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Further Characterization and Aquation of the Thiolopentaaquochromium(III) Complex, $CrSH^{2+}$, and Its Equilibration with Thiocyanate

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The sulfate salt of the thiolochromium(III) complex has been prepared. Analyses and ir spectra together with solution Raman and charge per Cr determinations support Ardon and Taube's $CrSH^{2+}$ formulation. Kinetic studies on the aquation reaction, $CrSH^{2+} + H^+ \rightarrow Cr^{3+} + H_2S$, give a hydrogen ion dependence $k_{obsd} = k_0 + k_1[H^+]$, $[H^+] = 0.01–1.00$ M, with $k_0 = (3.09 \pm 0.07) \times 10^{-5}$ s^{-1} and $k_1 = (3.82 \pm 0.16) \times 10^{-5}$ M^{-1} s^{-1} at 40 °C, $I = 1.00$ M ($LiClO_4$). Activation parameters for k_0 are $\Delta H^{\ddagger} = 27.7 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = 9.4 \pm 0.9$ cal K^{-1} mol^{-1}. The kinetics of the equilibration reaction with thiocyanate, $CrSH^{2+} + NCS^- \rightleftharpoons Cr(NCS)SH^+$, have also been studied. The $[H^+]$ dependence of the forward reaction ($k_2 + k_3[H^+]$) and the reverse are of the same form, where at 25 °C $k_2 = (8.57 \pm 0.15) \times 10^{-4}$ M^{-1} s^{-1} and $k_3 = (1.61 \pm 0.05) \times 10^{-3}$ M^{-2} s^{-1}, $I = 1.00$ M ($NaClO_4$). The equilibrium constant of 2.8 ± 0.08 M^{-1} from the kinetics is to be compared with a spectrophotometric value ($[H^+] = 0.1$ M) of 4.8 ± 0.1 M^{-1} at 25 °C.

Although various studies on sulfur-containing complexes have been reported and reviewed,[1,2] the important complex $CrSH^{2+}$ reported by Ardon and Taube[3] has not as yet been further investigated and detailed mechanistic studies have not been made. The substitution properties of this species are relevant in the assessment of not only the lability of Cr–S bonds[4-6] but also the labilizing effect which the SH^- group has on other ligands as compared to OH^- in $Cr(H_2O)_5OH^{2+}$. In this paper we report experiments concerned with the further purification and characterization of the complex as well as the kinetics of the aquation reaction and the equilibration of the complex with thiocyanate.

Experimental Section

Preparation of Solutions of Complex. Deaerated polysulfide solution, prepared by diluting a mixture of elemental sulfur (0.32 g) with hydrated sodium sulfide (2.4 g in 3 ml of H_2O) to 250 ml, was added dropwise to Cr^{2+} (ca. 0.08 M, 400 ml) in perchloric acid (ca. 0.08 M) with shaking. Oxygen-free conditions were maintained throughout. After the addition was complete, a vigorous current of nitrogen was passed through the solution for 45–60 min to expel all the H_2S generated. Oxygen was then passed through the solution for 5–7 min to oxidize excess Cr^{2+}. The reaction mixture was deaerated again with a brisk current of N_2 for 20–30 min.

The total volume was divided into two portions and passed down two deaerated, ice-cooled Dowex 50W-X8 (100–200 mesh) ion-exchange columns (1.8-cm diameter, 23 cm long) under air-free conditions. A bluish green complex formed a diffuse first band and was followed by the required brownish green complex. Other complexes including $Cr(H_2O)_6^{3+}$ and higher charged species were observed but remained on the top of the columns. The bluish green complex was eluted with 0.12 M $HClO_4$ (200 ml). The required brownish green band was eluted with a solution of 0.5 M $HClO_4$ and 0.5 M $NaClO_4$. About 7–10 cm separation was obtained between $Cr(H_2O)_6^{3+}$ and the required band.

The solution obtained (0.03–0.05 M, 50–75 ml) was contaminated with small amounts of impurities. Two subsequent ion-exchange separations using three different types of Dowex 50W resins did not remove the impurities effectively. Instead further purification was achieved by mixing the ion-exchange fraction containing the desired complex at near 0 °C with Cr^{2+} (0.5 ml of 0.8 M for 50 ml of 0.05 M complex) under rigorously air-free conditions. Nitrogen was further purified by passing through alkaline pyrogallol following this stage. The solution was diluted with ice-cold deaerated water (200 ml) and passed down another air-free Dowex 50W-X8 column at 0 °C. The column was washed with perchloric acid (0.10 M, 150 ml) and the required complex, which formed the first of three or four colored bands was eluted with a solution of 0.10 M $HClO_4$ and 0.90 M $NaClO_4$ or $LiClO_4$. About 120–150 ml of the eluent passed through the column before the desired complex (ca. 0.04 M, ca. 30 ml) could be collected under N_2. Teflon needles were used throughout in the transferrance of solutions.

The acid concentration of the eluate $I = 1.00$ M ($NaClO_4$) was determined on a Radiometer (Type PHM 4d) pH meter calibrated with 0.100 M $HClO_4$, $I = 1.00$ M ($NaClO_4$). Analyses relating to the assignment of the $CrSH^{2+}$ formula and the spectrum of the complex are given below. The entire procedure described took 30–35 h. The most suitable break is prior to the second ion-exchange separation. A sample stored as a frozen solid at ca. −6 °C gave no spectrophotometric changes at 350–600 nm over a period of 20 h.

