

Chalcogenide-bridged cuboidal clusters with M_4Q_4 ($M = Mo, W$; $Q = S, Se, Te$) cores

Rita Hernández-Molina^a and A. Geoffrey Sykes^{*b}

^a Department of Inorganic Chemistry, University of La Laguna, 38200 La Laguna, Tenerife, Canary Islands, Spain

^b Department of Chemistry, The University of Newcastle, Newcastle upon Tyne, UK NE1 7RU

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Cuboidal cluster complexes having M_4Q_4 cores made up of transition and main group metals (M), and non-metallic e.g. chalcogenide elements (Q), constitute a rapidly expanding area of inorganic chemistry. Extensive preparation, structural and reactivity studies have been carried out on the Group 6 metals ($M = Mo, W$) and chalcogenide ($Q = S, Se, Te$) clusters, and are the main focus of this perspective. The aqueous solution chemistry provides an important reference point in considering redox and other relevant properties.

1 Introduction

Homometallic cuboidal clusters with bridging chalcogenide ligands ($Q = S, Se, Te$) are now known for a wide variety of transition metals such as Mo,¹ W,² Fe,³ Ru,⁴ Co,⁵ Rh,⁶ Ir,⁷ Ti,⁸ V,⁹ etc. The clusters of general formula $Mo_4S_4L_{12}$ with L ligands either neutral or anionic,^{1,10–14} have been known for some 20 years. The oxidation state of Mo within the clusters can vary from III to IV. The cubes $[Mo_4Q_4(H_2O)_{12}]^{4+/5+/6+}$ ($Q = S, Se$) have been prepared as aqua ions. The different states can be accessed by cyclic voltammetry as well as controlled redox interconversions.^{15,16} Also many examples of heterometallic clusters¹² are known, among them special attention has focused on the mixed-metal clusters formed by incorporation of a single metal atom into the metal depleted incomplete cube $[Mo_3S_4(H_2O)_9]^{4+}$. Solid state molybdenum compounds $Mo_4S_4X_4$ ($X = Cl, Br, I$) and MMo_4Q_8 ($M = Al, Ga, Q = S; M = Ga, Q = Se$) are known to contain Mo_4Q_4 cores with each Mo octahedrally coordinated by three chalcogen and three halogen atoms or six chalcogen atoms.^{17–19}

In this review, M_4Q_4 cores are referred to as cube, distorted cube or cuboidal shapes, and reference to cubane (the C_8H_8 molecule) is avoided. The cubes are distorted having two interpenetrating tetrahedra M_4 and Q_4 of different dimensions. The metal atoms are octahedrally coordinated.

Much of the interest in the chemistry of molybdenum–sulfur cluster complexes derives from their relevance in a number of interdisciplinary areas. These range from the bioinorganic chemistry of Mo/S and W/S(Se) containing enzymes^{20,21} to the synthesis of highly dispersed/amorphous metal chalcogenides, which are important catalysts for hydrogenation/dehydrogenation reactions as well as C–S bond formation i.e. crude-oil hydrodesulfurization (HDS) processes.^{22,23}

A number of reviews on chalcogenide-bridged clusters are referenced.^{1,3,11–14,24} The present review focusses on the chemistry of Mo/W incomplete cubes M_3Q_4 ($M = Mo, W; Q = S, Se$), which are considered first, and cubes M_4Q_4 ($M = Mo, W; Q = S, Se, Te$). The emphasis is on aqueous solution chemistry. As compared to molybdenum the number of tungsten chalcogenide cuboidal clusters is limited, and the aqua ions $[W_4S_4(H_2O)_{12}]^{4+/5+/6+}$ have not as yet been reported.

2 Incomplete cuboidal clusters with M_3Q_4 cores

2.1 Preparation and structural information

The first cluster reported as having an Mo_3S_4 core was the cyclopentadienyl complex $[Mo_3S_4Cp_3]^+$.²⁵ Subsequently clusters with three anionic or neutral ligands instead of Cp coordinated to each Mo of Mo_3S_4 were prepared. If Mo–Mo bonds are ignored, the Mo atoms are hexa-coordinated and in a distorted octahedral environment (angles $\approx 10^\circ$ from regular geometries).



