Preparation and Properties of the Heterometallic Cuboidal Complex $[Mo_3CrS_4(H_2O)_{12}]^{4+}$: Comparisons with $[Mo_4S_4(H_2O)_{12}]^{4+}$ †

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A Cr-containing heterometal cuboidal cluster has been prepared for the first time by the reaction of $[Cr(H_2O)_6]^{2+}$ with the Mo^{IV}_3 incomplete cuboidal $[Mo_3S_4(H_2O)_9]^{4+}$ ion. The product has a formula $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ analogous to $[Mo_4S_4(H_2O)_{12}]^{4+}$, where the stoichiometries and the products for the hexaaquairon(III) and $[Co(dipic)_2]^-$ (dipic = pyridine-2,6-dicarboxylate) oxidations are consistent with the 4+ overall charge. Stopped-flow complexation studies with NCS^- are assigned as 1 : 1 NCS^- for H_2O substitution at the Cr. From the behaviour observed it is concluded that the Cr is in oxidation state III, and is labilised by the three μ_3-S ligands. In contrast the Mo^{III}_4 ion $[Mo_4S_4(H_2O)_{12}]^{4+}$ is substituted at a much slower rate, with rate constants similar to those for $[Mo(H_2O)_6]^{3+}$, and with no apparent influence of the μ_3-S ligands. While substitution on $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ exhibits an $[H^+]^{-1}$ dependence indicating a conjugate-base pathway (and $\geqslant 2$ H_2O per Cr), no similar dependence was observed for $[Mo_4S_4(H_2O)_{12}]^{4+}$. The behaviour thus parallels substitution on $[Cr(H_2O)_6]^{3+}$ ($3d^3$) and $[Mo(H_2O)_6]^{3+}$ ($4d^3$) where in the molybdenum case no $[H^+]^{1}$ dependence is observed. Kinetic studies (25 °C) on the hexaaquairon(III) and $[Co(dipic)_2]^-$ oxidations of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ to give $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Cr(H_2O)_6]^{3+}$, and of $[Mo_4S_4(H_2O)_{12}]^{4+}$ to give $[Mo_4S_4(H_2O)_{12}]^{5+}$ have also been made.

Incorporation of chromium into the Mo^{IV}_3 incomplete cuboidal $[Mo_3S_4(H_2O)_9]^{4+}$ ion,[1-4] to produce the heterometallic cuboidal cluster Mo_3CrS_4, and comparisons with the Mo_4S_4 analogue are of interest in view of the position of chromium as a Group 6 congener of molybdenum in the Periodic Table. The preparative procedure used here is somewhat different from other methods employed for heterometallic derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$. Previously procedures involving direct reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with the metal,[5-12] and in one case the metal ion (Sn^{2+}),[8] or $NaBH_4$ reduction of $[Mo_3S_4(H_2O)_9]^{4+}$ in the presence of M^{2+}, have been successfully employed.[13,14] In the present case no reaction with chromium metal was observed, but $[Cr(H_2O)_6]^{2+}$ is itself a strong enough reducing agent ($E^{\circ\prime} = -0.41$ V) to serve as a reductant for $[Mo_3S_4(H_2O)_9]^{4+}$ prior to incorporation and to give a product characterised here as $[Mo_3CrS_4(H_2O)_{12}]^{4+}$.

Some eight different metals (M) have so far been incorporated into $[Mo_3S_4(H_2O)_9]^{4+}$ yielding Mo_3MS_4 (and related) products, Fig. 1. In addition to the single heterometal cubes, where tetrahedral (**A**) and octahedral (**B**) co-ordination of the heterometal (Fe, Ni, Pd or Sn) are possible,[5-8] edge-linked double cubes (**C**) formed by the heterometal atom (Co, Cu or Pd) binding to a sulfide in the second cube[7,9-10] and (**D**) heterometal (Hg, Sn or Sb) corner-shared cubes[8,10-12] have been characterised as the toluene-*p*-sulfonate (pts^-) salts of the aqua ion by X-ray crystallography.[15] A turquoise-blue thallium derivative has also been prepared, where the high charge (Dowex column behaviour) indicates a corner-shared double cube structure.[16] In aqueous acidic solution the edge-linked double cubes give single cubes spontaneously or upon addition of complexing anions.[3,10,17]

There are three oxidation states of the $[Mo_4S_4(H_2O)_{12}]^{n+}$ cube with n = 4, 5 or 6.[18] All three have been characterised by X-ray crystallography as the $[Mo_4S_4(edta)_2]^{n-8}$ (edta = ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate) derivatives.[15] The air-sensitive $[Mo_4S_4(H_2O)_{12}]^{4+}$ is here selected for comparison

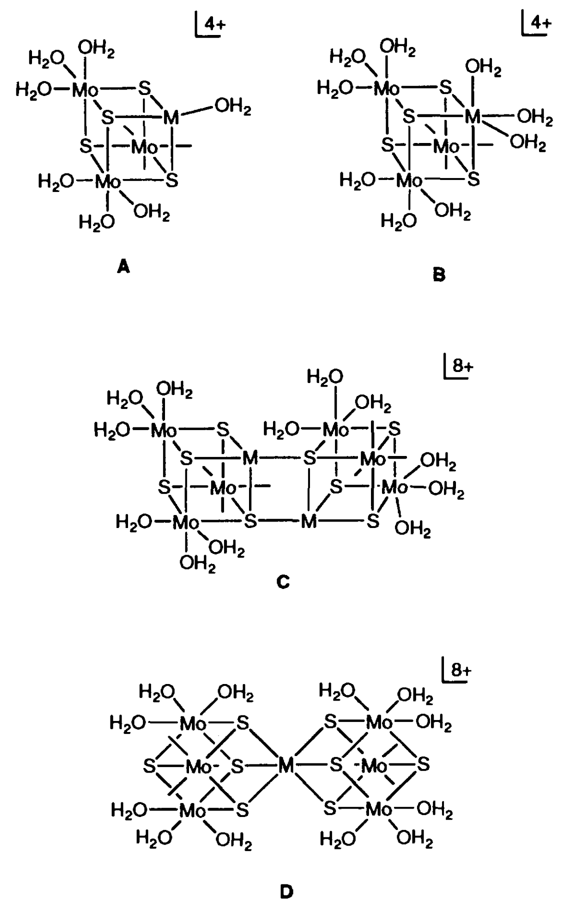

Fig. 1 Different types of heterometallic cuboidal clusters obtained from $[Mo_3S_4(H_2O)_9]^{4+}$: single cube with a tetrahedral heterometal atom, **A**; single cube with an octahedral heterometal atom, **B**; edge-linked double cube, **C**; and corner-shared double cube, **D**

