is important to note that the ZnH_2 formed in all these reactions of KH with $ZnCl_2$ gives the same powder pattern as the ZnH_2 prepared by the reaction of LiH with $ZnBr_2$ and NaH with ZnI_2.

The reaction of NaH with $ZnCl_2$ in 1:1 molar ratio proceeds according to eq 15. The filtrate from this reaction

$$\mathrm{NaH + ZnCl_2 \rightarrow {}^1/_2ZnCl_2 + NaCl + {}^1/_2ZnH_2} \tag{15}$$

contained Na, Zn, Cl, and H in molar ratios of 0.00:1.00:1.96:0.00 and half the starting zinc. The solid contained Na, Zn, Cl, and H in molar ratios of 1.94:1.00:1.97:1.27. The analytical data support the reaction as written and the X-ray powder pattern of the solid (Table I) contained lines only for NaCl and zinc metal. The powder pattern for ZnH_2 seen in the other cases was not observed. Also, this was the only reaction between an alkali metal hydride and zinc halide where the ZnH_2 produced turned black after just a few days. Why the ZnH_2 from this reaction behaved thus is unknown at present.

Several salient points about ZnH_2 are worth noting at this point. First, ZnH_2 is an isolable species which has moderate stability at or below room temperature. Second, ZnH_2 is the most thermally stable of the group IIb hydrides. Cadmium hydride[12,13] and mercury hydride[12] decompose rapidly even below 0°. Third, ZnH_2 exhibits ready reactivity in situations where the product is soluble.[12,14] The ZnH_2 prepared in this study remains stable longer and is more reactive than ZnH_2 prepared by the Schlesinger method. In view of point 3 we are presently studying ZnH_2 as a reducing agent toward organic substrates.[15]

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Registry No. KH, 7693-26-7; KCl, 7447-40-7; AlH_3, 7784-21-6; NaH, 7646-69-7; LiH, 7580-67-8; ZnH_2, 14018-82-7; $ZnCl_2$, 7646-85-7; $ZnBr_2$, 7699-45-8; ZnI_2, 10139-47-6; KZn_2Cl_5, 52002-83-2.

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(15) Note Added in Proof. The reaction of NaH with ZnI_2 in 2:1 molar ratio in THF produces ZnH_2 in essentially quantitative yield when the reaction mixture is allowed to stir for 24–48 hr. It has been suggested that the reaction time might be reduced by using triethylaluminum as a catalyst to solubilize the NaH as $NaAl(C_2H_5)_3H$. This idea was tested by repeating the above reaction in the presence of a catalytic amount of triethylaluminum. The reaction time was reduced considerably in the initial stages of the reaction; however, at least 24 hr was required for complete reaction and the final product turned black during the reaction period unlike the uncatalyzed reaction.

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A Study of the Products of the Reactions of Thiocyanate with Chromium(III) Ion in Water–Methanol Solvent Mixtures[1,2]

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The thiocyanate anation of hexaaquochromium(III) and pentaaquomethanolchromium(III) ions in a water–methanol mixed solvent of 0.308 mol of methanol gives three products, isothiocyanatopentaaquochromium(III), and *cis*- and *trans*-isothiocyanatotetraaquomethanolchromium(III). The rate law was found to be: rate = $\{[\mathrm{Cr(OH_2)_6}^{3+}]k_1 + (k_2 + k_3 + k_4)[\mathrm{Cr(OH_2)_5(CH_3OH)}^{3+}]\}[\mathrm{SCN^-}]$ where k_1 and k_2 correspond to pathways involving the formation of isothiocyanatopentaaquochromium(III) while k_3 and k_4 involve the formation of *trans*- and *cis*-isothiocyanatotetraaquomethanolchromium(III). The methanol and the trans water replacement accelerate the thiocyanate reaction in mixed solvents. Single site reactivities relative to the replacement of a single water on hexaaquochromium(III) at 30° in 0.1 *M* $HClO_4$ and 0.42 *M* ionic strength were found to be $k_2^*:k_1^* = 3.0$, $k_3^*:k_1^* = 2.0$, and $k_4^*:k_1^* = 1.0$. Solvent exchange equilibrium quotients and rate coefficients were measured for the products. The fluoride anation of hexaaquochromium(III) and pentaaquomethanolchromium(III) ion in 0.308 mol of methanol are also reported. In this case the products were not separated and analyzed.

Introduction

Previous kinetic studies of methanol-catalyzed association of chromium(III) with thiocyanate[4] and chloride[5] ions in water–methanol solvents have been limited to the measurement of the total concentration of products, CrX^{2+}. The slowness of the solvent exchange reaction[5]

$$\mathrm{CrO_6}^{3+} + \mathrm{M} \rightarrow \mathrm{CrO_5M}^{3+} + \mathrm{O} \tag{1}$$

$$(\mathrm{O = H_2O,\ M = methanol})$$

makes it possible to identify two reactants, pentaaquomethanolchromium(III) and hexaaquochromium(III) ions, for the association reactions with various nucleophiles. In this work the thiocyanate–chromium(III) association was further studied in order to separate and measure the three possible products of the reactions

$$\mathrm{CrO_6}^{3+} + \mathrm{N}^- \xrightarrow{k_1} \mathrm{CrO_5N}^{2+} + \mathrm{O} \tag{2}$$

$$\mathrm{CrO_5M}^{3+} + \mathrm{N}^- \xrightarrow{k_2} \mathrm{CrO_5N}^{2+} + \mathrm{M} \tag{3}$$

$$\mathrm{CrO_5M}^{3+} + \mathrm{N}^- \xrightarrow{k_3} trans\text{-}\mathrm{CrO_4MN}^{2+} + \mathrm{O} \tag{4}$$

$$\mathrm{CrO_5M}^{3+} + \mathrm{N}^- \xrightarrow{k_4} cis\text{-}\mathrm{CrO_4MN}^{2+} + \mathrm{O} \tag{5}$$

$$(\mathrm{N^- = SCN^-}\ \text{coordinated through nitrogen},\ \mathrm{M = CH_3OH})$$

The interchange of solvent on the products of the thiocy-

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[3] Undergraduate research participant from College of Saint Teresa, Winona, Minn.