Preparation of Solid. A more concentrated solution of $CrSH^{2+}$ (0.05–0.01 M, 50 ml) was prepared by eluting with 1.00 M $HClO_4$ instead of a mixture of $HClO_4$ and $NaClO_4$. This stock was then poured into a degassed and ice-cooled mixture of absolute alcohol (50 ml) and diethyl ether (150 ml). The solution was cooled with dry ice–acetone (−78 °C) under a current of N_2. Concentrated H_2SO_4 (0.5 ml) at 0 °C was added and immediately followed by degassed diethyl ether (250 ml) cooled in dry ice–acetone. Flaky crystals of the brownish green complex separated out. The crystals were filtered under a current of N_2 and dried in vacuo over P_2O_5 for 5–6 h. Anal. Calcd. for $[Cr(H_2O)_5SH]SO_4$: Cr, 19.2; S(as sulfate), 11.8; S(total), 23.6. Found: Cr, 19.4; S(as sulfate) 11.85; S(total), 23.6.

Determination of Charge per Atom. The complex (15 ml; 4.75×10^{-2} M) in 1.00 M $HClO_4$ was diluted with 75 ml of deaerated water at 0 °C and loaded onto an ice-cooled deaerated Dowex 50W-X2 (100–200 mesh) ion-exchange column (0.8-cm diameter, 8.0 cm long) at a flow rate of 1.5 ml min^{-1}. The column was washed with acid at pH 2.0 (20 ml). A brownish green band, 0.5–0.7 cm in length was obtained. A deaerated and precooled solution of thorium(IV) perchlorate (G. F. Smith Chemical Co.) (9.45×10^{-3} M), $[HClO_4] = 0.145$ M, was used to displace the Cr(III) species and the flow rate was maintained at 1 ml/min. About 25 ml of displaced solution was collected before any Cr(III) was displaced from the resin. The first fraction (5–10 ml) was rejected and the next fraction (20 ml) was collected. The Cr(III) concentration in the collected fraction was estimated by H_2O_2–NaOH oxidation and measurement of the absorbance of CrO_4^{2-} at 372 nm, ϵ 4.82×10^3 M^{-1} cm^{-1}. The free acid in the Cr(III) solution was determined by measurement of the pH of a solution diluted threefold, using a pH meter which had been calibrated according to the $[H^+]$ of the Th(IV) solution used in the displacement procedure as well as standard acid at $I = 1.00$ M ($NaClO_4$). The charge per atom, m, was determined from

$$m = \frac{4[\mathrm{Th(IV)}] + [H^+]_1 - [H^+]_2}{[\mathrm{Cr(III)}]}$$

where $[H^+]_1$ and $[H^+]_2$ are the hydrogen ion concentrations of the Th(IV) and Cr(III) solutions, respectively.[7]

Spectrum and Stability. The uv–visible spectrum of $CrSH^{2+}$ is given in Figure 1. The peaks and absorption coefficients (M^{-1} cm^{-1}) at 575 nm (27.5), 435 nm (43.1), and also 258 nm (6520) are in excellent agreement with those reported by Ardon and Taube.[3] Solutions obtained after just one ion-exchange separation (see preparative procedure) invariably contained impurities which led to higher absorbancies at <400 nm, Figure 1. Solutions were of limited stability and were generally used within 24 h of preparation. The spectrum obtained on anaerobic aquation at 40 °C, $[H^+] = 0.01–1.00$ M, corresponds to $Cr(H_2O)_6^{3+}$, Figure 1. Ion-exchange isolation of the product from solutions aquated at $[H^+] = 0.01$, 0.10, and 1.00 M for 24 h indicated >98% of the product was $Cr(H_2O)_6^{3+}$, (1). Some

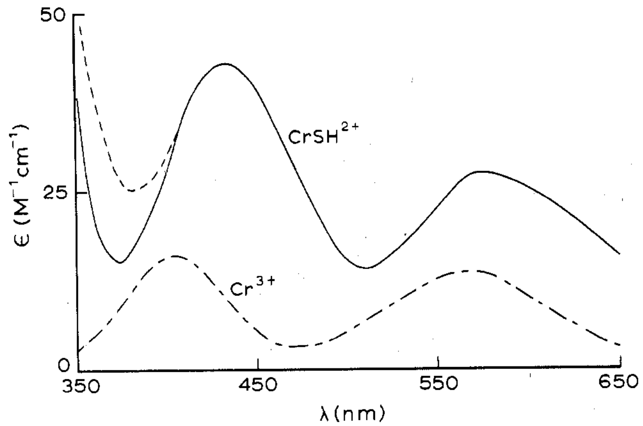

Figure 1. Uv-visible spectra of the aquo ions of CrSH^{2+} and Cr^{3+} in 0.10 M HClO$_4$, I = 1.00 M (NaClO$_4$). Impure samples of CrSH^{2+} generally have additional absorption at λ <400 nm as indicated (broken line).