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† *Non-SI unit employed:* M = mol dm^{-3}.

because it has the same number of valence electrons as $[Mo_3CrS_4(H_2O)_{12}]^{4+}$. Oxidations with cobalt(III) complexes[19] and NCS^- substitution have been studied previously.[20]

Solution properties of the heterometallic single cubes $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ (ref. 13) and $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ (ref. 14) have also been reported. The 2:1 oxidations of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ and $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ with $[Fe(H_2O)_6]^{3+}$ and $[Co(dipic)_2]^-$ (dipic = pyridine-2,6-dicarboxylate) result in the formation of $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Ni(H_2O)_6]^{2+}$ or $[Fe(H_2O)_6]^{2+}$.[13,14] For each heterometallic structure so far identified only a single oxidation state has been obtained except in the case of $[Mo_3CuS_4(H_2O)_{10}]^{4+/5+}$.[16] With Sn as the heteroatom the single cube $Mo_3SnS_4^{6+}$ and corner-shared double cube $Mo_3S_4SnS_4Mo_3^{8+}$ have been prepared, but these do not appear to interconvert readily.[8]

Experimental

Preparation of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$.—Solutions of $[Mo_3S_4(H_2O)_9]^{4+}$ in the acid required (generally HCl) were first prepared.[2-4] The reactant $[Cr(H_2O)_6]^{2+}$ and product $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ are very air-sensitive and rigorous O_2-free conditions are required throughout. The procedure used involves syphoning a solution of green $[Mo_3S_4(H_2O)_9]^{4+}$ (≈3 M, 30 cm^3) under N_2 onto a 10-fold excess of solid (sky-blue) $CrCl_2{\cdot}4H_2O$ (0.11 g). An immediate reaction with a colour change to red-brown was observed, which is summarised by equation (1). After dilution to $[H^+]$ ≈0.3 M the solution was

$$Mo_3S_4^{4+} + 3Cr^{2+} \longrightarrow Mo_3CrS_4^{4+} + 2Cr^{3+} \quad (1)$$

loaded onto a Dowex 50W-X2 cation-exchange column (20 x 1.0 cm). The column was washed with 0.5 M HCl (50 cm^3) and 1.0 M HCl (50 cm^3), and the product eluted with 2.0 M HCl. The first band was identified as unreacted $[Cr(H_2O)_6]^{2+}$, the second (green) band as $[CrCl(H_2O)_5]^{2+}$, and the third (violet) band as $[Cr(H_2O)_6]^{3+}$ (both minor components). The substantial fourth red-brown band was $[Mo_3CrS_4(H_2O)_{12}]^{4+}$. An unidentified brown band remained at the top of the column. Solutions in Hpts were obtained by loading the complex as described and washing extensively with 0.5 M Hpts (100 cm^3) and 1.0 M Hpts (50 cm^3), and eluting with either 2.0 or 4.0 M Hpts as required. Typically solutions (≈20 cm^3) of concentration 10–20 mM in 2.0 M Hpts were obtained. Solutions eluted in 2.0–4.0 M $HClO_4$ were less stable. A concentrated band of the cube eluted in 4 M Hpts gave a sample of non-crystalline solid material. Other procedures for crystallisation were attempted, but were difficult because of the extreme air-sensitivity of the cluster, and the tendency to revert to $[Mo_3S_4(H_2O)_9]^{4+}$.

The Mo:Cr ratio in the product was determined by inductively coupled plasma (ICP) atomic emission spectroscopy at Laporte plc, Widnes. The ratio was found to be 3.05 ± 0.09:1 (average of three determinations).

No reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ was observed with Cr metal (Johnson Matthey; Electrolytic Flake), which had previously been immersed in 2 M HCl for ≈15 min.

The UV/VIS spectrum of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ is shown alongside that of $[Mo_3S_4(H_2O)_9]^{4+}$ in Fig. 2. Peak positions λ/nm (ε/M cm^{-1} per cluster) are at 255 (12 000) and 510 (387) respectively, where the ε values are based on the ICP analyses. In addition there are shoulders at 368 (975), 415 (650) and 700 (38). No absorbance is observed in the NIR spectrum up to 1300 nm.

Preparation of $[Mo_4S_4(H_2O)_{12}]^{4+}$.—Solutions (≈0.5 M) of the green cuboidal complex $[Mo_4S_4(H_2O)_{12}]^{5+}$ in 2 M $HClO_4$ were first prepared by a standard procedure.[2] Formation of the orange 4+ cube was achieved by reduction at a carbon-cloth electrode (RVG 1000; Le Carbonne, Brighton, UK) at a potential of −120 mV *vs.* saturated calomel electrode (SCE) for ≈2 h as previously described.[19] The product, peak at 378 nm (ε = 1000 M^{-1} cm^{-1}), is very air-sensitive and rigorous air-free techniques were required throughout. The UV/VIS spectra of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ and $[Mo_4S_4(H_2O)_{12}]^{4+}$ are compared in Fig. 3.

Other Reagents.—A sample of chromium(III) chloride, $CrCl_2{\cdot}4H_2O$, was prepared under rigorous air-free conditions by dissolving chromium metal in hydrochloric acid.[21] A literature method[22] was used to prepare $[NH_4][Co(dipic)_2]{\cdot}H_2O$. Solutions were standardised spectrophotometrically using the peak at 510 nm (ε = 630 M^{-1} cm^{-1}). Solutions of

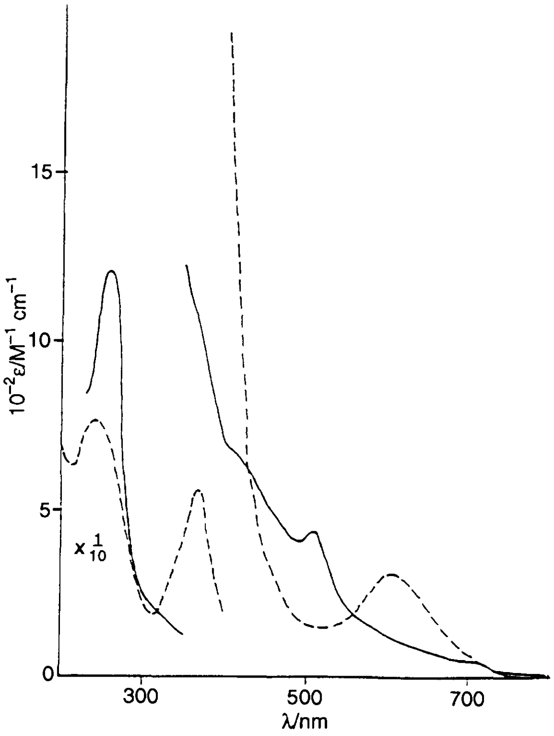

Fig. 2 The UV/VIS spectra of the heterometallic cuboidal complex $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ (——) and trinuclear Mo^{IV}_3 incomplete cuboidal $[Mo_3S_4(H_2O)_9]^{4+}$ (– – – –)

