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New procedures for the preparation of $[Mo_3S_4(H_2O)_9]^{4+}$, $[Mo_4S_4(H_2O)_{12}]^{5+}$ and $[Mo_7S_8(H_2O)_{18}]^{8+}$ and their Se analogues: redox and substitution studies on the double cube $[Mo_7S_8(H_2O)_{18}]^{8+}$ †

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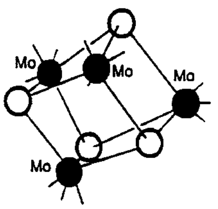
Alternative improved methods for the preparation of $[Mo_3S_4(H_2O)_9]^{4+}$, $[Mo_4S_4(H_2O)_{12}]^{5+}$ and $[Mo_7S_8(H_2O)_{18}]^{8+}$ are described from polymeric $\{Mo_3S_7Br_4\}_x$ (obtained by heating together the elements), *via* water soluble $[Mo_3S_7Br_6]^{2-}$. Abstraction of neutral sulfur with phosphines and aquation of terminal ligands in dilute acids gives $[Mo_3S_4(H_2O)_9]^{4+}$ in yields of up to 85%. The single cube $[Mo_4S_4(H_2O)_{12}]^{5+}$, and corner-shared double cube $[Mo_7S_8(H_2O)_{18}]^{8+}$, are obtained by treating $[Mo_3S_4(H_2O)_9]^{4+}$ with different reductants. The best procedure for $[Mo_7S_8(H_2O)_{18}]^{8+}$ is with hypophosphorous acid (H_3PO_2), when yields of up to 20% are obtained. Yields of $[Mo_4S_4(H_2O)_{12}]^{5+}$ are variable and in the range 10–65% depending on the reductant and procedure employed. The reactions provide examples of Mo^{III} and Mo^{IV}–sulfido reassembly from $[Mo_3S_4(H_2O)_9]^{4+}$ following reduction. Surprisingly, the more direct approach for the preparation of $[Mo_7S_8(H_2O)_{18}]^{8+}$, involving addition of $[Mo_3S_4(H_2O)_9]^{4+}$ to $[Mo_4S_4(H_2O)_{12}]^{4+}$, gives only ≈3% yield, most likely due to the inertness of $[Mo_4S_4(H_2O)_{12}]^{4+}$. The procedures described are effective also for $[Mo_3Se_7Br_6]^{2-}$, and in exploratory studies the double cube $[Mo_7Se_8(H_2O)_{18}]^{8+}$ has been prepared for the first time. The kinetics of substitution of H_2O on $[Mo_7S_8(H_2O)_{18}]^{8+}$ by NCS^- have been investigated, and two stages identified. One of these is a $[NCS^-]$-dependent equilibration, with rate constants (25 °C) for formation $k_f = 0.173\ M^{-1}\ s^{-1}$ and aquation $k_{aq} = 0.20 \times 10^{-3}\ s^{-1}$ at $[H^+] = 1.96$ M, $I = 2.00$ M (Lipts), $pts^- = p$-toluenesulfonate. The other is a $[NCS^-]$-independent step assigned as isomerisation of the S-bonded thiocyanato product ($k \approx 1.5 \times 10^{-3}\ s^{-1}$). With $[Co(dipic)_2]^-$ (dipic = pyridine-2,6-dicarboxylate) as oxidant, second-order kinetics are observed with the rate constant $0.31\ M^{-1}\ s^{-1}$ at 25 °C independent of $[H^+]$ in the range 0.87–2.00 M, $I = 2.00$ M (Lipts). The stoichiometry indicates higher than expected consumption (≈7 equivalents) of $[Co(dipic)_2]^-$. A mechanism involving transient formation of $[Mo_7S_8(H_2O)_{18}]^{9+}$, which fragments to $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_4S_4(H_2O)_{12}]^{5+}$, is proposed. In separate experiments the latter was found to be oxidised by $[Co(dipic)_2]^-$ yielding first $[Mo_4S_4(H_2O)_{12}]^{6+}$, which itself fragments with formation of $[Mo_3S_4(H_2O)_9]^{4+}$, the $Mo^V{}_2$ dimer $[Mo_2O_2S_2(H_2O)_6]^{2+}$, and other products.

Studies on the $Mo^{IV}{}_3$ incomplete cuboidal $[Mo_3S_4(H_2O)_9]^{4+}$, and cuboidal clusters $[Mo_4S_4(H_2O)_{12}]^{n+}$ ($n = 4$–6), of which the 5+ cube is most readily accessed, have been the subject of earlier work.[1–6] The preparations take ≈6 d, however, and yields are generally small (<20%).[1] Similar comments apply also in the case of the Se analogues. In this paper we describe alternative routes using as starting material polymeric $\{Mo_3Y_7Br_4\}_x$ (Y = S or Se), obtained by heating Mo, S (or Se) and Br_2 in sealed quartz tubes. The latter can be converted into $[NEt_4]_2[Mo_3Y_7Br_6]$ (Y = S or Se),[7,8] followed by chalcogenide abstraction and Br^- aquation to give $[Mo_3Y_4(H_2O)_9]^{4+}$.[9] Procedures for the conversion of $[Mo_3S_4(H_2O)_9]^{4+}$ to $[Mo_4S_4(H_2O)_{12}]^{5+}$ **I** and $[Mo_7S_8(H_2O)_{18}]^{8+}$ **II** on a preparative scale are considered in this paper. Structures of all but one of the clusters indicated have been reported previously,[7,8,10–12] the exception being $[Mo_7Se_8(H_2O)_{18}]^{8+}$, which in exploratory studies has been identified for the first time. The earlier procedure used to prepare the corner-shared double cube $[Mo_7S_8(H_2O)_{18}]^{8+}$ involves reacting $[Mo_3S_4(H_2O)_9]^{4+}$ with Mg.[12] However, we have experienced some problems with the reproducibility of this method, and the procedures now reported give much improved yields.