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anate association was studied in order to determine if significant product redistribution occurred during association

$$\mathrm{CrO_5N^{2+} + M \underset{k_7}{\overset{k_5}{\rightleftarrows}} \textit{trans}\text{-}CrO_4NM^{2+} + O} \tag{6}$$

$$\mathrm{CrO_5N^{2+} + M \underset{k_8}{\overset{k_6}{\rightleftarrows}} \textit{cis}\text{-}CrO_4NM^{2+} + O} \tag{7}$$

Equilibrium constants for reactions 6 and 7 were obtained from an equilibrium solution as an additional check on the individual rate constants.

The reactions of chromium(III) with various ligands are of interest for two reasons. The presence of methanol in the first coordination sphere of chromium(III) ion accelerates the rate of reaction as shown by the values of $(k_2 + k_3 + k_4)/k_1$ equal to 3.7 for chloride,[5] 1.5 for thiocyanate,[4] and 1.5 ± 0.1 for hydrofluoric acid as reported in this work. The greater reactivity of the methanol-substituted species could be due to the replacement of methanol (reaction 3) or to labilizing of the coordinated water (reaction 4 or 5). Measurement of the products of the association reaction of chromium(III) and thiocyanate ions will answer this question. In addition, the study will show the importance of the entering group in the association reactions in water-methanol solvents. Espenson[6] has shown that in aqueous solution chromium(III) anation rates cover a sizable range which is consistent with mechanisms where both the outgoing and the incoming ligands are important. Swaddle and Guastalla[7] correlated the aquation rates and stability quotients of $\mathrm{Cr(OH_2)_5X^{2+}}$ using the method of Langford.[8] The data obtained are consistent with an interchange mechanism, I_a, where X^- is about half-separated and half-hydrated in the transition state.

Experimental Section

Reagents. Reagent grade chemicals were used without further purification. Chromium(III) perchlorate used in this work was prepared from reagent grade potassium dichromate. The details of the synthesis are described in earlier work.[4,5] Triply distilled water was used in the preparation of all solutions. Reagent grade methanol (Fischer Scientific) was used without further purification. Bio-Rad cation exchange resin, reagent grade, was used in the ion-exchange procedures.

Analyses. Analyses for hydrofluoric acid content were carried out by titration with standard sodium hydroxide. Sodium nitrate and sodium perchlorate used in this work were determined by titration with standard base after the salt solution was passed through a Dowex 50W -X8 cation-exchange column in the hydrogen form. Thiocyanate ion was analyzed by titration with standard silver nitrate solution. Chromium(III) species were analyzed by conversion to chromate ion in basic peroxide solution and measuring the absorbance at 372 nm.[5]

Methanol coordinated to chromium(III) was determined in acid solution by oxidation with excess Ce(IV) and back titration with Fe(II). The details of the methanol determination were described earlier.[5] To determine methanol coordinated to isothiocyanatochromium(III) additional steps were necessary to eliminate thiocyanate ion interference. Excess silver nitrate and Ce(IV) were added and the sample was centrifuged to remove the precipitated AgSCN. Two aliquots were removed. One was titrated with Fe(II) and served as a blank for the amount of Ce(IV) decomposed by SCN^- at room temperature during the precipitation. The second aliquot was analyzed as earlier described.[5] The end points were followed potentiometrically since ferroin indicator interfered.

Instrumentation. Spectral measurements of solutions containing chromate ion and of solutions used for molar absorptivity determinations were carried out with a Cary Model 14 spectrophotometer. $\mathrm{CrN^{2+}}$ species were determined by monitoring the eluent of ion-exchange columns. The monitoring system was composed of a Beckman DB spectrophotometer, a Model 93500 Beckman recorder that was geared to deliver 0.0952 in. of chart paper per minute, and a modified 1-cm quartz cell that would fill and empty at constant volume. A steady flow rate of eluent was maintained using a constant head device. With a steady flow rate, the modified cell delivered 1.3 ml per aliquot and a Gaussian elution profile was obtained. The transmittance went to 0% *T* when the meniscus passed through the light beam and then returned to the transmittance reading of the eluent. The filling and emptying of the cell, therefore, marked each separate elution volume. The average transmittance reading of each aliquot was then converted to concentration units by the use of the proper molar absorptivity value. Since Gaussian elution curves were obtained, the concentrations were adjusted by extrapolation, as shown in Figure 1, to account for any peak overlap. Careful resin bed preparation, instrument calibration and equilibration, and flow rate control enabled changes of 0.2% *T* units to be observed. The monitoring system was sensitive to 10^{-9} mol of CrN species which would yield an elution peak maximum of 99% *T*. All calculations were performed with a programmed Wang 700 calculator.

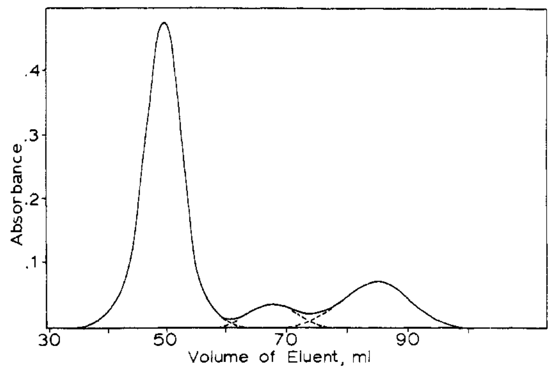

Figure 1. Elution of the isothiocyanatochromium(III) species in solution with composition 0.308 mol of methanol. The elution procedure is described in the text. The absorbance was measured at 292 nm.

Table I. Isothiocyanatochromium(III) Species Equilibration in 0.308 Mol Fraction of Methanol at 30°[a]

Elution order	Principal species	Flow cell[b] [Cr] × 10^4	Chromate ion[b] [Cr] × 10^4	Corrected[c] [Cr] × 10^4
(1)	$\mathrm{CrO_5N^{2+}}$	6.7	6.6	6.56
(2)	*trans*-$\mathrm{CrO_4NM^{2+}}$	0.73	0.78	0.37
(3)	*cis*-$\mathrm{CrO_4NM^{2+}}$	2.23	2.13	2.64
	Total $\mathrm{CrN^{2+}}$	9.6	9.5	
(4)	$\mathrm{CrO_3M_2N^{2+}}$		0.54	
(5)	$\mathrm{CrO_6{}^{3+}}$		0.4	
	Total Cr		10.4	

[a] Nine days equilibrium, $I = 0.413\ M$, $[\mathrm{H^+}] = 0.1\ M$ perchloric acid, initial $[\mathrm{CrO_4N^{2+}}] = 10.0 \times 10^{-4}\ M$. [b] For comparison purposes these concentrations were not adjusted for aliquot and peak overlap. [c] Since Gausian elution profiles were obtained, the initial and final portions of the curve were used to obtain a normal *trans*-$\mathrm{CrNM^{2+}}$ peak.