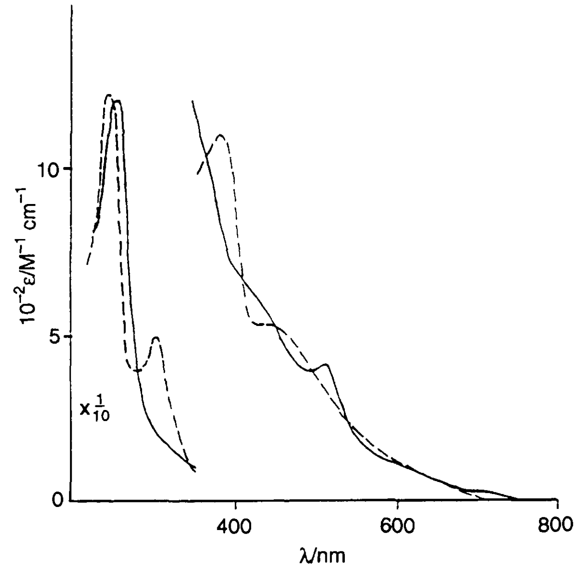

Fig. 3 Comparison of the UV/VIS spectra of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ (——) and $[Mo_4S_4(H_2O)_{12}]^{4+}$ (– – – –)

hexaaquairon(III) were obtained by Dowex 50W-X2 cation-exchange column purification of $Fe(ClO_4)_3{\cdot}6H_2O$ (Fluka). The solid was dissolved in 0.3 M acid and loaded onto the column. Extensive washing with 0.1 M Hpts or $HClO_4$ (100 cm^3) was followed by elution with a 1.0 M solution of the acid. Hydrochloric acid, 70% perchloric acid and sodium thiocyanate (BDH, AnalaR), and toluene-*p*-sulfonic acid (Sigma, 99%) was used as supplied. Lithium toluene-*p*-sulfonate was prepared by neutralisation of 4 M Hpts with lithium carbonate (BDH, Reagent Grade). The product was recrystallised twice from water.

Stability of Cuboidal Complexes.—In the presence of air immediate changes in the UV/VIS absorbance spectra of both $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ and $[Mo_4S_4(H_2O)_{12}]^{4+}$ were observed, in accordance with equations (2) and (3). With dioxygen in

$$4Mo_3CrS_4{}^{4+} + 3O_2 + 12H^+ \longrightarrow 4Mo_3S_4{}^{4+} + 4Cr^{3+} + 6H_2O \quad (2)$$

$$4Mo_4S_4{}^{4+} + O_2 + 4H^+ \longrightarrow 4Mo_4S_4{}^{5+} + 2H_2O \quad (3)$$

> 10-fold excess reaction (2) occurs in more than one step. All studies were done using high-purity N_2, rubber seals for containment, Teflon tubing, and Hamilton microsyringes. On varying the concentration of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ over the range 0.05–1.7 mM in 2.00 M Hpts, Beer's Law was obeyed at 510 (± 3) and 600 nm (± 6%).

Owing to the instability of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ in $HClO_4$ solutions all kinetic studies were done in Hpts. The conversion of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ into $[Mo_3S_4(H_2O)_9]^{4+}$ in 2.00 M $HClO_4$ is biphasic with $t_{\frac{1}{2}} \approx 35$ min for the first phase of reaction. No similar decay is observed in 2.00 M Hpts.

The air-sensitivity of $[Mo_4S_4(H_2O)_{12}]^{4+}$ has been commented on previously.[19]

Stoichiometries for the Oxidation of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$.—The oxidations of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ with hexaaquairon(III) and $[Co(dipic)_2]^-$ were studied. The final product is $[Mo_3S_4(H_2O)_9]^{4+}$. The iron(III) oxidation produces $[Fe(H_2O)_6]^{2+}$ which was determined as follows.[23] Glacial acetic acid (2 cm^3) was added with swirling to ammonium dihydrogenphosphate (10%, 5 cm^3) in a 100 cm^3 separating funnel. A sample of reaction mixture (2 cm^3) and water (8 cm^3) were then added. The pH was checked and if necessary adjusted to ≈2. Isopentyl acetate (10 cm^3) was added with a minimum of intermixing, followed by 0.01 M 4,7-diphenyl-1,10-phenanthroline (dpphen) (1 cm^3). After vigorous shaking the mixture was left to stand for 1 h. The aqueous layer was discarded and the spectrum of the upper isopentyl acetate layer containing $[Fe(dpphen)_3]^{2+}$ was recorded at the 535 nm peak (ε = 17 850 M^{-1} cm^{-1}). A 2.95 ± 0.12 : 1 ratio of Fe^{2+} produced per mole of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ consumed (five determinations) was obtained consistent with equation (4). An alternative titration procedure

$$Mo_3CrS_4{}^{4+} + 3Fe^{III} \longrightarrow Mo_3S_4{}^{4+} + Cr^{III} + 3Fe^{II} \quad (4)$$

involved monitoring changes in the UV/VIS spectrum of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ with successive addition of aliquots of a concentrated solution of hexaaquairon(III). Such studies confirmed a 1 : 3 stoichiometry.

The stoichiometry with $[Co(dipic)_2]^-$ as oxidant was also determined by the addition of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ from a Hamilton microsyringe to a solution of $[Co(dipic)_2]^-$ in a spectrophotometric cell. The decrease in absorbance at 510 nm and increase at 367 nm were monitored. Measurements indicated a 2.95 ± 0.15 : 1 (three determinations) stoichiometry in accordance with equation (5).

$$Mo_3CrS_4{}^{4+} + 3[Co(dipic)_2]^- \longrightarrow Mo_3S_4{}^{4+} + Cr^{3+} + 3[Co(dipic)_2]^{2-} \quad (5)$$

Together with the ICP analyses the stoichiometries require a formula $Mo_3CrS_4{}^{4+}$ with an overall 4+ charge. The conjugate-base pathway observed in kinetic studies on the 1 : 1 complexing of NCS^- at the Cr (see below) provides evidence for $\geqslant 2H_2O$ attached to the Cr, and a formula $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ which is analogous to $[Mo_4S_4(H_2O)_{12}]^{4+}$. The similarity of UV/VIS spectra in Fig. 3 is also noted. An oxidation-state assignment $Mo^{III}{}_3Cr^{III}$ corresponding to $Mo^{III}{}_4$ for $[Mo_4S_4(H_2O)_{12}]^{4+}$ is consistent with all these observations.