The better yields for $[Mo_7S_8(H_2O)_{18}]^{8+}$ have enabled us to investigate the aqueous solution chemistry of this cluster for the first time, including kinetic studies on substitution (with NCS^-) and oxidation (with $[Co(dipic)_2]^-$; dipic = pyridine-2,6-dicarboxylate). The double cube is of particular interest because, although there are a number of corner-shared double-cube derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$ with p-block metals (M) at the nodal position, general formula $[Mo_6MS_8(H_2O)_{18}]^{8+}$, this is the only one so far identified with a transition metal at the nodal position. From crystal structure information metal–metal bonding is clearly apparent in all transition-metal containing heterometallic derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$, including $[Mo_7S_8(H_2O)_{18}]^{8+}$, but not the heterometallic main-group derivatives $[Mo_6MS_8(H_2O)_{18}]^{8+}$, as will be discussed.[13]



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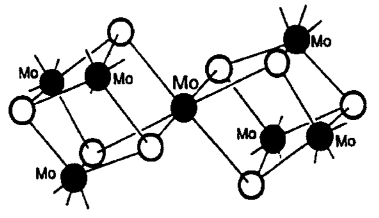

II

Experimental

Starting materials

The polymeric compounds $\{Mo_3S_7Br_4\}_x$ and $\{Mo_3Se_7Br_4\}_x$ were prepared by heating mixtures of elements in sealed tubes at temperatures to 350 °C. These were then converted into water-soluble compounds, *e.g.* $[Et_4N]_2[Mo_3S_7Br_6]$ and $[Ph_4P]_2[Mo_3Se_7Br_6]$ by procedures described.[7,8] Samples of the green coloured clusters $[Mo_3S_4(H_2O)_{12}]^{4+}$, UV/VIS peak at 603 (ε = 362 $M^{-1}\ cm^{-1}$ per Mo_3) and $[Mo_4S_4(H_2O)_{12}]^{5+}$, peak at 635 nm (ε = 435 $M^{-1}\ cm^{-1}$ per Mo_4) were prepared in 2 M Hpts (*p*-toluenesulfonic acid) by procedures as described in ref. 1.

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† Dedicated to Professor R. G. Wilkins on the occasion of his 70th birthday.

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

The complex $K_3[MoCl_6]$ was a gift from the Climax Molybdenum Co, a sample of $K_4[Mo_2Cl_8]$ was obtained by a literature method[14] and molybdic acid (99.5% MoO_3) was from Sigma Chemicals. The water soluble phosphine tris(3-sulfonatophenyl)phosphine, $Na_3[(3\text{-}SO_3C_6H_4)_3P]\cdot 4H_2O$, abbreviated here to PR_3^{3-}, was from Strem Chemicals,[15] and sodium thiocyanate (Analar) from BDH. Other reagents included *p*-toluenesulfonic acid ($CH_3C_6H_4SO_3H$), lithium carbonate (Li_2CO_3), triphenylphosphine, hypophosphorous acid (H_3PO_2) and vanadium metal turnings (99.7% purity); were all from Aldrich. Solutions of Lipts were prepared by Li_2CO_3 neutralisation of Hpts and recrystallising. The complex $[Co(dipic)_2]^-$, UV/VIS peak 510 nm ($\varepsilon = 630\ M^{-1}\ cm^{-1}$), reduction potential 767 mV, was as used in other reports from these laboratories.[13] Much of the preparative work requires good fumehood facilities since H_2S and H_2Se gases are evolved.

Determination of products

The products $[Mo_3S_4(H_2O)_9]^{4+}$, $[Mo_4S_4(H_2O)_{12}]^{5+}$ and $[Mo_7S_8(H_2O)_{18}]^{8+}$ were purified by Dowex cation-exchange chromatography. Yields were determined by UV/VIS spectrophotometry, peak position λ/nm ($\varepsilon/M^{-1}\ cm^{-1}$ per Mo_3, Mo_4 or Mo_7) for $[Mo_3S_4(H_2O)_9]^{4+}$ 366 (5550), 603 (362); $[Mo_4S_4(H_2O)_{12}]^{5+}$ 635 (435), 1100 (122); $[Mo_7S_8(H_2O)_{18}]^{8+}$ 416 (7190), 480 (sh) (9065), 518 (10 280), 635 (8860), 950 (4242), all in 2 M Hpts.

Stability of $[Mo_7S_8(H_2O)_{18}]^{8+}$

The violet coloured double cube $[Mo_7S_8(H_2O)_{18}]^{8+}$ does not react significantly with O_2 over periods of ≈1 d. It is eluted from a Dowex column with 4 M Hpts, but not by 4 M $HClO_4$, due to the weaker complexing properties of ClO_4^-. On evaporating solutions in 3 M HCl to dryness at ≈50 °C a green product was obtained, and fragmentation to *e.g.* $[Mo_3S_4(H_2O)_9]^{4+}$ is evident. This does not therefore provide a means of preparing solutions in 2 M $HClO_4$ as in earlier work with $[Mo_3S_4(H_2O)_9]^{4+}$.[16] Stock solutions of $\approx 10^{-3}$ M $[Mo_7S_8(H_2O)_{18}]^{8+}$ could be stored under N_2 for >3 weeks at ≈4 °C.

Kinetic studies

The NCS^- (for H_2O) substitution, and $[Co(dipic)_2]^-$ oxidation of $[Mo_7S_8(H_2O)_{18}]^{8+}$ were studied by conventional ($t_{\frac{1}{2}} > 1$ min) UV/VIS spectrophotometry on Perkin-Elmer Lambda 9 and Phillips-Unicam 8740 instruments. Preliminary runs with $[Co(dipic)_2]^-$ showed that $HClO_4$ replacement of Hpts in reactant solutions, $[H^+] = 2.00$ M, gave on extrapolation only a small (14%) decrease in rate constants for full replacement. Subsequent studies were in pts^- solutions. The temperature was 25.0 ± 0.1 °C, and ionic strengths were adjusted to $I = 2.00 \pm 0.01$ M with Lipts. Absorbance *vs.* time data (150–200 points) were transferred to Software SX-17MV (Spectra Kinetic Work Station) on an Applied Photophysics stopped-flow spectrophotometer in order to fit consecutive equilibria for the reaction of NCS^- with $[Mo_7S_8(H_2O)_{18}]^{8+}$ at 640 nm.

Results

New procedure for the preparation of $[Mo_3S_4(H_2O)_9]^{4+}$

The compound $[Et_4N]_2[Mo_3S_7Br_6]$ (5.5 g, 4.3 mmol) was dissolved in hot concentrated HCl. Solid PPh_3 (3.3 g, 12.7 mmol) was then added to the hot solution. It is important to ensure that no solid is left before adding PPh_3. The colour begins to change immediately to the characteristic green of the product. A copious precipitate of $SPPh_3$ forms. Heating was continued for a further 10–15 min, after which the solution was diluted (with stirring) with 4 times the volume of water, and the $SPPh_3$ filtered off. The filtrate was evaporated to dryness on a rotary evaporator, and the solid taken up in dilute HCl. The product in 0.5 M HCl was loaded onto a Dowex 50W-X2 cation-exchange column, washed with 0.5 M acid (100 cm^3), and a single green band eluted with 2 M Hpts or HCl as required. Yield 85%. Use of the more expensive water-soluble phosphine PR_3^{3-} in a modified procedure had no obvious advantages. The method has also been tested starting from $[Mo_3S_7Cl_6]^{2-}$ or $[Mo_3S_7I_6]^{2-}$, when similar yields are obtained. The procedure with $[Mo_3Se_7Br_6]^{2-}$ gives similar amounts of $[Mo_3Se_4(H_2O)_9]^{4+}$.