Table I. Rate Constants k_{obsd} for the Aquation of CrSH^{2+} [λ 450 nm, I = 1.00 M (LiClO$_4$)]

Temp, °C	[H$^+$], M	10^3[CrSH^{2+}], M	10$^5k_{obsd}$, s^{-1}
40.0	0.01	6.8	3.46[a]
	0.01	2.34	3.34
	0.01	4.68	3.39
	0.025	4.17	3.42
	0.025	4.7	3.28[b]
	0.050	5.68	3.33
	0.0825	1.88	3.42
	0.10	2.35	3.35[b]
	0.10	4.17	3.36
	0.10	4.7	3.48[b]
	0.10	18.75	3.54
	0.25	1.88	4.16
	0.50	3.76	5.0
	0.75	3.76	5.84
	1.0	3.76	6.97
47.5	0.01	4.05	10.3
	0.10	3.83	9.97
	0.10	11.5	9.85
55.0	0.01	4.05	27.7
	0.10	3.83	27.9
	0.10	11.5	27.4

[a] λ 575 nm. [b] Ionic strength adjusted with NaClO$_4$; not included in computation of rate constant parameters.

$$\mathrm{CrSH^{2+} + H^+ \rightarrow Cr^{3+} + H_2S} \tag{1}$$

unreacted CrSH^{2+}, ca. 2%, was recovered. On exposure of solutions of CrSH^{2+} to O$_2$ sulfur is deposited.

Kinetic Measurements. The kinetics of (1) were studied by monitoring the absorbance (A) at 450 nm,, at which wavelength ε is 39.4 M^{-1} cm^{-1} for CrSH^{2+} and ε is 5.3 M^{-1} cm^{-1} for Cr^{3+}. Oxygen-free conditions were used throughout. Rate constants k_{obsd} were obtained from the slopes (×2.303) of plots of log ($A_t - A_\infty$) against time, which were linear for 4–5 half-lives. The ionic strength was adjusted to 1.00 M with LiClO$_4$ in most cases. Runs in which NaClO$_4$ was used gave excellent agreement, Table I. The kinetics of the equilibration reaction with NCS$^-$, were followed at 428 nm, ε 41.8 M^{-1} cm^{-1}, for CrSH^{2+}, an isosbestic point for slow secondary reaction. Infinity-time absorbance readings were stable for at least 2–3 half-lives. The [NCS$^-$] was always in at least tenfold excess. Plots of log ($A_\infty - A_t$) against time were typically linear to >75% and gave k_{eq}. The ionic strength was adjusted to 1.00 M with NaClO$_4$.

Infrared and Raman Spectra. Infrared spectra were run on a Perkin-Elmer 457, and Raman spectra using a Coderg instrument. The latter were recorded using the 488-nm line of a Spectra Physics 125A argon laser source (Model 52).

Results

Further Characterization. The sulfate salt which was isolated analyzed for [Cr(H$_2$O)$_5$SH]SO$_4$. Infrared spectra of a Nujol mull give weak bands at 2560 and 340 cm^{-1} which are assigned to ν(S–H) and ν(M–S) stretching frequencies, respectively. Metal–sulfur stretching frequencies in similar complexes lie in the region 480–210 cm^{-1}.[8] Raman spectra of 0.05–0.13 M aqueous solutions (0.1 M HClO$_4$ and 1.9 M NaClO$_4$) also give a sharp band at 337 cm^{-1} which can be assigned to ν(M–S) stretch. The fact that ν(M–S) is both ir and Raman active is consistent with C_s symmetry of a bent triatomic system, in this case Cr–S–H. This observation rules out alternative bridged structures having a center of symmetry. The absence of ν(S=O) splitting in the infrared spectra indicates that the sulfate is in the ionic state and not coordinated.

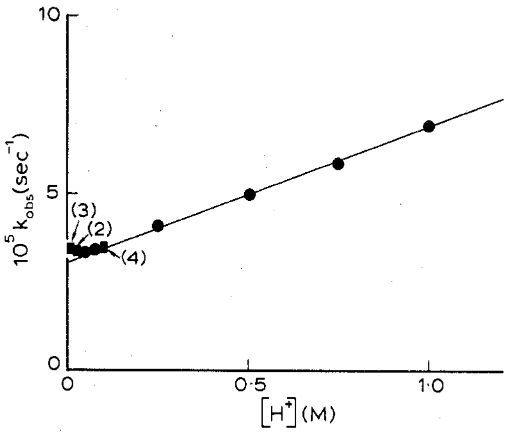

Figure 2. [H$^+$] dependence of rate constants k_{obsd} for the aquation of CrSH^{2+} at 40 °C, I = 1.00 M (LiClO$_4$).

The charge per Cr atom of the complex in solution was determined and found to be 1.95 and 1.82 (two determinations), consistent with the formulation CrSH^{2+} at [H$^+$] = 0.1–0.2 M.

