Solution Properties of the Cuboidal Mixed-metal Cluster $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ including Complexing (at Ni) and Redox Properties†

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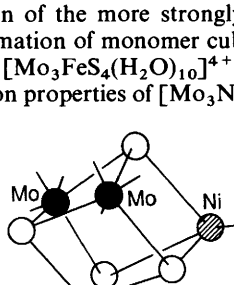
The green-blue complex $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ has been prepared by $NaBH_4$ reduction of a 1:10 solution of $[Mo_3S_4(H_2O)_9]^{4+}$ and $NiCl_2{\cdot}6H_2O$ in 0.5 M HCl, and purified by Dowex 50W-X2 cation-exchange chromatography. Solutions (0.1–2.0 mM) in 2 M $HClO_4$ obey Beer's law, consistent with the single cube formulation. Complexation equilibration reactions, $Mo_3NiS_4^{4+} + X^- \rightleftharpoons Mo_3NiS_4X^{3+}$, studied by stopped-flow spectrophotometry (25 °C), give forward and back rate constants for $X^- = Cl^-$ of $k_f = 9.4$ M^{-1} s^{-1}, $k_b = 0.097$ s^{-1}, and for $X^- = NCS^-$ of $k_f = 45$ M^{-1} s^{-1}, $k_b = 0.062$ s^{-1}. Complexation, assigned to substitution at the tetrahedrally ligated (and metal–metal bonded) nickel centre, is unusually slow, and slower than substitution on $[Ni(H_2O)_6]^{2+}$. Redox reactions, *e.g.* $Mo_3NiS_4^{4+} + 2Co^{III} \longrightarrow Mo_3S_4^{4+} + Ni^{2+} + 2Co^{II}$, with $[Co(dipic)_2]^-$ (dipic = pyridine-2,6-dicarboxylate) and $[Fe(H_2O)_6]^{3+}$ as oxidants, have also been studied. Rate laws are in both cases first order in the concentration of each reactant. Whereas at 25 °C the $[Co(dipic)_2]^-$ reaction is $[H^+]$-independent and outer sphere (0.35 M^{-1} s^{-1}), the reaction with $[Fe(H_2O)_6]^{3+}$ gives a dependence $k_a + k_b[H^+]^{-1}$, with $k_a = 5.4 \times 10^{-4}$ M^{-1} s^{-1} and $k_b = 5.3 \times 10^{-4}$ s^{-1}, assigned to outer- and inner-sphere mechanisms respectively. All studies were in aqueous perchloric acid solutions, $I = 2.00$ M ($LiClO_4$).

The incomplete cuboidal molybdenum(IV) trimer $[Mo_3S_4(H_2O)_9]^{4+}$ has been the subject of earlier studies,[1,2] and is now structurally well characterised.[3] One particularly interesting property is the ease with which it forms cuboidal mixed-metal complexes $[Mo_3MS_4(H_2O)_{10}]^{4+}$, M = Fe,[4] Co,[5] Ni[6] or Cu,[7] the structures of which have been determined as toluene-*p*-sulphonate (pts⁻) salts by Shibahara and colleagues. Whereas the even-number-electron cubes $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ and $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ are obtained as single cubes, the corresponding odd-electron clusters of Co and Cu form dimer cubes. It would appear that, in the latter two cases, weakly co-ordinating anions ClO_4^- and pts^- induce dimer-cube formation. Addition of the more strongly co-ordinating Cl^- results in the reformation of monomer cubes. Previous studies have been on the $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ cluster.[8,9] Here we consider the solution properties of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$.



Experimental

Preparation of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$.—Solutions of $[Mo_3S_4(H_2O)_9]^{4+}$ in the appropriate acid were first prepared as already described.[1,2] To convert into $[Mo_3NiS_4(H_2O)_{10}]^{4+}$, $NaBH_4$ reduction of a solution of $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Ni(H_2O)_6]^{2+}$, method (*a*), was used (< 1 min). Procedures involving (*b*) direct interaction of nickel metal with $[Mo_3S_4(H_2O)_9]^{4+}$ (> 7 d at 25 °C) and (*c*) electrolytic reduction of $[Mo_3S_4(H_2O)_9]^{4+}$ in the presence of $NiCl_2{\cdot}6H_2O$ (2 h) were much less favoured. In the case of $[Mo_3FeS_4(H_2O)_{10}]^{4+}$, method (*b*) was the preferred route.[8,9] The method used here involved syphoning a solution of $[Mo_3S_4(H_2O)_9]^{4+}$ (2.6 mM, 48 cm³) with excess of $NiCl_2{\cdot}6H_2O$ (26 mM) in 0.5 M HCl onto a 100-fold excess of $NaBH_4$ (0.46 g) under N_2. The reaction is summarised by equation (1). Solutions were left for 30 min.