In order to determine the accuracy of the flow analysis procedure, the eluents were collected in volumetric flasks after passage through the flow cell and the chromium content was determined by chromate analysis. Table I presents a comparison of the concentrations determined for a solution containing isothiocyanatochromium(III) in equilibrium with a 0.308 mol fraction of methanol–water solvent. Due to some peak overlap the comparison has been made using the actual volume of eluent collected. The molar absorptivity of the principal species present was used in the calculations of concentrations. The values obtained after extrapolation and adjustment are also presented in Table I. The total chromium analysis between the two analytical procedures agreed within less than 5%.

Separation and Identification of Isothiocyanatochromium(III) Species. Three isothiocyanatochromium(III) species are formed as the major products of the association of 0.03 *M* chromium(III) and 0.1 *M* thiocyanate ion in 0.308 mol of methanol solvents. Figure 1 shows the elution curve typical of the separation of these three species in 0.4 *M* sulfuric acid. In order to minimize the aqua-

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(8) C. H. Langford, *Inorg. Chem.*, 4, 265 (1965).

tion of the species the ion-exchange column was jacketed and operated at 1° at all times during the separation. Prior to use, the 10 × 0.7 cm column of Bio-Rad 50W-X12, 200–400 mesh, resin was backwashed to remove fines and voids. An aliquot of a reaction mixture containing a maximum of 10^{-6} mol of isothiocyanatochromium(III) species was diluted to an ionic strength of about 0.1 *M* with 0.01 *M* sulfuric acid above the resin bed. The column was then washed with 0.05 *M* sulfuric acid until all the chromium species were absorbed. Any diisothiocyanatochromium(III) formed in the reaction would elute at this time. The amount of diisothiocyanato species formed was less than 1% of the isothiocyanatochromium(III) formed. Elution profiles were obtained for acid concentrations between 0.4 and 0.7 *M* with perchloric, hydrochloric, and sulfuric acids. Optimum elution profiles were obtained for the isothiocyanatochromium species having a charge of +2 with 0.4 to 0.5 *M* sulfuric acid at a flow rate of 0.30 ml/min.

A number of the isothiocyanatochromium(III) species were collected separately in aliquots of 1.3 ml. The center fractions of each elution peak were analyzed for methanol content and the spectra were recorded. The species eluted first was found to contain no methanol. The visible and uv spectra of this species matched that of isothiocyanatopentaaquochromium(III) reported by Dismukes and King.[9] The spectra of the next four eluted species were found to be quite similar to that of isothiocyanatochromium(III). Methanol analysis of the species showed the second and third species eluted contained 1 mol of methanol per mole of chromium. The last two eluted species contained 2 mol of methanol per mole of chromium. Table II presents the molar absorptivity values measured at the four maxima regions observed. The two monomethanol species were identified as *trans-* and *cis-*isothiocyanatotetraaquomethanolchromium(III). The two dimethanol species were not identified and were never present in concentrations greater than 0.5% of the total CrN^{2+} product formed in kinetic solutions.

The assignment of the second eluted isothiocyanatomethanol species as the trans isomer and the third as the cis isomer is based on the following information. The equilibration of CrN^{2+} in water–methanol solution shown in Table I results in a 7:1 ratio of the *cis-* to *trans-*$CrNM^{2+}$. This would indicate a stability of the trans position to be about one-half that of a single cis site. In previous work by King, *et al.*, the cis and trans isomers of bis(dimethyl sulfoxide)chromium(III)[10] and bis(pyridine *N*-oxide)chromium(III)[11] have been isolated. At equilibrium in each case the assignment of the cis isomer was to the species produced in the largest quantity and when compared statistically the per site stability was similar. In this work if the assignment were made opposite, the per site stability of the trans position would be 28 times that of the cis position. The cis isomer has a slightly larger visible molar absorptivity than the trans species which is indicative of the cis isomer.[12] Finally, the trans species is usually eluted first.[13] King and Vanderheiden have recently reported the separation of two very similar complex ions, *cis-* and *trans-*$Cr(OH_2)_4(OS(CH_3)_2I)^{2+}$.[14] In this case the trans isomer was observed to be eluted first from a cation-exchange column.

Table II. The Molar Absorptivities (l. mol^{-1} cm^{-1}) for Isothiocyanatochromium(III) Species in 0.5 *M* Aqueous Sulfuric Acid at 30°

Species	222 nm[a]	292 nm	410 nm	564 nm
CrN	6800	2880	33.0	31.8
trans-CrNM	6650	3000	33.1 (412)	32.8 (570)
cis-CrNM	6660 (223)	2980 (293)	34.6 (413)	32.6 (570)
$CrNM_2$[b]	6430 (224)	3220 (295)	35.7 (413)	34.6 (571)
$CrNM_2$[b]	6610 (224)	3010 (296)	36.8 (418)	34.2 (572)

[a] The wavelengths of the exact position of the maxima are given in parentheses. The molar absorptivities were also calculated at the wavelength in parentheses. [b] These molar absorptivities were determined in 0.5 *M* perchloric acid.

Table III. Rate of Formation of Fluorochromium(III) Ion at 30° [a]

X_{CH_3OH}	$\bar{n}_{av}$	[HF], *M*	$[Cr^{3+}]$, *M*	$10^6 k_f$, M^{-1} sec^{-1}
0	0	0.400	0.0600	1.1 ± 0.1[b]
0	0	0.400	0.0300	1.0 ± 0.1
0	0	0.600	0.0060	1.1 ± 0.1
0.308	0.02 ± 0.02[c]	0.400	0.0300	0.75 ± 0.1
0.308	0.02 ± 0.02	0.600	0.0300	0.82 ± 0.1
0.308	0.19 ± 0.01	0.400	0.0300	0.87 ± 0.1
0.308	0.24 ± 0.01	0.400	0.0300	0.88 ± 0.1
0.308	0.31 ± 0.02	0.400	0.0300	0.91 ± 0.1
0.308	0.38 ± 0.04	0.400	0.0300	0.96 ± 0.1

[a] $[H^+] = 0.100\,M$, $I = 0.448\,M$, $k_f = \Delta[CrF^{2+}]/\Delta t[Cr^{3+}]_t[HF]$. [b] 95% confidence level, 6 to 10 points. [c] Range of $\bar{n}$, the average number of methanol molecules per chromium(III) ion, over the 10-hr study.