Kinetics of Aquation Reaction. Rate constants k_{obsd} are given in Table I. The variation of k_{obsd} with [H$^+$] at 40 °C, Figure 2, gives a good fit to (2). Points at [H$^+$] = 0.01–0.05 M deviate up to 10% from this linear dependence and suggest that a term k_{-1}[H$^+$]$^{-1}$ may contribute. From a least-squares treatment of data [H$^+$] ≥ 0.1 M, weighting $1/k_{obsd}^2$, k_0 = (3.09 ± 0.07) × 10^{-5} s^{-1} and k_1 = (3.82 ± 0.16) × 10^{-5} M^{-1} s^{-1} at 40 °C, I = 1.00 M (LiClO$_4$). With the inclusion of k_{-1}, values of k_0 and k_1 are essentially (<1%) unchanged and k_{-1} = (2.74 ± 0.72) × 10^{-8} M s^{-1}. From the temperature dependence at 40–55 °C, [H$^+$] = 0.10 M, when k_{obsd} may be assumed equal to k_0, activation parameters for k_0 are $\Delta H^\ddagger$ = 27.7 ± 0.3 kcal mol^{-1} and $\Delta S^\ddagger$ = 9.4 ± 0.9 cal K^{-1} mol^{-1}. An extrapolated value of k_0 at 25 °C is 4.27 × 10^{-6} s^{-1}.

$$k_{obsd} = k_0 + k_1[\mathrm{H^+}] \tag{2}$$

Equilibrium Constant for Thiocyanate Anation. The constant K refers to the equilibrium in (3). At constant [H$^+$] and [CrSH^{2+}] and with a large (>tenfold) excess of [NCS$^-$], absorbance changes can be expressed as in (4), where ϵ_0, ϵ_c, and ϵ_{obsd} are the molar absorption coefficients for CrSH^{2+}, Cr(NCS)SH$^+$, and a mixture of the two at any particular [NCS$^-$].[9] Plots of $(\epsilon_{obsd} - \epsilon_0)^{-1}$ against [NCS$^-$] are linear and give no evidence for higher complexes, Figure 3. At 25 °C and [H$^+$] = 0.1 M, I = 1.00 M (NaClO$_4$), K = 4.8 ± 0.1 M^{-1}. The dependence of K on [H$^+$] was investigated and gave 10%

$$\mathrm{CrSH^{2+} + NCS^- \overset{K}{\rightleftharpoons} Cr(NCS)SH^+} \tag{3}$$

$$\frac{1}{\epsilon_{obsd} - \epsilon_0} = \frac{1}{\epsilon_c - \epsilon_0}\left(1 + \frac{1}{K[\mathrm{NCS^-}]}\right) \tag{4}$$

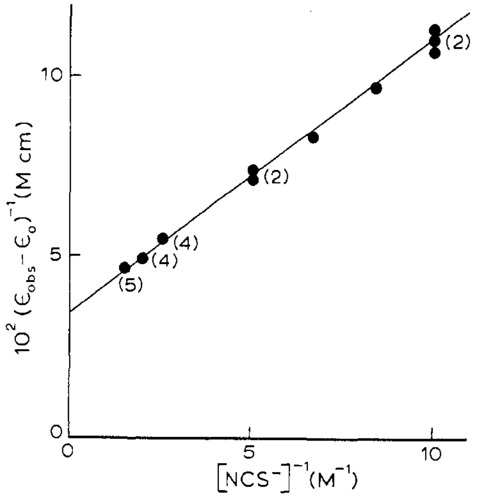

Figure 3. Spectrophotometric determination of the equilibrium constant K at λ 428 nm, for the 1:1 complex of NCS^- with $CrSH^{2+}$ at 25 °C, $[H^+] = 0.10$ M, $I = 1.00$ M ($NaClO_4$). Coincident points are indicated by numbers in parentheses.

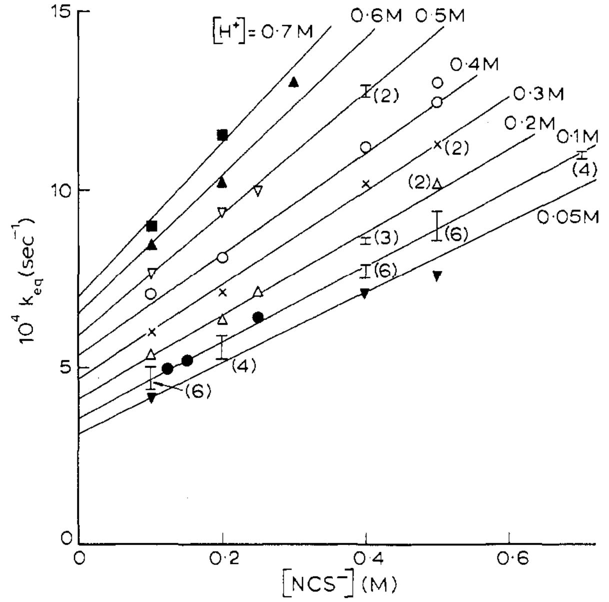

Figure 4. $[NCS^-]$ dependence of rate constants k_{eq} for the 1:1 equilibration of NCS^- with $CrSH^{2+}$, at 25 °C, λ 428 nm, $I = 1.00$ M ($NaClO_4$).

variation as $[H^+]$ was varied from 0.1 to 0.4 M. Since values of ϵ_0 and ϵ_c may also be $[H^+]$ dependent due to the participation of $CrSH_2^{3+}$ and $Cr(NCS)SH_2^{2+}$ species, no attempt was made to analyze further this variation of K.

