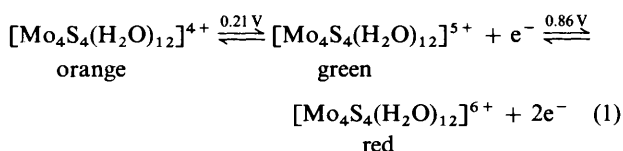


# Preparation and Properties of the High-oxidation-state Cuboidal $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$ Ion in Aqueous Acidic Solutions†

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Oxidation of the green mixed-valence  $\text{Mo}^{\text{III}}\text{Mo}^{\text{IV}}$  cuboidal ion  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$  with a limited (2:1) excess of *cis*- $[\text{VO}_2(\text{H}_2\text{O})_4]^+$  in 2 M Hpts (Hpts = toluene-*p*-sulfonic acid) yields two red products. From Dowex cation-exchange chromatography, elution with 2M Hpts, these were identified as  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  and a less strongly held product with the same 6+ core but with lower ( $\approx 4+$ ) overall charge. The spectrum of the latter approaches that of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  as solution pts<sup>-</sup> is replaced by  $\text{ClO}_4^-$  and co-ordinated pts<sup>-</sup> is aquated (2–3 h). The reactivity of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  was studied, including substitution and redox properties, and the tendency of the cube to fragment to the trinuclear molybdenum(IV) ion,  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ , and (initially) monomeric Mo is noted. This property is more pronounced than with  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ , and is attributed to the lower core electron count ( $10 e^-$ ) and higher charge. Substitution of the 6+ ion ( $\text{H}_2\text{O}$  by  $\text{NCS}^-$ ) is substantially faster than for the 4+ and 5+ cubes (factors of up to  $10^3$ ), and involves in addition a conjugate-base pathway. A statistical factor of two is observed, consistent with two identical centres for substitution on the  $\text{Mo}^{\text{III}}_2\text{Mo}^{\text{IV}}_2$  cluster. The reaction is monophasic and substitution at the  $\text{Mo}^{\text{IV}}$  is proposed, in which case there is no detectable substitution at the  $\text{Mo}^{\text{III}}$ . The stopped-flow reduction of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  by  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  is first order in the concentration of each reactant, and shows no unusual features. The second phase of reaction corresponds to reduction of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$  to  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{4+}$ . The first but not the second phase includes an  $[\text{H}^+]^{-1}$ -dependent term.

It has been shown that there are three different oxidation states of the cuboidal  $\text{Mo}_4\text{S}_4$  core, equation (1).<sup>1</sup> A crystal structure of



the green 5+ ion has demonstrated the presence of 12 co-ordinated  $\text{H}_2\text{O}$  groups.<sup>2</sup> Reduction potentials have been determined by cyclic voltammetry for this ion, which is the most readily accessed state.<sup>3</sup> Redox<sup>4</sup> and substitution studies<sup>5</sup> have been reported on the air-sensitive  $\text{Mo}^{\text{III}}_4$  ion  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{4+}$ , and on the mixed-valence  $\text{Mo}^{\text{III}}_3\text{Mo}^{\text{IV}}$  ion  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ .<sup>1,5</sup>

We now turn to the higher-oxidation-state product  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$ . The preparation of this ion is not as straightforward in that constant-potential electrochemical oxidation of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$  leads to a breakdown of the cube with formation of the trinuclear incomplete cuboidal  $\text{Mo}^{\text{IV}}_3$  ion  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ ,<sup>6</sup> and chemical oxidation with a large excess of the vanadium(V) ion *cis*- $[\text{VO}_2(\text{H}_2\text{O})_4]^+$  yields the same product.<sup>1</sup> However, as previously indicated,<sup>1</sup> by using limited amounts of  $\text{V}^{\text{V}}$  it is possible to trap the red higher-oxidation-state cuboidal product. Using Hpts (toluene-*p*-sulfonic acid) solutions and Dowex cation-exchange chromatography it is now clear that there are two red products. These are the upper (more strongly held)  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  ion, and a lower-charged (less strongly held) product which elutes prior to  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ . We are concerned here in the main with solution properties of the first of these products. Although the lower product has the same oxidation state and is believed to

retain the  $\text{Mo}_4\text{S}_4^{6+}$  core, its precise composition is less certain. The overall charge approximates to 4+ (or less) and we refer to it here as the lower '6+' product. The latter was the only product isolated in previous studies,<sup>1</sup> and the procedure and purification here described are therefore a development of the previous work. Crystal structures of the ethylenediamine-*N,N,N',N'*-tetraacetate (edta) complexes  $[\text{Mo}_4\text{S}_4(\text{edta})_2]^{n-}$  ( $n = 2-4$ ) have indicated identical co-ordinated structures,<sup>7</sup> and redox interconversions have been studied.<sup>8</sup> The structures of the 6+ cores in  $[\text{NH}_4]_6[\text{Mo}_4\text{S}_4(\text{NCS})_{12}] \cdot 10\text{H}_2\text{O}$  and  $[\text{Mo}_4\text{S}_4(\text{C}_5\text{H}_4\text{Pr}^i)_4][\text{I}_3]_2$  containing the singly substituted cyclopentadienyl ligand have also been reported.<sup>9,10</sup> Relevant reviews are contained in refs. 11–13.

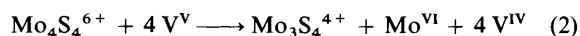
## Experimental

**Preparation of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$ .**—Green cuboidal  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$  was first prepared by  $\text{BH}_4^-$  reduction of the di- $\mu$ -sulfido-molybdenum(V) complex  $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{cys})_2]^{2-}$  [*cys* = cysteinate(2-)], containing a  $\text{Mo}_2\text{S}_2$  ring, using the procedure described.<sup>3</sup> Solutions of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$  in 2 M Hpts can be stored under  $\text{N}_2$  at 4 °C for weeks, with only a slow build-up of trinuclear  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ . To a solution of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$  (20 cm<sup>3</sup>, 5.0 mM) in 2 M Hpts a two-fold excess of the vanadium(V) ion *cis*- $[\text{VO}_2(\text{H}_2\text{O})_4]^+$  (2 cm<sup>3</sup>, 0.10 M) in 2 M Hpts was added under  $\text{N}_2$  at 0 °C. The solution turned red-brown within 5 min. This was left at 4 °C for 2 h, and undiluted (*i.e.* in 2 M Hpts) was loaded onto a jacketed ice-cooled  $\text{O}_2$ -free Dowex 50W-X2 column. The latter was washed with 0.50 M Hpts (20 cm<sup>3</sup>), and eluted with 2.0 M Hpts. Four bands were obtained. The red-purple lower '6+' eluted first, followed by small amounts of green  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$  and  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$  as second and third bands respectively. Red, or more precisely red-purple,  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  was eluted as the fourth band. The ratio of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  to lower '6+' was around 2:3. On leaving solutions of lower '6+' to stand for more than 2 h at 4 °C more  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$

† Non-SI unit employed: M = mol dm<sup>-3</sup>.

was obtained (see below). Solutions of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  stored under  $\text{N}_2$  at  $4^\circ\text{C}$  can be kept for only limited periods ( $\approx 2$  d).

