Synthesis and Characterization of the μ-Disulphido Complexes CrS_2Cr^{4+} and CrS_2HFe^{4+}

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Summary Novel chromium(III) complexes with μ-disulphido(S–S) bridging ligands have been prepared by I_2 and Fe^{III} oxidation of $CrSH^{2+}$.

Addition of I_2 (*ca.* 10^{-3} M, 50 ml) to mercaptopenta-aquochromium(III),† $CrSH^{2+}$,[1,2] (*ca.* $1{\cdot}50 \times 10^{-2}$M, 25 ml) in non-complexing $0{\cdot}1$M$HClO_4$–$0{\cdot}9$M $LiClO_4$ (from ion-exchange separation), under air-free conditions, yields a yellow-brown complex (A). The latter was separated from excess of $CrSH^{2+}$ using a Sephadex SP C25 column (18—20 cm long, 1·8 cm diameter, 0 °C) pre-equilibrated with 0·10M $HClO_4$. The $CrSH^{2+}$ band was eluted with 0·2M $HClO_4$, and (A) with a solution of 0·1M $HClO_4$ and 0·9M $LiClO_4$.

Solutions of (A) were stored under N_2 and were characterized as follows. An aliquot portion (1×10^{-3}M, 50 ml) was mixed with NaOH (1M, 10 ml), and H_2O_2 (30%, 1 ml), and heated at 70 °C for 1 h. The chromate(VI) produced was determined spectrophotometrically at 372 nm (ϵ $4{\cdot}82 \times 10^3$ l mol^{-1} cm^{-1}), and the sulphate as $BaSO_4$ after first reducing Cr^{VI} to Cr^{III} with H_2O_2 under acidic conditions. The validity of the procedure was checked using solutions of S^{2-} and S_2^{2-} in the presence of chromium(III) and perchlorate. The ratio of S:Cr was found to be 0·96 ±0·01:1.

Procedures involving I_2 oxidation of S^{2-} to elemental sulphur have previously been used in the estimation of sulphur compounds.[3] In this study I_2 was used to determine the number of redox equivalents of (A) (1·01 ± 0·01 per Cr). It was also found that complex (A) is eluted more slowly than Cr^{3+} using Dowex cation-exchange resin, indicating a charge > 3. Accordingly (A) is formulated as the μ-disulphido-bis[penta-aquochromium(III)] complex, CrS_2Cr^{4+}. The spectrum of (A) is shown in the Figure. The equation for formation can be expressed as in (1).

$$I_2 + 2\,CrSH^{2+} \rightarrow CrS_2Cr^{4+} + 2H^+ + 2I^- \qquad (1)$$

On addition of Fe^{2+} (0·037M) to CrS_2Cr^{4+} ($1{\cdot}3 \times 10^{-4}$M), $[H^+] = 0{\cdot}10$—$0{\cdot}55$M, spectrophotometric changes ($t_{\frac{1}{2}}$ *ca.* 10 min at 25 °C) are observed, with an isosbestic point at 376 nm, and the yellow-green complex (B) is formed (Figure). The same product is obtained in good yield, along with hexa-aquochromium(III), by hexa-aquoiron(III) oxidation of $CrSH^{2+}$, $[H^+] = 0{\cdot}10$—$0{\cdot}55$M. Separation using a Sephadex resin, followed by determination of the S:Cr ratio (1·98 ± 0·10:1) was as above. The Fe content (Cr:Fe ratio 0·94 ± 0·02:1) was determined by iodometric titration after exhaustive oxidation with $HClO_4$, HNO_3, and H_2SO_4 until no more SO_2 was evolved. The Fe^{III} and Cr^{VI} were titrated together, and the Cr^{VI} separately after the addition of ethylenediaminetetra-acetic acid and acetate buffer to complex the Fe^{III} and thus prevent the oxidation of I^- to I_2. The Cr^{VI} was also estimated spectrophotometrically. Redox equivalents of a solution of (B) were determined as before (0·98 ± 0·03 per Cr), and the charge on the complex (3·8) by the method of Cady and Connick.[4] Complex (B) is accordingly formulated as CrS_2HFe^{4+} and the relevant equations are (2) and (3).

$$CrS_2Cr^{4+} + Fe^{2+} + H^+ \rightarrow CrS_2HFe^{4+} + Cr^{3+} \qquad (2)$$

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

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† Elsewhere[1,2] this complex has been referred to as thiolopenta-aquochromium(III).

The $CrSH^{2+}$ complex must be in excess in reaction (3), to avoid further oxidation of the S-ligand and precipitation of sulphur. The 1 : 1 stoicheiometry of reaction (3) was confirmed from a detailed analysis of spectrophotometric changes. Ion-exchange separation and determination of the Cr^{3+} and Fe^{2+} products were also carried out using Dowex 50W-X8 resin.

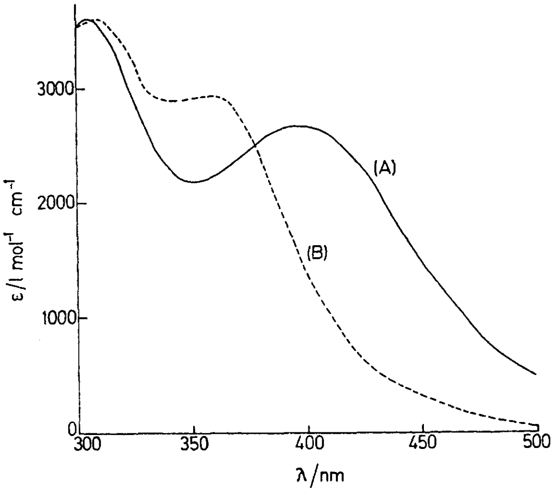

FIGURE. Spectra of CrS_2Cr^{4+} (A) and CrS_2HFe^{4+} (B) $[H^+] =$ 0·1M. Absorption coefficients are per dimer unit.

Interesting features of reaction (2) are the displacement of Cr^{3+} by Fe^{2+} which is known to have a high affinity for S-ligands.[5] Reaction (3) also gives as much as 20% of CrS_2Cr^{4+} at low $[H^+]$ (0·10M) which suggests that a radical mechanism is involved. Complex (B) is not formed *via* (A) in reaction (3). It is necessary to invoke protonation of the Cr–Fe binuclear complex to meet all the requirements of product analyses. Alternative structures with di-μ-sulphido or with non-bridging S_2^{2-} ligands are not consistent with the above findings (incorrect charge *etc.*).

From kinetic studies the rate law for reaction (2) takes the form of equation (4), where $k_1 = (3{\cdot}16 \pm 0{\cdot}05) \times 10^{-2}$

$$\text{Rate} = k_1[CrS_2Cr^{4+}][Fe^{2+}] + k_2[CrS_2Cr^{4+}] \qquad (4)$$

$l\ mol^{-1}\ s^{-1}$ and $k_2 = (9{\cdot}8 \pm 0{\cdot}4) \times 10^{-5}\ s^{-1}$ (both are independent of $[H^+]$) at 25 °C, $I = 1{\cdot}0M$ ($LiClO_4$). The rate law for reaction (3) is as in equation (5), where at 25 °C,

$$\text{Rate} = k_3[CrSH^{2+}][Fe^{3+}][H^+]^{-1} \qquad (5)$$

$k_3 = (1{\cdot}50 \pm 0{\cdot}02) \times 10^{-2}\ l\ mol^{-1}\ s^{-1}$, $I = 1{\cdot}0M$ ($LiClO_4$). The latter most likely involves a reaction of CrS^+ with Fe^{3+}.

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