Kinetics of Thiocyanate Anation. The first-order dependence of rate constants k_{eq} on $[NCS^-]$, Figure 4, is consistent with an equilibration process as in (3) with no evidence for ion-pair saturation involving NCS^- and $CrSH^{2+}$. Rate constants for both the forward (slope) and back reactions (intercepts, Figure 4) exhibit a dependence on $[H^+]$. From Figure 5 it is concluded that the dependence on $[H^+]$ is first order. These dependences are adequately explained by the reaction scheme of (5), where K_1 and K_2 are protonation constants. Evidence

$$\begin{array}{ccc} CrSH^{2+} + H^+ + NCS^- & \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} & Cr(NCS)SH^+ + H^+ \\ \upharpoonleft\downharpoonright K_1 & & \upharpoonleft\downharpoonright K_2 \\ CrSH_2^{3+} + NCS^- & \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} & Cr(NCS)SH_2^{2+} \end{array} \qquad (5)$$

supporting the inclusion of K_1 comes from the aquation study in which the term $k_1[H^+]$ contributes, (2). It is possible to replace k_{-2} and k_{-3} in the rate law, assuming K as defined in (3) is equal to k_2/k_{-2}, when (6) is obtained. Values of k_{eq},

$$k_{eq} = (k_2 + k_3K_1[H^+])([NCS^-] + K^{-1}) \qquad (6)$$

$[NCS^-]$, and $[H^+]$ were fitted to this equation using a nonlinear least-squares program with weighting $1/k_{eq}^2$,[10] and gave $k_2 = (8.57 \pm 0.15) \times 10^{-4}$ M^{-1} s^{-1}, $k_3K_1 = (1.61 \pm 0.05) \times 10^{-3}$ M^{-2} s^{-1}, and $K = 2.80 \pm 0.08$ M^{-1}.

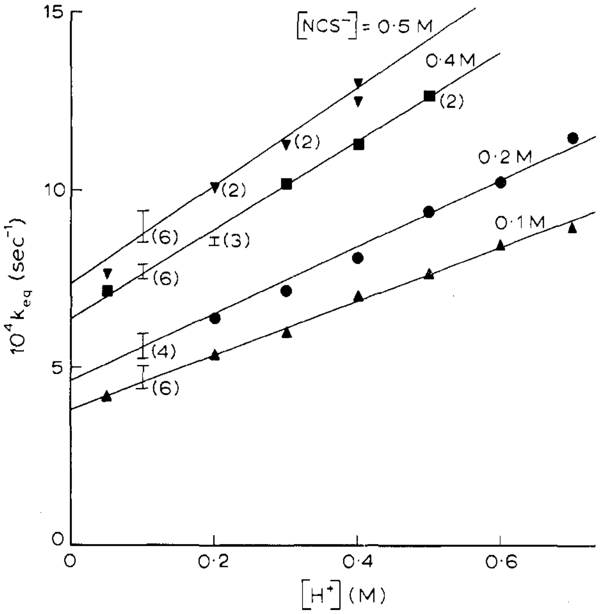

Figure 5. $[H^+]$ dependence of rate constants k_{eq} for the 1:1 equilibration of NCS^- with $CrSH^{2+}$ at 25 °C, λ 428 nm, $I = 1.00$ M ($NaClO_4$). The concnentration of $CrSH^{2+}$ was varied from 1.46 × 10^{-3} to 8.44 × 10^{-3} M at $[H^+] = 0.1$ M.

Discussion

Ardon and Taube's assignment of a thiolopentaaquochromium(III) structure[3] was based on ion-exchange elution behavior, the oxidation state of the sulfur, and the Cr:S ratio. Though these are consistent with a mononuclear structure, they do not rule out alternative binuclear structures. Evidence supporting their assignment has now been obtained from elemental analyses and ir studies on the sulfur salt, together with Raman and charge per Cr determinations of solutions of the complex. Evidence for the purity of $CrSH^{2+}$ solutions prepared by the procedure described comes from the aquation study which yields $Cr(H_2O)_6^{3+}$ (>98%) as the sole product of a single-stage kinetic process. Even after three successive ion-exchange separations in the preparative procedure it was found that, without treatment with Cr^{2+} following the first ion-exchange, an impurity or impurities were present. The latter gave increased absorbance at <400 nm (Figure 1) and in the aquation study resulted in an increase and then decrease in absorbance in the range 350–400 nm. A Sephadex SP C25 separation of such a solution yielded 0.3–1.0% of a greenish yellow species with an absorption coefficient of 2940 ± 20 M^{-1} cm^{-1} at 355 nm. When only one ion-exchange separation was made, a typical solution gave as much as 10% of a greenish yellow species besides 75–85% of $Cr(H_2O)_6^{3+}$ after 24 h of aquation at 40 °C.