Stoichiometries for the Reactions of $[Mo_4S_4(H_2O)_{12}]^{4+}$.—Reduction potentials for the one-electron changes (6) and (7)

$$[Mo_4S_4(H_2O)_{12}]^{5+} + e^- \rightleftharpoons [Mo_4S_4(H_2O)_{12}]^{4+} \quad (6)$$

$$[Mo_4S_4(H_2O)_{12}]^{6+} + e^- \rightleftharpoons [Mo_4S_4(H_2O)_{12}]^{5+} \quad (7)$$

are 0.21 and 0.86 V respectively.[18] The oxidants used have reduction potentials $[Fe(H_2O)_6]^{3+/2+}$ (0.77 V) and $[Co(dipic)_2]^{-/2-}$ (0.75 V).[24] The UV/VIS absorbance changes indicate a one-electron change as in (6) as the dominant process.

Kinetic Studies.—Reactions of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ were studied at 25.0 ± 0.1 °C with the ionic strength adjusted to I = 2.00 ± 0.01 M Li(pts). Rigorous air-free conditions were employed in all cases with the different reagents used generally in > 10-fold excess. All kinetic runs were carried out on a Dionex D110 stopped-flow spectrophotometer. The complexation of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ with NCS^- was monitored at 400 nm, I = 2.00 M Li(pts), with checks at 600 nm. The reaction of $[Mo_4S_4(H_2O)_{12}]^{4+}$ with NCS^- has been studied previously at 25 °C, I = 2.00 M ($LiClO_4$).[20] The reaction with hexaaquairon(III) as oxidant was monitored at 510 nm with some checks at 367 nm. With $[Co(dipic)_2]^-$ as oxidant runs were at 367 nm with checks at 603 nm. Studies on the reactions of $[Mo_4S_4(H_2O)_{12}]^{4+}$ with the same two oxidants were at I = 2.00 M ($LiClO_4$), and were monitored at the 645 nm peak of $[Mo_4S_4(H_2O)_{12}]^{5+}$.[18] Dissociation of the cobalt(II) product $[Co(dipic)_2]^{2-}$ does not effect the absorbance changes monitored.

Cyclic Voltammetry.—Cyclic voltammetry was carried out on a Princeton Applied Research (PAR) 173 potentiostat attached to an Apple II microcomputer *via* a PAR 276 interface. A Metrohm glassy carbon electrode, a platinum secondary electrode and a calomel reference electrode were used. No reversible behaviour was observed for the $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ cluster, and a decomposition process was observed.

Treatment of Data.—Stopped-flow rate constants were evaluated using exponential fitting programs supplied by On-Line Instrument Systems (OLIS). For rate law fits an unweighted least-squares treatment was used.

Results

Substitution of NCS^- *on* $[Mo_3CrS_4(H_2O)_{12}]^{4+}$.—With NCS^- in large (> 10-fold) excess, Table 1, the reaction is biphasic, with a first stage ($t_{\frac{1}{2}} \approx 8$ s) much faster than the second ($t_{\frac{1}{2}} \approx 10$ min). Substitution of NCS^- on $[Mo_4S_4(H_2O)_{12}]^{4+}$ is known to be in the conventional time range,[20] consistent with the faster phase of the reaction of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ being substitution at the Cr. Studies at 25 °C, I = 2.00 M Li(pts) were restricted to the first phase, Fig. 4, where the reaction can be expressed as in equation (8). Formation and aquation rate

$$[Mo_3CrS_4(H_2O)_{12}]^{4+} + NCS^- \rightleftharpoons [Mo_3CrS_4(H_2O)_{11}(NCS)]^{3+} + H_2O \quad (8)$$

constants, k_f and k_{aq}, are as defined in equations (9) and (10). No

$$k_{eq} = k_f[Mo_3Cr^{4+}] + k_{aq} \qquad (9)$$

$$k_{eq} = (k_f[NCS^-]/n) + k_{aq} \qquad (10)$$

statistical factor is required, *i.e.* $n = 1$, to obtain a coincidence of rate constants k_f and k_{aq} defined with first $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ and then NCS^- in large excess, Fig. 4. A plot of k_f against $[H^+]^{-1}$, with $[H^+]$ in the range 0.50–2.00 M, Fig. 5, indicates a dependence (11) where $a = 25.2 \pm 2.1$ M^{-1} s^{-1} for

$$k_f = a + b[H^+]^{-1} \qquad (11)$$

the reaction of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ and $b = 21.4 \pm 1.6$ s^{-1} for the pathway involving the conjugate base $[Mo_3CrS_4(H_2O)_{11}(OH)]^{3+}$. Since K_a for the formation of Cr–OH is not known the second-order rate constant b/K_a cannot be determined. A similar relationship holds for k_{aq}. Values of k_f and k_{aq} at different $[H^+]$ values are listed in Table 2. The

Table 1 First-order rate constants, k_{eq} (25 °C), for the reaction of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ with NCS^-, I = 2.00 M Li(pts)

$[H^+]$	$10^3[Mo_3CrS_4{}^{4+}]$ M	$10^3[NCS^-]$ M	$10k_{eq}/s^{-1}$
2.00	0.05	0.50	0.63
	0.05	1.00	0.81
	0.05	1.50	0.98
	0.05	2.00	1.19
	0.05	2.50	1.33
	0.50	0.05	0.58
	1.35	0.50	0.93
1.00	0.05	0.50	0.78
	0.04	1.00	1.03
	0.05	1.50	1.27
	0.05	1.92	1.43
0.75	0.04	0.50	0.89
	0.05	1.00	1.18
	0.05	1.50	1.43
	0.05	2.00	1.67
0.50	0.05	0.50	0.98
	0.05	1.00	1.37
	0.05	1.50	1.67

Table 2 Formation, k_f, and aquation, k_{aq}, rate constants (25 °C) for the equilibration of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ with NCS^-, I = 2.00 M Li(pts)

$[H^+]$/M	k_f/M^{-1} s^{-1}	$10^2k_{aq}/s^{-1}$
2.00	37 ± 1	4.2 ± 0.2
1.00	46 ± 2	5.6 ± 0.3
0.75	52 ± 2	6.5 ± 0.2
0.50	69 ± 5	6.9 ± 0.6

