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Kinetic Studies on the Oxidation of the Thiolopentaaquochromium(III) Complex CrSH²⁺ with Fe³⁺ (and I₂) and the Reaction of Fe²⁺ with the μ-Disulfido-bis[pentaaquochromium(III)] Complex CrS₂Cr⁴⁺

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Anaerobic oxidation of thiolopentaaquochromium(III), $CrSH^{2+}$, by hexaaquoiron(III) at 25 °C and $I = 1.00$ M (LiClO₄) yields the chromium(III) products CrS_2Fe^{3+} (which is assigned the formula CrS_2HFe^{4+} at $[H^+] = 0.50$–1.00 M) and CrS_2Cr^{4+} with μ-disulfido (S–S) bridging ligands. Relative amounts of the two are dependent on the hydrogen ion concentration. At 25 °C with $[H^+] \geq 0.10$ M, CrS_2HFe^{4+} is the major product ($\geq 80\%$). The kinetics have been followed by monitoring formation of CrS_2HFe^{4+} and CrS_2Cr^{4+} at the 376-nm isosbestic for these complexes and conform to the rate law

$$\text{rate} = k_1[CrSH^{2+}][Fe^{3+}][H^+]^{-1} \tag{i}$$

where $k_1 = 1.50\ (\pm 0.02) \times 10^{-2}\ s^{-1}$ at 25 °C and $I = 1.00$ M (LiClO₄). The reaction of hexaaquoiron(II) with CrS_2Cr^{4+} also yields CrS_2HFe^{4+} with a rate law

$$\text{rate} = k_2[CrS_2Cr^{4+}] + k_3[CrS_2Cr^{4+}][Fe^{2+}] \tag{ii}$$

where $k_2 = 9.8\ (\pm 0.4) \times 10^{-5}\ s^{-1}$ and $k_3 = 3.16\ (\pm 0.05) \times 10^{-2}\ M^{-1}\ s^{-1}$. Oxidation of $CrSH^{2+}$ by I₂ (with $CrSH^{2+}$ excess) yielding CrS_2Cr^{4+} as the sole product is too fast to follow by the stopped-flow method; $k_4 > 3 \times 10^6\ M^{-1}\ s^{-1}$ with $[H^+] = 0.50$ M at 25 °C.

Many studies on redox reactions involving organic thiols and metal ions have been carried out.[1,2] Little is known however about the redox behavior of simple ligands such as SH⁻ (or H₂S) when coordinated to a metal ion. The important complex $CrSH^{2+}$ was first reported by Ardon and Taube in 1967.[3] Further characterization together with studies of the aquation and anation (with NCS⁻) have recently been reported.[4] A communication from this laboratory on the synthesis and characterization of the μ-disulfido complexes CrS_2Cr^{4+} and CrS_2HFe^{4+} resulting from the I₂ and Fe(III) oxidation of $CrSH^{2+}$ has already appeared.[5] Iron(III) is also known to catalyze the aquation of $Cr(H_2O)_5(SC_6H_4NH_3)^{3+}$.[6] The present paper describes kinetic studies on the Fe(III) (and I₂) oxidation of $CrSH^{2+}$, as well as the Fe²⁺ displacement of Cr³⁺ from CrS_2Cr^{4+} to give CrS_2HFe^{4+}.

Experimental Section

Materials. Solutions of the complex $CrSH^{2+}$ typically ca. 0.04 M in 0.10 M HClO₄ and 0.9 M LiClO₄ were prepared as described elsewhere.[3,4] The μ-disulfido complex CrS_2Cr^{4+} was obtained by reacting I₂ with $CrSH^{2+}$ and separating the product using a column of Sephadex SP C25.[5] Concentrations of complex obtained were ca. 1×10^{-3} M in 0.1 M HClO₄ and 0.9 M LiClO₄. Hexaaquoiron(III) (G. F. Smith, Chemical Co.) was purified by elution from Amberlite IR-120(H) (BDH) cation-exchange column using 0.5 M HClO₄, while hexaaquoiron(II) perchlorate (G. F. Smith) was eluted from an air-free Dowex 50W-X8 (200–400 mesh) column using solutions of 0.1 M HClO₄ with 0.9 M LiClO₄. Solutions of iron(II) were stored under N₂. Lithium perchlorate was prepared from perchloric acid (Analar grade) and lithium carbonate and recrystallized until free from Cl⁻ and SO₄²⁻ impurities. Sephadex SP C25 resin (Pharmacia Fine

Table I. Reaction of $CrSH^{2+}$ (1.52×10^{-2} M) with Fe(III) (2.5×10^{-4} M) at 25 °C and $I = 1.00$ M (LiClO₄): Yield of CrS_2Cr^{4+} with Varying $[H^+]$

[H⁺], M	% CrS₂Cr⁴⁺ [a]	[H⁺], M	% CrS₂Cr⁴⁺ [a]
0.10	18	0.40	8
0.25	12	0.55	4

[a] Percentage of total binuclear product formed.

Chemicals, 40–120 μ) was prepared for use by washing extensively with water and 0.1 M HClO₄ (3× resin volume) to remove any free polyelectrolytes and then equilibrating with 0.1 M HClO₄ for at least 24 h. Trapped air was removed by placing the slurry in a desiccator under vacuum.