The UV-VIS-NIR absorption spectrum of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  is shown in Fig. 1. Absorption coefficients were determined as follows. First an approximate concentration of the cube was determined by oxidation with standardised *cis*- $[\text{VO}_2(\text{H}_2\text{O})_4]^+$ , equation (2), which gives a red  $\rightarrow$  green



colour change. A solution of  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  (see below), in 2.0 M Hpts ( $2.5 \text{ cm}^3$ , 1.06 mM) and under argon, was titrated into  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  ( $5.0 \text{ cm}^3$ ,  $\approx 0.5$  mM) in 2.0 M Hpts at  $0^\circ\text{C}$  over  $\approx 30$  min. The decay of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  was monitored at the 467 and 556 nm peaks. A slight excess of  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  was added. The solution was then exposed to air for 10 min to allow conversion of any  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{4+}$  into  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ . The concentration of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$  was obtained from the absorbance at the 645 nm peak ( $\epsilon = 435 \text{ M}^{-1} \text{ cm}^{-1}$  per cube),<sup>1</sup> and hence  $\epsilon$  values for  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  were determined. The spectrum of the lower '6+' was quantified in a similar manner, Fig. 1. Peak positions  $\lambda/\text{nm}$  ( $\epsilon/\text{M}^{-1} \text{ cm}^{-1}$  per cube):  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$ , 467 (1395), 556 (1280) and 935 (295); lower '6+', 492 (945), 555 (995) and 795 (385).

The spectrum of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  has similar features to that of the edta complex  $[\text{Mo}_4\text{S}_4(\text{edta})_2]^{2-}$ ,  $\lambda/\text{nm}$  ( $\epsilon/\text{M}^{-1} \text{ cm}^{-1}$  per cube) 572 (825) and 945 (665),<sup>8</sup> which has been characterised by X-ray crystallography.<sup>7</sup> Reversible electrochemical behaviour is observed for the  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+/5+}$  couple.

**Interconversion of Red Products.**—A sample of lower '6+' (0.8 mM,  $20 \text{ cm}^3$ ) in 2 M Hpts was left to aquate at  $\approx 4^\circ\text{C}$  for 20 h under air-free conditions. Small  $1 \text{ cm}^3$  ( $\approx 2$  mM) samples of  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$  and  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$  were added as markers, and the solution loaded onto an air-free Dowex 50W-X2 column at  $0^\circ\text{C}$ . The column was eluted with 2.0 M Hpts. Four bands were observed. The first and second of these were eluted with 2.0 M Hpts and the third and fourth with 4.0 M Hpts. Over the time of the experiment some decomposition of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  to  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$  and molybdenum monomer product occurs. The  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  and lower '6+' bands were identified by their colour (and spectra). The ratio of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  to lower '6+' obtained was around 1:1.

A sample of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  (0.6 mM,  $25 \text{ cm}^3$ ) in 2.0 M Hpts was likewise left to undergo pts<sup>-</sup> anation. On elution the amount of lower '6+' obtained was 7–10% of that of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$ . When anation was in 4.0 M Hpts over 20 h 8–13% of lower '6+' was obtained. Solutions of the lower '6+' product eluted are very dilute, hence the range of values indicated.

**Reaction with 1 M NCS<sup>-</sup>.**—On treating  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  with 1 M NCS<sup>-</sup> a new peak at 500 nm replaces the 467 and 556 nm peaks.<sup>1,10</sup> Solutions of lower '6+' in 2.0 M Hpts gave a similar colour change (to brighter red), but noticeably the 500 nm peak was no longer resolved, and a shoulder only was observed.

**Preparation of V<sup>V</sup>.**—Ammonium metavanadate,  $\text{NH}_4\text{VO}_3$  (1.17 g), was dissolved in water ( $50 \text{ cm}^3$ ) at  $\approx 50^\circ\text{C}$ . After cooling to  $\approx 20^\circ\text{C}$  an equal volume of 4.0 M Hpts was added with stirring to give a 0.10 M solution of yellow *cis*- $[\text{VO}_2(\text{H}_2\text{O})_4]^+$  in 2.0 M Hpts. The solution was filtered, and the concentration determined by titration against ammonium iron(II) sulfate (BDH, Analar) in 2.0 M  $\text{H}_2\text{SO}_4$  with ferroin as indicator. The reduction potential of the *cis*- $[\text{VO}_2(\text{H}_2\text{O})_4]^+ - [\text{VO}(\text{H}_2\text{O})_5]^{2+}$  couple is 1.0 V.<sup>14</sup>

**Preparation of  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ .**—A sample of  $[\text{Ru}$

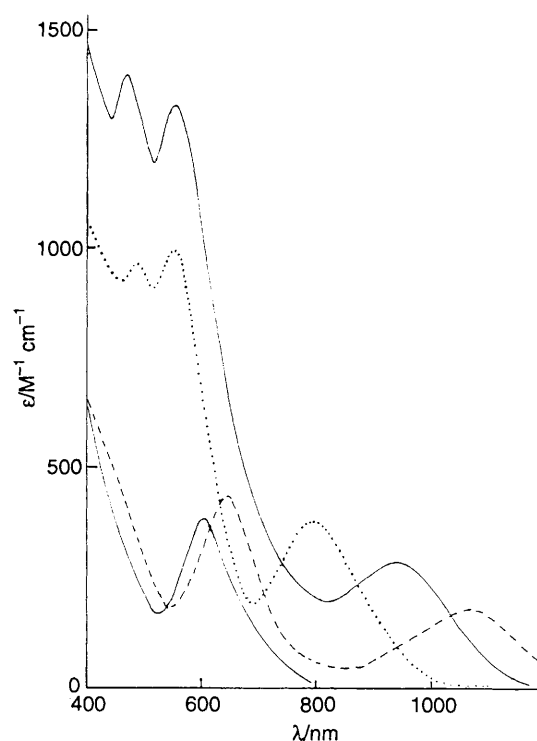


Fig. 1 Spectra of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  (more intense —), lower '6+' (···),  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$  (---), and  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$  (less intense —) in 2.00 M Hpts;  $\epsilon$  values are per cube or trinuclear complex respectively