Dr Rita Hernández-Molina

Dr R. Hernández-Molina was born in La Palma (Canary Islands) in 1965. She obtained her first degree at the University of La Laguna (Tenerife) in 1988 and her Ph.D at the University of La Laguna in 1995, under the supervision of Professor A. Mederos and Professor P. Gili. She joined Professor Sykes' group in Newcastle as a post-doctoral researcher in 1996. Currently she is a Lecturer in Inorganic Chemistry at the University of La Laguna. Current research interests include the chalcogenide-bridged cluster complexes.



Professor A. G. Sykes

Professor A. G. Sykes FRS has BSc, Ph.D, and DSc degrees in chemistry from the University of Manchester where he researched under the supervision of Professor W. C. E. Higginson. After post-doctoral work in Princeton and Adelaide he was appointed a Lecturer at the University of Leeds, became a Reader in 1970 and moved to the Chair of Inorganic Chemistry at the University of Newcastle upon Tyne in 1980. His research interests are in the area of kinetic/mechanistic studies of inorganic and bioinorganic (metalloprotein) reactions, with studies on Mo/W aqueous solution chemistry a long term interest.

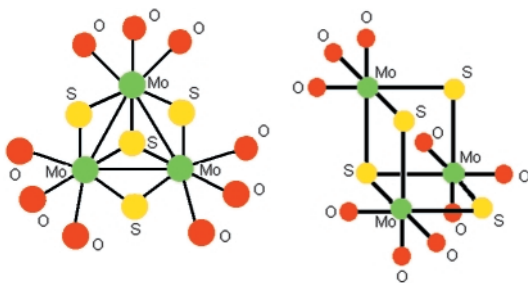


Fig. 1 Two alternative views of the trinuclear cluster $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$, the structure is also adopted by $[\text{W}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$.

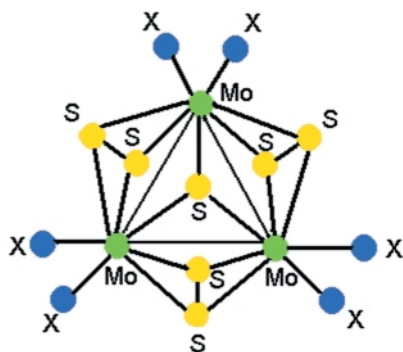
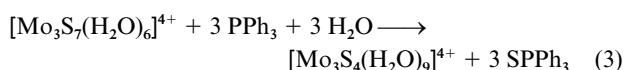
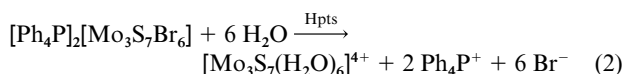


Fig. 2 The structure of $[\text{Mo}_3\text{S}_7\text{X}_6]^{2-}$ ($\text{X} = \text{Cl}^-, \text{Br}^-$), also applies to $[\text{W}_3\text{S}_7\text{Br}_6]^{2-}$.

The three molybdenum atoms are in oxidation state IV and this framework is remarkably stable. The trinuclear species are electron-precise, and contain the required number of electrons (six) necessary to give three Mo–Mo bonds. The triangular Mo_3 core is capped by a μ_3 -S atom and the Mo–Mo edges are bridged by μ -S (Fig. 1). Alternatively the cores can be referred to as one metal depleted incomplete cube forms.

A procedure involving the reduction of the di- μ -sulfido Mo_2^{V} cysteinato complex $[\text{Mo}_2\text{O}_2\text{S}_2(\text{cys})_2]^{2-}$ with NaBH_4 in diluted HCl (under N_2), followed by air oxidation,^{26,27} and purification by Dowex 50W-X2 cation-exchange chromatography gives the green cuboidal cluster $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$. Yields of up to 20% can be achieved.²⁸ Heating of such solutions in 1 M HCl to $\approx 90^\circ\text{C}$ for 10 h results in air oxidation with loss of one Mo, and formation of the green incomplete cube $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$.