Determination of Products Obtained from Fe(III) Oxidation of $CrSH^{2+}$. Because of the air sensitivity of both $CrSH^{2+}$ and the products of the Fe(III) oxidation, isolation was performed anaerobically under N₂. To a solution of $CrSH^{2+}$ (ca. 2×10^{-2} M, 3–4 mL) at $[H^+] = 0.1$ M and $I = 1.0$ M (LiClO₄) was added Fe(III) (1.5×10^{-2} M, 1 mL) and the mixture maintained at 25 °C for 20 min. The reaction mixture was cooled to 0 °C and passed down a dearated Sephadex SP C25 column (18–20 cm long, 1.8-cm diameter, at 0 °C) which had been preequilibrated with 0.1 M HClO₄. Four colored bands were observed. The first diffuse brownish green band was identified as unreacted $CrSH^{2+}$ by its visible spectrum, peak positions 575 nm (ϵ 27.5 M⁻¹ cm⁻¹) and 435 nm (ϵ 43.1 M⁻¹ cm⁻¹).[4] The second blue band was identified as Cr³⁺, peak positions 575 nm (ϵ 13.7 M⁻¹ cm⁻¹) and 408 nm (ϵ 15.5 M⁻¹ cm⁻¹). The two remaining bands were both slow moving possibly because of the high charge. Washing the column first with 0.2 M HClO₄ eluted the Fe(II) product. This was identified by addition of thiocyanate and H₂O₂ which produced an

intense red-brown color characteristic of iron(III)–thiocyanate complexes. Before complete elution of Fe(II) had been achieved, elution of CrSH^{2+} began. Elution of the blue band required a solution of 0.1 M HClO$_4$ and 0.4 M LiClO$_4$. Continued elution with a solution of 0.1 M HClO$_4$ and 0.9 M LiClO$_4$ finally produced a 3-cm separation between yellow-brown (CrS$_2$Cr^{4+}) and yellow-green (CrS$_2$HFe^{4+}) species. The CrS$_2$Cr^{4+} was eluted first without any apparent contamination. Peak positions and absorption coefficients [λ, nm (ϵ, M^{-1} cm^{-1})] determined were as follows: 310 (3600), 355 (2940), 585 (70) for CrS$_2$HFe^{4+} and 230 (6450), 305 (3600), 399 (2660) for CrS$_2$Cr^{4+} in agreement with spectra in ref 5. A crossover point is observed at 376 nm. On varying the [H$^+$] for the Fe(III) oxidation of CrSH^{2+} the relative amounts of CrS$_2$HFe^{4+} and CrS$_2$Cr^{4+} as estimated by the analyses of spectra of the products varied as shown in Table I. Although these results indicate the formation of CrS$_2$Cr^{4+} (4–18% depending on [H$^+$]), in the preparative chromatographic column separations (involving prolonged periods, ca. 36 h) CrS$_2$Cr^{4+} was not detected.

To prepare larger quantities of CrS$_2$HFe^{4+} a solution of CrSH^{2+} (25–40 mL, 2 × 10^{-3} M) was transferred under air-free conditions to a dearated vessel and deoxygenated Fe(III) (2–4 mL, 9.25 × 10^{-2} M) was added under N$_2$. The reaction mixture at [H$^+$] = 0.1 M was kept thermostated at 25 °C for 45 min. After fourfold dilution with 0.1 M HClO$_4$ at near 0 °C the Sephadex separation as described above was carried out. The yellow-green band was eluted with 0.1 M HClO$_4$–0.9 M NaClO$_4$, to give a (5–15) × 10^{-4} M solution of complex. By use of 0.1 M HClO$_4$–1.9 M NaClO$_4$ for the final elution a higher concentration (1–8) × 10^{-3} M in Cr(III) was obtained, the separation procedure taking about 36 h. The solution was stored by freezing solid at –6 °C under air-free conditions. In view of the self-decomposition and Fe^{2+}-catalyzed reaction of CrS$_2$Cr^{4+}, it is hardly surprising that, over prolonged periods required for the separation procedure, the CrS$_2$Cr^{4+} species was not detected.

Analytical procedures as used in the characterization of the CrS$_2$HFe^{4+} and CrS$_2$Cr^{4+} complexes have been described.[5] On the basis of an S:Cr ratio of 0.96 ± 0.01:1 and an I$_2$ oxidation equivalent of 1.01 ± 0.01 per sulfur atom, assuming Cr to be in the III state, the yellow-brown species is formulated as CrS$_2$Cr^{4+}. The Cr–Fe complex gave a S:Cr ratio of 1.98 ± 0.10:1 and a Cr:Fe ratio of 0.94 ± 0.02:1, as well as a charge[7] of 3.8 consistent with the formula CrS$_2$HFe^{4+}. One determination which was carried out requires further elaboration and comment here. Thus iodometry[3,8] was used to determine the oxidation state of sulfur S(−I) → S(0) and gave 0.98 ± 0.03 equiv/Cr for the complex CrS$_2$HFe^{4+}. For the formula given, a value of 2 equiv/Cr would have been expected. The implication is that only one of the sulfur atoms is being oxidized to free sulfur. We have demonstrated that such a situation does pertain. After oxidation with iodine, the precipitated sulfur was removed by Millipore filtration, and the filtrate was treated with Br$_2$. Subsequent treatment with BaCl$_2$ revealed the presence of SO$_4^{2-}$ and a quantitative determination indicated that 0.88 equiv of sulfur/mol was not oxidized by iodine. The reason for this is not clear but is possibly due to the formation of some iron–sulfur species which is resistant to further oxidation.

