrictions preclude anchimeric cis assistance by the uncoordinated oxygen[17] in chelate cleavages.

The cleavage of a $Cr(H_2O)_4^{3+}$–alcohol bond (k_1) occurs ~7 times faster with carboxylate as the cochelating function than with alcohol,[12] the former rates exceeding even the aquation rates of $Cr(H_2O)_5ClO_4^{2+}$ and $Cr(H_2O)_5(O_3SCF_3)^{2+}$.[20,21] The slightly slower loss of a thiol function (k_1) from $Cr(en)_2(HSCH_2COO)^{2+}$,[3b] which should be relatively insensitive to ionic strength differences,[12] is surprising since RSH normally is a better leaving group than ROH and the aquations of amminechromium(III) complexes are usually faster than with analogous aquochromium(III) complexes.[3b,22,23] However, chelating spectator ligands can retard aquation rates.[24]

The rates of ring cleavage of $Cr(H_2O)_4(en)^{3+}$ and aquation of $Cr(H_2O)_5(NH_2CH_2CH_2NH_3)^{4+}$ are quite similar at 60 °C[11] and, by extrapolation, even more so at 25 °C (2.1×10^{-8} vs. $2.2 \times 10^{-8}\ s^{-1}$). Thus, it is notable that chromium–sulfur bond rupture in $(H_2O)_5CrSCH_2CH_2NH_3^{3+}$ is faster than in $(H_2O)_4Cr(SCH_2CH_2NH_2)^{2+}$ along both pathways by factors of ~8 and ~17, respectively. The difference presumably arises from the nonbonded electron pair(s) on sulfur, suggesting intramolecular general-acid acceleration of aquation (by the pendent ammonium function of $(H_2O)_5Cr(SCH_2CH_2NH_3)^{3+}$) as has been proposed for the acid-independent aquation of $(H_2O)_5Cr(OOCCH_2COOH)^{2+}$.[5b]

The rate advantage along the primary pathway for chelate ring closure by RSH (k_{-1}) over monodentate ligation of $Cr(H_2O)_6^{3+}$ by HF or HN_3,[13] by factors of ~10–380 after statistical corrections of 4 and 6 are applied, has been previously noted.[2] A more direct comparision can be made with alcohol ligands based on our calculation of $k_{-1} \simeq 8.3 \times 10^{-6}$ $M^{-1}\ s^{-1}$ (25 °C) for the substitution of one methanol on $Cr(H_2O)_6^{3+}$ from $k_1 \approx 5.4 \times 10^{-6}\ s^{-1}$ for its dissociation ($I \simeq 0.23$ M) and an apparently temperature-insensitive equilibrium quotient.[25] While possibly being complicated by media variations, the statistically corrected rate advantage is ~170 for ethylene glycol ring closure.[12]

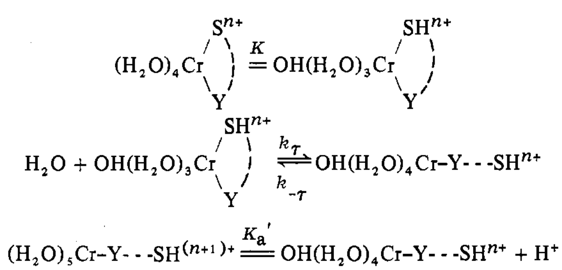
Secondary Pathway for Chromium(III)–Sulfur Bond Breaking and Making. As has been found with a variety of moderately basic ligands,[26] an acid-independent pathway for chromium(III)–sulfur bond cleavage seems indicated by three criteria: (a) *large* intercepts of k_f vs. $[H^+]$ plots with amine ligands, (b) small intercepts of such plots with carboxylate ligands which appear, nevertheless, to be larger than can be attributed to activity effects,[3b] and (c) a *substantial* slope of the k_r vs. $[H^+]^{-1}$ plot for closure on $(H_2O)_5Cr(NH_2CH_2CH_2SH)^{3+}$ and a smaller, but apparently real, slope with $(H_2O)_5Cr(OOCCH_2SH)^{2+}$ (Table II), both cases

Table V. Rate Parameters for Secondary Cr^{III}–S Bond Breaking-Making (Schemes I-III)