$(\text{NH}_3)_6\text{Cl}_3$  (Johnson Matthey) was converted into  $[\text{Ru}(\text{NH}_3)_5(\text{CF}_3\text{SO}_3)]_2^{2+}$ .<sup>15</sup> The latter was then reduced with Zn/Hg amalgam under argon, and a solid sample of  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})][\text{PF}_6]_2$  obtained,<sup>16</sup> which could be stored under argon for  $\approx 4$  weeks. The reduction potential for the  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+/2+}$  couple is 0.08 V.<sup>17</sup>

**Other Reagents.**—White (not pink) crystalline toluene-*p*-sulfonic acid (Aldrich Chemicals) was used. A sample of Li(pts) was prepared by neutralising the acid with LiOH and recrystallising twice. Sodium thiocyanate (BDH) was recrystallised once from ethanol.

**Kinetic Studies.**—Both the NCS<sup>-</sup> substitution and  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  reduction of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  were studied using a Dionex-D110 stopped-flow spectrophotometer. Rate constants,  $25.0 \pm 0.1^\circ\text{C}$ , were obtained using fitting procedures and programs from OLIS (Bogart, GA, USA). Reactant solutions were adjusted to an ionic strength  $I = 2.00$  M  $[\text{Li}(\text{pts})]$  prior to mixing. Unweighted linear least-squares fits were used in the treatment of all data.

## Results

**Stability of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$ .**—There is little or no change ( $< 2\%$  at 467 nm) in the UV-VIS-NIR spectrum of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  on varying  $[\text{H}^+]$  in the range 0.50–2.00 M,  $I = 2.00$  M  $[\text{Li}(\text{pts})]$ . Solutions of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  (0.25 mM) in Hpts,  $I = 2.00$  M  $[\text{Li}(\text{pts})]$ , decompose within 40 h in air at  $25^\circ\text{C}$ . From absorbance readings at 460 and 555 nm the products are 89%  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$  and 11%  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ . First-order rate constants are  $2.46 \times 10^{-5}$  (2.0 M Hpts) and  $2.23 \times 10^{-5} \text{ s}^{-1}$  (1.0 M Hpts) indicating no significant dependence on  $[\text{H}^+]$ . The same reaction under  $\text{N}_2$  requires  $\approx 80$  h, and the products are 71%  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$  and 29%  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ . The rate constant is less at  $0.96 \times 10^{-5} \text{ s}^{-1}$ . Decomposition with and without oxidation to the '7+' state seems likely, equations (3) and (4), followed by oxidation of

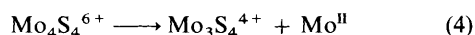
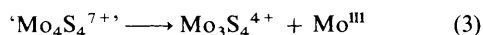
**Table 1** Equilibration rate constants  $k_{eq}$  (25 °C) for the reaction of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  with  $\text{NCS}^-$  in Hpts solutions,  $I = 2.00 \text{ M}$  [Li(pts)]

M	$10^2 k_{eq}/\text{s}^{-1}$		
	$[\text{H}^+]$	$10^4[\text{Mo}_4\text{S}_4^{6+}]$	$10^3[\text{NCS}^-]$
0.51	0.53	1.00	1.64
	0.53	1.49	2.22
	0.53	2.00	2.84
	0.53	2.51	3.36
0.67	0.53	2.98	4.00
	0.55	1.01	1.46
	0.55	1.50	2.00
	0.55	2.02	2.55
1.0	0.55	2.50	2.97
	0.55	3.00	3.58
	0.79	1.48	1.78
	0.79	2.04	2.28
1.5	0.79	2.50	2.74
	0.79	2.96	3.10
	0.79	4.02	4.13
	0.79	4.02	4.13
2.0	0.74	1.50	1.56
	0.74	2.01	2.02
	0.74	2.50	2.49
	0.74	3.00	2.90
2.0	0.74	4.02	3.76
	0.77	1.52	1.42
	0.77	2.04	1.80
	0.77	2.48	2.22
	0.77	2.96	2.62
	0.77	4.08	3.35
	5.2	0.05	1.04
	4.8	0.05	1.01

**Table 2** Summary of rate constants (25 °C) for formation ( $k_f$ ) and aquation ( $k_b$ ) in the reaction of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  with  $\text{NCS}^-$ ,  $I = 2.00 \text{ M}$  [Li(pts)]

$[\text{H}^+]/\text{M}$	$k_f/\text{M}^{-1} \text{ s}^{-1}$	$10^3 k_b/\text{s}^{-1}$
0.51	23.4	4.6
0.67	20.8	4.2
1.00	18.7	3.8
1.50	16.9	3.2
2.00	15.2	3.0

$\text{Mo}^{\text{III}}$  and  $\text{Mo}^{\text{II}}$  by trace amounts of  $\text{O}_2$ , and by the reaction as in equation (5).

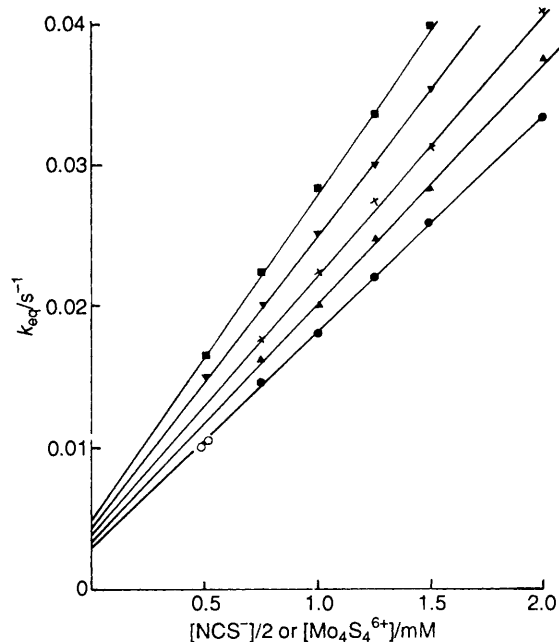
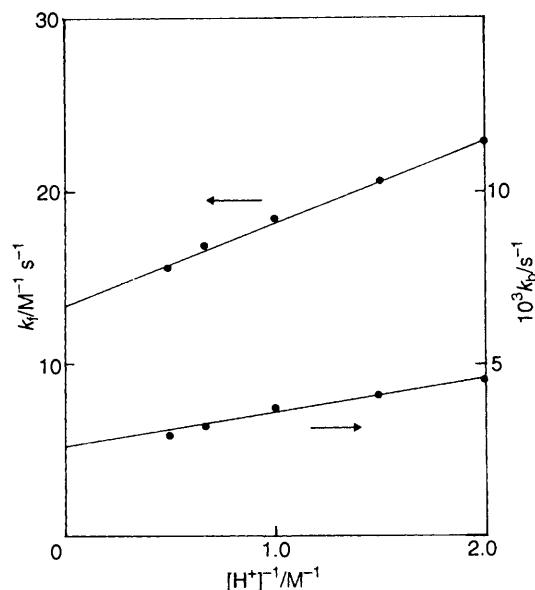