Results

Rate of Association of Cr^{3+} with HF. The initial rates of association of hexaaquochromium(III) and pentaaquomethanolchromium(III) ion with hydrofluoric acid were determined in acidic media for 10 hr at 30°. Experimental procedures were the same as those used by Baltisberger and Hanson in a study where total CrN^{2+} species were determined.[4] The dissociation of CrF^{2+} is unimportant during the 10-hr study. The initial rate of the reaction is the form

$$\frac{d[CrF^{2+}]}{dt} = k_f[Cr^{3+}]_t[HF]$$

where $[Cr^{3+}]_t$ equals the sum of $[Cr^{3+}]$, $[CrM^{3+}]$, and any $[CrM_2{}^{3+}]$ (less than 3% at $\bar{n} = 0.308$). The reaction was found to be first order in both reactants. The uncertainty in the values of k_f reported on Table III is ±10% at the 95% confidence level for 6 to 10 points obtained over a 10-hr period. At a constant mole fraction of methanol of 0.308, the second-order rate coefficient will fit a two-term expression

$$k_f = (1 - \bar{n}_{av})k_1 + \bar{n}_{av}k_t$$

where k_1 and k_t are the rate coefficients for reactions 2 and the sum of 3, 4, and 5, respectively. The term $\bar{n}$ is the average number of methanol bound to chromium(III) and in this kinetic study is equal to the fraction of chromium(III) present as CrM^{3+} assuming $CrM_2{}^{3+}$ can be neglected. The term $\bar{n}_{av}$ is the average value of $\bar{n}$ over the 10-hr study. The value of k_1 was found to be $7.8 \pm 0.08 \times 10^{-7}\,M^{-1}\,sec^{-1}$ and k_t was $1.2 \pm 0.1 \times 10^{-6}\,M^{-1}\,sec^{-1}$ in 0.308 mol fraction of methanol.

Values of k_1 equal to $0.9 \pm 0.5 \times 10^{6}\,M^{-1}\,sec^{-1}$ and k_t equal to $3.1 \pm 0.9 \times 10^{-6}\,M^{-1}\,sec^{-1}$ in 0.308 mol fraction of methanol were measured for nitrate association at an ionic strength of 1.44 *M*. The reactions were studied in a time period of less than 1 hr. The scatter in the values renders any determination of the amount of acceleration impossible.

Solvation of Isothiocyanatochromium(III) Species. Before considering the actual rates for the association of thiocyanate with Cr^{3+} and CrM^{3+}, it is necessary to establish if the products of those reactions will undergo any rapid solvolysis reactions which could negate any knowledge of the product distribution. Solutions containing only *cis-* or *trans-*$CrNM^{2+}$ were obtained by ion-exchange separation of an equilibrium solution of CrN^{2+} in methanol–water solvent. The species were allowed to aquate at 30°. The concentrations of the cis and trans isomers were measured by the flow cell monitoring technique. The dissociation of CrN^{2+} in water to pro-

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Table IV. The Aquation of *cis*-Isothiocyanatotetraaquomethanolchromium(III) in Aqueous 0.2 *M* Perchloric Acid at 30° [a]

	$X_{cis\text{-}CrNM}$	
Time, sec × 10^{-4}	Obsd	Calcd[b]
0	0.885	0.887
0.656	0.806	0.826
1.56	0.811	0.749
1.99	0.670	0.716
2.55	0.692	0.673
4.62	0.527	0.538
11.10	0.268	0.267

[a] $[H^+] = 0.202\ M$, $[CrN^{2+}]_{total} = 2.08 \times 10^{-4}\ M$, $I = 0.42\ M$.
[b] $X_t = X_0e^{-kt}$ where $k_5 = 1.1 \times 10^{-5} \pm 0.1\ sec^{-1}$.

Table V. The Aquation of *trans*-Isothiocyanatotetraaquomethanolchromium(III) in Aqueous 0.1 *M* Perchloric Acid at 30° [a]

Time, sec	[*trans*-$CrNM^{2+}$], *M* × 10^5
30	8.46
2670	7.84
8010	7.26

[a] $[H^+] = 0.20\ M$, $I = 0.412\ M$, sodium perchlorate used to adjust the ionic strength.

Table VI. Concentration of Products in the Association of the Chromium(III)–Thiocyanate Ion in 0.308 mol of Methanol[a]

Time, sec × 10^{-4}	[CrN], *M* × 10^4	[*trans*-CrMN], *M* × 10^4	[*cis*-CrMN], *M* × 10^4
0			
1.784	1.77	0.155	0.380
3.170	3.08	0.320	0.638
3.551	3.24	0.349	0.789

[a] Temperature 30°, $[Cr(OH_2)_6{}^{3+}] = 0.0222\ M$, $[Cr(OH_2)_5(CH_3OH)^{3+}] = 0.0084\ M$, $[SCN^-] = 0.140\ M$, $[H^+] = 0.100\ M$, $I = 0.42\ M$.

duce Cr^{3+} and SCN^- is negligible since the rate coefficient is 9×10^{-9} sec^{-1} at this temperature.[15] In the case of the cis isomer the fraction of this species aquated from 88.5 to 26.7% over 24 hr. Both reactions were found to follow first-order kinetics, $X = X_0[\exp(-kt)]$, where X_0 equals the initial concentration of the trans or cis isomer and X equals the concentration at any time, t. Table IV presents the results of the aquation of *cis*-$CrNM^{2+}$ and Table V the aquation of *trans*-$CrNM^{2+}$. The rate coefficients for the aquation of *cis*-$CrNM^{2+}$, k_6, and of *trans*-$CrNM^{2+}$, k_5, were found to be $1.1 \pm 0.1 \times 10^{-5}$ sec^{-1} and $2.1 \pm 0.3 \times 10^{-5}$ sec^{-1}, respectively.