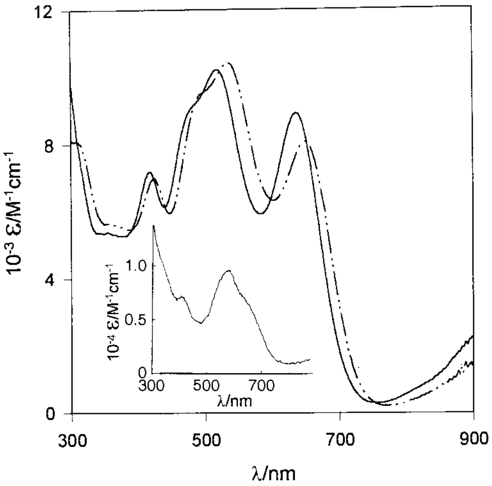
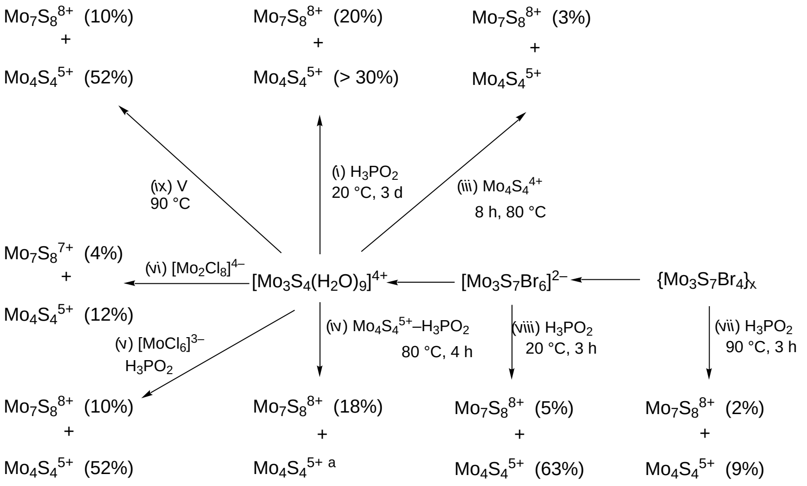


Fig. 1 The UV/VIS absorbance spectrum of $[Mo_7S_8(H_2O)_{18}]^{8+}$ in 2 M Hpts (——), 2 M HCl (– ·· –) and inset the spectrum of $[Mo_7Se_8(H_2O)_{18}]^{8+}$ in 4 M HCl

Preparation of $[Mo_7S_8(H_2O)_{18}]^{8+}$ and $[Mo_4S_4(H_2O)_{12}]^{5+}$

At the outset the aim was to improve yields of $[Mo_7S_8(H_2O)_{18}]^{8+}$. At the same time, and equally important as it emerges, significantly improved yields of the single cube are obtained. The single cube which separates first on a Dowex 50W-X2 column eluted with 2–3 M Hpts is orange $[Mo_4S_4(H_2O)_{12}]^{4+}$. In the course of the chromatography, as the reductant is removed, green $[Mo_4S_4(H_2O)_{12}]^{5+}$ forms as a result of air oxidation, UV/VIS peaks at 635 (435) and 1100 nm (122 $M^{-1}\ cm^{-1}$ per Mo_4).[5,17] Violet $[Mo_7S_8(H_2O)_{18}]^{8+}$ eluted with 4 M Hpts has absorbance peak positions λ/nm ($\varepsilon/M^{-1}\ cm^{-1}$ per Mo_7) at 416 (7190), 480 (sh) (9065), 518 (10 280), 635 (8860) and 950 (4242) in 2 M Hpts,[12] Fig. 1. The spectrum in 2 M HCl is also indicated in Fig. 1.

Some ten different procedures as listed were explored, Scheme 1, reactions carried out under N_2. The best method for formation of $[Mo_7S_8(H_2O)_{18}]^{8+}$ is (*i*) the treatment of $[Mo_3S_4(H_2O)_9]^{4+}$ in 2 M HCl (10 cm^3, 16 mM) with H_3PO_2 (5 cm^3, 50% aqueous solution). After 3 d at room temperature yields were up to 20% with amounts of $[Mo_4S_4(H_2O)_{12}]^{5+}$ in excess of 30%. Alternatively (*ii*) by heating to 90 °C for 60 min, only 9% of the double cube and 11% of $[Mo_4S_4(H_2O)_{12}]^{5+}$ were obtained. A procedure (*iii*) involving addition of $[Mo_3S_4(H_2O)_9]^{4+}$ (2 cm^3, 16 mM) to $[Mo_4S_4(H_2O)_{12}]^{4+}$ (34 cm^3, 0.96 mM), generated *in situ* by reduction of $[Mo_4S_4(H_2O)_{12}]^{5+}$ gave only 3% of $[Mo_7S_8(H_2O)_{18}]^{8+}$ after 8 h at 80 °C. Procedures involving addition of $[Mo_3S_4(H_2O)_9]^{4+}$ (6.3 cm^3, 2.5 mM) to (*iv*) $[Mo_4S_4(H_2O)_{12}]^{5+}$ (9 cm^3, 1.8 mM) with heating to 80 °C for 4 h, and (*v*) $K_3[MoCl_6]$, both in 2 M HCl and in the presence of excess H_3PO_2 (3 cm^3, 50%), gave 18% and 10% yields respectively of double cube, but with no enhancement attributable to the second Mo component. Similarly (*vi*) heating $[Mo_3S_4(H_2O)_9]^{4+}$ (two-fold excess) with $K_4[Mo_2Cl_8]$ for 70 min at 80 °C, no H_3PO_2 added, gave only a 4% yield of $[Mo_7S_8(H_2O)_{18}]^{8+}$ and 12% $[Mo_4S_4(H_2O)_{12}]^{5+}$. On treating (*vii*) polymeric $\{Mo_3S_7Br_4\}_x$ for 3 h at 90 °C, or (*viii*) $[Mo_3S_7Br_6]^{2-}$ for 3 h at room temperature, with H_3PO_2 (5 cm^3, 50%), 2 and 5% yields respectively of $[Mo_7S_8(H_2O)_{18}]^{8+}$ with 9 and 63% of $[Mo_4S_4(H_2O)_{12}]^{5+}$ were obtained. It was also found (*ix*) that addition of $[Mo_3S_4(H_2O)_9]^{4+}$ in 2 M