**Substitution Studies on  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$ .**—The reaction of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  with  $\text{NCS}^-$  in large > 10-fold excess,  $I = 2.00 \text{ M}$  [Li(pts)], was monitored at 420 nm. Amounts of  $\text{NCS}^-$  were such that only 1:1 reaction occurs at each Mo. First-order equilibration rate constants  $k_{eq}$  are listed in Table 1. Two runs were included with the  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  reactant in 10-fold excess. The latter indicate that a statistical factor of 2 is required for the runs with  $\text{NCS}^-$  in excess, with the rate equation (6) defining the forward ( $k_f$ ) and back ( $k_b$ ) rate constants, Fig. 2. On varying the  $[\text{H}^+]$  in the range 0.51–2.00 M, both  $k_f$  and  $k_b$  (Table 2) exhibit  $[\text{H}^+]^{-1}$  dependencies, equations (7) and (8), Fig. 3. From the fitting procedures

$$k_{eq} = k_f[\text{NCS}^-]/2 + k_b \quad (6)$$

$$k_f = a + b[\text{H}^+]^{-1} \quad (7)$$

$$k_b = c + d[\text{H}^+]^{-1} \quad (8)$$

**Fig. 2** Dependence of equilibration rate constants  $k_{eq}$  (25 °C) on  $[\text{NCS}^-]$  (reactant in > 10-fold excess) at  $[\text{H}^+] = 0.51$  (■),  $0.67$  (▼),  $1.00$  (×),  $1.50$  (▲) and  $2.00 \text{ M}$  (●)  $I = 2.00 \text{ M}$  [Li(pts)]. The open circles with  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  in 10-fold excess indicate that a statistical factor of 2 is required for all  $[\text{NCS}^-]$  runs**Fig. 3** Dependences on  $[\text{H}^+]^{-1}$  of  $k_f$  (for formation) and  $k_b$  (for aquation) at 25 °C, from the slopes and intercepts respectively in Fig. 2,  $I = 2.00 \text{ M}$  [Li(pts)]

described  $a = 13.3 \pm 0.4 \text{ M}^{-1} \text{ s}^{-1}$ ,  $b = 5.13 \pm 0.18 \text{ s}^{-1}$ ,  $c = (2.53 \pm 0.19) \times 10^{-3} \text{ s}^{-1}$  and  $d = (1.08 \pm 0.05) \times 10^{-3} \text{ M s}^{-1}$ . Since stock solutions of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  were at high  $[\text{H}^+]$  it was not easy to carry out runs at  $[\text{H}^+] < 0.50 \text{ M}$ . The plot of  $k_f$  against  $[\text{H}^+]^{-1}$  in Fig. 3 shows no pronounced curvature, and it can be concluded that the  $\text{p}K_a$  for  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  is  $> 1.0$ .

**Reduction of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  with  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ .**—With a > 10-fold excess of reductant, the orange  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{4+}$  cube, peak at 378 nm ( $\epsilon = 1100 \text{ M}^{-1} \text{ cm}^{-1}$  per cube),<sup>4</sup> was obtained. From the stopped-flow biphasic kinetics monitored at 555 nm first-order rate constants  $k_{1\text{obs}}$  and  $k_{2\text{obs}}$  (25 °C) were determined, Table 3. Both gave first-order

**Table 3** First-order rate constants  $k_{1\text{obs}}$  and  $k_{2\text{obs}}$  (25 °C) from the biphasic studies on the reduction of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  (0.040–0.052 mM), with  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  in Hpts solutions,  $I = 2.00$  M [Li(pts)]. The last four entries are for separate studies with  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$  (0.051 mM) as oxidant

$[\text{H}^+]/\text{M}$	$10^3[\text{Ru}^{\text{II}}]/\text{M}$	$k_{1\text{obs}}/\text{s}^{-1}$	$k_{2\text{obs}}/\text{s}^{-1}$
0.49	0.38	85	21
	0.63	138	33
	0.87	190	42
0.66	0.50	99	27
	0.75	144	42
	1.01	197	55
1.0	0.51	87	27
	0.75	130	44
	1.02	178	55
1.5	0.50	81	26
	0.74	122	43
	1.00	162	54
	1.24	199	67
2.0	0.51	74	25
	0.75	116	39
	1.02	152	50
	1.25	188	65
1.96	0.49	29	44
	0.75	57	44
	0.98	57	57
	1.25	73	73

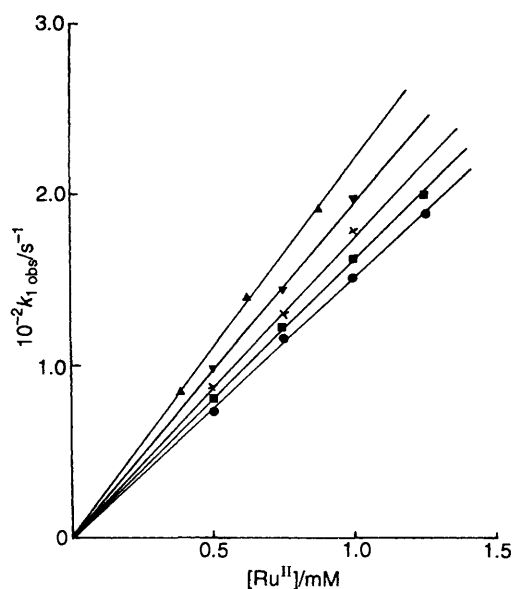
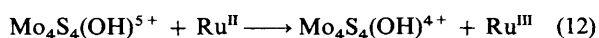
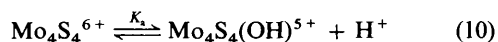
**Table 4** Summary of rate constants (25 °C)  $k_1$  and  $k_2$  for the  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  reduction of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$ ,  $I = 2.00$  M [Li(pts)]