However a greatly improved method for the preparation of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ from polymeric $\{\text{Mo}_3\text{S}_7\text{Br}_4\}_x$ has been described.^{29,30} This reaction is simpler than that from Mo_2^{V} and gives much better yields. Polymeric $\{\text{Mo}_3\text{S}_7\text{Br}_4\}_x$ is prepared³⁰ by heating mixtures of the elements in a sealed glass ampoule to $\approx 350^\circ\text{C}$. The polymeric compound is then heated (under N_2) with Ph_4PBr ($\approx 250^\circ\text{C}$) for 3 h to convert it into the water-soluble compound $[\text{Ph}_4\text{P}]_2[\text{Mo}_3\text{S}_7\text{Br}_6]$,^{31,32} the structure of which is shown in Fig. 2. The Br^- can be aquated with 4 M Hpts (pts⁻ = *p*-toluenesulfonate), and the S_7 converted to S_4 by S abstraction with PPh_3 in dichloromethane. Relevant equations to these processes are as in (1), (2) and (3).



The aqueous solution is again purified by Dowex 50W-X2 chromatography giving $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ in good yield (80%). A similar procedure,^{30,33} has been reported for the preparation of yellow-brown $[\text{Mo}_3\text{Se}_4(\text{H}_2\text{O})_9]^{4+}$ from polymeric $\{\text{Mo}_3\text{Se}_7$

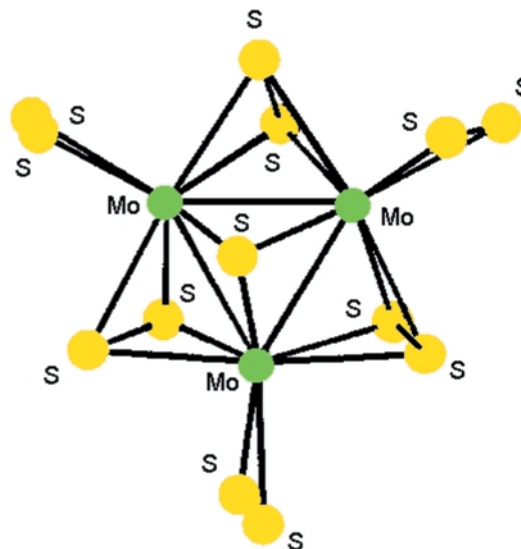


Fig. 3 The structure of $[\text{Mo}_3\text{S}_{13}]^{2-}$.

$\text{Br}_4\}_x$.³³ The reaction of $[\text{Ph}_4\text{P}]_2[\text{Mo}_3\text{Se}_7\text{Br}_6]$ with PPh_3 is slower than for the S analogue and longer reaction times are required for Se abstraction.

In another related reaction³⁴ $[\text{Mo}_3\text{S}(\text{S}_2)_6]^{2-}$ (Fig. 3) can be reacted with CN^- and results in the formation of $[\text{Mo}_3\text{S}_4(\text{CN})_9]^{5-}$ as in eqn. (4).



The crystal structure of $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9] \cdot 3\text{KCN} \cdot 4\text{H}_2\text{O}$ has been determined by X-ray diffraction. In the trinuclear cluster the Mo–Mo bond distances are 2.775 Å, with each Mo atom surrounded by a distorted octahedral array of three CN^- groups and three sulfur atoms. Many other derivatives have been prepared by replacement of H_2O .²⁴ It is however difficult to replace the CN^- . The existence of the $\text{Mo}_3\text{S}_4^{4+}$ core has been confirmed by X-ray structure analysis on a number of complexes (Table 1).^{1,11}