Scheme 1

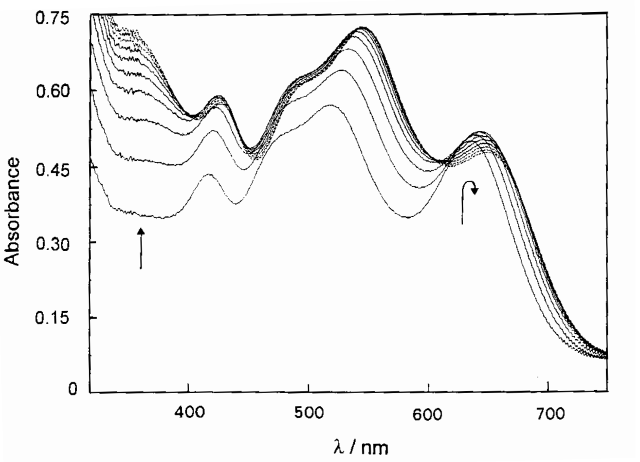


Fig. 2 The UV/VIS scan spectra (every 10 min) for the reaction of $[Mo_7S_8(H_2O)_{18}]^{8+}$ (4.0×10^{-5} M) with $[NCS^-]$ (2.0×10^{-3} M) at 25 °C in 2.0 M Hpts, $I = 2.0$ M

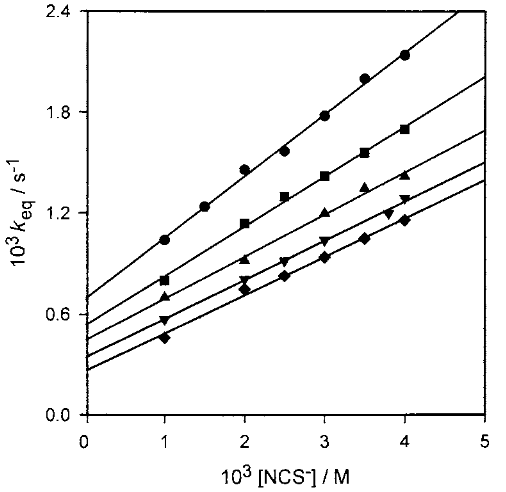


Fig. 3 Dependence of rate constants k_{eq} (25 °C) for the equilibration NCS^- with $[Mo_7S_8(H_2O)_{18}]^{8+}$ (4.0×10^{-5} M) at different $[H^+]$ 0.41 (●), 0.72 (■), 0.96 (▲), 1.46 (▼) and 1.96 (◆) M, from absorbance changes at 360 nm, $I = 2.00$ M (Lipts)

HCl to vanadium metal turnings, and heating to 90 °C for 2 h, gives 10% of $[Mo_7S_8(H_2O)_{18}]^{8+}$ and 30% of $[Mo_4S_4(H_2O)_{12}]^{5+}$. Finally, in a somewhat different approach, (*x*) on heating MoS_3 (0.17 g) for 3 h at 90 °C with H_3PO_2 (5 cm^3, 50%) in concentrated HCl, only 1% $[Mo_7S_8(H_2O)_{18}]^{8+}$ but 26% of $[Mo_4S_4(H_2O)_{12}]^{5+}$ was obtained. In some procedures H_3PO_2 was replaced by BH_4^-, but the latter is generally less satisfactory since precipitation can occur.

Preparation of $[Mo_7Se_8(H_2O)_{18}]^{8+}$ and $[Mo_4Se_4(H_2O)_{12}]^{5+}$

In the first procedure polymeric $\{Mo_3Se_7Br_4\}_x$ (1 g) was heated with concentrated HCl (20 cm^3) and H_3PO_2 (5 cm^3, 50% aqueous solution) for 4.5 h under N_2. A pale brown solution was obtained, and the greater part of the solid remained undissolved. The above procedure was modified to include Et_4NBr (≈3 g) thus simulating the conditions for generation of $[Mo_3Se_7Br_6]^{2-}$. The brown solution (darker than in the previous experiment) was filtered, diluted to $[H^+]$ ≈0.3 M and loaded onto a Dowex 50W-X2 column. The latter was washed with 0.5 M Hpts and then 3 M Hpts, giving two bands. These were a faster moving green band (peak at 658 nm) identified as $[Mo_4Se_4(H_2O)_{12}]^{5+}$,[11] and a second violet band, both yields small (≈2%). The latter was concentrated by Dowex chromatography, elution with 4 M HCl to give a violet solution with UV/VIS absorption peaks λ/nm (ε/M^{-1} cm^{-1} per Mo$_7$) at 407 (7200), 579 (9700) and ≈630 (≈7000), inset to Fig. 1. Inductively coupled plasma (ICP) analyses for Mo/ppm (4 determinations) gave 14.61, 14.12, 17.62, 15.10 and Se/ppm 14.11, 14.22, 13.77, 14.34 corresponding to a ratio Mo : Se of 7 : 7.9. The Se-containing double cube is less stable in air than $[Mo_7S_8(H_2O)_{18}]^{8+}$, especially on heating. Storage was under N_2 at 4 °C. In preliminary studies using procedure (*i*) above, better yields were obtained from $[Mo_3Se_4(H_2O)_9]^{4+}$.

Kinetics of NCS^- for H_2O substitution on $[Mo_7S_8(H_2O)_{18}]^{8+}$

The early stages of substitution with replacement of a minimum number of H_2O molecules were studied. Scan spectra for the reaction with $[NCS^-] = 2 \times 10^{-3}$ M are shown in Fig. 2. Absorbance changes monitored at 360 nm (≈2 h) are uniphasic, and plots of $\ln(A_\infty - A_t)$ *vs.* time, linearity to ≈80% completion, gave first-order equilibration rate constants k_{eq}, Table 1. A linear dependence of k_{eq} on $[NCS^-]$ is observed, Fig. 3, defining formation (k_f) and aquation (k_{aq}) rate constants, equation (1).

$$k_{eq} = k_f [NCS^-] + k_{aq} \qquad (1)$$

From $[H^+]$ variations in the range 0.41–2.00 M both k_f and k_{aq}, Table 2, are dependent on $[H^+]^{-1}$, Fig. 4, as in equations (2) and (3).

$$k_f = a + b [H^+]^{-1} \qquad (2)$$

$$k_{aq} = a' + b' [H^+]^{-1} \qquad (3)$$

Individual constants evaluated from an unweighted least-squares fit give $a = 0.173(4)$ M^{-1} s^{-1}, $b = 0.079(3)$ s^{-1}, $a' = 2.0(2) \times 10^{-4}$ s^{-1} and $b' = 2.2(1) \times 10^{-4}$ M s^{-1}.