$$Mo_3S_4^{4+} + Ni^{2+} + 2e^- \longrightarrow Mo_3NiS_4^{4+} \qquad (1)$$

Black solid material was filtered off, the solid residue washed several times with 0.5 M HCl (until the filtrate is clear), and the combined green-blue filtrate purified on a Dowex 50W-X2 cation-exchange column (20 × 1.5 cm). After loading the column was washed with 0.5 M HCl (100 cm³), and then eluted with 1 M HCl. The first green band was excess of Ni^{2+}, the second green-blue $[Mo_3NiS_4(H_2O)_{10}]^{4+}$, and the third unreacted $[Mo_3S_4(H_2O)_9]^{4+}$. The yield was 43% based on the conversion of $[Mo_3S_4(H_2O)_9]^{4+}$. To obtain solutions in perchloric acid the complex was reloaded on a Dowex column, and after thorough washing with 0.5 M acid (100 cm³) eluted with 2.0 M $HClO_4$. At least two such columns were required to ensure removal of all Cl^-. Solutions were stored under N_2. Concentrations obtained were typically 15–20 mM in 2.0 M HCl, 4–5 mM in 2.0 M $HClO_4$. Metal analyses were carried out by atomic absorption spectroscopy, and gave a Mo:Ni ratio of 3.10 ± 0.11:1.

UV/VIS/NIR Spectrum. The spectrum of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ in 2.0 M $HClO_4$ is shown alongside that of $[Mo_3S_4(H_2O)_9]^{4+}$ in Fig. 1. Peak positions, λ/nm, are at 237, 495 and 677, with a shoulder at 350. From the nickel analysis by Inductively Coupled Plasma (ICP) emission spectroscopy the absorption coefficient at 677 nm is 610 M^{-1} cm^{-1} in reasonable agreement with an earlier value of 601 M^{-1} cm^{-1}.[6] No absorbance is observed in the NIR up to 1300 nm.

Other Reactants.—A literature method[10] was used to prepare $NH_4[Co(dipic)_2]{\cdot}H_2O$, where dipic is pyridine-2,6-dicarboxylate (or dipicolinate), having an absorption peak at 510nm (ε = 630 M^{-1} cm^{-1}). Solutions of $[Fe(H_2O)_6]^{3+}$ were obtained by Dowex 50W-X2 cation-exchange column

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† *Non-SI unit employed:* M = mol dm⁻³.

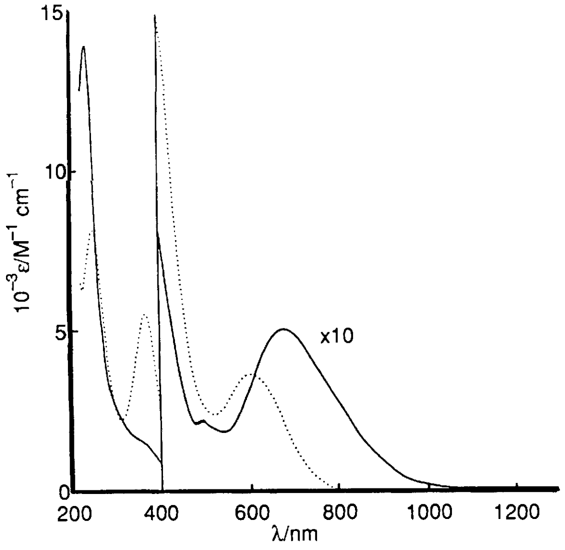

Fig. 1 UV/VIS/NIR spectra of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ (——) and $[Mo_3S_4(H_2O)_9]^{4+}$ (.....) in 2.0 M $HClO_4$; ε per cluster

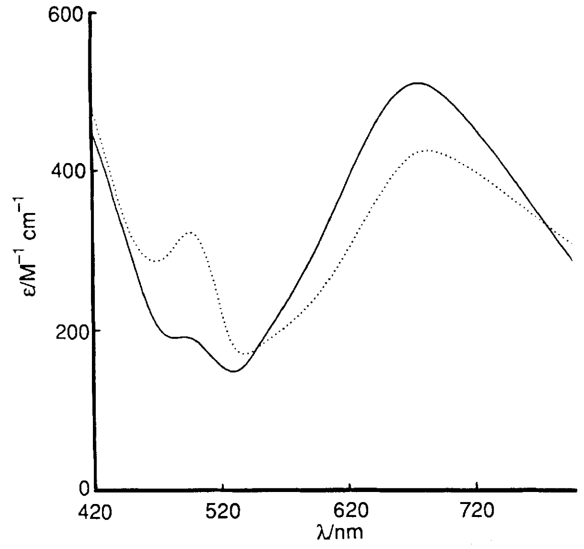

Fig. 2 Effect of 0.1 M Cl^- (as HCl) (.....) on the spectrum of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ (——) at 25 °C, $I = [H^+] = 2.00$ M ($HClO_4$)