The trinuclear complex $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ can be stored over long periods (years!) in air, the only prerequisite being that $[\text{H}^+]$ should be above 0.3 M so that the OH^- conjugate-base form and oligomerisation do not become relevant. Interestingly, addition of BH_4^- to $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ followed by cation-exchange chromatography yields $\mu\text{-O}^{2-}$ for $\mu\text{-S}^{2-}$ products.³⁵ Thus, $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ can be a source of $[\text{Mo}_3\text{OS}_3(\text{H}_2\text{O})_9]^{4+}$ and $[\text{Mo}_3\text{O}_2\text{S}_2(\text{H}_2\text{O})_9]^{4+}$ on a preparative scale. The derivatives of the $[\text{Mo}_3\text{O}_3\text{S}(\text{H}_2\text{O})_9]^{4+}$ incomplete cube have also been prepared and a μ_3 -sulfido structure is indicated (Fig. 4 and 5 of ref. 11).

Similarly the trinuclear complex $[\text{Mo}_3\text{Se}_4(\text{H}_2\text{O})_9]^{4+}$ is obtained¹⁵ by NaBH_4 reduction of $[\text{Mo}_2\text{O}_2\text{Se}_2(\text{cys})_2]^{2-}$ in HCl solutions. The products from cation-exchange chromatography give several bands corresponding to trinuclear $[\text{Mo}_3\text{O}_2\text{Se}_2(\text{H}_2\text{O})_9]^{4+}$, $[\text{Mo}_3\text{OSe}_3(\text{H}_2\text{O})_9]^{4+}$ and $[\text{Mo}_3\text{Se}_4(\text{H}_2\text{O})_9]^{4+}$, and cuboidal $[\text{Mo}_4\text{Se}_4(\text{H}_2\text{O})_{12}]^{5+}$. The yield of the last two products is $\approx 10\%$. The crystal structure of $[\text{NMe}_4]_5[\text{Mo}_3\text{Se}_4(\text{NCS})_9]$ has been reported.¹⁵ The Mo–Mo bond lengths of 2.82 Å are consistent with metal–metal bonding. For $\text{Mo}_3\text{S}_4^{4+}$ structures (Table 1) the Mo–Mo distance is 2.76 Å, with smaller distances between Mo– μ_3 -S (2.34 Å) and Mo– μ -S (2.29 Å). The Mo– μ_3 -Se (2.45 Å) and Mo– μ -Se (2.41 Å) bond lengths are consistent with the 0.14 Å larger ionic radius of selenide compared with sulfide.¹⁵

Trinuclear $[\text{W}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ can be prepared³⁶ by NaBH_4 reduction of yellow $[\text{NH}_4]_2[\text{WS}_4]$. Using Dowex purification different products including $[\text{W}_3\text{S}_2\text{O}_2(\text{H}_2\text{O})_9]^{4+}$, $[\text{W}_3\text{OS}_3(\text{H}_2\text{O})_9]^{4+}$, and $[\text{W}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ were separated. In this preparation the yield of the latter was $\approx 25\%$. Alternatively, $[\text{W}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ can

Table 1 Structural parameters (Å) for incomplete cubes with M_3Q_4 cores ($M = Mo, W; Q = S, Se$)