Ion-exchange separation of the reaction products was carried out on an air-free, ice-cooled Dowex 50W-X8 (100–200 mesh) column in order to separate the lower charged Fe^{2+} and CrSH^{2+} species. The binuclear complexes could not be eluted easily from the ion-exchange column and therefore the above Sephadex separation was preferred for isolation of these species.

Stoichiometry. The products of the reaction of Fe(III) (1.54 × 10^{-3} M) with CrSH^{2+} (1.52 × 10^{-2} M) at [H$^+$] = 0.1 M, I = 1.00 M (NaClO$_4$), and 25 °C were isolated using ion-exchange and Sephadex separation techniques. The Fe^{2+} was determined by Ce(IV) titration, and fractions containing Cr^{3+}, CrS$_2$HFe^{4+}, and CrS$_2$Cr^{4+} by oxidation of Cr(III) with H$_2$O$_2$ (in 1 M NaOH), followed by the spectrophotometric determination of Cr(VI) at 372 nm (ϵ 4.82 × 10^3 M^{-1} cm^{-1}). The stoichiometric ratio for the conversion of Fe^{3+} to free Fe^{2+} was 1:0.52 and of Cr^{3+} to CrS$_2$HFe^{4+} was 0.89:1 from product analyses. All observations were consistent with a 1:1 stoichiometry as in (1). The stoichiometry observed for the reaction implies that

$$2CrSH^{2+} + 2Fe^{3+} \rightarrow CrS_2HFe^{4+} + Fe^{2+} + Cr^{3+} + H^+ \quad (1)$$

the iron adduct could be formulated only as CrS$_2^{3-}$Fe^{III} or Cr(S$_2^{2-}$)Fe^{II} and not as Cr(S$_2^{2-}$)Fe^{III}, which requires a CrSH^{2+}:Fe^{3+} ratio of 1:1.5. For the conditions [H$^+$] ≥ 0.1 M at 25 °C and I = 1.0 M reaction

Table II. Pseudo-First-Order Rate Constants, k_{obsd}, and Second-Order Rate Constants, k_1, for the Reaction of CrSH^{2+} with the Fe(III) at 25 °C, I = 1.00 M (LiClO$_4$), and λ 376 nm

| [H$^+$], M	10^2[Cr-SH^{2+}], M	10^3[Fe-(III)], M	10$^3k_{obsd}$,[a] s^{-1}	10$^2k_1$, M^{-1} s^{-1}
0.10	0.37	0.05	0.53 (0.55)	1.41
	1.01	0.25	1.55 (1.51)	1.53
	1.52	0.25	2.32 (2.28)	1.53
	2.53	0.25	3.75 (3.80)	1.49
0.15	1.52	0.25	1.54 (1.52)	1.51
0.20	0.37	0.05	0.295 (0.28)	1.38
0.25	0.37	0.05	0.245 (0.22)	1.65
	1.01	0.25	0.60 (0.60)	1.48
	1.52	0.25	0.96 (0.91)	1.57
0.30	0.37	0.05	0.205 (0.18)	1.65
0.40	1.52	0.25	0.53 (0.57)	1.39
0.55	0.37	0.05	0.10 (0.09)	1.49
	1.01	0.25	0.30 (0.27)	1.64
	1.52	0.25	0.385 (0.41)	1.39
0.70	0.37	0.05	0.082 (0.080)	1.53

[a] k_{calcd} values in parentheses.

2, accounting for ≤20% of the reaction, is a minor pathway. At the

$$2CrSH^{2+} + 2Fe^{3+} \rightarrow CrS_2Cr^{4+} + 2Fe^{2+} + 2H^+ \quad (2)$$

isosbestic point 376 nm for CrS$_2$Cr^{4+} and CrS$_2$HFe^{4+} the spectrophotometric determination of stoichiometry at varying [H$^+$] yields a ratio of precisely 1 equiv of CrS$_2$Cr^{4+} or CrS$_2$HFe^{4+} for every 2 equiv of Fe^{3+} added.

The reaction of Fe^{2+} with CrS$_2$Cr^{4+} proceeds with the retention of the isosbestic point at 376 nm. Displacement of Cr^{3+} by Fe^{2+} with quantiative formation of CrS$_2$HFe^{4+} as in (3) is observed. Spec-

$$CrS_2Cr^{3+} + Fe^{2+} + H^+ \rightarrow CrS_2HFe^{4+} + Cr^{3+} \quad (3)$$
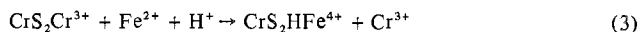
trophotometric investigations indicated that even under second-order conditions CrS$_2$HFe^{4+} was the major product and reaction 3 is essentially complete. Further reaction 1 as well as reaction 3 yields the same CrS$_2$HFe^{4+} species and the observed stoichiometry for reaction 1 favors a 1:1 stoichiometry as in (3) also.