Similarities in spectrum of $CrSH^{2+}$ (Figure 1) as compared with that of $CrSCH_2CH_2NH_3^{3+}$, peak positions 578 nm (ϵ 26 M^{-1} cm^{-1}), 438 nm (ϵ 46 M^{-1} cm^{-1}), and 274 nm (ϵ 7000 M^{-1} cm^{-1}),[5] are very striking. The change in polarizability in going from H_2S to R_2S species (R = alkyl group) is <5% as compared with an increase of 24% going from H_2O to R_2O.[1] The possibility that transitions occur between d levels with

Table II. Kinetic Data (25 °C) for the Aquation of S-Bonded Ligands from Pentaaquochromium(III)

Complex	k_0, s^{-1}	$\Delta H_0^{\ddagger}$, kcal mol^{-1}	$\Delta S_0^{\ddagger}$, cal K^{-1} mol^{-1}	Ref
$(H_2O)_5CrSC_6H_5NH_3^{3+}$	4.0×10^{-6} [a]	29.8	16.7	4
$(H_2O)_5CrS(CH_2)_2NH_3^{3+}$	4.5×10^{-5} [a]	27.6	14	5
$(H_2O)_5CrSH^{2+}$	4.3×10^{-6} [b]	27.7	9.4	This work

[a] $I = 2.00$ M ($LiClO_4$). [b] Extrapolated from data at 40–55 °C, $I = 1.00$ M ($LiClO_4$).

different amounts of p character cannot be ruled out in these complexes. Though similarities in the spectra of $CrSH^{2+}$ and $CrSH_2^{3+}$ are possible, our kinetic results indicate that the concentration of $CrSH_2^{3+}$ at $[H^+] = 0.01$–1.00 M is very small. The strongly acidic nature of coordinated H_2S is to be expected since as Ardon and Taube pointed out,[3] the first acid dissociation constant of H_2O is increased from 2×10^{-16} to 10^{-4} M on coordination to Cr(III) in $Cr(H_2O)_6^{3+}$. Hence it is not surprising that H_2S, with a dissociation constant of 1.3×10^{-7} M,[11] will behave as a strong acid when coordinated to Cr(III).

Our attempts to determine protonation constants by spectrophotometry at λ 225 nm, $[H^+] = 0.10$–1.00 M, were unsuccessful. Kuehn and Taube[12] have determined an acid dissociation constant of 10^{-4} M at 25 °C for $Ru(NH_3)_5(SH_2)^{2+}$, suggesting that the species is 5×10^6 times more acidic than $Ru(NH_3)_5(H_2O)^{2+}$.[13] Therefore, allowing for the higher oxidation state in the case of Cr(III), the acid dissociation constant of $CrSH_2^{3+}$ would be expected to be around 10 M or higher. If there is an acid dissociation constant below pH 2, it is not possible to distinguish between processes giving $Cr(H_2O)_4(OH)SH^+$ and $Cr(H_2O)_5S^+$, a point which is also important in the interpretation of the kinetic data.

The dependence of rate constants on $[H^+]$ for the aquation reaction indicates that two terms, $k_0 + k_1[H^+]$, are effective within the $[H^+]$ range 0.05–1.00 M. Small deviations from this dependence are apparent at $[H^+] < 0.05$ M, Figure 2, indicating a possible $[H^+]^{-1}$ path as observed for many other reactions of aquochromium(III) complexes.[14] Due to difficulties in attaining and working at lower $[H^+]$ values it was not possible to determine with accuracy contributions made by such a path.

Kinetic data for the k_0 term for other complexes with Cr–S bonding are listed in Table II. Bearing in mind the different charges on the reactants, the rate constants and activation parameters are remarkably similar. The rate constant for the aquation of $CrSCN^{2+}$ (4.0×10^{-5} s^{-1} at 25 °C) is similar to those in Table II but the activation parameters, $\Delta H^{\ddagger} = 23.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = 1.0$ cal K^{-1} mol^{-1}, do not give the same correspondence.[15] The rate constant (25 °C) for the aquation of CrI^{2+} (8.5×10^{-5} s^{-1}),[16] but not that for CrF^{2+} (6.2×10^{-10} s^{-1}),[16] is of similar magnitude which is as predicted by the hard–soft acid–base concept,[17] where Cr(III) is a hard center and as such exhibits an affinity for harder ligands. As with other Cr(III) complexes of weak acids, the aquation of $CrSH^{2+}$ (and other complexes in Table II) gives a k_1 term, eq 2, consistent with the sulfur atom undergoing partial protonation in the $[H^+]$ range 0.1–1.0 M. The aquation of $CrSCN^{2+}$ does not exhibit such a path for the $[H^+]$ range up to 1.00 M investigated, which is presumably related to the strong acidity of HSCN.

The protonation constant for $CrSH^{2+}$ has to be $<<1$ M^{-1}, since there is no curvature in Figure 2 as $[H^+]$ approaches 1.0 M. Hence it can be concluded that the aquation rate of $CrSH_2^{3+}$ is $>>3.8 \times 10^{-5}$ s^{-1} at 40 °C, which exceeds k_0 for the aquation of $CrSH^{2+}$ (3.05×10^{-5} s^{-1} at 40 °C). It has been demonstrated that oxygen exchange involving $Co(NH_3)_5OH^{2+}$ is much slower than that for $Co(NH_3)_5H_2O^{3+}$,[18] and the same is likely to be the case for the aquo ions $CrOH^{2+}$ and Cr^{3+}. The water-exchange rate constant for Cr^{3+}, 3.67×10^{-6} s^{-1} at 40 °C,[19] is much smaller than that obtained for aquation of $CrSH_2^{3+}$.