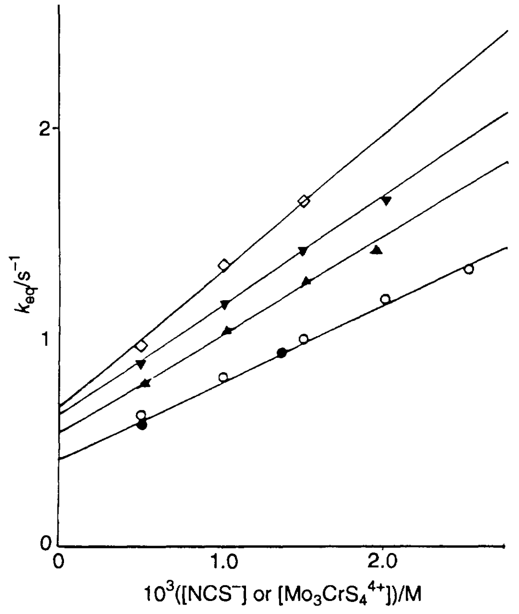

Fig. 4 Dependence of first-order rate constants k_{eq} (25 °C) for the equilibration of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ with NCS^- in > 10-fold excess with $[H^+]$ = 2.00 (○), 1.00 (▲), 0.74 (▼) and 0.50 M (◇). Runs at $[H^+]$ = 2.00 M with $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ in > 10-fold excess are also indicated (●); I = 2.00 M Li(pts)

Table 3 Variation of first-order rate constants, k_{obs} (25 °C), for the oxidation of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ (5×10^{-5} M) with hexaaquairon(III) as the concentration of oxidant and $[H^+]$ are varied, I = 2.00 M Li(pts)

$[H^+]$/M	$10^3[Fe^{III}]$/M	$10^2k_{obs}/s^{-1}$
1.80	3.00	1.60
	4.00	2.15
	5.00[a]	2.67
	6.00	3.2
	7.00	3.7
1.40	3.00[b]	1.70
	4.00	2.27
	5.00	2.78
	6.00	3.4
1.00	3.00	1.85
	4.00[a]	2.45
	5.00	3.1
	5.80	3.6
0.70	2.00	1.86
	3.00	2.15
	3.75	2.65
	4.50	3.2
	5.00	3.6
0.50	2.00	1.75
	3.20	2.73
	3.70[b]	3.1
	4.50	4.0
	5.00	4.3

[a] $[Mo_3CrS_4(H_2O)_{12}{}^{4+}] = 4 \times 10^{-5}$ M. [b] $[Mo_3CrS_4(H_2O)_{12}{}^{4+}] = 3 \times 10^{-5}$ M.

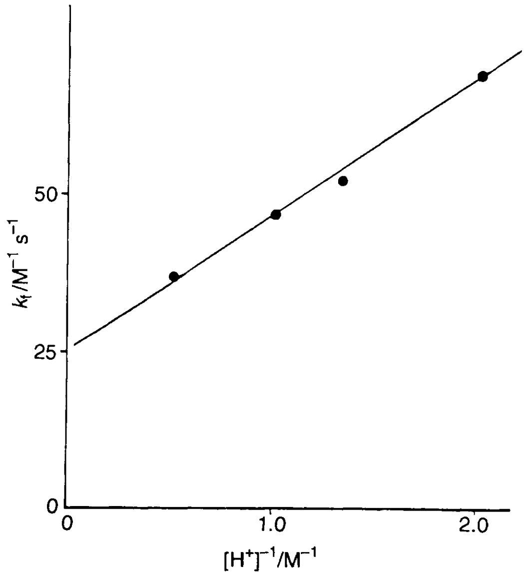

Fig. 5 Dependence of formation rate constants k_f (25 °C) on $[H^+]^{-1}$ for the equilibration of NCS^- with $[Mo_3CrS_4(H_2O)_{12}]^{4+}$, I = 2.00 M Li(pts)

equilibrium constant $K = k_f/k_{aq}$ at $[H^+] = 2.00$ M is 880 ± 45 M^{-1}.

Oxidation of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ *with* $[Fe(H_2O)_6]^{3+}$.—A uniphasic reaction is observed with first-order rate constants, k_{obs}, Table 3, showing a linear dependence on $[Fe^{III}]$, equation (12). The rate law and 1:3 stoichiometry (4) are

$$d[Mo_3S_4^{4+}]/dt = k_{Fe}[Mo_3CrS_4^{4+}][Fe^{III}] \quad (12)$$

consistent with a reaction sequence (13)–(15). On varying $[H^+]$

$$Mo_3CrS_4^{4+} + Fe^{III} \xrightarrow{k_{Fe}} Mo_3CrS_4^{5+} + Fe^{II} \quad (13)$$

$$Mo_3CrS_4^{5+} + Fe^{III} \xrightarrow{\text{fast}} Mo_3S_4^{4+} + Cr^{II} + Fe^{II} \quad (14)$$

$$Cr^{II} + Fe^{III} \xrightarrow{\text{fast}} Cr^{III} + Fe^{II} \quad (15)$$

within the range 0.50–1.80 M, Table 4, an inverse dependence is observed, Fig. 6, which can be expressed as in equation (16).

$$k_{Fe} = c + d[H^+]^{-1} \quad (16)$$

This suggests contributions to k_{Fe} from $[Fe(H_2O)_6]^{3+}$ (path *c*) and $[Fe(H_2O)_5(OH)]^{2+}$ (path *d*), the two being related by the acid dissociation process (17). At 25 °C, $I = 2.00$ M Li(pts), $c = 4.0 \pm 0.1$ M^{-1} s^{-1} and $d = 2.30 \pm 0.08$ s^{-1}.

$$[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H^+ \quad (17)$$

Oxidation of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ *with* $[Co(dipic)_2]^-$.—First-order rate constants, k_{obs} (Table 5), for the uniphasic reaction give a linear dependence on $[Co(dipic)_2^-]$, Fig. 7, in accord with equation (18). The rate law and stoichiometry

$$d[Mo_3S_4^{4+}]/dt = k_{Co}[Mo_3CrS_4^{4+}][Co^{III}] \quad (18)$$

indicate a reaction sequence (19)–(21) which is similar to (13)–(15). No dependence of rate constants on $[H^+]$ in the range 0.55–2.00 M was observed. From the slope in Fig. 7, $k_{Co} = 16.2 \pm 3.0$ M^{-1} s^{-1}, at 25 °C, $I = 2.00$ M Li(pts).

$$Mo_3CrS_4^{4+} + Co^{III} \xrightarrow{k_{Co}} Mo_3CrS_4^{5+} + Co^{II} \quad (19)$$

$$Mo_3CrS_4^{5+} + Co^{III} \xrightarrow{\text{fast}} Mo_3S_4^{4+} + Cr^{II} + Co^{II} \quad (20)$$

$$Cr^{II} + Co^{III} \xrightarrow{\text{fast}} Cr^{III} + Co^{II} \quad (21)$$

Oxidation of $[Mo_4S_4(H_2O)_{12}]^{4+}$ *with* $[Fe(H_2O)_6]^{3+}$.—The 1:1 oxidation to $[Mo_4S_4(H_2O)_{12}]^{5+}$ was monitored at 645 nm. In the time range up to 0.3 s the reaction was uniphasic. First-