Any possible isomerization reactions due to water-water exchange on *cis*- or *trans*-$CrNM^{2+}$ or isomerization during column separations could be observed during this study. While observing the aquation of *cis*-$CrNM^{2+}$, only CrN^{2+} was observed as a product. *trans*-$CrNM^{2+}$ was considered absent since 100% *T* values were obtained at its elution profile maximum. Likewise when starting with *trans*-$CrNM^{2+}$ only the product CrN^{2+} and starting material were observed. The experiments indicate that isomerization of cis to trans or trans to cis was not occurring during the reaction or column separation.

The rate coefficients for the methanol solvolysis of 1.00×10^{-3} *M* isothiocyanatopentaaquochromium(III) in 0.308 mol fraction of methanol were estimated by measurement of the fraction of the various CrN^{2+} species present after 1.32×10^4 sec at 30° in 0.1 *M* perchloric acid at an ionic strength of 0.413 *M*. The concentration of CrN^{2+} was 9.77×10^{-4} *M*, of *cis*-$CrNM^{2+}$ was 3.23×10^{-5} *M*, and of *trans*-$CrNM^{2+}$ was 9.8×10^{-6} *M*. Calculations were made for the rate coefficients of methanol solvolysis both considering the backward rate coefficients measured in the aquation studies and without considering them. The first-order rate coefficients calculated for reactions 6 and 7 were k_7 equal to 7.6×10^{-7} sec^{-1} if uncorrected and 8.0×10^{-7} sec^{-1} if corrected for the back reaction and k_8 equal to 2.5×10^{-6} sec^{-1} if uncorrected and 2.6×10^{-6} sec^{-1} if corrected. These rate coefficients represent single analyses so that a fit of the data to linear graph is not possible. The uncertainty on any individual CrN^{2+} concentration is about 5%. The same solution that was used for the measurement of the methanol solvolysis rate was allowed to go to equilibrium. The equilibration at 30° was for 9 days which is sufficient time for the equilibration of chromium(III) with water-methanol solutions.[5] After 9 days the solution was found to contain 6.56×10^{-4}, 0.37×10^{-4}, and 2.64×10^{-4} *M* CrN^{2+}, *trans*-, and *cis*-$CrNM^{2+}$, respectively. At equilibrium the ratio of cis to CrN^{2+} is 0.41 while trans to CrN^{2+} is 0.055. The consistency of the data can be checked from the ratios k_8/k_6 and k_7/k_5 which would be the equilibrium constants for the dissociation of *cis*- and *trans*-$CrNM^{2+}$ to form CrN^{2+}. The values of k_5 and k_6 were not measured in 0.308 mol of methanol. However, values for these two rate coefficients can be estimated. The methanol and aquo solvolysis rates for chromium(III) in water-methanol mixtures have been measured from 0.2 to 0.6 mol fraction of methanol and the rates are nearly constant when corrected for solvent by either using the molar or mole fraction ratios.[5] Since the solvolysis of CrN^{2+} seems to be very similar to that of Cr^{3+}, it seems reasonable to expect that the correction of k_5 and k_6 using solvent molarities should not introduce more than 10% uncertainty. To obtain corrected values, k_5 and k_6 were multiplied by 28/55, the ratio of water molarities in 0.308 mol of methanol and water. Equilibrium constants of $(k_8/k_6)(55/28) = 0.45$ and $(k_7/k_5)(55/28) = 0.065$ are obtained. The consistency indicates that the data are good and that isomerization is not important under the conditions studied.

Rate of Association of Cr(III) Species with Thiocyanate. The rate coefficients for the formation of the three isothiocyanatochromium(III) aquo and methanol complex ions were calculated from values measured for the initial rates of formation of each species during the first 10 hr of the reactions. In the experiment chromium(III) was preequilibrated with 0.308 mol of methanol solution for 10 days at 30° to establish the equilibrium concentration of hexaaquochromium(III) and pentaaquomethanolchromium(III). At this solvent composition less than 2% of the chromium(III) exists in higher methanol substituted forms.[16] The preequilibrated mixture was then added to sodium thiocyanate, sodium perchlorate, and perchloric acid media to bring the solution to the initial compositions indicated in Table VI. The production of the thiocyanatochromium(III) species was then followed by means of the ion-exchange separation and uv analysis techniques previously described.

During the initial 10-hr period less than 1.5% of the chromium(III) reactants and 0.5% of the thiocyanate are consumed. In addition the ratio of haxaaquochromium(III) to pentaaquomethanolchromium(III) was constant because both substances were in equilibrium initially. The initial rates, $\Delta CrN^{2+}/\Delta t$, $\Delta cis/\Delta t$, and $\Delta trans/\Delta t$, were constant. The

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overall rate coefficient for the association reaction was previously shown to be first order in chromium(III) and in thiocyanate.[4] The backward rate coefficient for the dissociation of CrN^{2+} is unimportant during the first 10 hr. The concentrations of CrN^{2+} and *cis*- and *trans*-$CrNM^{2+}$ observed depend upon the amount of rearrangement due to isomerization and/or solvolysis during the 10-hr study. No evidence for isomerization was observed. Calculations indicate that no noticeable solvolysis rearrangement occurs during this period. The concentrations of products at 17,840 sec were used with the earlier reported solvolysis constants to calculate the expected changes due to solvation at 35,500 sec. An increase of 10% in the concentration of *cis*-$CrNM^{2+}$ would be expected. A decrease of 3% of the trans species was indicated. Since the changes are near those of the analysis uncertainty, no corrections for solvolysis were made.

The rate coefficient for the formation of *cis*-$CrNM^{2+}$ was calculated from the equation

$$k_4 = \frac{\Delta[cis\text{-}CrNM^{2+}]}{\Delta t[CrM^{3+}][SCN^-]}$$

The value of k_4 was found to be $1.9 \pm 0.07 \times 10^{-6}\ M^{-1}\ sec^{-1}$. The uncertainty reported is based on the fit of the data to a linear plot at the 95% confidence level for the four data points in Table VI. The rate coefficient, k_3, was found to be $0.87 \pm 0.04 \times 10^{-6}\ M^{-1}\ sec^{-1}$ from the initial rate of formation of *trans*-$CrNM^{2+}$.