Kinetic Studies. The reaction of Fe(III) with CrSH^{2+} was monitored at the 376-nm isosbestic point for CrS$_2$HFe^{4+} and CrS$_2$Cr^{4+} (ϵ 2500 M^{-1} cm^{-1}), using conventional spectrophotometric techniques. The CrSH^{2+} reactant was in excess; otherwise further oxidation occurred and sulfur was precipitated. Sulfur is also formed on exposure of CrSH^{2+} to oxygen and all studies were carried out under N$_2$. The reaction of Fe^{2+} (in large excess) with CrS$_2$Cr^{4+} was monitored at 420 nm at which wavelength absorption coefficients for CrS$_2$Cr^{4+} and CrS$_2$HFe^{4+} differ markedly. Rate constants were obtained from slopes (×2.303) of graphs of log ΔA against time, where ΔA is the difference in absorbance reading A_t (at time t) and A_∞. Measured A_∞ values were used. Plots were linear to >90%. Analysis of kinetic data was performed with the aid of a nonlinear least-squares program.[9] Data points were weighted by a factor 1/k^2. Attempts to study the I$_2$ and I$_3^-$ oxidation of CrSH^{2+} required the use of the Durrum–Gibson stopped-flow spectrophotometer.

Results

Reaction of CrSH^{2+} with Fe(III). First-order rate constants k_{obsd} gave a *good* fit to (4). Values of k_{obsd} and k_1 are given

$$k_{obsd} = k_1 [CrSH^{2+}] [H^+]^{-1} \quad (4)$$

in Table II, and the [H$^+$] dependence is illustrated in Figure 1. From a least-squares analysis of data k_1 = (1.50 ± 0.02) × 10^{-2} s^{-1} at 25 °C and I = 1.00 M (LiClO$_4$). Inclusion of an [H$^+$]-independent term k_0[CrSH^{2+}] in (3) gives k_0 = (0.07 ± 1.28) × 10^{-3} M^{-1} s^{-1} and k_1 = (1.50 ± 0.05) × 10^{-2} s^{-1}, from which it is concluded that k_0 makes no significant contribution.

At the end of the primary reaction a secondary reaction is incident giving a decrease in absorbance at ca. 420 nm. No absorbance changes were observed at the 376-nm isosbestic point. These changes were assigned to the reaction of Fe^{2+} with CrS$_2$Cr^{4+}. With Fe^{2+} (4.8 × 10^{-3} M) present initially,
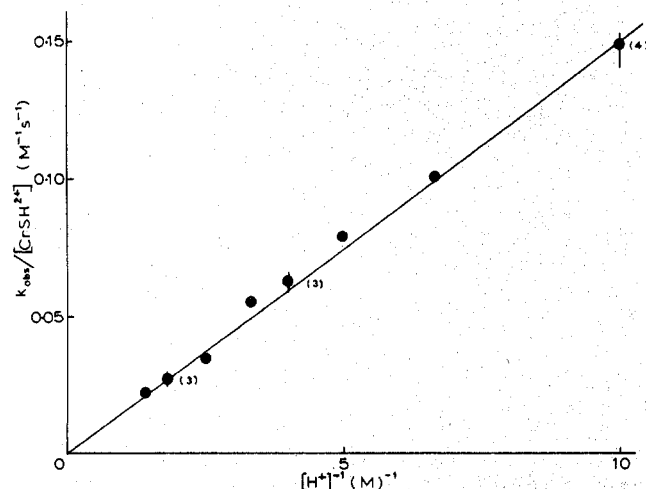
Figure 1. Dependence of second-order rate constants, $k_{obsd}/[CrSH^{2+}]$, on the hydrogen ion concentration for the reaction of $CrSH^{2+}$ with Fe(III) at 25 °C, I = 1.00 M (LiClO$_4$). Number of points averaged indicated in parentheses.

Table III. First-Order Constants, k'_{obsd}, for the Reaction of CrS_2Cr^{4+} with Iron(II) (in Large Excess) at 25 °C, I = 1.00 M (LiClO$_4$), and λ 420 nm

10^2 [Fe^{2+}], M	[H$^+$], M	10^4[CrS$_2$-Cr^{4+}], M	$10^3 k_{obsd}$,^{a} s^{-1}
0.23	0.10	1.34	0.17 (0.17)
	0.10	0.40	0.17 (0.17)
0.91	0.10	1.34	0.38 (0.39)
	0.25	1.34	0.38 (0.39)
	0.40	1.34	0.38 (0.39)
	0.55	1.34	0.41 (0.39)
1.82	0.10	0.67	0.70 (0.67)
	0.10	1.34	0.69 (0.67)
	0.10	2.68	0.69 (0.67)
2.74	0.10	1.62	1.01 (0.97)
3.65	0.10	1.34	1.20 (1.25)
	0.10	1.34	1.21^b (1.25)
	0.55	1.34	1.22 (1.25)

^{a} Calculated values in parentheses. ^{b} λ 450 nm.

[H$^+$] = 0.1 M, the amount of minority product CrS$_2$Cr^{4+} formed was reduced by ca. 40%.