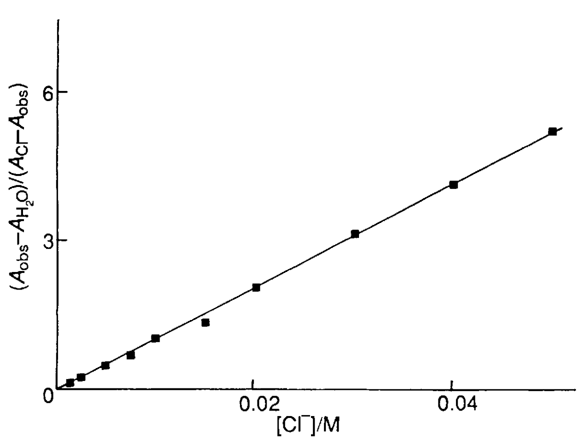

Fig. 3 Determination of K for the 1:1 complexing of Cl^- with $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ at 25 °C, $I = [H^+] = 2.00$ M ($HClO_4$)

purification of $Fe(ClO_4)_3{\cdot}6H_2O$ (Fluka), the final elution being with 1.0 M $HClO_4$. Other reagents including HCl, $HClO_4$ and NaNCS were of Analar grade purity. Samples of $LiClO_4$ (Aldrich) were recrystallised from water three times.

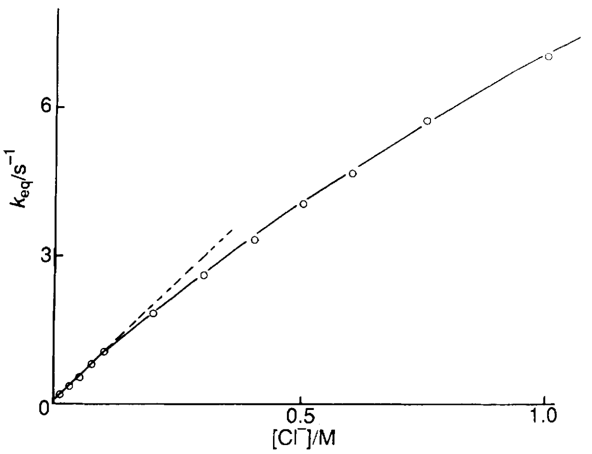

Fig. 4 Variation of stopped-flow equilibration rate constants (k_{eq}) with $[Cl^-]$ for the 1:1 complexing of Cl^- with $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ at 25 °C, $I = [H^+] = 2.00$ M ($HClO_4$)

EPR Spectroscopy.—A solution of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ (5 mM) in 2.0 M $HClO_4$ was loaded into an EPR tube under air-free conditions and frozen in liquid N_2. Spectra were run on a Bruker ER 200D spectrometer fitted with an Oxford Instrument Cryostat at 4.2 K. No EPR spectrum was observed. We are grateful to Dr. W. J. Ingledew at the University of St. Andrews for carrying out this measurement.

Electrochemistry.—Cyclic voltammetry was carried out on a Princeton Applied Research (PAR) 173 potentiostat attached to an Apple II microcomputer *via* a PAR 276 interface. Electrodes used were a Metrohm glassy carbon working electrode, a platinum secondary electrode, and a standard calomel reference electrode. No reversible behaviour was observed, and decomposition occurs.

Treatment of Data.—Unweighted linear and non-linear least-squares programs were used.

Results

Stability of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$.—As compared to $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ the $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ cluster is only very slowly air oxidised, equation (2). Thus at room temperature

$$2Mo_3NiS_4^{4+} + O_2 + 4H^+ \longrightarrow 2Mo_3S_4^{4+} + 2Ni^{2+} + 2H_2O \quad (2)$$

with the cluster < 5 mM some reaction is detected after > 1 h exposure, but oxidation is not complete for 1–2 weeks, with $k < 10^{-6}\ M^{-1}\ s^{-1}$ in 2.0 M $HClO_4$. Stock solutions were stored under N_2, and the slower kinetic runs, *i.e.* the redox studies, were carried out under N_2. Beer's law was obeyed on varying the concentration of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ over the range 0.1–2.0 mM in 2.0 M $HClO_4$, at the peak positions 495 (± 6%) and 677 nm (± 1%). No evidence was obtained for dimer forms as in the case of the cobalt and copper analogues. The Dowex-column elution characteristics using 2 M $HClO_4$ were also consistent with a 4+ monomer cube, whereas the corresponding 8+ dimer cube of Co is extremely difficult to elute even with 4 M $HClO_4$.[11]