The rate coefficient, k_2, the direct replacement of methanol, must be obtained by differences. The rate of formation of CrN^{2+} is due to two paths: the association of thiocyanate with hexaaquochromium(III), and the direct replacement of methanol on CrM^{3+}. The apparent rate coefficient at any time would be given by

$$k_{app} = \frac{\Delta[CrN^{2+}]}{\Delta t[SCN^-]([Cr^{3+}] + [CrM^{3+}])}$$

The k is then related to individual rate coefficients, k_1 and k_2, by the following expression

$$k_{app} = \frac{k_1[Cr^{3+}] + k_2[CrM^{3+}]}{[Cr^{3+}] + [CrM^{3+}]} \qquad (8)$$

The value of k_{app} was found to be $2.18 \pm 0.08 \times 10^{-6}\ M^{-1}\ sec^{-1}$. The value of k_1 at the same temperature, ionic strength, and mol fraction was found to be $2.5 \pm 0.1 \times 10^{-6}\ M^{-1}\ sec^{-1}$ in earlier work.[4] The value of k_2 calculated from eq 8 is $1.3 \pm 0.3 \times 10^{-6}\ M^{-1}\ sec^{-1}$. Baltisberger and Hanson[4] have measured the values of k_1 and k_t in 0.308 mol of methanol. The value of k_f calculated from eq 9 using k_1 and k_t turns out to be $2.9 \times 10^{-6}\ M^{-1}\ sec^{-1}$ for the concentrations of Cr^{3+} and CrM^{3+} given in Table VI. The total rate coefficient, k_f, calculates to be $2.9 \times 10^{-6}\ M^{-1}\ sec^{-1}$ using the Cr^{3+} concentrations given in Table VI and the individually measured k values reported in this paper. The total rate coefficient was also calculated to be $2.9 \times 10^{-6}\ M^{-1}\ sec^{-1}$ using eq 9 where the total concentration of products, $CrNM^{2+}$ and CrN^{2+}, was used in place of CrN^{2+}. The close comparison indicates that the data are internally consistent and that the acceleration observed in mixed solvents has been accounted for.

$$[Cr^{3+}]_{total}k_f = k_1[Cr^{3+}] + (k_2 + k_3 + k_4)[CrM^{3+}] \qquad (9)$$

Discussion

Thiocyanate Anation. Table VII summarizes the data so that rapid comparisons of rate coefficients can be made. The greater reactivity of pentaaquomethanolchromium(III) compared to hexaaquochromium(III) is due to two pathways. The direct replacement of the methanol ligand relative to one single water site on hexaaquochromium(III) by thiocyanate is given by k_2^*/k_1^* equal to 3.1 ± 0.7. The values k^* are corrected statistically for the number of reactive sites. The second acceleration is due to the replacement of a trans water where the ratio, k_3^*/k_1^*, is equal to 2.1 ± 0.1. The relative reactivity of a cis water on pentaaquomethanolchromium(III) is identical with a single water on hexaaquochromium(III), $k_4^*/k_1^* = 1.0$. The ease of breaking the methanol bond relative to water is expected.[5] The greater reactivity of the trans anation may be due to steric hindrance of the cis site by the bulky methanol ligand. This would be consistent with an I_a mechanism for chromium(III). The general fate of Co(III) or Cr(III) substitution reactions is for the cis isomer to react with almost total retention of configuration. Trans species on the other hand react with some scrambling of configuration particularly in cases where π bonding of the ligand to the metal could aid in the formation of a trigonal bipyramidal structure in the transition state.[17] No scrambling would be expected with methanol in the cis or trans position.

The cis and trans site reactivity depends on the ability of other ligands in the complex ion to π bond to or to polarize the activated complex in the transition state. Methanol and water would have similar abilities in this regard. The more reactive trans site may be more indicative of a steric problem in the cis position. This is evidenced in part by the unusally high equilibrium constant for the formation of *cis*-$CrNM^{2+}$.

Solvolysis of Thiocyanatochromium(III) Species. Thiocyanate has the effect of labilizing the aquation of trans methanol relative to cis methanol of $CrNM^{2+}$, $k_5/k_6 = 2.0$. In the reverse reaction, the methanol solvolysis of CrN^{2+}, k_7^*/k_8^* is equal to 1.2 ± 0.1. The values k_7 and k_8 are corrected to the basis of a single site for comparison. Labilization of either site by different ligands has been reported. Moore, Basolo, and Pearson have postulated that iodide labilizes the trans water position of CrI^{2+}.[18] King and Vanderheiden[14] in more recent work with the solvolysis of $Cr(OH_2)_5I^{2+}$ have shown that in a mixed solvent of water-DMSO, *trans*-$Cr(OH_2)_4(DMSO)I^{2+}$ is formed confirming the suggestion of Moore, Basolo, and Pearson. Garner, *et al.*,[19-21] found the cis chloro site to be more reactive than the trans position of $Cr(en)_2Cl_2^+$ and $Cr(en)_2ClOH^+$. Tobe[22] has shown in the aquation of X in $Co(en)_2AX^+$ ion that when A equals thiocyanate the ratio of k_{trans}/k_{cis} for X^- equal to chloride is 5×10^{-3}. When X^- is equal to Br^- the ratio is 2×10^{-2}. In this work we see that the presence of thiocyanate in the cis position labilizes the replacement of water by methanol, $k_8^*/k_{-H_2O}^*$ is equal to 1.5, and the replacement of methanol by water where $k_6^*/k_{-CH_3OH}^*$ is equal to about 2. The last two rate coefficients are in different solvents so the comparison is difficult. This labilization could be due just to a decrease in charge of the central ion. The presence of thiocyanate in the trans position labilizes

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Table VII. Rate Coefficients of Chromium(III) Substitution Reactions in Water–Methanol Solvents at 30°