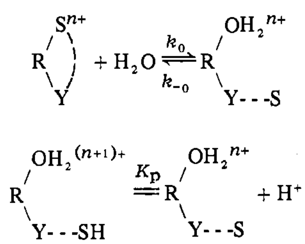
Complex	I, M	Kk_{τ} (k_0), s^{-1}	$K_a'k_{-\tau}$ (K_pk_{-0}), $M\ s^{-1}$	$k_0 + k_{-1}$, s^{-1}	k_0, s^{-1}	Ref
$(H_2O)_5CrSC_6H_4NH_3^{3+}$	2.0	4.0×10^{-6}				3c
$(H_2O)_5CrSCH_2CH_2NH_3^{3+}$	1.0^b	2.8×10^{-5}				*a*
	1.0	3.2×10^{-5}				3a
	2.0	4.5×10^{-5}				3a
$(H_2O)_4Cr(SCH_2COO)^+$	0.25	8×10^{-7}	8×10^{-8}			*a*
$(H_2O)_4Cr(SCH_2CH_2NH_2)^{2+}$	1.0	1.9×10^{-6}	3.6×10^{-7}			*a*
$(en)_2Cr(SCH_2COO)^+$	1.0			2.5×10^{-5}		3b
	4.0			$<2 \times 10^{-4}$		3b
$(en)_2Cr(SCH_2CH_2NH_2)^{2+}$	1.0				1.3×10^{-6}	3b
	4.0			1.7×10^{-7}		3b

^{a} This work. ^{b} $NaClO_4$; all others with $LiClO_4$.

Scheme II

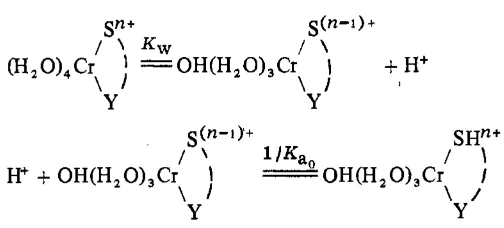


Scheme III



corresponding to the microscopically reversible closure required of any real acid-independent cleavage. These observations are collectively consistent with such a pathway being real rather than being a media effect.

Accepting this, a critical mechanistic ambiguity must be confronted.[3,13,14,15,27-30] One widely favored mechanism for such ligands on aquo ions involves an intramolecular protonation of the leaving group (Scheme II), where, for the secondary pathway, $k_f' = Kk_{\tau}$, $k_r' = K_a'k_{-\tau}[H^+]^{-1}$, and K can be formally analyzed as equal to K_w/K_{a0}



whether or not the proton is actually released to solution.[3a]

A second mechanism (Scheme III), thought to be operative with weakly basic ligands,[13-15,27,28,30] is kinetically indistinguishable from Scheme II. In Scheme III R = $Cr(H_2O)_4^{3+}$ or $Cr(en)_2^{3+}$, $k_f' = k_0$ and $k_r' = K_pk_{-0}[H^+]^{-1}$. Our results are summarized with others[3] in Table V where column headings correspond to the designations of the three mechanisms outlined above with parentheses enclosing interpretations based on Scheme III. Estimates of K_a' and K_p can be made.[31] Combination with observed k_r' values yields alternative estimates of $k_{-\tau} \approx 2.7 \times 10^{-3}\ s^{-1}$ vs. $k_{-0} > 8$–$80\ s^{-1}$ with $(H_2O)_5Cr(OOCCH_2SH)^{2+}$ and $k_{-\tau} \approx 9 \times 10^{-3}\ s^{-1}$ vs. $k_{-0} >$ 0.4–4 s^{-1} with $(H_2O)_5Cr(NH_2CH_2CH_2SH)^{3+}$.

Our preference[2] for Scheme II reflected the consensus that substitution on aquochromium(III) centers was dominantly dissociative[13,36-38] whereas the above estimates for k_{-0} would require a substantial degree of incoming group participation. While our $k_{-\tau}$ estimates exceed statistically adjusted water exchange on $Cr(H_2O)_6^{3+}$,[39] they could reflect the labilization of a dissociative process by coordinated hydroxide[13,45] and carboxylate or amine. Also, the $k_{-\tau}$ values preserve the rate advantage of $\sim 10^2$ for chelate closure, compared to monodentate ligation of $Cr(H_2O)_5OH$ by HF or HN_3,[13] and seem in reasonable correspondence with the k_{-1} value (Table IV) observed for ring closure by ethylene glycol.[12] Finally, positive evidence has been presented in favor of Scheme II for the acid-independent hydrolysis pathway for $Cr(H_2O)_5SCH_2CH_3NH_3^{3+}$.[3a]

While these observations provide support for Scheme II, several results suggest a reconsideration of Scheme III with thiolate as the entering group. In studying the Cr^{III}–S cleavage of $Cr(en)_2(SCH_2COO)^+$ at I = 1.0 and 4.0 M and $Cr(en)_2(SCH_2CH_2NH_2)^{2+}$ at I = 4.0 M, Weschler and Deutsch[3b] employed a kinetic analysis in which intercepts were equal to ($k_0 + k_{-1}$) as listed in Table V. These intercepts may be dominantly due to k_{-1}, at least for the one case where a calculation of k_{-1} is possible (Table IV).