Reaction of Fe^{2+} with CrS$_2$Cr^{4+}. A large >20-fold excess of Fe^{2+} was used. First-order rate constants k'_{obsd} for (3), Table III, are independent of [H$^+$] and give a dependence (5),

$$k'_{obsd} = k_2 + k_3[Fe^{2+}] \tag{5}$$

Figure 2. A least-squares treatment gives $k_2 = (9.8 \pm 0.4) \times 10^{-5}$ s^{-1} and $k_3 = (3.16 \pm 0.05) \times 10^{-2}$ M^{-1} s^{-1} at 25 °C and I = 1.00 M (LiClO$_4$). Final product spectra with [Fe^{2+}] = (0.23–2.73) × 10^{-2} M corresponded to the formation of CrS$_2$HFe^{4+}. The 376-nm isosbestic point was retained under all conditions investigated. The k_2 term almost certainly corresponds to Fe^{2+}-independent aquation of Cr^{3+} from CrS$_2$Cr^{4+}, where the product is the same as for k_3. The initial rate constant for such a process as determined in separate experiment in the absence of Fe^{2+}, with [CrS$_2$Cr^{4+}] = 1.34 × 10^{-4} M, [H$^+$] = 0.1 M, and I = 1.00 M (LiClO$_4$), is ca. 5 × 10^{-5} s^{-1} at 25 °C. Although of the same magnitude as k_2, the first-order plot is markedly curved, and the products are uncertain. The addition of hexaaquochromium(III) to the product CrS$_2$HFe^{4+} did not give any reaction, suggesting that (3) is not an equilibrium.

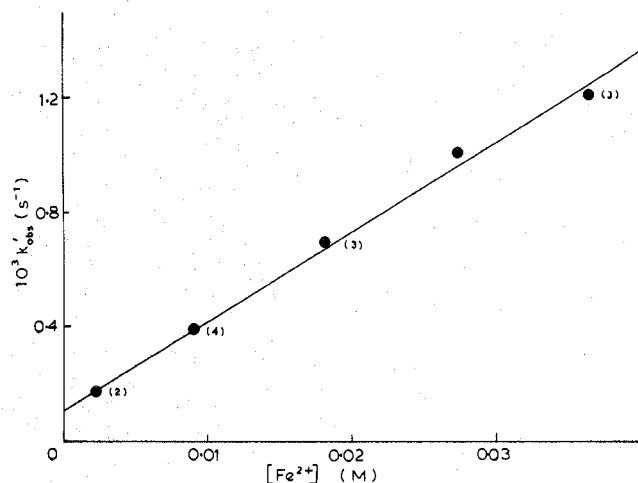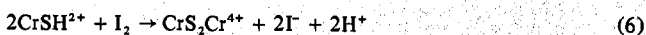**Reaction of CrSH^{2+} with I$_2$.** Oxidation of CrSH^{2+} by I$_2$ to give CrS$_2$Cr^{4+}

$$2CrSH^{2+} + I_2 \rightarrow CrS_2Cr^{4+} + 2I^- + 2H^+ \tag{6}$$

Figure 2. Dependence of first-order rate constants for the reaction of Fe^{2+} (in large excess) with CrS$_2$Cr^{4+} on [Fe^{2+}] at 25 °C, I = 1.00 M (LiClO$_4$). Number of points averaged indicated in parentheses.

is rapid. The reaction was too fast to monitor by the stopped-flow method with [CrSH^{2+}] = 1.55 × 10^{-4} M, [I$_2$] = 1.1 × 10^{-5} M, and [H$^+$] = 0.5 M, at 25 °C and I = 1.00 M (LiClO$_4$). By assuming a second-order rate law, a lower limit on the rate constant for the rate-determining step in (6) of k_4 > 3 × 10^6 M^{-1} s^{-1} can be estimated. On addition of [I$^-$] = 0.01 M, so that [I$_3^-$] $\approx$ 1.0 × 10^{-5} M and [I$_2$] $\approx$ 1.3 × 10^{-6} M, the reaction remained too fast to follow.

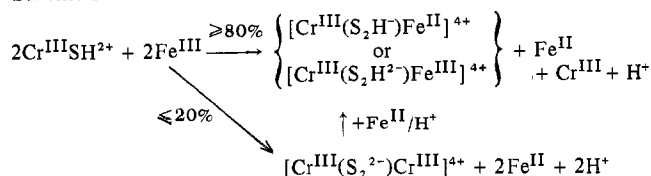**Discussion**

The lower limit of 3 × 10^6 M^{-1} s^{-1} for the rate constant for the I$_2$ oxidation of CrSH^{2+} implies an outer-sphere reaction. Mechanistic implications are that a radical–ligand Cr(III) species, CrS^{2+} or CrSH^{3+} (depending whether or not loss of a proton from CrSH^{2+} occurs), is formed and that this dimerizes subsequently in a rapid step to yield the product CrS$_2$Cr^{4+}. This is not to say that a nucleophilic attack of thiol sulfur on iodine leading to the displacement of an iodide ion and the formation of a sulfenyl iodide is not possible. If under the conditions (excess thiol) used, sulfenyl iodide was indeed formed, it would be transformed to disulfide in a second step. Since little is known about the stability of a precursor CrSI species, a simpler radical mechanism similar to that suggested by Asher and Deutsch[6] for the Fe(III) oxidation of CrS-(C$_6$H$_4$NH$_3$)$^{3+}$ appears preferable.