Complexing with Cl^-.—Complexing of Cl^- to $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ is rapid. Equation (3) defines the 1:1 complexing

$$Mo_3NiS_4^{4+} + Cl^- \xrightleftharpoons{K} Mo_3NiS_4Cl^{3+} \quad (3)$$

constant K. For solutions of cube 6.9×10^{-4} M and with Cl^- (as HCl) in the range 0–0.050 M, $I = [H^+] = 2.00$ M ($HClO_4$),

Table 1 Equilibration rate constants (25 °C) for the 1:1 complexing of Cl^- (as HCl) with $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ (4.1×10^{-4} M), $I = [H^+] = 2.00$ M ($HClO_4$)

$[Cl^-]$/M	k_{eq}/s^{-1}	$[Cl^-]$/M	k_{eq}/s^{-1}
0.010	0.185	0.300	2.64
0.030	0.39	0.400	3.4
0.050	0.57	0.500	4.0
0.075	0.79	0.60	4.7
0.100	1.04	0.75	5.7
0.200	1.83	1.00	7.0

Table 2 Equilibration rate constants (25 °C) for the complexing of NCS^- with $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ ($(0.53–1.05) \times 10^{-4}$ M, with $I = [H^+] = 2.00$ M ($HClO_4$)

$10^3[NCS^-]$/M	$10^2k_{eq}/s^{-1}$
0.50	8.1
0.75	9.8
1.00	11.0
1.50	12.9
2.00	14.9
2.50	17.5

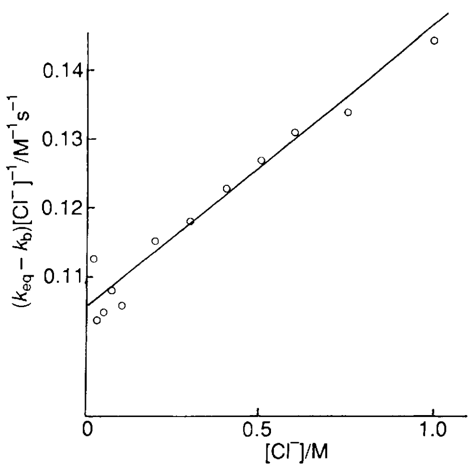

Fig. 5 Dependence of equilibration rate constants (k_{eq}) on $[Cl^-]$ for the 1:1 reaction of Cl^- (full range of values) with $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ at 25 °C, $I = [H^+] = 2.00$ M ($HClO_4$)

absorbance changes at 500 nm (Fig. 2) can be fitted by the expression (4) where A_{H_2O}, A_{obs} and A_{Cl} are absorbance readings with no Cl^-, a specified amount of $[Cl^-]$, and for the 1:1 chloro complex respectively. From the graph shown in Fig. 3, $K = 106 \pm 2$ M^{-1} at 25 °C.

$$\frac{A_{obs} - A_{H_2O}}{A_{Cl} - A_{obs}} = K[Cl^-] \qquad (4)$$

The kinetics of the equilibration (3) was monitored by the stopped-flow method at 500 nm. Rate constants k_{eq} are listed in Table 1. From values up to 0.10 M Cl^-, Fig. 4, a linear dependence is obtained, equation (5), from which the forward

$$k_{eq} = k_f[Cl^-] + k_b \qquad (5)$$

and back rate constants in (3), $k_f = 9.4 \pm 0.1$ M^{-1} s^{-1}, $k_b = 0.097 \pm 0.007$ s^{-1}, are obtained. These give $K = 97 \pm 8$ M^{-1}, in satisfactory agreement with that from Fig. 3.

More detailed information is obtained by considering values of k_{obs} to $[Cl^-] = 1.0$ M, Table 1. Thus the curvature, Fig. 4, is consistent with a two-stage process as in equations (6) and (7),

$$Mo_3Ni^{4+} + Cl^- \overset{K_{os}}{\rightleftharpoons} Mo_3Ni^{4+},Cl^- \qquad (6)$$

$$Mo_3Ni^{4+},Cl^- \xrightarrow{k} Mo_3NiCl^{3+} \qquad (7)$$

and making due allowance for k_b, equation (8) can be derived.