Scan spectra, Fig. 2, indicate a two phase reaction at other wavelengths, *e.g.* 640 nm, Fig. 5. Rate constants for the second phase from the slope of $\ln(A_t - A_\infty)$ *vs.* *t*, Fig. 5, are with

Table 1 The variation of first-order equilibrium rate constants k_{eq} (25 °C) determined at 360 nm for the reaction of NCS^- with $[Mo_7S_8(H_2O)_{18}]^{8+}$ (4×10^{-5} M), $I = 2.0$ M (Lipts)

$[H^+]$/M	$10^{-3}[NCS^-]$/M	10^3k_{eq}/s^{-1}
0.41	1.00	1.04
	1.50	1.24
	2.00	1.46
	2.50	1.57
	3.00	1.78
	3.50	2.00
	4.00	2.14
0.72	1.00	0.80
	2.00	1.14
	2.50	1.30
	3.00	1.42
	3.50	1.56
	4.00	1.70
0.96	1.00	0.70
	2.00	0.92
	3.00	1.20
	3.50	1.35
	4.00	1.42
1.46	1.00	0.57
	2.00	0.81
	2.50	0.92
	3.00	1.04
	3.80	1.20, 1.18*
	4.00	1.29
1.96	1.00	0.46
	2.00	0.75
	2.50	0.82, 0.84*
	3.00	0.94
	3.50	1.04, 1.06*
	4.00	1.16

* Duplicate runs.

Table 2 The variation of rate constants (25 °C) for formation (k_f) and aquation (k_{aq}) steps in the equilibration of $[Mo_7S_8(H_2O)_{18}]^{8+}$ with NCS^-, $I = 2.00$ M (Lipts)

$[H^+]$/M	k_f/M^{-1} s^{-1}	10^3k_{aq}/s^{-1}
0.42	0.364	0.73
0.72	0.291	0.53
0.96	0.258	0.42
1.46	0.224	0.36
1.96	0.213	0.30

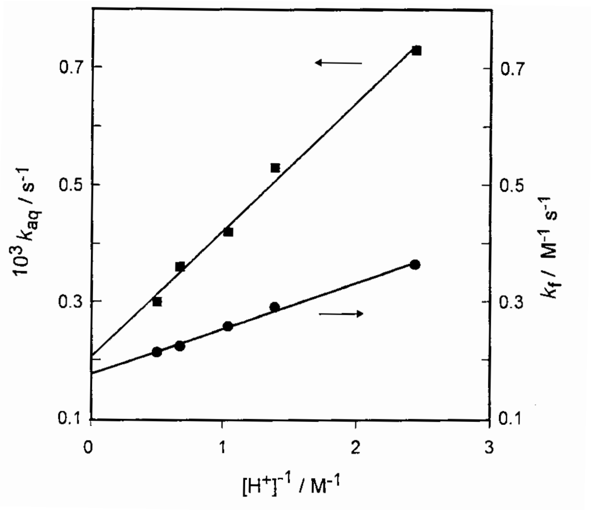


Fig. 4 Dependence of formation (k_f) and aquation (k_{aq}) rate constants (25 °C) on $[H^+]^{-1}$, $I = 2.00$ M (Lipts)

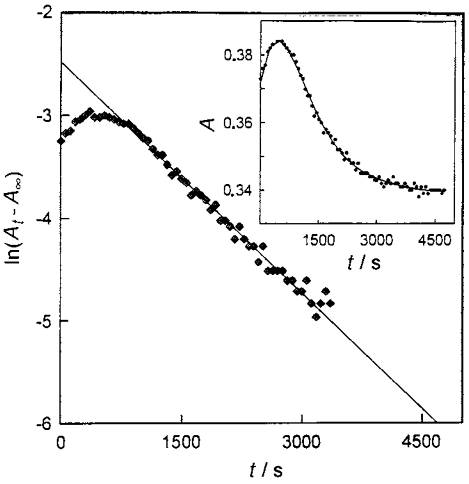


Fig. 5 First-order plot of UV/VIS absorbance (A) changes at 640 nm with time (25 °C) for the NCS^- (3.0×10^{-3} M) reaction with $[Mo_7S_8(H_2O)_{18}]^{8+}$ (4.0×10^{-5} M) at $[H^+] = 0.96$ M, $I = 2.00$ M (Lipts). The slope of the linear portion gives k_{eq} absorbance *vs.* time changes consistent with the two-stage reaction

$[NCS^-]$ in the range (2–4) $\times 10^{-3}$ M, $[H^+] = 0.96$ M, in good agreement with those obtained at 360 nm. The initial absorbance increase, inset Fig. 5, is independent of $[NCS^-]$, and an isomerisation step is proposed. Formation of N- and S-bonded products is proposed, equations (4) and (5), and isomerisation

$$Mo_7S_8^{8+} + NCS^- \underset{k_{aq}'}{\overset{k_f'}{\rightleftharpoons}} Mo_7S_8(NCS)^{7+} \tag{4}$$

$$Mo_7S_8^{8+} + NCS^- \underset{k_{aq}''}{\overset{k_f''}{\rightleftharpoons}} Mo_7S_8(SCN)^{7+} \tag{5}$$

as in equation (6). The isomerisation rates are slightly faster

$$Mo_7S_8(SCN)^{7+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mo_7S_8(NCS)^{7+} \tag{6}$$

than for formation and aquation, and this process is the first observable phase of reaction. Since crystal structures of thiocyanato complexes of Mo, *e.g.* $[Mo_3O_4(NCS)_8H_2O]^{4-}$,[18] $[Mo_3O_2S_2(NCS)_9]^{5-}$[19] and $[Mo_4S_4(NCS)_{12}]^{6-}$,[20] are N-bonded, the isomerisation process observed is assigned as a reaction from left to right in equation (6). Four runs were fitted all at $[H^+] = 0.96$, $I = 2.00$ M (Lipts). From fitting procedures carried out values of k_1 are $\approx 1.5 \times 10^{-3}$ s^{-1} and k_{-1} is an order of magnitude smaller at $\approx 3 \times 10^{-4}$ s^{-1}. The sum of the rate constants $k_f' + k_f''$ (range of values 0.16–0.35 M^{-1} s^{-1}) is in agreement with $a + b[H^+]^{-1}$ (0.252 M^{-1} s^{-1}) determined above, and $k_{aq}' + k_{aq}''$ of 3×10^{-4} s^{-1} is close to 4.2×10^{-4} s^{-1} from $a' + b'[H^+]^{-1}$ above. Owing to the need to include other $[NCS^-]$-dependent steps at higher values of $[NCS^-]$, we did not attempt to extend further these fitting procedures.