Of more compelling interest is their observation[3b] of a substantial intercept in a parallel study of $Cr(en)_2(SCH_2CH_2NH_2)^{2+}$ at I = 1.0 M under conditions where no more than 5% of reaction was followed, such that k_{-1} contributes negligibly to the intercept, which yields $k_0 = 1.3 \times 10^{-6}\ s^{-1}$. If the rate of acid-independent cleavage is of this magnitude, Scheme III would seem required[3b] since the equilibrium constant for loss of an amine proton (corresponding to the K_w of Scheme II) is likely to be at least 10^9 smaller than K_w[40] without any sufficiently compensating change in $1/K_{a0}$. Thus, cleavage by Scheme II can be anticipated to be $\sim 10^9$ slower for $Cr(en)_2(SCH_2CH_2NH_2)^{2+}$ than for the more acidic aquo ion analogue.

Acceptance of such an acid-independent path carries with it consequences that arise from microscopic reversibility. From our combined results, an estimate of $K_{eq} \approx 20$ for the reaction $H_3O^+ + Cr(en)_2(SCH_2CH_2NH_2)^{2+} = Cr(en)_2(H_2O)(NH_2CH_2CH_2SH)^{3+}$ seems within reason at I = 1.0 M. An estimate of $K_p \approx 10^{-6.5}$ for the latter ion leads to a calculated $k_{-0} = k_0/K_pK_{eq} = 0.2\ s^{-1}$. The K_{eq} and estimated k_0 and K_p of Weschler and Deutsch[3b] lead to $k_{-0} \simeq 250\ s^{-1}$ for ring closure of $Cr(en)_2(H_2O)(OOCCH_2SH)^{2+}$ at I = 1.0 M. The latter value appears high in relation to that for the mercaptoethylamine complex, perhaps from the k_0 estimate being too high. However, it does not seem likely that k_0 would be less than with mercaptoethylamine which leads to an estimated lower limit of $\sim 25\ s^{-1}$ for k_{-0} with mercaptoacetate.

It should be emphasized that these k_{-0} estimates are *quite large* in comparison to most substitutions on related chromium(III) centers. Since our previous report,[2] important evidence has been presented which suggests, "an I_a (associative interchange) mechanism is operative in acid-independent substitutions of cationic chromium(III) complexes in aqueous solution",[41,42] as had been predicted earlier.[43] Such a mechanism appears to extend to other M(III) centers with the exception of cobalt(III).[41,42] To the extent that bond making is influential for substitution on Cr(III), pendent thiolate chelate functions offer significant advantages to ring closure via Scheme III arising from their proximity to the leaving group and their combined uniqueness in base strength and nucleophilicity,[44,45] relative to previously studied substitutents, which may overcome their resistance to deprotonation at sulfur (K_p).

The marked similarity for chromium(III)–sulfur cleavage of mercaptoethylamine on $Cr(H_2O)_4^{3+}$ and $Cr(en)_2^{3+}$ along *both* pathways raises the temptation to invoke Scheme III for our acid-independent ring closure in view of its apparent applicability to the $Cr(en)_2^{3+}$ case. On the other hand, the fact that the cleavage data for $Cr(H_2O)_4(SCH_2CH_2NH_2)^{2+}$ lie quite close to the lines for stronger bases in Figures 1 and 2 of ref 3a (in spite of the presence of the amine function in the coordination sphere) seems supportive of Scheme II.[46] It seems prudent to withhold judgment until studies with strongly basic and nucleophilic ligands establish that rates as high as the k_{-0} values we have estimated are realistic for substitution on aquochromium(III) centers.

Pathways for Carboxylate Ring Closure. The results on carboxylate ring closures are less reliable because they are less extensive and the rapid rates precluded separation and identification of reactants generated for study in situ (see Results). Nevertheless, they require mention since the only isolable chromium(III) carboxylate species were the chelates which could not have arisen directly from the redox reactions for steric reasons.