$$(k_{obs} - k_b) = \frac{K_{os}k[Cl^-]}{1 + K_{os}[Cl^-]} \qquad (8)$$

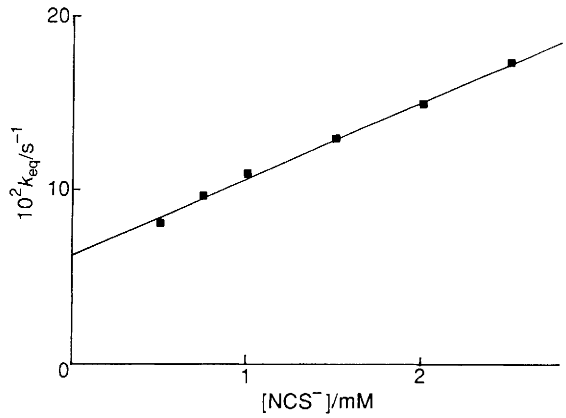

Fig. 6 Dependence of stopped-flow equilibration rate constants (k_{eq}) on $[NCS^-]$ for the 1:1 complexing of NCS^- with $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ at 25 °C, $I = [H^+] = 2.00$ M ($HClO_4$)

From a graph of $[Cl^-]/(k_{obs} - k_b)$ against $[Cl^-]$, Fig. 5, the intercept $(1/kK_{os})$ and slope $(1/k)$ give $k = 25.5 \pm 2.0$ s^{-1} and $K_{os} = 0.37 \pm 0.03$ M^{-1}. Rate constants at $[Cl^-] = 0.10$ M were independent of $[H^+]$ over the range 0.5–2.0 M, $I = 2.00$ M ($HClO_4$–$LiClO_4$).

Complexing with NCS^-.—Studies were restricted to those listed in Table 2. At higher NCS^- concentrations or with $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ the reactant in large excess, biphasic kinetics was observed. The former may be due to secondary substitution, and the latter to bridging by NCS^-. The main reaction can be expressed as in equation (9), which defines

$$Mo_3Ni^{4+} + NCS^- \rightleftharpoons Mo_3NiNCS^{3+} \qquad (9)$$

forward and back rate constants used in the rate-law dependence (10). The data can be fitted by this equation, Fig. 6.

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

From a least-squares treatment $k_f = 45 \pm 2$ M^{-1} s^{-1} and $k_b = 0.062 \pm 0.003$ s^{-1}. These give $K = 720$ M^{-1} at 25 °C, $I = 2.00$ M ($HClO_4$).

Oxidation with $[Co(dipic)_2]^-$.—The conversion of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ into $[Mo_3S_4(H_2O)_9]^{4+}$ was monitored by UV/VIS spectrophotometry. Addition of aliquots of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ (Hamilton microsyringe) to $[Co(dipic)_2]^-$ in a spectrophotometer optical cell was monitored at the $[Co(dipic)_2]^-$ peak at 510 nm ($\varepsilon = 630$ M^{-1} cm^{-1}). A stoichiometry of 2.11 ± 0.15 was obtained, consistent with equation (11).

$$Mo_3NiS_4^{4+} + 2Co^{III} \longrightarrow Mo_3S_4^{4+} + Ni^{2+} + 2Co^{II} \qquad (11)$$

First-order kinetic plots of absorbance (A) changes at 367 nm, ln ΔA *vs* time, with oxidant in large (> 10-fold) excess, were linear to 3–4 half-lives. First-order rate constants k_{obs} gave a linear dependence on $[Co(dipic)_2^-]$, Fig. 7, consistent with the rate law (12). The 2:1 stoichiometry (11), and existence of an

$$d[Mo_3S_4^{4+}]/dt = k_{Co}[Mo_3NiS_4^{4+}][Co(dipic)_2^-] \qquad (12)$$

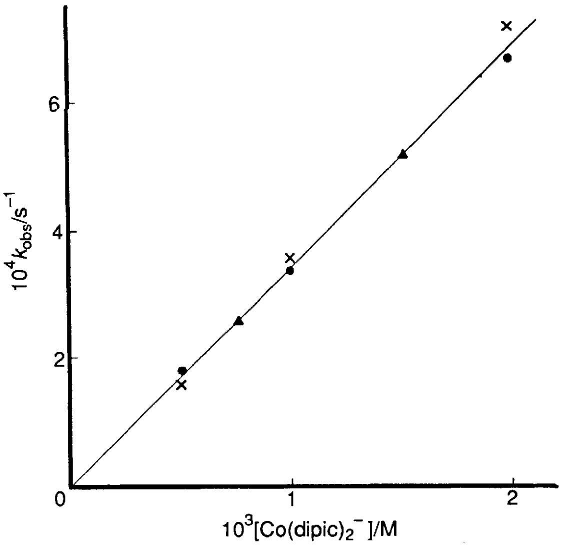

Fig. 7 Dependence of first-order rate constants k_{obs} (25 °C) on $[Co(dipic)_2^-]$ (reactant in excess) for the oxidation of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ (0.05–0.10 mM). The various symbols indicate different $[H^+]$ values. No variation of k_{obs} with $[H^+]$ (0.5–1.8 M) is observed, I = 2.00 M ($LiClO_4$)