It was not possible to monitor runs with the reactant $[Mo_7S_8(H_2O)_{18}]^{8+}$ (2.3×10^{-4} M) in ten-fold excess (absorbance changes too small), in order to determine statistical factors applying.[4]

Kinetics of the $[Co(dipic)_2]^-$ oxidation of $[Mo_7S_8(H_2O)_{18}]^{8+}$

The kinetics monitored at 635 nm are relatively straightforward. With $[Co(dipic)_2]^-$ in large excess, single-phase absorbance changes are observed, and first-order plots linear to 80% completion give rate constants k_{obs} as in Table 3. A linear plot of k_{obs} against $[Co(dipic)_2^-]$ is observed, Fig. 6, with no dependence of k_{obs} on $[H^+]$ in the range 0.87–2.00 M. The slope gives $k_{Co} = 0.31 \pm 0.02$ M^{-1} s^{-1}. It is concluded that equation (7), giving transient $[Mo_7S_8(H_2O)_{18}]^{9+}$, is rate controlling and is

$$Mo_7S_8^{8+} + Co^{III} \longrightarrow Mo_7S_8^{9+} + Co^{II} \tag{7}$$

Table 3 First-order rate constants k_{obs} (25 °C) for the $[Co(dipic)_2]^-$ oxidation of $[Mo_7S_8(H_2O)_{18}]^{8+}$ (5.00 × 10^{-5} M), I = 2.00 M (Lipts)

$10^3[Co(dipic)_2^-]$/M	$[H^+]$/M	$10^3k_{obs}/s^{-1}$
1.00	2.00	0.22
2.00	2.00	0.57
3.00	0.87	0.96
	1.50	1.10
	2.00	1.04
4.00	2.00	1.38
5.00	2.00	1.55
7.00	2.00	2.22

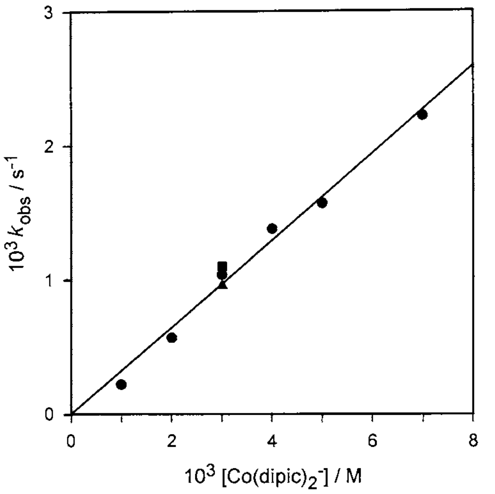


Fig. 6 Dependence of the first-order rate constants k_{obs} (25 °C) for the $[Co(dipic)_2]^-$ oxidation of $[Mo_7S_8(H_2O)_{18}]^{8+}$ on oxidant. The reaction is independent of $[H^+]$ = 0.87 (▲), 1.50 (■), 2.00 (●), I = 2.00 M (Lipts)

followed by reaction (8). Determination of the products and

$$Mo_7S_8^{\ 9+} \xrightarrow{\text{fast}} Mo_3S_4^{\ 4+} + Mo_4S_4^{\ 5+} \qquad (8)$$

stoichiometry were less straightforward. Thus for the reaction of $[Mo_7S_8(H_2O)_{18}]^{8+}$ (1.1 × 10^{-4} M) with $[Co(dipic)_2]^-$ (2.6 × 10^{-3} M) in 2.0 M HCl the products were separated after 3 h by Dowex 50W-X8 cation-exchange chromatography. Loading was carried out after diluting to $[H^+]$ = 0.2 M, and washing was with 0.2 M HCl. Unreacted $[Co(dipic)_2]^-$ was collected, and a stoichiometry of 7 (±10%) mol of $[Co(dipic)_2]^-$ to 1 of $[Mo_7S_8(H_2O)_{18}]^{8+}$ was obtained from UV/VIS spectrophotometry. Three other bands were eluted with 0.5 M HCl and UV/VIS spectra recorded. It was not possible to quantify the first (yellow) and second (pink) bands. The yellow band was identified as the Mo^V_2 ion $[Mo_2O_2(\mu\text{-}S)_2(H_2O)_6]^{2+}$, peak at 370 nm (ε = 1940 M^{-1} cm^{-1} per Mo_2). The pink band is tentatively assigned as $[Mo_3O_4(H_2O)_9]^{4+}$ (505 nm) and/or $[Mo_3SO_3(H_2O)_9]^{4+}$ (512 nm). A green band (peak at 603 nm) was quantified as 0.89 mol of $[Mo_3S_4(H_2O)_9]^{4+}$ per $[Mo_7S_8(H_2O)_{18}]^{8+}$, supportive of reaction (8). However, no $[Mo_4S_4(H_2O)_{12}]^{5+}$ product, peak at 645 nm (ε = 470 M^{-1} cm^{-1} per Mo_4) was detected. In separate experiments the further reaction of $[Mo_4S_4(H_2O)_{12}]^{5+}$ (≈1 mM) with $[Co(dipic)_2]^-$ (9.9 × 10^{-3} M) was studied, and the products determined by the same procedure. The products included yellow $[Mo_2O_2(\mu\text{-}S)_2(H_2O)_6]^{2+}$ (0.67 mol), a pink band peak at 505 nm (not quantified) and green $[Mo_3S_4(H_2O)_9]^{4+}$ (0.41 mol per mol of $[Mo_4S_4(H_2O)_{12}]^{5+}$). The reactions occurring cannot be summarised by a single equation, and there is a shortfall in the Mo detected, suggesting that Mo^{VI} may also be formed. The product pattern is similar to that previously reported for the decay of $[Mo_4S_4(H_2O)_{12}]^{6+}$, and intermediate formation of the 6+ cube is a strong possibility.[21]

Discussion

The double cube $[Mo_7S_8(H_2O)_{18}]^{8+}$ is of particular interest as the only example with a transition metal (M = Mo) at the nodal position. Heterometallic corner-shared double cubes $[Mo_6MS_8(H_2O)_{18}]^{8+}$ of p-block metals with M = Hg,[22] In,[23,24] Tl,[25] Sn,[26] Pb,[27] Sb[28] and Bi,[29] have been reported. In the case of $[Mo_7S_8(H_2O)_{18}]^{8+}$ there is evidence for Mo–Mo bonding. Thus Mo–Mo distances involving the nodal Mo (3.05 Å) indicate a considerably shorter separation than Mo–M for the d^{10} or higher heterometal atoms in double cubes with, *e.g.* Mo–Hg 3.88 in $[Mo_6HgS_8(H_2O)_{18}]^{8+}$,[22] Mo–In 3.45–3.81 in $[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$[23] and Mo–Sn 3.71 Å in $[Mo_6SnS_8(H_2O)_{18}]^{8+}$.[26] The same observation holds for heterometallic single cubes Mo_3M, which have short Mo–Fe (2.68) and Mo–Ni (2.64 Å) distances,[10] as compared with Mo–In (3.73)[30] and Mo–Sn (3.73 Å).[13]