Based on both electrostatic and covalent models the lability of the Cr–S bond as compared to Cr–O can be explained in terms of the greater size and lower electronegativity of S as compared to O. This will have the effect of reducing the coordinating ability of H_2S as compared to H_2O. However such an approach takes no account of the π-acceptor properties which H_2S (but not H_2O) is likely to exhibit. This will decrease the electron density on the metal and will tend to favor associative processes which are believed to prevail in the substitution reactions of hexaaquo- and pentaaquochromium(III) species.[19-21] A similar comparison is difficult for $CrSH^{2+}$ and $CrOH^{2+}$ since the π-donor and π-acceptor properties of the SH^- ligand are more complicated.

The equilibration of $CrSH^{2+}$ with NCS^- is believed to yield $Cr(NCS)SH^+$ as the only identifiable primary product. Attempts to isolate the product by ion-exchange chromatography were unsuccessful because of the low charge and equilibrium constant, as well as the relatively high rate of aquation. Formation of $CrNCS^{2+}$ or $CrSCN^{2+}$ as the dominant process can be ruled out since, at the wavelength (428 nm) at which the kinetics were studied, these species are less absorbing[15,22] than the reactant $CrSH^{2+}$ so that a decrease rather than an increase in absorbance would be observed. Furthermore the equilibration kinetics observed do not support the formation of $CrNCS^{2+}$ which has a very slow rate of aquation[23] and a high formation constant.[24] Aquation of $CrSH^{2+}$ at 25 °C is considerably slower and does not interfere in the NCS^- equilibration. A dependence on $[H^+]$ (viz., $k_2 + k_3K_1[H^+]$) is observed in the anation with NCS^-. Using the same arguments as above that the protonation constant for $CrSH^{2+}$ must be $<<1$ M^{-1}, the anation rate constant (k_3) for $CrSH_2^{3+}$ is $>>16.1 \times 10^{-4}$ M^{-1} s^{-1}. The anation rate constant (k_2) for $CrSH^{2+}$ is 8.6×10^{-4} M^{-1} s^{-1}. When these values are compared with corresponding values (25 °C) for NCS^- anation of Cr^{3+} (1.8×10^{-6} M^{-1} s^{-1}) and $CrOH^{2+}$ (4.9×10^{-5} M^{-1} s^{-1}), the labilizing influences of coordinated sulfur as H_2S and HS^- are evident. A ratio of $\geq 10^3$ between the anation rates of $CrSH_2^{3+}$ and Cr^{3+} is quite dramatic. An enhancement by a factor of 17 is observed for $CrSH^{2+}$ as compared to $CrOH^{2+}$. The ratio of $\geq 10^3$ between $CrSH_2^{3+}$ and Cr^{3+} is believed to stem from the different bonding characteristics of S as opposed to O. An explanation of the factor of 17 between $CrSH^{2+}$ and $CrOH^{2+}$ is more difficult. The labilizing effect of the Cr–S bond is also manifest in equilibrium constants (25 °C) for the complexing with NCS^-. Thus from the $[H^+]$ dependence of the intercepts in Figure 5 k_{-2} and k_{-3} can be evaluated and equilibrium constants for the complexing of $CrSH^{2+}$ and $CrSH_2^{3+}$ with NCS^- obtained. Both are ca. 3 M^{-1} whereas the equilibrium constant for the complexing of NCS^- with Cr^{3+} is 130 M^{-1}. The geometric position of the labilization by H_2S and SH^- was not identified. Previous instances in which the metal–sulfur bond introduces a trans-labilizing effect have been reported.[25-27] Relevant MO theory calculations for the Pt^{IV}–H_2S system have also been made.[28]

Another feature of interest in this study is the ratio of ≤ 0.5 for the thiocyanate anation rate constant of $CrSH^{2+}$ to that for $CrSH_2^{3+}$. The corresponding ratio for $CrOH^{2+}$ and Cr^{3+} is 30. Though the possible difference in ion-pairing constants of $CrSH_2^{3+}$ and NCS^- and of $CrSH^{2+}$ and NCS^- could be one of the reasons, it alone may not explain the observed differences in rate constants. A difference in the mechanism of substitution between $CrSH^{2+}$ and $CrSH_2^{3+}$ is a possibility.

Such a difference has previously been envisaged for $CrOH^{2+}$ and Cr^{3+} substitution processes.

The comparison made between analogous $CrSH_2^{3+}$ and Cr^{3+} reactions and those of $CrSH^{2+}$ and $CrOH^{2+}$ shows that the Cr–S bond is more labile than the Cr–O bond. In addition the Cr–S bond exercises a quite dramatic effect on other replaceable aquo ligands.

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Registry No. $[Cr(H_2O)_5SH]SO_4$, 58342-01-1; NCS^-, 302-04-5; $[Cr(H_2O)_4(NCS)SH]^+$, 58281-49-5.