It is not as easy to designate the reaction pathway for the Fe(III) oxidation and say whether this is an inner- or outer-sphere process. Clearly the rate constants as determined must represent an upper limit for an outer-sphere contribution, and it is of interest that I$_2$ (the weaker oxidant in terms of standard reduction potentials[10]) reacts much faster than Fe(III) by the outer-sphere path. This difference in reactivity is unlikely to stem from the fact that I$_2$ is a 2-equiv oxidant since two-electron oxidation of CrSH^{2+} does not seem a reasonable possibility. In the oxidation of various organic thiols by I$_2$, schemes involving two single-electron steps have been suggested,[11] and this is preferred to a termolecular reaction involving 2 mol of thiol and 1 mol of I$_2$.

The Fe(III) oxidation proceeds exclusively by an [H$^+$]$^{-1}$-dependent path, eq 4. There are various possible interpretations involving loss of a proton from a water ligand on one or other reactant or loss of a proton from the SH$^-$ ligand. There seem to be no obvious advantages resulting from loss of a proton from the Fe^{3+} reactant, and formation of CrS$^+$ seems more likely. An inner-sphere reaction would then give CrSFe^{4+}, whereas an outer-sphere pathway, as in the I$_2$ case, would generate CrS^{2+}. Either way subsequent steps leading to formation of CrS$_2$HFe^{4+} as the majority and CrS$_2$Cr^{4+} as

Scheme I

$$2Cr^{III}SH^{2+} + 2Fe^{III} \xrightarrow{\geqslant 80\%} \left\{ \begin{array}{c} [Cr^{III}(S_2H^-)Fe^{II}]^{4+} \\ \text{or} \\ [Cr^{III}(S_2H^{2-})Fe^{III}]^{4+} \end{array} \right\} + \begin{array}{c} Fe^{II} \\ + Cr^{III} + H^+ \end{array}$$

$$\xrightarrow{\leqslant 20\%} \qquad \uparrow + Fe^{II}/H^+$$

$$[Cr^{III}(S_2{}^{2-})Cr^{III}]^{4+} + 2Fe^{II} + 2H^+$$

the minority product are not at this stage easy to define. If dissociation of $CrSFe^{4+}$ to CrS^{2+} or FeS^+ species is involved, then it is interesting that no binuclear Fe_2 species is formed. Many examples are known in organic reactions where there is a cross-exchange between two disulfides of the form RSSR and R′SSR′ to give RSSR′ which is the dominant product. The reaction of Fe^{2+} with CrS_2Cr^{4+} is too slow for CrS_2Cr^{4+} to be the precursor of CrS_2HFe^{4+}.

It is of course remarkable that Fe^{2+} is able to react at all with CrS_2Cr^{4+} and displace substitution-inert Cr^{3+}. With reactants $[Fe^{2+}] = 0.037$ M, $[CrS_2Cr^{4+}] = 1.3 \times 10^{-4}$ M, and $[H^+] = 0.10$–0.55 M, the half-time for reaction is ca. 10 min. at 25 °C. Two terms are observed in the rate law (5). For the $[Fe^{2+}]$-independent step k_2, loss of Cr^{3+} from CrS_2Cr^{4+} by aquation is the most likely rate-determining process. The initial rate of decay of the CrS_2Cr^{4+} absorption in an experiment with no Fe^{2+} added is consistent with such an explanation. The second-order term k_3 carries with it the implication of an Fe^{2+} attack on one of the S atoms of CrS_2Cr^{4+}. Since Fe^{2+} is labile, it could form a transient intermediate (by electrophilic attack at a sulfur lone pair), the Fe^{2+} having a sufficiently long residence time to labilize the adjacent $Cr(III)$.[13] The rate constant for the hydrogen ion independent aquation of $CrSH^{2+}$ to yield Cr^{3+} has been determined previously and is 3.09×10^{-5} s^{-1} at 40 °C.[4] This is to be compared with the k_2 value of 9.8×10^{-5} s^{-1} at 25 °C ($I = 1.00$ M in both cases). If we assume an association constant <2 M^{-1} for the formation of the Fe^{2+} adduct with CrS_2Cr^{4+} (no curvature is observed in kinetic plots), then from k_3 the rate constant for the aquation of Cr^{3+} from this adduct is $>1.5 \times 10^{-2}$ s^{-1}.