In the case of the single cubes $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ and $[Mo_3InS_4(H_2O)_{12}]^{5+}$, conversion to double cubes can be achieved by addition of $[Mo_3S_4(H_2O)_9]^{4+}$ together with BH_4^- or H_3PO_2 as reducing agent, equations (9) and (10), yields 50–80%.[13,24] As far as reaction (11) is concerned, prior reduction of $[Mo_4S_4(H_2O)_{12}]^{5+}$ occurs, but only ≈3% addition as in equation (12). The reaction requires substitution of three H_2O molecules on one Mo of $[Mo_4S_4(H_2O)_{12}]^{4+}$ by three μ_2-S ligands of $[Mo_3S_4(H_2O)_9]^{4+}$. The low yield for this straightforward reaction is at first surprising, but is most likely due to the substitution inertness of $[Mo_4S_4(H_2O)_{12}]^{4+}$.[6]

$$Mo_3SnS_4^{\ 6+} + Mo_3S_4^{\ 4+} + 2e^- \longrightarrow Mo_6SnS_8^{\ 8+} \qquad (9)$$

$$Mo_3InS_4^{\ 5+} + Mo_3S_4^{\ 4+} + 1e^- \longrightarrow Mo_6InS_8^{\ 8+} \qquad (10)$$

$$Mo_4S_4^{\ 5+} + Mo_3S_4^{\ 4+} + e^- \longrightarrow Mo_7S_8^{\ 8+} \qquad (11)$$

$$Mo_4S_4^{\ 4+} + Mo_3S_4^{\ 4+} \longrightarrow Mo_7S_8^{\ 8+} \qquad (12)$$

The $[Mo_7S_8(H_2O)_{18}]^{8+}$ double cube is obtained in vastly improved yields of up to 20% by procedures described herein, the most successful of which involves treating $[Mo_3S_4(H_2O)_9]^{4+}$ with the reducing agent H_3PO_2. No advantage stems from using an Mo complex, *e.g.* $[MoCl_6]^{3-}$, $[Mo_2Cl_8]^{4-}$ or $[Mo_4S_4(H_2O)_{12}]^{4+}$, as reducing agent. A significant observation is that $[Mo_4S_4(H_2O)_{12}]^{5+}$, in amounts up to 60%, is produced alongside the $[Mo_7S_8(H_2O)_{18}]^{8+}$. A breaking down and reassembly of Mo_3S_4 units is required to explain the overall reaction yielding $[Mo_7S_8(H_2O)_{18}]^{8+}$ and $[Mo_4S_4(H_2O)_{12}]^{5+}$. The reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with vanadium metal is also of interest, since the metal does not react with H^+, and there must therefore be a reduction of $[Mo_3S_4(H_2O)_9]^{4+}$ at the metal surface, possibly with some incipient formation of an Mo_3VS_4 cluster. We have not as yet been able to identify such an intermediate by spectrophotometry.

It is also possible to use $[Mo_3S_7Br_6]^{2-}$, or the more inert polymeric $\{Mo_3S_7Br_4\}_x$, as a lead-in compound to obtain $[Mo_7S_8(H_2O)_{18}]^{8+}$ and $[Mo_4S_4(H_2O)_{12}]^{5+}$. This can be achieved directly by the use of H_3PO_2 as reductant. However a better procedure is to first use $\{Mo_3S_7Br_4\}_x$ as a source of $[Mo_3S_4(H_2O)_9]^{4+}$, when quite remarkable 80–90% yields are obtained. The polymeric material is prepared by heating the elements together (350 °C for 24 h) in a sealed quartz tube, and the product can then be converted into $[Mo_3S_7Br_6]^{2-}$ by treating with ammonium polysulfide, equation (13), followed by concentrated HBr, equation (14), in a relatively simple pro-

$$\{Mo_3S_7Br_4\}_x + S_n^{\ 2-} \xrightarrow[3\,h]{90\,°C} [Mo_3S_{13}]^{2-} \qquad (13)$$

Table 4 Comparison of rate and equilibrium constants (25 °C) for NCS^- substitution on $[Mo_7S_8(H_2O)_{18}]^{8+}$ with those obtained for the $[Mo_4S_4(H_2O)_{12}]^{n+}$ ions (n = 4–6), I = 2.00 M (Lipts)

Reaction	Assignment	$k_f/M^{-1}\ s^{-1}$	k_{aq}/s^{-1}	K/M^{-1}
(i) $[Mo_4S_4(H_2O)_{12}]^{4+}$	Mo^{III}	1.95	1.44×10^{-3}	1300
(ii) $[Mo_4S_4(H_2O)_{12}]^{5+}$	Mo^{III}	0.116	4.3×10^{-5}	2700
	Mo^{IV}	0.0166	5.0×10^{-6}	3300
(iii) $[Mo_4S_4(H_2O)_{12}]^{6+}$	$Mo^{III}Mo^{IV\,a}$	13.3	2.53×10^{-3}	5220
Conjugate-base path	$Mo^{III}Mo^{IV\,a}$	5.1^{b}	$1.08 \times 10^{-3\,c}$	4720
(iv) $[Mo_7S_8(H_2O)_{18}]^{8+}$	Not made	0.173	2.0×10^{-4}	870
Conjugate-base path	Not made	0.079^{b}	$2.2 \times 10^{-4\,c}$	360

[a] Substitution on a delocalised $Mo^{III}Mo^{IV}$, ref. 21. [b] Units s^{-1}. [c] Units $M\ s^{-1}$.

$$[Mo_3S_{13}]^{2-} \xrightarrow[30\ \text{min}]{30\ °C} [Mo_3S_7Br_6]^{2-} \qquad (14)$$

cedure. The S-abstraction reaction of $[Mo_3S_7Br_6]^{2-}$ with triphenylphosphine,[9] and aquation in 4 M Hpts to give $[Mo_3S_4(H_2O)_9]^{4+}$ gives the much improved route referred to. The procedure is based on a self-assembly process which yields initially the polymeric material with $Mo^{IV}{}_3$ units.