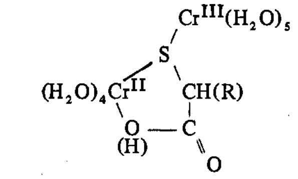
Subsequent to the rapid redox processes with slightly *deficient* chromium(II), the first-order rate of absorbancy increase at the chelate maxima increased with acid concentration according to $k = a + b[H^+]$ (Table III) and was taken at the time as reflective of the net process

$$(H_2O)_5Cr(SCH(R)COOH)^{2+} \rightarrow (H_2O)_4Cr(SCH(R)COO)^{+} + H_3O^{+}$$

with $a = 5.6 \times 10^{-3}$ and 10×10^{-3}, $b = 13 \times 10^{-3}$ and 26×10^{-3} (M and s), for R = H and CH_3, respectively. Precedent for such behavior was found in similar in situ observations by Huchital and Taube[47] on the analogous malonato system for which $k = (4.0 + 22[H^+]) \times 10^{-6}$ was reported. Meanwhile, a detailed study[5b] on isolated samples for the latter system has brought the previous conclusions into question by finding no acid dependence for ring closure ($k = 2.3 \times 10^{-5}$ s^{-1}) and an acid dependence for ring opening ($k = 3.1 \times 10^{-6}[H^+]$) as is reasonable from the microscopically reversible nature of the equilibrium and the related acid-dependent hydrolysis of $Cr(H_2O)_5(OOCCH_3)^{2+}$.[10] Agreement with the previous data[47] was found only at $[H^+] = 1.0$ M.[5b]

We find ourselves in the position of having similar in situ results which, however, are suspect in interpretation both in analogy to the malonato closure (particularly regarding the acid dependence) and in the rapidity with which the changes occur. We initially interpreted the enhanced reactivity, relative to the malonato report,[47] as being due to substitution occurring at carbon[47] with a steric advantage for closing a five-membered ring compared to a six-membered ring which appears to be well-documented in comparable organic systems.[48,49] It now seems advisable to postpone conclusions on the details of ring closure in in situ systems until more definitive studies are available.

The simplest interpretation of the absence of isolable monodentate products and observable absorbancy increases at the chelate maxima subsequent to the redox reactions with *excess* $Cr(H_2O)_6^{2+}$ is that this ion catalyzes chelate closure via a reductant-chelated transition state[5a,7,47,50,51]



with $k \gtrsim 10^4$ M^{-1} s^{-1} at $[H^+] = 0.10$ M. This estimate seems high relative to $k = 1.1 \times 10^{-4}$ M^{-1} s^{-1} for the $Cr(H_2O)_6^{2+}$–$Cr(en)_2(SCH_2CH_2NH_2)^{2+}$ reaction.[52] Comparison with reductions by $Cr(H_2O)_6^{2+}$ of $Cr(NH_3)_5X^{2+}$ and $Cr(H_2O)_5X^{2+}$ (where X = F,[53,54] Cl,[53,55] and OH[56,57]) might be construed to suggest a $k \approx (4 \pm 2.5) \times 10^{-2}$ M^{-1} s^{-1} for monodentate, thiolate-bridged chromous reduction of $Cr(H_2O)_5SR^{2+}$ if a common mechanism, e.g., resonance transfer, is assumed.

The diminished efficiency of thiolate bridging on Cr^{III}(amine)$_5$ has been partially attributed[52] to a lack of the ground-state elongation of the trans metal–nitrogen bond found in $Co(en)_2(SCH_2CH_2NH_2)^{2+}$.[58] While no comparable aquochromium(III) structures are available, a diminished inner-sphere reorganization energy may be reflected in 10^3–10^4 enhancements of trans ligation on $Cr(H_2O)_5SR^{2+}$ relative to $Cr(H_2O)_6^{3+}$.[59] Rate enhancement by the pendent carboxyl function of $Cr^{III}(H_2O)_5SCH(R)COO(H)^{+(2+)}$ is expected from related redox behavior[7,47,50] but by a smaller factor than the discrepancy noted above.[60]

An additional factor that may be missing in the previous rate comparisons is a bridging ligand, X, that is comparably reducing to RS^- [44,45] combined with the possibility that a superexchange mechanism[50,62–64] might be operative with such easily oxidizable bridging ligands. In such a mechanism the state in which an electron is transferred from RS^- to Cr(III) is not directly involved, as in one form of the radical ion mechanism, but mixes with the ground states of the bridged complex to lower the energy barrier for electron transfer.[64]