Oxidation-state ambiguities in particular with regard to CrS_2HFe^{4+} are present in this work. It is of interest that by one-electron reduction of various organic disulfides R_2S_2 with e_{aq}^-, $R_2S_2^-$ species have been generated and found to undergo protonation to R_2S_2H at pH ca. 1.0.[14] It has also been reported that when R contains a β NH_3^+ function, the positively charged group has a retarding influence on the rate of decay of $R_2S_2^-$ by interacting with the electron on the disulfide radical.[15] It is possible in the light of these observations that coordination of S_2^{3-} (or S_2H^{2-}) radical anions may attain stability by way of ligand to metal charge-transfer interactions and that formulations such as $[Cr(S_2{}^{3-})Fe^{III}]^{3+}$ and under acid conditions $[Cr(S_2H^{2-})Fe^{III}]^{4+}$ are therefore feasible. A comparison of spectra of $R_2S_2^-$ and R_2S_2H, with peaks at 410 and 385 nm, respectively, with the CrS_2HFe^{4+} peak at 355 nm (ϵ 2940 M^{-1} cm^{-1}) is consistent with this formulation. However the recent report on $[Fe(C_5H_5)(SC_2H_5)]_2S_2^{16}$ emphasizes the need to invoke a high degree of, if not complete, transfer of an electron from the disulfide bridge to the Fe atoms. In our case a similar situation will yield $[Cr(S_2H^-)Fe^{II}]^{4+}$, and for an unambiguous assignment of formal oxidation states magnetic measurements and the determination of the S–S bond distance may be necessary.

With the CrS_2Cr^{4+} complex the iodine oxidation equivalence suggests an $S_2{}^{2-}$ bridge, and without invoking any partial oxidation of $Cr(III)$ to $Cr(IV)$, the peak at 399 nm cannot be directly related to that of $R_2S_2^-$ at 410 nm. It is plausible that peaks at 310 and 355 nm for CrS_2HFe^{4+} as well as those at 305 and 399 nm for CrS_2Cr^{4+} may be due to S→ Cr charge

transfer since the energy levels of sulfur orbitals are close together. Protonation of a disulfide bridge and the existence of cis–trans arrangements, as well as steric strain, are known to influence the UV absorption spectra of disulfides.[17] Further the ligand to metal π donation and metal to ligand π back-donation that are possible in the Fe–S and Cr–S systems can also be expected to influence UV spectra. Therefore the red shift observed for CrS_2Cr^{4+} as compared to CrS_2HFe^{4+} absorption peaks may be due to the different nature of S–Cr bonding in the two complexes.

Finally other examples of complexes with S_2 bridges are known. Raman spectroscopy has revealed that the ν(S–S) frequency for $(CN)_5CoS_2Co(CN)_5^{6-}$ [18] and L-$(NH_3)_4RuS_2Ru(NH_3)_4L^{(4-2n)+}$, $L^{n-} = H_2O$, NH_3, Cl$^-$,[19] is in the range 490–526 cm^{-1}, which is in good agreement with values observed for H_2S_2 and R_2S_2 (R = alkyl) species. Thus there is strong evidence in such complexes for an S–S single bond and $S_2{}^{2-}$ structure. Our attempts to obtain Raman spectra for our species were unsuccessful due to photodecomposition of the two complexes in an argon laser beam. Crystallographic studies on complexes $[Fe(CO)_3]_2S_2$,[20] $[Fe(C_5H_5)(SC_2H_5)]_2S_2$,[16] and $[Co_3S(CO)_7]_2S_2$ [21] as well as H_2S_2 [22] and R_2S_2 [23] gives S–S single-bond distances of 2.1–2.05 Å. In some cases for consistency with magnetic data[16,19] magnetic coupling through the S_2 bridges must be present. This can be regarded as a mixing in of some S_2^- or S_2^0 character. The preferred dihedral angle between two substituents attached to an S–S group in R_2S_2 has been reported to be close to 90°.[24] When the geometrical constraints and resulting torsional strain on an S–S bond coordinated to two transition metal ions (along with ligands in their coordination spheres) are known, it may be easier to further rationalize the thermodynamic stability as well as mechanistic features of the formation of CrS_2HFe^{4+} and CrS_2Cr^{4+} complexes.

To summarize, the complex CrS_2Cr^{4+} is obtained by I_2 oxidation of $CrSH^{2+}$ as in eq 6. Reactions described by equations 1–3 can be summarized in terms of oxidation-state changes by Scheme I. In this scheme it is assumed that the chromium is in oxidation state III. Attention is drawn to the ambiguity existing for the product CrS_2HFe^{4+}, where the bridging ligand is assigned as $S_2{}^{2-}$ or $S_2{}^{3-}$ and the ion is in the II or III oxidation state.

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Reaction Sequence in the Hydroxo-Bridge Cleavage of the Tri-μ-hydroxo-bis[triamminecobalt(III)] Complex. Identification of an Isomerization Step

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Further details of hydroxo-bridge cleavage of the tri-μ-hydroxo-bis[triamminecobalt(III)] complex, $[(NH_3)_3Co(\mu$-$(OH,OH,OH))Co(NH_3)_3]^{3+}$, have been obtained, $I = 1.00$ M (LiClO₄). The faster equilibration stopped-flow step, forward rate constant $k_a = 4.22$ M⁻¹ s⁻¹ at 25 °C, which was previously assigned to slow protonation, is here alternatively assigned to first bridge cleavage. Activation parameters ($\Delta H^* = 11.2$ kcal mol⁻¹, $\Delta S^* = -18.3$ cal K⁻¹ mol⁻¹) and deuterium isotope effects support such an assignment. The slower equilibration stopped-flow step is now believed to correspond to a process involving isomerization of water ligands into trans (opposed) positions. Details of the [H⁺] dependence for the slower (conventional) third observable step, involving cleavage of the second bridge, are clarified. The final product *fac*-[Co-$(NH_3)_3(H_2O)_3]^{3+}$ is formed with cleavage of the third bridge in a relatively fast non-rate-determining step. Rate constants and activation parameters have now been obtained for three forward and two reverse steps in the reaction sequence.