Reaction	Solvent	$k \times 10^6$	Corrected $k^* \times 10^6$	Ref
k_1, CrO + N → CrN[a]	0.308 mol CH_3OH	2.5[b]	0.42[c]	*d*
k_2, CrM + N → CrN	0.308 mol CH_3OH	1.3	1.3	
k_3, CrM + N → *trans*-CrNM	0.308 mol CH_3OH	0.87	0.87	
k_4, CrM + N → *cis*-CrNM	0.308 mol CH_3OH	1.9	0.48	
k_{exchange}, CrO + O → CrO	Water	32	5.3	*e*
k_{-H_2O}, CrO + M → CrM	0.308 mol CH_3OH	2.4	0.40	*f*
k_{-CH_3OH}, CrM + O → CrO	0.308 mol CH_3OH	5.3	5.3	*f*
k_5, *trans*-CrNM + O → CrN	H_2O	21	21	
k_6, *cis*-CrNM + O → CrN	H_2O	11	11	
k_7, CrN + M → *trans*-CrNM	0.308 mol CH_3OH	0.76	0.76	
k_8, CrN + M → *cis*-CrNM	0.308 mol CH_3OH	2.5	0.62	

[a] Charges eliminated in order to simplify the equations, where Cr^{3+} = Cr, O = H_2O, N = SCN^- (coordinated iso), M = CH_3OH. [b] Units either in sec^{-1} or M^{-1} sec^{-1}. [c] Statistically corrected $k^* = k$/number of reacting sites. In cases involving mixed solvents, the value of k was not corrected for the mole fraction of the solvent. [d] Reference 4. [e] J. P. Hunt and R. A. Plane, *J. Amer. Chem. Soc.*, 76, 5760 (1954). [f] Reference 5.

the replacement relative to a cis position for a similar reaction, $k_7^*/k_8^* = 1.2$ and $k_5^*/k_6^* = 1.9$. The fact that these numbers are not closer together may be either due to scrambling of configuration in the trans reaction or because the trans position does not labilize water and methanol to the same extent. This point cannot be distinguished in this work. The results of a study by Swaddle and Guastalla[23] of the aquation of chromium(III) aquoamines indicate that the aquations are stereoretentive and that isomerization is slow. The fact that we observed no isomerization in this study indicates the chromium(III) aquomethanol system is behaving in a similar manner.

The equilibrium concentrations of thiocyanatochromium(III) give a ratio of cis to trans equal to 7:1. The equilibrium concentration of cis and trans is also given by

$$\frac{[cis\text{-CrNM}^{2+}]}{[trans\text{-CrNM}^{2+}]} = \frac{k_6k_8}{k_7k_5} = 6.3$$

The ratio of the solvolysis products at equilibrium agrees with the rate coefficients measured. The equilibrium $\bar{n}$ value 0.32 for CrN^{2+} in 0.308 mol of methanol is similar to the value of 0.33 measured for chromium(III) in the same solvent.[5,16] King and Baltisberger have found that chlorochromium(III) has a similar $\bar{n}$ value to chromium(III) in several different methanol–water mixtures.[5] A rational comparison of equilibrium quotients would be to correct for the statistical contribution. The corrected value of $\bar{n}$ of Cr-X^{2+} would be 0.064 compared to 0.055 for Cr^{3+}. King in several papers has shown that statistical corrections alone do not yield constant values for stepwise reactions in mixtures of water–methanol, water–ethanol,[24] water–dimethyl sulfoxide,[10] and water–pyridine *N*-oxide.[11] In the case of methanol–water–chromium(III) equilibria, King based an explanation on a two-term steric repulsion model or on a two-term logarithmic relationship. Both models were consistent with the data. In the repulsion model proposed by King[16] the relative amounts of *cis*- to *trans*-dimethanolchromium(III) at equilibrium would be 2.4:1. The model is consistent with an expected methanol–methanol steric interaction at the cis position. In the study they were unable to isolate isomers and test the model completely, although the total calculated equilibrium quotient for the formation of dimethanolchromium(III), *Q*(trans) + *Q*(cis), agreed with the experimentally measured value. The model gives a calculated value of $Q(trans\text{-CrM}_2{}^{3+})$ to be 0.059 and $Q(cis\text{-CrM}_2{}^{3+})$ to be 0.144. Solvent activities are included in the calculation of the quotients. In our work the presence of thiocyanate greatly increases the cis to trans ratio to a value of 7:1. The measured value of $Q(trans\text{-CrNM}^{2+})$ is 0.047 using a_{CH_3OH}/a_{H_2O} equal to 1.17, which is the same activity ratio used in the work of Mills and King.[16] The quotient at 0.4 *M* ionic strength is remarkedly close to the value of $Q(trans\text{-CrM}_2{}^{3+})$ predicted by the model at 0.16 *M* ionic strength. The values of $\bar{n}$ increase slightly with ionic strength below 0.5 *M*. The number further confirms the validity of the repulsion model treatment. The value of $Q(cis\text{-CrMN}^{2+})$ calculates to be 0.350 which is several times larger than $Q(cis\text{-CrM}_2{}^{3+})$. The data are consistent with much less steric hindrance due to the thiocyanate–methanol interaction at the cis site. This is apparently an explanation of the larger than expected $\bar{n}$ values for $CrCl^{2+}$.

Table VIII. Effect of Entering Group on the Rates of Association with Chromium(III) Ions in Mixed Solvents[a]

Ligand	X_{CH_3OH}	10^6k_1, M^{-1} sec^{-1}	10^6k_t, M^{-1} sec^{-1}	k_t/k_1
HF	0	1.2		
HF	0.308	0.78	1.2	1.5
NO_3^-	0	1.2[b]		
NO_3^-	0.308	1.2	2.3	2.5[e]
SCN^- [c]	0	2.9		
SCN^-	0.128	2.6	3.7	1.4
SCN^-	0.308	2.5	3.7	1.4
Cl^- [d]	0	0.16		
Cl^-	0.128	0.15	0.52	3.5
Cl^-	0.308	0.22	0.83	3.7

[a] $I = 0.42$ *M*, temperature 30°. [b] $I = 1.44$ *M*. [c] Reference 4. [d] Reference 5. [e] The uncertainty (2σ) of this value is ±1.0; the other values of the ratios are ±0.1.