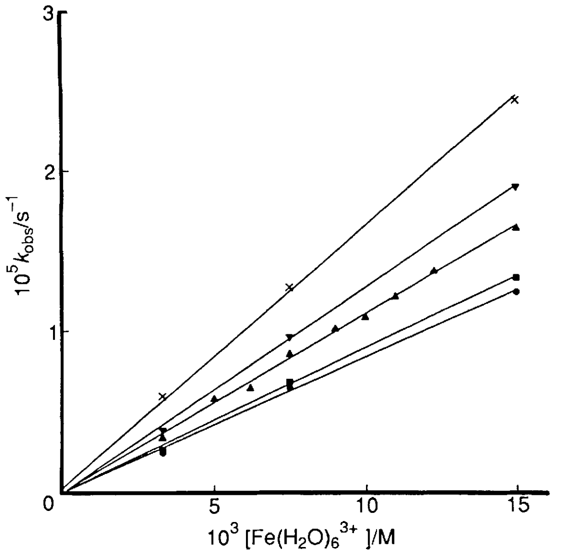

Fig. 8 Dependence of first-order rate constants, k_{obs} (25 °C), on $[Fe(H_2O)_6^{3+}]$ (reactant in excess) for the oxidation of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ at $[H^+]/M$ = 1.80 (●), 1.40 (■), 1.00 (▲), 0.70 (▼) or 0.50 (×), I = 2.00 M ($LiClO_4$)

isosbestic point at 445 nm in scan spectra, indicate a reaction sequence (13) and (14). No dependence of rate constants on

$$Mo_3NiS_4^{4+} + Co^{III} \xrightarrow{k_{Co}} Mo_3NiS_4^{5+} + Co^{II} \qquad (13)$$

$$Mo_3NiS_4^{5+} + Co^{III} \xrightarrow{fast} Mo_3S_4^{4+} + Ni^{2+} + Co^{II} \qquad (14)$$

$[H^+]$ in the range 0.50–2.00 M was observed. From the slope in Fig. 7, k_{Co} = 0.35 ± 0.01 $M^{-1}\ s^{-1}$, at 25 °C, I = 2.00 M ($LiClO_4$).

Oxidation with $[Fe(H_2O)_6]^{3+}$.—To obtain the stoichiometry the $[Fe(H_2O)_6]^{2+}$ product was determined by complexing with 4,7-diphenyl-1,10-phenanthroline and extracting with pentyl acetate.[12,13] The procedure involved taking a suitable aliquot of Fe^{2+}, adding a 100-fold excess of ligand, and adjusting the pH to 3.6 by addition of 0.1 M sodium acetate. This was followed by extraction into pentyl acetate and standardisation at 535 nm (ε 17 850 $M^{-1}\ cm^{-1}$). The value was 1.83 ± 0.3:1 (six determinations) consistent with equation (15).

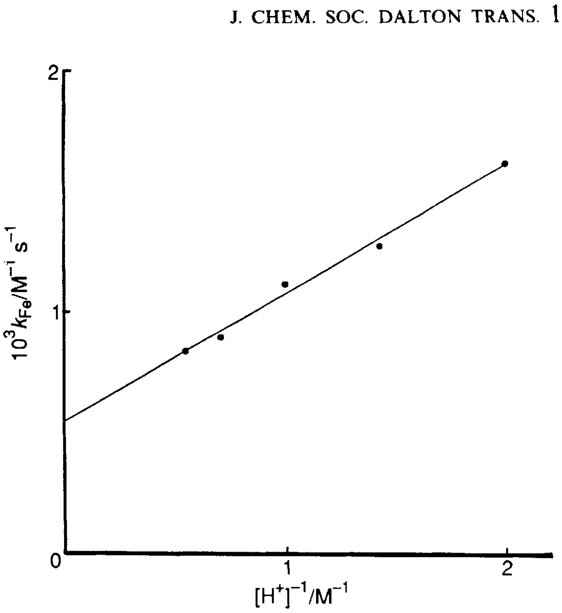

Fig. 9 Dependence of second-order rate constants, k_{Fe} (25 °C), on $[H^+]^{-1}$ for the $[Fe(H_2O)_6]^{3+}$ oxidation of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$, I = 2.00 M ($LiClO_4$)

$$Mo_3NiS_4^{4+} + 2Fe^{III} \longrightarrow Mo_3S_4^{4+} + Ni^{2+} + 2Fe^{2+} \qquad (15)$$