Introduction

Kinetic studies on the hydroxo-bridge cleavage of the tri-μ-hydroxo complex $[(NH_3)_3Co(\mu$-$(OH,OH,OH))Co(NH_3)_3]^{3+}$ have been reported previously.[1-3] Involvement of an isomerization step first became a possibility once it had been demonstrated that the di-μ-hydroxo-bisaquo intermediate $[(NH_3)_3(H_2O)Co(\mu$-$(OH,OH))Co(H_2O(NH_3)_3]^{4+}$ (isolated as the nitrate salt) had H₂O ligands in trans (opposed) positions.[4] Studies reported here have yielded further relevant information regarding the mechanism.

Experimental Section

Reactants. These were prepared as described previously.[2] To obtain a completely deuterated sample of the tri-μ-hydroxo complex, $[(NH_3)Co(\mu$-$(OH,OH,OH))Co(NH_3)_3](ClO_4)_3\cdot2H_2O$, the latter (6 g) was first left in vacuo over P₂O₅ for 2 weeks to remove the 2H₂O. The complex was then dissolved in D₂O (99.75%, Merck) and a few drops of 0.1 M NaOD in D₂O added. Analar (dehydrated) NaClO₄ was added after a few minutes and the solution cooled to 0 °C. Crystals of the perchlorate salt were filtered off, and the sample was recrystallized twice, when the IR spectrum showed no ν(O–H) or ν(N–H) stretching frequencies at 3600–3100 cm⁻¹. Dehydration experiments over P₂O₅ were consistent with the formula $[(ND_3)_3Co(\mu$-$(OD,OD,OD))Co(ND_3)_3](ClO_4)_3\cdot2D_2O$.

Kinetic Studies. There are three observable stages in conversion to a mononuclear complex, the first two of which can be monitored using a stopped-flow (Durrum Instrument). The first stage was monitored at 544 nm (increased in absorbance). A full study has already been made of the second stage at 450 and 544 nm (also an increase in absorbance).[2] Conventional spectrophotometry, Unicam SP500, was used to study the third stage at 362 nm (decrease in absorbance). The third stage was also studied at 295 nm, $I = 3.00$ M (LiClO₄). Incidence of the second stage prevented accurate absorbance A_∞ values for the first stage being obtained from oscilloscope traces. Instead the Guggenheim method of evaluating rate constants was used.[5]

The ionic strength was adjusted to $I = 1.00$ M (LiClO₄) or (for more extensive range of [H⁺] for third stage) $I = 3.00$ M (LiClO₄).

First-order plots of log ΔA against time for the third stage were linear to 95% completion.

An unweighted nonlinear least-squares program[6] was used in evaluating all parameters.

Results

First-order rate constants k_{eq}, Table I,[7] give a dependence (eq 1) on [H⁺] (Figure 1), where k_a and k_{-a} are believed to

$$k_{eq} = k_a[H^+] + k_{-a} \qquad (1)$$

correspond to forward and reverse (equilibration) steps. Rate constants and activation parameters are summarized in Table IV. Rate constants k_{eq}^D for the deuterated complex in D₂O solution [D⁺] = 0.05, 0.10, 0.25, and 0.50 M were $k_{eq}^D = 1.58$ (3), 2.12 (2), 2.91 (5), and 4.76 (2) s⁻¹, respectively (number of runs averaged in parentheses). These give at 25 °C $k_a/k_a^D = 0.64$ and $k_{-a}/k_{-a}^D = 1.3$, where k_a^D and k_{-a}^D are parameters as defined in eq 1 for the deuterated complex.

Crossover points from spectra of tri-μ-hydroxo and di-μ-hydroxo-bisaquo (trans) complexes are at 269 ± 3, 341 ± 5, and 511 ± 3 nm. By varying the wavelength setting on the stopped-flow three isosbestic points were identified for the first stage at 265 ± 3, 339 ± 10, and 524 ± 2 nm ([H⁺] = 0.25 and 1.00 M). For the second stage (the study reported in ref 2) isosbestics were at 265 ± 6, 358 ± 10 and 504 ± 3 ([H⁺] = 1.0 M; with [H⁺] = 0.25 M the latter was at 513 ± 2).

Rate constants k_{obsd} for the third stage are given in Table II.[7] The best fit of data is given by eq 2 where k'_c is small.

$$k_{obsd} = k_c[H^+] + k'_c \qquad (2)$$

This same dependence was observed for a wider [H⁺] range, 0.05–3.00 M at $I = 3.00$ M (LiClO₄), Table III.[7] No evidence was obtained for a less than first-order dependence on [H⁺] as suggested in ref 1. Since the final step yielding *fac*-Co-$(NH_3)_3(H_2O)_3]^{3+}$ is believed to be rapid, k_{obsd} is not an equilibration process, and k'_c is therefore assigned to an [H⁺]-independent contribution to bridge cleavage. Rate constants and activation parameters are again listed in Table IV.