Effects of Variation of Entering Group. The rate coefficients for a number of anation reactions are presented in Table VIII. The solvent effect on an individual rate coefficient is variable, but the ratio of k_t/k_1 remains constant in going from one solvent to another. We have just completed an nmr study of the relative solvation of hexaaquochromium(III) and pentaaquomethanolchromium(III) in water–methanol solvents. The study indicates a preferential second sphere solvation of both ions by methanol, but the solvation of each ion is nearly identical. The constancy of k_t/k_1 would be expected if the solvent environment around each ion and transition state changed in the same manner in going from one mixed solvent to another. Langford has shown in previous work that chromium(III) solvation rates are better correlation with second sphere solvation populations than mixed solvent bulk compositions.[25]

A variation of k_t/k_1 with entering group is noted in Table VIII. The acceleration effects in the case of hydrofluoric

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acid and thiocyanate are similar. Chloride dramatically increases the acceleration rate. It is possible that only in the chloride substitution reaction is the accelerating nature of the cis site showing up. The other bulky ions cannot get into the cis site as rapidly. This interpretation would be consistent with the I_a nature of the chromium(III) substitution reactions. The nitrate acceleration is uncertain due to scatter in the data.

Registry No. $Cr(OH_2)_6{}^{3+}$, 14873-01-9; $Cr(OH_2)_5(CH_3OH)^{3+}$, 29827-16-5; $Cr(OH_2)_5(NCS)^{2+}$, 22258-89-5; *trans*-$Cr(OH_2)_4(CH_3OH)(NCS)^{2+}$, 52003-12-0; *cis*-$Cr(OH_2)_4(CH_3OH)(NCS)^{2+}$, 52079-27-3; $Cr(OH_2)_3(CH_3OH)_2(NCS)^{2+}$, 52063-97-5; SCN^-, 302-04-5; F^-, 16984-48-8; CH_3OH, 67-56-1.

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Oxidation of Free and Coordinated Thiols by Neptunium(VI)[1a]

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The Np(VI) oxidation of thioglycolic acid (tga) has been quantitatively investigated under conditions where the reaction involves a 1-equiv oxidation at sulfur. This reaction follows the rate law $-d(\ln [Np(VI)])/dt = (a + b/[H^+])[tga]$; at 25° and $\mu = 1.00\ F$ ($LiClO_4$), $a = 3.5 \pm 0.7\ F^{-1}\ sec^{-1}$, $b = 34.2 \pm 0.3\ sec^{-1}$, and the corresponding activation parameters are $\Delta H^*_a = 6 \pm 3$ and $\Delta H^*_b = 14.2 \pm 0.2$ kcal/mol and $\Delta S^*_a = -37 \pm 11$ and $\Delta S^*_b = -3.7 \pm 0.5$ eu. The Np(VI) oxidation of methyl thioglycolate follows a similar rate law with values of a and b at 25° and $\mu = 1.00\ F$ ($LiClO_4$) of $58 \pm 2\ F^{-1}\ sec^{-1}$ and $2.7 \pm 0.1\ sec^{-1}$, respectively. These results are interpreted as indicating that the net rate of oxidation of tga deprotonated at the carboxyl group (b^{COO}) is 12 times greater than the net rate of oxidation of tga deprotonated at the sulfhydryl group (b^S); however, the specific rate of oxidation of the latter form ($k_2{}^S = b^S/K^S$) is 10^3 times greater than that of the former ($k_2{}^{COO} = b^{COO}/K^{COO}$) since the acid dissociation constant of the carboxyl group (K^{COO}) is about 10^4 times greater than that of the sulfhydryl group (K^S). Qualitative observations have also been made on the Np(VI) oxidation of coordinated thiolato ligands in the complexes $[Cr(en)_2(SCH_2COO)]^+$, $[Co(en)_2(SCH_2COO)]^+$, $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$, $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$, $[Cr(en)_2(SCH_2CH_2COO)]^+$, $[Cr(en)_2(SC_6H_4COO)]^+$, and $[Cr(en)_2(OH_2)(OOCCH_2SH)]^{2+}$. The last two complexes consume roughly 1 equiv of Np(VI)/mol of complex and can be considered to undergo the same type of oxidation as free thiols. The other complexes undergo multiequivalent, multistep oxidations often involving oxidation of the thiol carbon backbone. Chromium(III)-thiolato complexes are oxidized much more rapidly than analogous cobalt(III) complexes and coordinated tga is oxidized much more rapidly than coordinated cysteamine or coordinated thiopropionic acid. Rationalizations to account for these observations are presented.

Introduction

Thiols contain the chemically most reactive functionality found in biological systems. A prominent feature of this reactivity is the ease of oxidation of thiols (RSH) to disulfides (RSSR), which in turn are resistant to further oxidation under mild conditions. The RSH-RSSR redox pair comprises an essential part of many electron-transport systems, the myriad biochemical roles of these systems having recently been reviewed.[2] Of particular interest to the inorganic chemist are the observations that in biological systems (1) transition metal complexes (*e.g.*, vitamin B_{12}[3]) are often associated with thiols and (2) the RSH-RSSR conversion is often mediated by metal-containing enzymes in relatively complicated reaction sequences (*e.g.*, phosphorylation of adenosine monophosphate can be coupled to the transfer of electrons from glutathione to cytochrome *c* in a reaction which requires oxidized glutathione as a catalyst[4]). In the hope of shedding some light on the chemistry of these complex natural processes, we have undertaken a detailed kinetic study of the relatively simple Np(VI) oxidation of free thioglycolic acid (tga) and its methyl ester in dilute aqueous solutions. Analogous studies with other metal ion oxidants have been reported,[5] but conclusions reached therein must be considered suspect in light of recent work showing that the stoichiometry of thiol oxidations is very sensitive to reaction conditions.[6] Indeed, the results reported in this study demonstrate that under properly controlled conditions the kinetics of metal ion oxidation of thiols are much simpler than previously appreciated.

Kinetic studies on the oxidation of free thiols also provide a standard to which the rates of oxidation of coordinated thiols may be compared. The oxidation of thiolato metal complexes is of considerable current interest in both biological and inorganic chemistry as evidenced by the following reports as to the possible courses such reactions may take: (a) autoxidation of $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$ leads to metal-sulfur bond fission and formation of the free disulfide;[7] (b) H_2O_2 oxidation of tris(cysteinato)cobaltate(III) proceeds by oxidation at the coordinated sulfur, with no cleavage of the metal-sulfur bond, to yield the S-bonded tris(cysteine)-sulfinato complex;[8] (c) oxidation of *O,S*-mercaptoacetatobis-

(1) (a) A portion of this investigation was conducted under the auspices of the United States Atomic Energy Commission. (b) ANL-AUA-AEC Laboratory Graduate Participant, 1972-1973. (c) University of Chicago. (d) Argonne National Laboratory. (e) Presently located at University of Cincinnati.

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