Table 4 Variation of second-order rate constants, k_{Fe} (25 °C), with $[H^+]$ for the oxidation of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ with hexaaquairon(III), $I = 2.00$ M Li(pts)

$[H^+]$/M	k_{Fe}/M^{-1} s^{-1}
1.80	5.3 ± 0.1
1.40	5.7 ± 0.1
1.00	6.2 ± 0.1
0.70	7.2 ± 0.1
0.50	8.6 ± 0.1

Table 5 First-order rate constants, k_{obs} (25 °C), for the $[Co(dipic)_2]^-$ oxidation of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ showing a dependence on the concentration of oxidant but not $[H^+]$, $I = 2.00$ M Li(pts)

$[H^+]$/M	$10^3[Co^{III}]$/M	10^2k_{obs}/s^{-1}
1.80	0.50	0.91
	1.00	1.55
	1.25	1.95
	2.50	4.1
1.00	0.50	0.91
	1.00	1.62
	1.50	2.45
	2.25	3.7
0.55	0.75	1.25
	1.38	2.25
	2.00	3.3

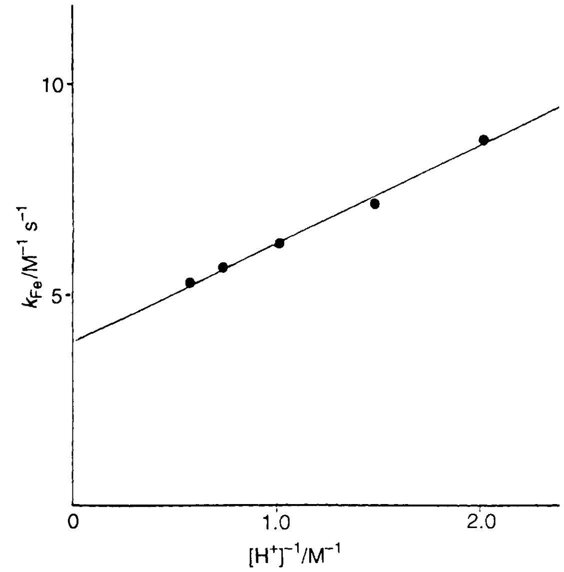

Fig. 6 Dependence of second-order rate constants k_{Fe} (25 °C) on $[H^+]$ for the hexaaquairon(III) oxidation of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$. $I = 2.00$ M Li(pts)

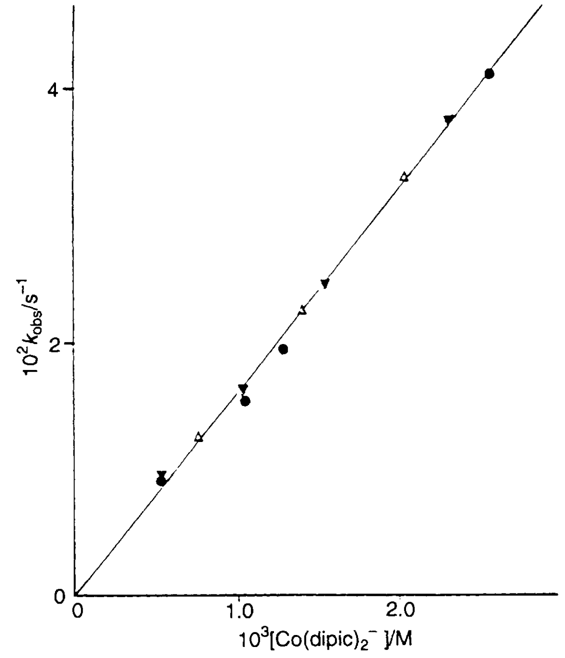

Fig. 7 Rate constants k_{obs} (25 °C) for the $[Co(dipic)_2]^-$ oxidation of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ illustrating no dependence on $[H^+] = 2.00$ (▼), 1.00 (●) and 0.55 M (△), $I = 2.00$ M Li(pts)

order rate constants, k_{obs}, Table 6, for the reaction (22), give a

$$Mo_4S_4^{4+} + Fe^{III} \longrightarrow Mo_4S_4^{5+} + Fe^{II} \quad (22)$$

rate law (23), Fig. 8. From $[H^+]$ variations in the range 0.5–2.0

$$d[Mo_4S_4^{5+}]/dt = k_{Fe}[Mo_4S_4^{4+}][Fe^{III}] \quad (23)$$

M no dependence on $[H^+]^{-1}$ was observed and k_{Fe} = (4.4 ± 0.1) × 10^4 M^{-1} s^{-1}.

Oxidation of $[Mo_4S_4(H_2O)_{12}]^{4+}$ *with* $[Co(dipic)_2]^-$.—From studies in 2.00 M $HClO_4$ solutions and a similar treatment of first-order rate constants, k_{Co} = (3.7 ± 0.3) × 10^5 M^{-1} s^{-1}, Table 7.

Discussion

The aqua ions $[Cr(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{3+}$ are known for their extreme lability and inertness,[25] with H_2O-exchange rate constants of $\approx 10^9$ and $\approx 10^{-6}$ s^{-1} respectively. From studies with $[Cr(H_2O)_6]^{2+}$ as reductant for inorganic complexes, a distinction between inner- and outer-sphere electron transfer is possible as has been well documented. The $[Cr(H_2O)_6]^{2+}$ reduction of $[Mo_3O_4(H_2O)_9]^{4+}$ has been studied previously.[26] The formation of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ by the reaction of $[Cr(H_2O)_6]^{2+}$ with $[Mo_3S_4(H_2O)_9]^{4+}$ represents a new preparative route for a heterometal cluster. The presence of strongly reducing $[Cr(H_2O)_6]^{2+}$ obviates the need for $NaBH_4$ as a reductant in the preparative procedure used.