$[\text{H}^+]/\text{M}$	$10^{-4}k_1/\text{M}^{-1}\text{s}^{-1}$	$10^{-4}k_2/\text{M}^{-1}\text{s}^{-1}$
0.49	22.0	5.4
0.66	19.3	5.2
1.00	17.6	5.2
1.50	16.0	5.3
2.00	15.2	5.5

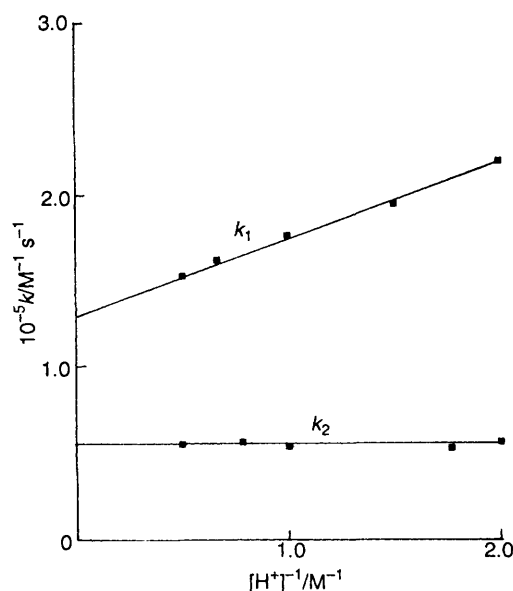
dependencies on  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}]$ , e.g. Fig. 4, hence second-order rate constants  $k_1$  and  $k_2$  were obtained, Table 4. The rate constant  $k_1$  (Fig. 5) is dependent on  $[\text{H}^+]^{-1}$ , equation (9), from which  $e = (13.0 \pm 0.3) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  and  $f =$

$$k_1 = e + f[\text{H}^+]^{-1} \quad (9)$$

$(4.4 \pm 0.1) \times 10^4 \text{ s}^{-1}$ . However  $k_2$  (Fig. 5) is independent of  $[\text{H}^+]$  over the range studied, 0.49–2.00 M, from which  $k_2 = (5.4 \pm 0.3) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . In separate experiments on the  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  reduction of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ , Table 3, the rate constant  $(5.8 \pm 0.4) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  at  $[\text{H}^+] = 1.96$  M reproduced  $k_2$  to within 7%, confirming the second stage as further reduction of the 5+ cube. The reductant  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  has been reported to have a high  $\text{p}K_a$  (values 12.3 and 13.1).<sup>17–19</sup> It seems likely therefore that  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  and not  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  undergoes acid dissociation, equation (10), and the reaction scheme can be written as in (10)–(13), where (11) and (12) give rise to  $e$  and  $f$  respectively in (9), and (13) to the  $[\text{H}^+]$ -independent reaction  $k_2$ .



**Fig. 4** Dependence on reductant concentration of first-order rate constants  $k_{1\text{obs}}$  (25 °C) for the first stage of the  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  reduction of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  at  $[\text{H}^+] = 0.49$  ( $\blacktriangle$ ), 0.66 ( $\blacktriangledown$ ), 1.00 ( $\times$ ), 1.50 ( $\blacksquare$ ) and 2.00 M ( $\bullet$ ),  $I = 2.00$  M [Li(pts)]



**Fig. 5** Dependence of second-order rate constants  $k_1$  and  $k_2$  (25 °C) on  $[\text{H}^+]^{-1}$  for the  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  reduction of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$ ,  $I = 2.00$  M [Li(pts)]

**Effects of  $[\text{H}^+]$  and  $[\text{pts}^-]$  on Lower '6+'.**—The effect of varying  $[\text{H}^+]$  and  $[\text{pts}^-]$  on the UV–VIS–NIR spectrum of lower '6+' was explored. On decreasing  $[\text{H}^+]$  in the range 0.50–2.00 M, lower '6+' at 0.64 mM,  $I = 2.00$  M [Li(pts)], absorbance decreases complete in  $\approx 10$  min are observed at 492 and 555 nm, Fig. 6. The changes are believed to correspond to an equilibration process involving  $\text{pts}^-$  aequation. First-order rate constants  $k_{\text{obs}}$  (linearity 85%), Table 5, can be expressed as in equation (14), Fig. 7, where  $g = (0.73 \pm 0.04) \times 10^{-3} \text{ s}^{-1}$  and  $h = (0.36 \pm 0.03) \times 10^{-3} \text{ M s}^{-1}$ .

$$k_{\text{obs}} = g + h[\text{H}^+]^{-1} \quad (14)$$

On decreasing  $[\text{pts}^-]$  to 0.40 M by addition of  $\text{ClO}_4^-$  (1.60 M) while retaining  $[\text{H}^+] = 2.00$  M, the lower '6+' (0.32 mM) gives absorbance changes as in Fig. 8 over 150 min. A particularly important feature is the decrease in the 795 nm peak and increase in absorbance at  $\approx 900$  nm suggesting incomplete

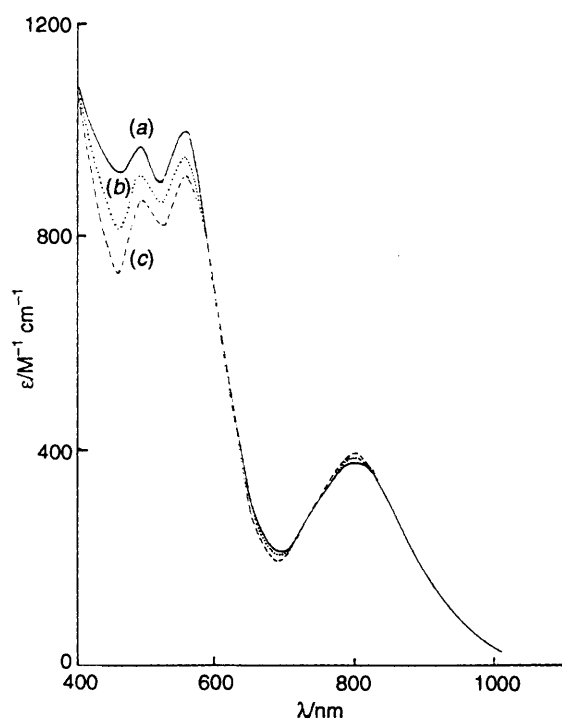


Fig. 6 Effect of  $[H^+]$  as Hpts on the spectrum of lower '6+': (a) 2.00, (b) 1.00 and (c) 0.5 M, all at  $I = 2.00$  M [Li(pts)]. Solutions were left to equilibrate for  $\approx 10$  min at  $25^\circ\text{C}$