The corresponding Se (for S) studies have been carried out in an exploratory manner. Similar procedures can be used to prepare the Se cluster $[Mo_3Se_4(H_2O)_9]^{4+}$, as well as $[Mo_4Se_4(H_2O)_{12}]^{5+}$. The violet coloured corner-shared double cube $[Mo_7Se_8(H_2O)_{18}]^{8+}$ has also been obtained for the first time. The yields (and stability) are at present less than for $[Mo_7S_8(H_2O)_{18}]^{8+}$, but an extension to include the preparative route involving treatment of $[Mo_3Se_4(H_2O)_9]^{4+}$ with H_3PO_2 gives improved yields.

Using NCS^- to probe the substitution of H_2O on the double cube $[Mo_7S_8(H_2O)_{18}]^{8+}$, it has been shown that the latter has a substitution inertness comparable to $[Mo_4S_4(H_2O)_{12}]^{5+}$, Table 4. The 4+ and 6+ single cubes substitute one and two orders of magnitude faster respectively. Formation (k_f) and aquation (k_{aq}) rate constants for $[Mo_7S_8(H_2O)_{18}]^{8+}$ exhibit dependences on $[H^+]$ of the kind $a + b[H^+]^{-1}$. The 6+ but not the 4+ and 5+ single cubes exhibits a similar dependency on $[H^+]^{-1}$, in keeping with the greater tendency of water ligands on the 6+ and 8+ clusters to acid dissociate, *e.g.* equilibrium (15).[6,21] Formation of

$$[Mo_7S_8(H_2O)_{18}]^{8+} \rightleftharpoons [Mo_7S_8(H_2O)_{17}OH]^{7+} + H^+ \qquad (15)$$

a hydroxo conjugate-base form labilises water co-ordinated to the same Mo. The isomerisation step detected at 690 nm results from the ambidentate nature of NCS^-. Isomerisation steps have been observed previously for NCS^- substitution on $[Mo_4S_4(H_2O)_{12}]^{4+}$ ($1.17 \times 10^{-4}\ s^{-1}$ in 2 M $HClO_4$; 3.6×10^{-5} in 2 M Hpts)[6] and $[W_3S_4(H_2O)_9]^{4+}$ ($1.02 \times 10^{-4}\ s^{-1}$ in 2 M $HClO_4$),[31] which compare with $\approx 1.5 \times 10^{-3}\ s^{-1}$ for $[Mo_7S_8(H_2O)_{18}]^{8+}$ (in 2 M Hpts) in the present studies. The isomerisation is assigned to the formation of metastable S-bonded $Mo_7S_8(SCN)$, alongside $Mo_7S_8(NCS)$, and its isomerisation to $Mo_7S_8(NCS)$. Crystal structures of a range of Mo–thiocyanate complexes,[10,32] lend support to N-bonded forms being more stable. An unusual feature is that isomerisation occurs at a faster rate than complexation, and is observed as the first phase of reaction. The formation constants K obtained, Table 4, are less than for the single cubes in spite of the higher cationic charge.

The Sn and In containing double cubes, $[Mo_6SnS_8(H_2O)_{18}]^{8+}$ and $[Mo_6InS_8(H_2O)_{18}]^{8+}$, are converted into the corresponding single cube and $[Mo_3S_4(H_2O)_9]^{4+}$ using 1 : 1 amounts of $[Co(dipic)_2]^-$ as oxidant, equations (16) and (17).[13,24] Yields of up to 70% only of the heterometal cubes are obtained, because the oxidant reacts further with the single cubes $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ and $[Mo_3InS_4(H_2O)_{12}]^{6+}$ to give $[Mo_3S_4(H_2O)_9]^{4+}$ and Sn^{IV} or In^{III} as final products, equations (18) and (19). The double cube

$$Mo_6SnS_8{}^{8+} + 2Co^{III} \longrightarrow Mo_3SnS_4{}^{6+} + Mo_3S_4{}^{4+} + 2Co^{II} \qquad (16)$$

$$Mo_6InS_8{}^{8+} + Co^{III} \longrightarrow Mo_3InS_4{}^{5+} + Mo_3S_4{}^{4+} + Co^{II} \qquad (17)$$

$$Mo_3SnS_4{}^{6+} + 2Co^{III} \longrightarrow Mo_3S_4{}^{4+} + Sn^{IV} + 2Co^{II} \qquad (18)$$

$$Mo_3InS_4{}^{5+} + 2Co^{III} \longrightarrow Mo_3S_4{}^{4+} + In^{III} + 2Co^{II} \qquad (19)$$

$[Mo_7S_8(H_2O)_{18}]^{8+}$ gives a similar reaction sequence, equation (20), with the $[Mo_4S_4(H_2O)_{12}]^{5+}$ product undergoing further

$$Mo_7S_8{}^{8+} \longrightarrow Mo_7S_8{}^{9+} \xrightarrow{\text{fast}} Mo_4S_4{}^{5+} + Mo_3S_4{}^{4+} \qquad (20)$$

oxidation to $[Mo_4S_4(H_2O)_{12}]^{6+}$. The latter then fragments[21] with consumption of additional $[Co(dipic)_2]^-$, giving rise to the ≈7 : 1 stoichiometry.

To summarise, the preparative work highlights a self-assembly route in which polymeric $\{Mo_3S_7Br_4\}_x$ containing $Mo^{IV}{}_3$ units is obtained. This product provides a much more effective and quicker route to $[Mo_3S_4(H_2O)_9]^{4+}$, $[Mo_4S_4(H_2O)_{12}]^{5+}$ and $[Mo_7S_8(H_2O)_{18}]^{8+}$. Similar reactions have been demonstrated to occur with the Se polymeric form $\{Mo_3Se_7Br_4\}_x$. Studies on $[Mo_7S_8(H_2O)_{18}]^{8+}$ have provided evidence for substitution inert behaviour comparable to that of $[Mo_4S_4(H_2O)_{12}]^{5+}$.[6] No evidence for localised structures as in the case of $[Mo_4S_4(H_2O)_{12}]^{5+}$ (as $Mo^{III}{}_3Mo^{IV}$)[6] and $[Mo_4S_4(H_2O)_{12}]^{6+}$ (as $Mo^{III}Mo^{IV}$ pairs) was obtained.[21] Oxidation of $[Mo_7S_8(H_2O)_{18}]^{8+}$ with $[Co(dipic)_2]^-$ gives transient $[Mo_7S_8(H_2O)_{18}]^{9+}$ which fragments consuming further amounts of $[Co(dipic)_2]^-$, and giving a range of products similar to those obtained from $[Mo_4S_4(H_2O)_{12}]^{6+}$ (which is an intermediate).[21] To avoid the destabilising effect of high positive charge on such clusters, negatively charged ligands are required, as in the case of $[Re_4S_4(CN)_{12}]^{4-}$.[33]

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