First-order rate constants, k_{obs}, give a linear dependence on Fe^{III}, the reactant in large excess, Fig. 8. The rate law is first order in the concentration of both reactants, as in equation (12), and the reaction sequence can be written as in (16) and (17). On varying $[H^+]$ within the range 0.50–1.80 M the dependence (18) is observed, Fig. 9. Values of k_a = (5.4 ± 0.3) × 10^{-4} $M^{-1}\ s^{-1}$ and k_b = (5.3 ± 0.3) × 10^{-4} s^{-1} are obtained.

$$Mo_3NiS_4^{4+} + Fe^{3+} \xrightarrow{k_{Fe}} Mo_3NiS_4^{5+} + Fe^{2+} \qquad (16)$$

$$Mo_3NiS_4^{5+} + Fe^{3+} \xrightarrow{fast} Mo_3S_4^{4+} + Ni^{2+} + Fe^{2+} \qquad (17)$$

$$k_{Fe} = k_a + k_b[H^+]^{-1} \qquad (18)$$

Discussion

The structure of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ is identical to that of the iron analogue, with a unique tetrahedrally co-ordinated nickel subsite. The Ni atom is in an almost regular tetrahedral arrangement bonded to three μ_3-sulphido and one terminal H_2O ligand. It is also metal–metal bonded to the three Mo atoms in the cuboidal cluster arrangement.

The 1:1 complexing observed with Cl^- could correspond to addition of Cl^- at the Ni, with increase in co-ordination number from four to five, or substitution of the H_2O. In view of retention of absorption peak positions, Fig. 2, we consider the latter more likely. Assuming the same to be true for NCS^- the anation rate constants of 9.4 (Cl^-) and 45 $M^{-1}\ s^{-1}$ (NCS^-), ratio 4.8:1, are sufficiently similar as to suggest a dissociative interchange (I_d) mechanism.[14,15] Both substitution processes are however remarkable for their slow rates. The full treatment which has been possible with Cl^- gives an outer-sphere formation constant of 0.37 M^{-1}, and an interchange rate constant (Cl^- for H_2O within the ion pair) of 25.5 s^{-1}. The former is perfectly reasonable for a 4+ and 1− charge interaction at an ionic strength of 2.00 M.

The rate constant for substitution at the nickel subsite is substantially slower than the corresponding interchange rate constant of *ca.* 10^4 s^{-1} for octahedral $[Ni(H_2O)_6]^{2+}$. NMR studies on the five-co-ordinate tetraazamacrocyclic nickel(II) complexes show a very labile solvent H_2O molecule.[16] In non-aqueous ($CDCl_3$) solution substitution of sterically bulky phosphine ligands (PPh_3) at tetrahedral Ni^{II} is again relatively rapid.[17] Similarly tetrahedral Ni^{II}, which is normally high spin, is expected to undergo substitution at a very fast rate. There are a number of possible explanations for the behaviour observed. Foremost amongst these is that the formal oxidation state of the Ni has not been established and may not be Ni^{II}. Although the Ni goes in and out of the cube as Ni^{II} this does not rule out Ni^{III} as a possible oxidation state although no EPR signal was observed. In the case of $[Mo_3FeS_4(H_2O)_{10}]^{4+}$, where Fe goes in and out of the cube as Fe^{II}, Mössbauer studies favour a strongly coupled tetrahedral high-spin iron(III) assignment.[8] No corresponding assignment has yet been possible for the nickel cube using physical measurements. There is moreover no information available as to the substitution properties of tetrahedral Ni^{III}.[18] What is particularly relevant is that the Ni (like Fe) is in an unusual situation as part of a cluster, with metal–metal bonding in addition to the tetrahedral metal–ligand bonds. As a result there is electron delocalisation at the Ni, and it is difficult to indicate the electronic configuration and predict (or rationalise) substitution behaviour.

The kinetics of complexation gives equilibrium constants for 1:1 reactions of 97 (Cl^-) and 720 M^{-1} (NCS^-). The stability constant for 1:1 Cl^- substitution on $[Ni(H_2O)_6]^{2+}$ is 0.62 M^{-1} (I = 2.00 M).[19] The behaviour of the iron analogue is more easily understood. Substitution of Cl^- for H_2O at the tetrahedral Fe of $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ ($>2 \times 10^4$ M^{-1} s^{-1})[8] is faster than the 1:1 substitution on $[Fe(H_2O)_6]^{3+}$ (9.4 M^{-1} s^{-1}).[20] The corresponding formation constants of 560 and 3.3 M^{-1} (ref. 21) respectively are consistent with tetrahedral and octahedral co-ordination.