Table 5 First-order rate constants  $k_{\text{obs}}$  ( $25^\circ\text{C}$ ) for re-equilibration on decreasing the  $[H^+]$ , initially 2.00 M Hpts, of lower '6+' solutions,  $I = 2.00$  M [Li(pts)]

$[H^+]/\text{M}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$	
	at 492	at 556 nm
0.35	1.76	1.72
0.40	1.58	1.59
0.49	1.48	1.45
0.56	1.35	1.33
0.74	1.25	1.22
0.99	1.13	1.11
1.25	1.02	1.01
1.50	0.96	0.94
1.75	0.89	0.86

aquation of co-ordinated pts<sup>-</sup>. It is not possible to elute samples of lower '6+' in 2M HClO<sub>4</sub>, and 0.40 M is the smallest pts<sup>-</sup> concentration we were able to work with. This evidence again indicates inner-sphere complexing of pts<sup>-</sup> to lower '6+'.

**Substitution Studies on Lower '6+'.**—For completeness we report in an abbreviated form data obtained for the reaction of lower '6+' with NCS<sup>-</sup>. As in the case of the  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  reaction, uniphasic kinetics is observed. Rate equations are of the same form as (7) and (8) and give  $a' = 242 \pm 5 \text{ M}^{-1} \text{ s}^{-1}$ ,  $b' = 105 \pm 4 \text{ s}^{-1}$ ,  $c' = 0.133 \pm 0.071 \text{ s}^{-1}$  and  $d' = 0.053 \pm 0.006 \text{ M s}^{-1}$ . Particularly noteworthy is the formation rate constant  $a'$  which is 18 times the value of  $a$  for  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$ .

**Reduction of Lower '6+' with  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ .**—Two stages are observed as with  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$ . For the first stage the rate equation is of the same form as (9), with  $e' = (7.2 \pm 0.2) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  and  $f' = (2.73 \pm 0.13) \times 10^3 \text{ s}^{-1}$ . For the second stage the dominant  $[H^+]$ -independent pathway  $(0.78 \pm 0.02) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  is accompanied by a relatively small  $[H^+]^{-1}$ -dependent term  $(0.76 \pm 0.15) \times 10^2 \text{ s}^{-1}$ .

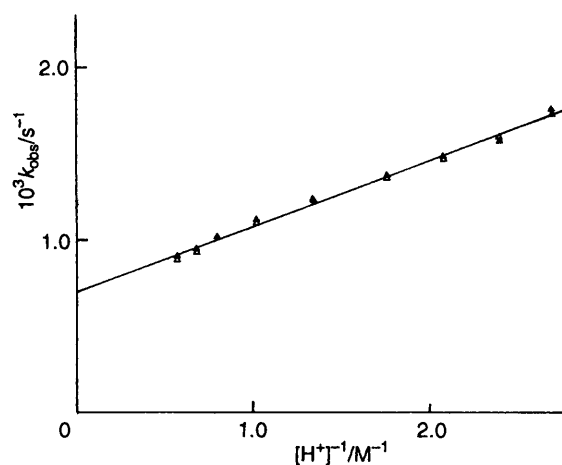


Fig. 7 Variation of first-order rate constants ( $25^\circ\text{C}$ ) for the re-equilibration of lower '6+' on decreasing  $[H^+]$  from 2.00 M Hpts,  $I = 2.00$  M [Li(pts)]

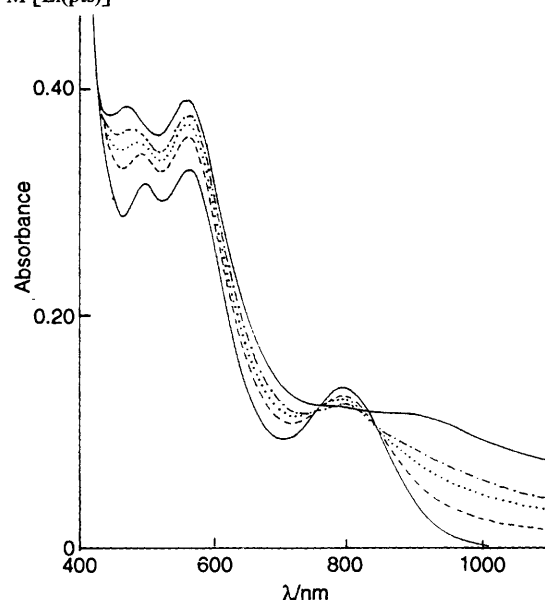


Fig. 8 Absorbance changes ( $25^\circ\text{C}$ ) for the re-equilibration of lower '6+' (0.32 mM) peak at 795 nm on changing the composition (initially 2.00 M Hpts) to 0.40 M Hpts and 1.60 M HClO<sub>4</sub>, after 30 (---), 60 (····), 90 (— · —) and 150 min (—)

## Discussion

The preparation and aqueous solution properties of the high-oxidation-state  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  ion is described in this work. A second (red) product, the lower '6+' ion, is obtained in the preparative procedure described. The new procedure requires that the crude product be left to stand for 2 h, and loading of the Dowex cation-exchange column be carried out without dilution of the 2.0 M Hpts. The more strongly held product, eluting less readily than  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ , has all the hallmarks of a 6+ ion. Its UV-VIS-NIR spectrum ( $\lambda/\text{nm}$   $\epsilon/\text{M}^{-1} \text{ cm}^{-1}$  per cube) has twin peaks at 467 (1395) and 556 (1280) and a less-intense inter-valence band at 935 (295), which compare favourably with the single peak at 572 (825) and NIR band at 945 (665) for the X-ray characterised  $[\text{Mo}_4\text{S}_4(\text{edta})_{12}]^{2-}$  complex. An NIR band is also observed for  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$  at 1100 nm ( $122 \text{ M}^{-1} \text{ cm}^{-1}$ ), and is likewise assigned as an inter-valence band. The spectrum of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  is not affected by changes in  $[H^+]$  in the range 0.50–2.00 M.