The high-intensity ultraviolet absorption of $Cr(H_2O)_5SCH_2CH_2NH_3^{3+}$ is ~7 kcal lower in energy than with $Cr(en)_2(SCH_2CH_2NH_2)^{2+}$ [3c] reflecting, presumably, the greater oxidizing power expected of the $Cr(H_2O)_5^{3+}$ moiety which would be more responsive to a superexchange influence than in the less oxidizing chromium(III)–amine systems. However, comparisons when moderately oxidizable iodide[44] is the bridging ligand on the significantly more oxidizing[65] $Co(NH_3)_5^{3+}$ center, $k = 3 \times 10^6$ M^{-1} s^{-1} ($I = 0.10$ M[66]), vs. $Cr(NH_3)_5^{3+}$, $k = 5.5$ M^{-1} s^{-1} ($I = 1.0$ M[53]), with results for $Co(en)_2(SCH_2CH_2NH_2)^{2+}$ [1] vs. $Co(en)_2(SCH_2CH_2NH_2)^{2+}$ [52] appear to require trans activation and chelate assistance to rationalize our observations even in view of the greater oxidizability of RS^-.[44,45]

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Registry No. $Cr(H_2O)_4(OOCCH_2S)^+$, 32696-60-9; $Cr(H_2O)_5(OOCCH_2SH)^{2+}$, 34872-84-9; $Cr(H_2O)_4(OOCCH_2O)^+$, 60745-59-7; $Cr(H_2O)_5(OOCCH_2OH)^{2+}$, 60745-60-0; $Cr(H_2O)_4(OOCCH(CH_3)S)^+$, 34872-87-2; $Cr(H_2O)_5(OOCCH(CH_3)SH)^{2+}$, 34872-85-0; $Cr(H_2O)_4(OOCCH(CH_3)O)^+$, 60745-61-1; $Cr(H_2O)_5(OOCCH(CH_3)OH)^{2+}$, 60745-62-2; $Cr(H_2O)_4(SCH_2CH_2NH_2)^{2+}$, 60745-63-3; $Cr(H_2O)_5(SCH_2CH_2NH_3)^{3+}$, 59033-97-5; $Cr(H_2O)_5(NH_2CH_2CH_2SH)^{3+}$, 60745-64-4; $Cr(H_2O)_5(HOCH_2CH_2NH_3)^{4+}$, 60745-65-5; $Cr(H_2O)_5(OOCCH_2SCH_3)^{2+}$, 60745-66-6; $Cr(H_2O)_5(OOCCH_2NH_3)^{3+}$, 60745-67-7; $Cr(H_2O)_4(OOCCH_2NH_2)^{2+}$,

60745-68-8; $Cr(H_2O)_5(SCH_2COOH)^{2+}$, 60745-69-9; $Cr(H_2O)_5(SCH(CH_3)COOH)^{2+}$, 60745-70-2; $(H_2O)_4Cr(HOCH(CH_3)COO)^{2+}$, 60745-71-3; $(H_2O)_4Cr(HOCH_2COO)^{2+}$, 60745-72-4.

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Synthesis and Optical Resolution of *cis,cis*-Dicyanodicarboxylatodiammine and *cis,cis*-Dinitrodicarboxylatodiammine Complexes of Cobalt(III)

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The *cis,cis*-$[Co(CN)_2(O\text{-}O)(NH_3)_2]^-$- and *cis,cis*-$[Co(NO_2)_2(O\text{-}O)(NH_3)_2]^-$-type complexes (O-O represents CO_3^{2-}, ox^{2-}, or mal^{2-}) and the related *cis*-$[Co(CN)_2(O\text{-}O)en]^-$- and *cis*-$[Co(NO_2)_2(O\text{-}O)en]^-$-type complexes have been synthesized essentially based on the successive substitution of CO_3^{2-} ion in the $[Co(CO_3)_3]^{3-}$ complex with desired ligands. The resolution of all the complexes into optically active enantiomers has also been achieved. The complexes have been characterized by their absorption and CD spectra. The absolute configurations of the enantiometric complexes have been discussed on the basis of the CD spectra.

Introduction

Most studies on the optically active metal complexes have been undertaken with those complexes which are dissymmetric because of either the distribution of chelate rings about a central metal ion or the conformations of individual chelate rings.[1] On the other hand, little attention has been paid to complexes that derive their dissymmetry solely from the distribution of unidentate ligands. Russian workers reported