Even with Cl^- as high as 1.0 M there is no evidence for substitution exceeding the 1:1 stoichiometry indicated in equation (3). The 1:1 substitution of NCS^- (amounts as used in the present work) on cuboidal $[Mo_4S_4(H_2O)_{12}]^{4+}$ and $[Mo_4S_4(H_2O)_{12}]^{5+}$ has been shown to be slow requiring *ca.* 1 d to proceed to completion at 25 °C, I = 2.00 M.[22] Stability constants are 10^2–10^3 M^{-1} which is substantially in excess of those expected for Cl^- complexing. The slowness of the reactions is accounted for by all the H_2O ligands being *trans* to μ_3-sulphido ligands. In the case of NCS^- for H_2O substitution on the $Mo^{IV}{}_3$ incomplete cuboidal clusters $[Mo_3O_4(H_2O)_9]^{4+}$ (refs. 23 and 24) and $[Mo_3S_4(H_2O)_9]^{4+}$,[25] substitution at the H_2O *trans* to μ-sulphido is *ca.* 10^3 times faster than at H_2O *trans* to μ_3-sulphido positions.

The oxidation of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ involves a two-electron change to give $[Mo_3S_4(H_2O)_9]^{4+}$. This is shown by the 2:1 stoichiometries in the reactions of $[Co(dipic)_2]^-$ and $[Fe(H_2O)_6]^{3+}$. A single rate-determining step is observed. The unlikely event of a concerted two-electron step can be ignored. Instead two-stage mechanisms with the second stage fast as in (13) and (14) and (16) and (17) are implicated. We have not yet identified the 5+ species, which can be regarded as a short-lived intermediate. Since we have no evidence for this intermediate a single-electron oxidation to give $Mo_3S_4{}^{3+}$ cannot be ignored as an alternative. In either case the presence of an isosbestic point in the scan spectra of the reaction with $[Co(dipic)_2]^-$ indicates that the intermediate is short lived.

The lack of any $[H^+]$ dependence and improbability of the dipic ligand dechelating to act as a bridge leads to an outer-sphere assignment for oxidation with $[Co(dipic)_2]^-$. The $[H^+]^{-1}$ dependence for the $[Fe(H_2O)_6]^{3+}$ oxidation can be assigned to the oxidant and carries the implication of an inner-sphere mechanism. Thus assuming the $[H^+]^{-1}$ dependence is due to acid dissociation of $[Fe(H_2O)_6]^{3+}$ ($K_a = 1.0 \times 10^{-3}$ M at 25 °C, I = 2.0 M $NaClO_4$),[26] and reaction of $[Fe(H_2O)_5(OH)]^{2+}$ with $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ the true rate constant for this path is given by k_b/K_a, which is 0.53 M^{-1} s^{-1}, and is to be compared directly with $k_a = 5.4 \times 10^{-4}$ M^{-1} s^{-1}. It is likely that, for a conjugate-base enhancement factor of this magnitude, $[Fe(H_2O)_5(OH)]^{2+}$ reacts by an inner-sphere mechanism.[27] Since H_2O is an unlikely bridging ligand for inner-sphere electron transfer, k_a is assigned an outer-sphere mechanism. On the evidence of the studies with the $[Mo_4S_4(H_2O)_{12}]^{4+/5+}$ complexes, acid dissociation of H_2O ligands attached to the molybdenum centres is unlikely to explain the $[H^+]^{-1}$ dependence.

A theoretical Marcus treatment[28] to calculate a self-exchange rate constant for the $[Mo_3NiS_4(H_2O)_{10}]^{4+/5+}$ couple is difficult due to the lack of a reliable reduction potential for the cube. A value of *ca* 1.0V *vs.* normal hydrogen electrode can be estimated from the cyclic voltammetry experiment. Using this value, a self-exchange rate constant of 10^{-1}–10 M^{-1} s^{-1} can be calculated after allowing for work terms. This value is less favourable than those obtained for the $[Mo_4S_4(H_2O)_{12}]^{4+/5+}$, $[Mo_4S_4(edta)_2]^{4-/3-}$, and $[Mo_4S_4(edta)_2]^{3-/2-}$ couples (edta = ethylenediaminetetraacetate).

A qualitative bonding model for clusters of the type $M_3M'S_4$ has been proposed and can be applied in this case.[29] As compared to $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ the nickel cube has two more electrons, both of which go into bonding orbitals. This increases the overall bonding and hence the overall stability of the cuboidal structure. The most obvious evidence of this increased stability is the resistance of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ to oxidation.

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