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Complex Halides of the Transition Metals. XXI.[1] Evidence for the Existence of Tertiary Phosphine Derivatives of the New $[Mo_6Cl_8]^{2+}$ Cluster Cation

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A novel reduction of the $[Mo_6Cl_8]^{4+}$ cluster has been discovered. Triethyl-, tri-*n*-propyl-, and diethylphenylphosphine react with $[Mo_6Cl_8]Cl_4$ and salts of the $[(Mo_6Cl_8)X_6]^{2-}$ anions, where X = Cl, Br, or I, to afford complexes of stoichiometry $Mo_6Cl_8X_3(PR_3)_3$. The less basic triphenylphosphine and diphenylethylphosphine do not reduce this cluster and only adducts of the type $Mo_6Cl_{12}(PR_3)_2$ can be isolated. On the basis of magnetic susceptibility and spectral measurements, these reduced phases are formulated as ionic $[(Mo_6Cl_8)(PR_3)_6]^{2+}[(Mo_6Cl_8)X_6]^{2-}$, in which the cation is a derivative of the previously unknown $[Mo_6Cl_8]^{2+}$ cluster, obtained by the two-electron reduction of $[Mo_6Cl_8]^{4+}$.

Introduction

Although niobium and tantalum halide clusters of the type $[M_6X_{12}]^{n+}$ undergo one-electron redox reactions within the series for $n = 2$–4,[2] without accompanying changes in the gross molecular structure of these species, the same has invariably not been found in the case of the molybdenum(II) and tungsten(II) halides which contain the $[M_6X_8]^{4+}$ cluster. The only exception involves the bromine oxidation of $[W_6Br_8]Br_4$, which leads to derivatives of the $[W_6Br_8]^{6+}$ ion.[3,4] In contrast to this, the chlorine oxidation of $[Mo_6Cl_8]Cl_4$ and $[W_6Cl_8]Cl_4$ leads to the phases $[Mo_6Cl_{12}]Cl_3$ and $[W_6Cl_{12}]Cl_6$, respectively, in which the original $[M_6Cl_8]$ cores are no longer present.[5,6] With these exceptions, previous studies of the chemistry of the molybdenum and tungsten halide clusters $[M_6X_8]X_4$[2b,7] have not revealed any redox behavior in which a cluster structure is preserved. We have now discovered a novel redox chemistry for $[Mo_6Cl_8]Cl_4$ in its reactions with certain tertiary phosphines in which derivatives of the unknown $[Mo_6Cl_8]^{2+}$ cluster are formed. This is the first instance where reduction of a metal halide $[M_6X_8]^{4+}$ cluster has been achieved.

Experimental Section

Molybdenum(II) chloride was prepared by the method of Sheldon, as modified by Jolly.[8] Samples of the complexes $(Et_4N)_2[(Mo_6Cl_8)Cl_6]$ and $[(n\text{-}Bu)_4N]_2[(Mo_6Cl_8)X_6]$, where X = Br or I, were prepared using the procedures described by Cotton et al.[9] All tertiary phosphines and solvents were obtained from commercial sources. Solvents were deoxygenated by purging with N_2 gas for several hours and *all reactions were carried out in a nitrogen atmosphere*.

(a) Triethylphosphine. (i) $[Mo_6Cl_8]Cl_4$ (0.1 g) was dissolved in 20 ml of ethanol, 0.2 ml of triethylphosphine syringed into this solution, and the reaction mixture refluxed for 5 min. The resulting yellow precipitate (0.12 g) was filtered off, washed with petroleum ether and diethyl ether, and then dried in vacuo. Microanalytical data showed that this product was the complex $Mo_6Cl_{12}(PEt_3)_2$ (Table I); yield 98%.

(ii) The reaction between $[Mo_6Cl_8]Cl_4$ (0.11 g) and triethylphosphine (0.5 ml) was repeated but with a reflux time of 14 days. During this period, the initial yellow product slowly turned orange. This complex (0.125 g) was filtered off, washed with ethanol (40 ml), petroleum ether (20 ml), and diethyl ether (20 ml), and finally dried in vacuo. Microanalytical data for this complex were consistent with the stoichiometry $Mo_6Cl_{11}(PEt_3)_3$ (Table I); yield 86%.

(iii) When the salt $(Et_4N)_2[(Mo_6Cl_8)Cl_6]$ (0.21 g) was used in place of $[Mo_6Cl_8]Cl_4$ in the reaction with triethylphosphine (1.4 ml), a much shorter reflux time (7 days) was necessary to produce the reduced species $Mo_6Cl_{11}(PEt_3)_3$ (0.18 g); yield 86%.

The related reactions between $(Bu_4N)_2[(Mo_6Cl_8)X_6]$, where X = Br or I, and triethylphosphine in ethanol produced the insoluble orange complexes of stoichiometry $Mo_6Cl_8X_3(PEt_3)_3$ (Table I) after a reflux time of only 1 day. Workup procedures were the same as those described in section a(ii); yields 79% (X = Br) and 72% (X = I).

(b) Tri-*n*-propylphosphine. The orange complexes of stoichiometry $Mo_6Cl_8X_3[P(n\text{-}Pr)_3]_3$, where X = Cl or I, were prepared from $(Et_4N)_2[(Mo_6Cl_8)Cl_6]$ and $(Bu_4N)_2[(Mo_6Cl_8)I_6]$ using procedures similar to those described in section a(iii). Reflux times of 18 days