Reduction of the $Mo_3S_4^{4+}$ core has been demonstrated to occur in the case of the CN^- and ida (= iminodiacetate) complexes,[27,28] and with $[Mo_3S_4(H_2O)_9]^{4+}$ formation of the $Mo_3S_4^{2+}$ transient is proposed for both $NaBH_4$ and $[Cr(H_2O)_6]^{2+}$. Initial $[Cr(H_2O)_6]^{2+}$ reduction of $[Mo_3S_4(H_2O)_9]^{4+}$ does not seem to result in permanent attachment of Cr^{III}. Incorporation of $[Cr(H_2O)_6]^{2+}$ follows in the sequence of changes (24). Air-free cation-exchange purification of

$$Mo_3S_4^{4+} \longrightarrow Mo_3S_4^{2+} \longrightarrow Mo_3CrS_4^{4+} \quad (24)$$

$[Mo_3CrS_4(H_2O)_{12}]^{4+}$ gives bands of unreacted $[Cr(H_2O)_6]^{2+}$ as well as $[Cr(H_2O)_6]^{3+}$. Any traces of O_2 would give green binuclear chromium(III) species as product, and formation of $[Cr(H_2O)_6]^{3+}$ is therefore explained by the stoichiometric equation (25).

$$Mo_3S_4^{4+} + 3Cr^{II} \longrightarrow Mo_3CrS_4^{4+} + 2Cr^{III} \quad (25)$$

The relative ease with which the heterometallic cluster elutes from a cation-exchange column with 2.00 M Hpts implicates a single cube structure of the type $Mo_3CrS_4^{4+}$, rather than an edge-linked or corner-shared double cube of higher charge. The 4+ charge is confirmed by the stoichiometry of the oxidations with Fe^{III} and $[Co(dipic)_2]^-$. Thus both oxidants give a three-equivalent conversion of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ to $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Cr(H_2O)_6]^{3+}$, which are formed in a 1 : 1 ratio.

Studies on the aqueous solution chemistry of Cr^{II} and Cr^{III} have demonstrated that tetrahedral co-ordination is not a common feature, and indeed is extremely rare for these ions.[29] In the case of Cr^{II} $t_{2g}^3e_g^1$, tetragonally distorted octahedral structures have been established, and octahedral co-ordination is favoured for the Cr^{III} t_{2g}^3 state. A number of Cr-containing homo- and hetero-metallic cuboidal sulfido clusters containing cyclopentadienyl terminal ligands have been prepared previously,[30–36] but none containing the Mo_3CrS_4 core has yet been described. In a recent study incorporation of the Mo_3CrO_4 core in a double cube was reported.[37]

Early transition metals with low d-electron populations favour six-co-ordination in chalcogenide cubes of the kind under discussion. Thus M = Mo and V in Fe_3MS_4 and Mo in Mo_4S_4 clusters are six-co-ordinate, whereas M = Fe, Co, Ni or Cu in Mo_3MS_4 and the Fe in Fe_4S_4 clusters are tetrahedral. Octahedral co-ordination to the Cr of Mo_3CrS_4 is supported by the substitution studies described. Thus with NCS^- a well defined $[H^+]^{-1}$ dependence is observed. This is consistent with a conjugate-base mechanism and $\geq 2H_2O$ attached to each Cr.

The oxidations of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ with $[Fe(H_2O)_6]^{3+}$, rate law term *c* in equation (16), and with $[Co(dipic)_2]^-$ (no $[H^+]$ dependence) are both assigned as outer-sphere processes, Table 8. Thus H_2O does not normally

Table 6 First-order rate constants, k_{obs} (25 °C), for the oxidation of $[Mo_4S_4(H_2O)_{12}]^{4+}$ with hexaaquairon(III), *I* = 2.0 M $LiClO_4$

$10^3[Mo_4S_4^{4+}]$/M	$10^3[Fe^{III}]$/M	k_{obs}/s^{-1}
$[H^+]$ = 2.0 M		
0.06	0.65	26
0.08	0.83	38
0.08	1.02	48
0.08	1.11	52
0.13	1.38	56
0.13	1.47	68
0.13	1.66	75
0.13	1.93	90
0.13	2.18	97
0.13	2.48	109
$[H^+]$ = 1.0 M		
0.08	0.83	38
0.08	1.11	51
0.13	1.52	61
0.13	2.21	92
$[H^+]$ = 0.50 M		
0.08	0.83	33
0.08	1.11	46
0.13	1.38	56

Table 7 Rate constants (25 °C) for the $[Co(dipic)_2]^-$ oxidation of $[Mo_4S_4(H_2O)_{12}]^{4+}$, $[H^+]$ = 2.00 M $HClO_4$

$10^4[Mo_4S_4^{4+}]$/M	$10^4[Co^{III}]$/M	$10^{-5}k_{Co}/M^{-1}\ s^{-1}$
4.6	4.6	3.5
2.3	2.3	3.8
2.3	4.6	4.0
2.3	6.9	3.5

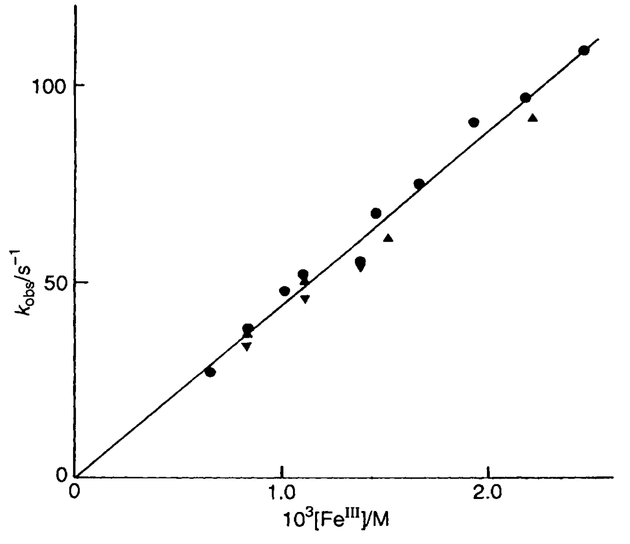

Fig. 8 Dependence of the first-order rate constants k_{obs} (25 °C) for the hexaaquairon(III) oxidation of $[Mo_4S_4(H_2O)_{12}]^{4+}$ on $[Fe^{III}]$ at different $[H^+]$ 2.00 (●), 1.00 (▲) and 0.50 M (▼); *I* = 2.00 M $LiClO_4$

Table 8 Comparison of kinetic data (35 °C) obtained for (*a*) $[Fe(H_2O)_6]^{3+}$ and $[Co(dipic)_2]^-$ redox reactions, and (*b*) NCS^- substitution reactions of cuboidal aqua ions, $I = 2.00$ M Li(pts) (Cr) and 2.00 M $LiClO_4$ (Mo and Ni[13])

(*a*) Redox studies

	$k_{Fe}/M^{-1}\ s^{-1}$	$k_{Co}/M^{-1}\ s^{-1}$	k_{Co}/k_{Fe}
$[Mo_3CrS_4(H_2O)_{12}]^{4+}$	4.0[a]	16.2[b]	4.1
$[Mo_4S_4(H_2O)_{12}]^{4+}$	4.4×10^4[b]	3.7×10^5[b]	8.4
$[Mo_3NiS_4(H_2O)_{10}]^{4+}$	5.4×10^{-3}[c]	0.35[b]	64.8