The second product, the lower '6+', elutes from the Dowex column as a well defined band prior to  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ . When the  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$  starting complex is prepared in 4 M HClO<sub>4</sub> and oxidised with V<sup>V</sup>, trinuclear  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$

**Table 6** Summary of rate and equilibrium constant data (25 °C) from this and previous work<sup>5</sup> for substitution of H<sub>2</sub>O in [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>n+</sup>, n = 4–6, I = 2.00 M [Li(pts)]

Reaction	Assignment	k <sub>f</sub> /M <sup>-1</sup> s <sup>-1</sup>	k <sub>b</sub> /s <sup>-1</sup>	K/M <sup>-1</sup>
Mo <sub>4</sub> S <sub>4</sub> <sup>4+</sup> + NCS <sup>-</sup>	Mo <sup>III</sup>	1.95	1.44 × 10 <sup>-3</sup>	1300
Mo <sub>4</sub> S <sub>4</sub> <sup>5+</sup> + NCS <sup>-</sup>	Mo <sup>III</sup>	0.116	4.3 × 10 <sup>-5</sup>	2700
	Mo <sup>IV</sup>	0.0166	5.0 × 10 <sup>-6</sup>	3300
Mo <sub>4</sub> S <sub>4</sub> <sup>5+</sup> + Cl <sup>-</sup>	Mo <sup>IV</sup>	0.0097	4.9 × 10 <sup>-3</sup>	1.98
Mo <sub>4</sub> S <sub>4</sub> <sup>6+</sup> + NCS <sup>-</sup>	Mo <sup>IV</sup>	13.3	2.53 × 10 <sup>-3</sup>	5220
Conjugate-base path	Mo <sup>IV</sup>	5.1 <sup>a</sup>	1.08 × 10 <sup>-3b</sup>	4720

<sup>a</sup> Units s<sup>-1</sup>. <sup>b</sup> Units M s<sup>-1</sup>.

but little or no red product is obtained. The similarity of spectra and experiments on the interconversion of the two red forms are consistent with the lower '6+' having a similar structure, but with pts<sup>-</sup> co-ordinated. Thus when 1.0 M NCS<sup>-</sup> is added to the lower '6+' the spectrum is shifted as compared to [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>6+</sup>,<sup>1</sup> suggesting that other ligands, *i.e.* pts<sup>-</sup>, are preventing more extensive complexing by NCS<sup>-</sup>. Whereas the visible spectrum of [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>6+</sup> is not affected by [H<sup>+</sup>] variations in the range 0.50–2.00 M, the lower '6+' exhibits changes in the 400–600 nm region, Fig. 6. This may be due to an acid dissociation process, but, since no similar change is observed for [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>6+</sup>, is more likely due to the extent of pts<sup>-</sup> complexing adjusting as the [H<sup>+</sup>] is varied. Interestingly the peak at 795 nm does not shift significantly towards 940 nm, Fig. 1, until the pts<sup>-</sup> is decreased to 0.4 M, Fig. 8. It seems likely therefore that two pts<sup>-</sup> ions are co-ordinated to the cube. It is not clear why a singly co-ordinated pts<sup>-</sup> '5+' ion should not have been observed in the Dowex chromatography. The attachment of two pts<sup>-</sup> ions most likely relates to the presence of two Mo<sup>IV</sup> (or two Mo<sup>III</sup>) in the 6+ cube.

The reduction potential of the [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>6+/5+</sup> couple (0.86 V) is consistent with moderately strong oxidising properties for the 6+ ion. The 6+ state has a tendency to fragment with and without addition of oxidant, a property not exhibited by [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>4+</sup>, and much less marked with [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>5+</sup>. Thus [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>6+</sup> yields trinuclear [Mo<sub>3</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>4+</sup> and mononuclear molybdenum products in the presence of *e.g.* *cis*-[VO<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>+</sup> (within 5 min), or in air (half-life ≈ 8 h at 25 °C). The first-order dependence of the latter reaction on [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>6+</sup> rules out a bimolecular disproportionation reaction. From limited observations it would appear that an incipient '7+' form decomposes to yield [Mo<sub>3</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>4+</sup> and Mo<sup>III</sup>, and that the latter is further oxidised by the oxidant<sup>20</sup> or by [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>6+</sup> to give [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>5+</sup>. Observations on the stability of [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>6+</sup> under N<sub>2</sub> suggest that the decomposition can also occur directly. The instability of the 6+ and 7+ forms is attributed to the high charge and low electron counts. In this respect [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>4+</sup>, with 12 electrons from the metal atoms, is more stable, and has sufficient electrons to give the maximum of six Mo–Mo bonds.<sup>21</sup>

Ligand substitution of H<sub>2</sub>O by NCS<sup>-</sup> on [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>6+</sup> shows a number of different features as compared to that on [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>5+</sup> and [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>4+</sup>. Whereas the latter do not give [H<sup>+</sup>]<sup>-1</sup> dependencies, in the case of [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>6+</sup> the dependence k<sub>f</sub> = a + b[H<sup>+</sup>]<sup>-1</sup> is observed for the formation step, implicating a conjugate-base form [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>11</sub>(OH)]<sup>5+</sup>. Similar behaviour is observed for the reverse process. Since plots of rate constants *vs.* [H<sup>+</sup>]<sup>-1</sup> exhibit little or no curvature it can be concluded that the acid dissociation constant pK<sub>a</sub> is > 1, in keeping with the weak acidic properties noted for the H<sub>2</sub>O groups *trans* to μ<sub>3</sub>-S core ligands.<sup>22</sup> Also although the 6+ ion is mixed-valence Mo<sup>III</sup><sub>2</sub>Mo<sup>IV</sup><sub>2</sub> only a single reaction phase is observed. In this respect the behaviour is different from [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>5+</sup>

which gives biphasic kinetics.<sup>5</sup> From the runs with [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>6+</sup> in 10-fold excess a statistical factor of 2 is observed indicating the number of equivalent sites. Of the two possible sites for substitution the Mo<sup>IV</sup> is favoured because, for otherwise identical sites, a conjugate base is more likely to be generated for the higher oxidation state. However the apparent non-reactivity of the molybdenum(III) centres is surprising. An alternative explanation is that the 6+ ion behaves as a pair of identical dimers, *i.e.* (Mo<sup>III</sup>Mo<sup>IV</sup>)<sub>2</sub>, much as has been suggested from Mössbauer studies on Fe<sub>4</sub>S<sub>4</sub> clusters.<sup>23,24</sup> In the case of [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>5+</sup> the first phase (statistical factor of 3) has been assigned to substitution at the three Mo<sup>III</sup>, and the second phase (statistical factor of unity) to substitution at the Mo<sup>IV</sup>, Table 6. Important in the present context is the observation that the second phase involving Mo<sup>IV</sup> gives a six-fold bigger absorbance change.

Even allowing for the conjugate-base path, the thiocyanate complex-formation step for [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>6+</sup> is substantially faster than both the corresponding processes observed for [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>5+</sup>. The higher overall charge and more favourable ion-pair formation is no doubt a contributing factor. Not easy to explain however is the extent of the effect, *i.e.* the ≈ 10<sup>3</sup> faster [H<sup>+</sup>]-independent substitution at the Mo<sup>IV</sup> of [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>6+</sup> as compared to substitution at Mo<sup>IV</sup> in [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>5+</sup>. Also, from the earlier studies,<sup>5</sup> the formation rate constants are 20 times more favourable for the Mo<sup>III</sup> of [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>4+</sup> than for those in [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>5+</sup>. These are large effects which require better understanding.

The fact that substitution on *e.g.* [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>5+</sup> is slow (≈ 1 d), and separate processes should be observed for reaction at Mo<sup>III</sup> and Mo<sup>IV</sup>, is we believe related to the lifetime of the rapid and electrostatically controlled ion-pair (*i.e.* outer-sphere) association of NCS<sup>-</sup> to a specific Mo, and whether the latter is Mo<sup>III</sup> or Mo<sup>IV</sup> at any one time. The time-scale for intervalence charge transfer between the molybdenum(-III) and (-IV) centres, and lifetime of any one distribution, is also relevant. Thus a comparable to longer lifetime of a particular distribution as compared to that of the ion pair is presumably responsible for a discrimination between Mo<sup>III</sup> and Mo<sup>IV</sup>, and the existence of two separate rate processes. It is possible that there are different intervalence charge-transfer rates for [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>n+</sup>, n = 5 or 6, resulting in different rate constants for substitution at the Mo<sup>III</sup> and Mo<sup>IV</sup>. The possibility that there are Mo<sup>III</sup>Mo<sup>IV</sup> pairs in the 6+ case might also help explain the different behaviour observed. With the paramagnetic 5+ cluster [Mo<sub>4</sub>-Se<sub>4</sub>(edta)<sub>2</sub>]<sup>3-</sup>, it has been shown from <sup>77</sup>Se (I = ½, natural abundance 7.6%) NMR studies at 95.5 MHz that there are two broad resonances at δ 1608 and 1931 relative to dimethyl selenide in an intensity ratio of 3:1, confirming the lowered symmetry of the cluster and that intervalence electron transfer occurs at a rate slower than the NMR time-scale.<sup>22</sup>

Formation constants (K) for the reaction of NCS<sup>-</sup> with [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>6+</sup> are more favourable than those for the corresponding reaction with [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>5+</sup>, which are more favourable than with [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>4+</sup>, see summary in Table 6. This is in keeping with an influence of overall charge.

Not only does the 6+ cube readily fragment to give trinuclear [Mo<sub>3</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>4+</sup>, but (perhaps coincidentally) both with regard to conjugate-base participation and the magnitude of rate constants, its substitution behaviour approaches more that of the trinuclear complex. Thus for [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>6+</sup>, equation (7), a = 13.3 M<sup>-1</sup> s<sup>-1</sup> and b = 5.13 s<sup>-1</sup>, while for [Mo<sub>3</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>4+</sup> the corresponding values are 108 M<sup>-1</sup> s<sup>-1</sup> and 248 s<sup>-1</sup>. A feature of the substitution properties of [Mo<sub>3</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>4+</sup> is the labilising influence of electron-rich μ-sulfido as opposed to μ<sub>3</sub>-sulfido core ligands.<sup>6,25,26</sup> The comparison here suggests a distortion of the 6+ cube towards a trinuclear structure. No other evidence has been reported however in support of such an effect.

One reason for studying the [Ru(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)]<sup>2+</sup> reduc-

tion of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  was to check whether a rate-determining structural change might possibly precede the  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  to  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$  conversion. A strictly first-order dependence on  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}]$  was however observed for all the conditions explored. Moreover the second stage was confirmed as the further reduction to  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{4+}$  by separate studies on the  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$  reduction of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ . Rate constants  $k_1$  for the reduction of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  were shown to have an  $[\text{H}^+]$  dependence,  $k_1 = e + f[\text{H}^+]^{-1}$ . From kinetic studies on the substitution of the  $\text{H}_2\text{O}$  of  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$  with a wide variety of neutral unhindered ligands, rate constants have been shown to vary over a small range  $0.05\text{--}0.30 \text{ M}^{-1} \text{ s}^{-1}$  only at  $25^\circ\text{C}$ .<sup>27,28</sup> This suggests a predominantly bond-breaking (dissociative) process. The pathway  $e$  ( $1.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ) is therefore assigned as outer sphere in view of the relative inertness of both the ruthenium and molybdenum centres. However the conjugate-base pathway  $f$  is not as readily assigned. Since  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$  has a high  $\text{p}K_a$ ,<sup>18,19</sup> the  $f$  term most likely arises from acid dissociation of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$ , equation (10). Whether the mechanism is inner sphere is not clear, where  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$  substitution into the acid-dissociated molybdenum co-ordination sphere is the only possibility to be considered. Since the  $\text{p}K_a$  is  $> 1$ , and  $f(4.4 \times 10^4 \text{ s}^{-1})$  is the product of  $K_a$  and the true rate constant, the latter is  $> 10^5 \text{ M}^{-1} \text{ s}^{-1}$  which does seem high for an inner-sphere process. Therefore the mechanism may well be outer sphere with the  $\text{OH}^-$  of the conjugate-base form,  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{11}(\text{OH})]^{5+}$ , alleviating electrostatic repulsion between the  $2+$  and  $6+$  reactants. If this mechanism holds the reaction has similar features to that of  $[\text{Fe}(\text{OH})]^{2+}$  with  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ , rate constant  $4.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  at  $10^\circ\text{C}$ , which has likewise been assigned as outer sphere.<sup>29</sup> No  $[\text{H}^+]$  dependence was observed for the  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$  reduction of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ , and this is a more straightforward outer-sphere assignment. The similarity of rate constants for the reduction of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  ( $13.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ) and  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$  ( $5.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ) is surprising in view of the different reduction potentials (0.86 and 0.21 V).

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