(*b*) Substitution studies (NCS^-)

	$k_f/M^{-1}\ s^{-1}$	k_{aq}/s^{-1}	K/M^{-1}
$[Mo_3CrS_4(H_2O)_{12}]^{4+}$	37[d]	0.042[d]	880
$[Mo_4S_4(H_2O)_{12}]^{4+}$	1.95[b]	0.001[b]	1390
$[Mo_3NiS_4(H_2O)_{10}]^{4+}$	45[b]	0.062[b]	720

[a] A conjugate-base pathway is also observed; rate constant for reaction of $[Fe(OH)]^{2+}$ is 2.3×10^3 M^{-1} s^{-1}. [b] No $[H^+]^{-1}$ dependence. [c] Conjugate-base pathway observed; rate constant for the reaction of $[Fe(OH)]^{2+}$ is 5.3 M^{-1} s^{-1} (results given in ref. 13 are in error by one order of magnitude). [d] [Hpts] = 2.00 M; conjugate-base pathway observed but relevant K_a not known.

act as a bridging ligand in inner-sphere reactions, and the tridentate dipic ligand has only carbonyl O atoms available to act as a potential bridging ligand(s). No evidence has been obtained for such a path which is considered most unlikely. Additionally there is no $[H^+]^{-1}$ dependence. With hexaaquairon(III) on the other hand an $[H^+]^{-1}$ dependence is clearly evident, and a conjugate-base pathway from the involvement of $[Fe(H_2O)_5(OH)]^{2+}$ and/or $[Mo_3CrS_4(H_2O)_{11}(OH)]^{3+}$ is proposed. Owing to the enhancement factor which is apparent for the second-order rate constant from *d* as compared to *c*, path *d* can be assigned as inner sphere.[38] Thus if it is assumed that the *d* term is due to acid dissociation of $[Fe(H_2O)_6]^{3+}$ giving $[Fe(H_2O)_5(OH)]^{2+}$ ($K_a = 1.0 \times 10^{-3}$ M at 25 °C, $I = 2.0$ M, $NaClO_4$),[39] which then reacts with $[Mo_3CrS_4(H_2O)_{12}]^{4+}$, a second-order rate constant (d/K_a) of 2.3×10^3 M^{-1} s^{-1} is obtained. However the rate constant for the NCS^- complexation (25.2 M^{-1} s^{-1}) suggests that 2.3×10^3 M^{-1} s^{-1} may be too high for substitution into the chromium coordination sphere to occur. Therefore contributions from the conjugate base $[Mo_3CrS_4(H_2O)_{11}(OH)]^{3+}$ and a path involving substitution into the Fe^{III} seems likely. The acid dissociation constant K_a for this process has not yet been determined.

No $[H^+]^{-1}$ dependence for NCS^- substitution on $[Mo_4S_4(H_2O)_{12}]^{4+}$ is observed, or for the oxidations with hexaaquairon(III) and $[Co(dipic)_2]^-$. Therefore for the range $[H^+]$ 0.5–2.0 M investigated the conjugate-base form of this cube is not influential. Also a rate constant of 4.4×10^4 M^{-1} s^{-1} for the hexaaquairon(III) oxidation of $[Mo_4S_4(H_2O)_{12}]^{4+}$ is too fast for an inner-sphere process, and the reaction is assigned as outer sphere.

Rate constants k_f and k_{aq} obtained from the 1:1 NCS^- complexation with $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ give an equilibrium constant $K = 880$ M^{-1} in 2.00 M Hpts. This is of the same magnitude as the value observed previously for $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ (720 M^{-1}). The reaction of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ is assigned as substitution at the chromium centre because rate constants k_{aq} determined with first NCS^- and then $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ in large (> 10-fold) excess give a statistical factor of 1, and not 3 which would be required for substitution at three identical Mo. The second stage, which is ≈ 100 times slower, has a half-life $t_{\frac{1}{2}} \approx 10$ min, which is of the same order of magnitude as NCS^- substitution on $[Mo_3S_4(H_2O)_{12}]^{4+}$ ($t_{\frac{1}{2}} \approx 4$ min).[20] The second stage is therefore assigned as substitution at Mo^{III}.

The similarity of the UV/VIS spectra for $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ and $[Mo_4S_4(H_2O)_{12}]^{4+}$, Fig. 3, suggests that $Mo^{III}{}_3Cr^{III}$ and $Mo^{III}{}_4$ oxidation states apply. The chromium(III) assignment is consistent with the substitution behaviour. However the formation rate constant (k_f) for NCS^- complexation, which can be expressed as $k_f = a + b[H^+]^{-1}$, gives $a = 25.2$ M^{-1} s^{-1} and $b = 21.4$ s^{-1}. Much smaller rate constants of 2.4×10^{-6} M^{-1} s^{-1} (*a*) and 1.8×10^{-4} s^{-1} (*b*) are observed for NCS^- substitution on $[Cr(H_2O)_6]^{3+}$.[26,40] Therefore the *a* term for substitution is 10^7 times faster in the case of the cube. From earlier studies on $[Cr(H_2O)_5(SH)]^{2+}$,[40] the protonated form $[Cr(H_2O)_5(SH_2)]^{3+}$ substitutes $\geqslant 10^3$ times faster than $[Cr(H_2O)_6]^{3+}$, and an enhancement factor of 17 is observed for $[Cr(H_2O)_5(SH)]^{2+}$ as compared to $[Cr(H_2O)_5(OH)]^{2+}$. We conclude that the presence of three μ_3-S ligands attached to the Cr^{III} in $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ is able to explain the substitution behaviour observed.

However $[Mo_4S_4(H_2O)_{12}]^{4+}$ behaves quite differently. Thus in the case of NCS^- substitution on $[Mo_4S_4(H_2O)_{12}]^{4+}$ (k_f = 1.95 M^{-1} s^{-1})[20] little difference is observed as compared to substitution on $[Mo(H_2O)_6]^{3+}$ (0.28 M^{-1} s^{-1}).[41] Nor is there any contribution from $[H^+]^{-1}$ terms for either of the molybdenum reactions. It would appear therefore that Mo^{III} is not as sensitive as Cr^{III} to the presence of μ_3-S ligands, and as has been indicated previously[41] does not respond to the conjugate-base pathways for substitution. This quite amazing contrast in behaviour is attributed to the low electron population on the III state ions, and the different sizes of the 3d and 4d orbitals. The extreme associative nature of substitution at the Mo^{III}[42] is already well developed for $[Mo(H_2O)_6]^{3+}$ which substitutes some 10^5 times more rapidly than does $[Cr(H_2O)_6]^{3+}$.

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