Cluster	M–M	M– μ_3 -S	M– μ_2 -S	M–L	Ref.
$[Mo_3S_4Cp_3][Sn(CH_3)_3Cl]$	2.812(1)	2.314(6)	2.294(6)	2.030(7)	11
$K_5[Mo_3S_4(CN)_9] \cdot 3KCN \cdot 4H_2O$	2.775(8)	2.363(7)	2.322(10)	2.189(10) ^b 2.220(3) ^c	11
$K_5[Mo_3S_4(CN)_9] \cdot 7H_2O$	2.765(7) 2.194(17) ^d	2.363(4)	2.312(5)	2.159(13) ^b	11
$Ca[Mo_3S_4(ida)_3] \cdot 11H_2O$	2.754(11)	2.348(9)	2.294(8)	2.166(13), O 2.274(5), N	11
$[NH_4]_3[Mo_3S_4(Hnta)_2(nta)] \cdot 3EtOH$	2.769(1)	2.344(5)	2.298(3)		11
$[Mo_3S_4(H_2O)_9][pts]_4 \cdot 9H_2O$	2.732(7)	2.332(4)	2.286(6)	2.190(14), O	11
$[bpyH]_5[W_3S_4(NCS)_9] \cdot 3H_2O$	2.767(4)	2.363(12)	2.310(7)	2.153(32), N	11
$[W_3S_4(H_2O)_9][pts]_4 \cdot 7H_2O^a$	2.723(15)	2.351(3)	2.283(5)	2.176(17), O	11
$[MoW_2S_4(H_2O)_9][pts]_4 \cdot 9H_2O$	2.723(6)	2.342(13)	2.284(5)	2.187(17), ^b O 2.172(15), ^c O	48
$[Mo_2WS_4(H_2O)_9][pts]_4 \cdot 9H_2O$	2.728(6)	2.332(6)	2.283(7)	2.190(12), ^b O 2.181(19), ^c O	48
$Na_2[MoW_2S_4(Hnta)_3] \cdot 5H_2O$	2.749(19)	2.348(4)	2.304(9)	2.110(17), O 2.311(9), N	48
$Na_2[Mo_2WS_4(Hnta)_3] \cdot 5H_2O$	2.754(20)	2.341(3)	2.295(12)	2.110(9), O 2.311(9), N	48
$Cs[W_3Se_4(CN)_9] \cdot CsCl \cdot 4H_2O$	2.829(3)	2.497(3)	2.449(3)	2.178(15), C	49
$[NMe_4]_5[Mo_3Se_4(NCS)_9]$	2.817(6)	2.453(6)	2.409(6)	2.19, N	15
$[Me_3NH]_5[W_3Se_4(NCS)_9]$	2.795(3)	2.458(5)	2.388(5)	2.18	45

Cp = cyclopentadienyl, ida = iminodiacetate, nta = nitrilotriacetate. ^a Other samples obtained give 9H₂O. ^b *trans* to μ_3 -S. ^c *cis* to μ -S. ^d *cis* to μ_3 -S.

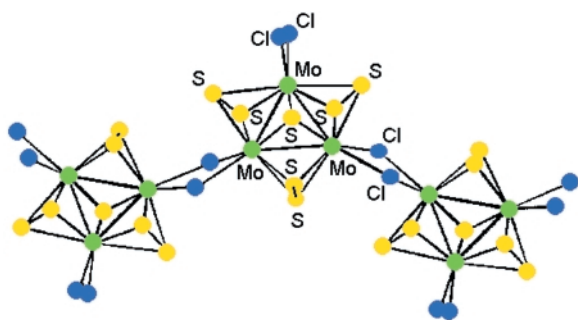


Fig. 4 The structure of polymeric $\{Mo_3S_7Cl_4\}_x$, also applies to $\{W_3S_7Br_4\}_x$.

be prepared³⁷ by heating polymeric $\{W_3S_7Br_4\}_x$ ³⁸ (Fig. 4) with excess of hypophosphorous acid (H_3PO_2) at $\approx 90^\circ C$ in concentrated HCl for 15 h. Dowex purification led to purple $[W_3S_4(H_2O)_9]^{4+}$ as the single product. This method is quicker and more efficient than the one from $[NH_4]_3[WS_4]$ and consequently is the preferred route to $[W_3S_4(H_2O)_9]^{4+}$. Other preparative routes to $M_3S_4^{4+}$ ($M = Mo, W$) have been reviewed.²⁴ Several crystal structures of the W_3S_4 core with different terminal ligands have been reported^{39–44} including the aqua ion $[W_3S_4(H_2O)_9][pts]_4 \cdot 9H_2O$.³⁶ The average W–W distance is 2.708 Å. The $[W_3S_4(H_2O)_9]^{4+}$ complex does not store as well as $[Mo_3S_4(H_2O)_9]^{4+}$, and slow air oxidation with loss of S^{2-} is observed.

From crystallographic studies the Mo_3S_4 and W_3S_4 cores have very similar dimensions, thus the average metal–metal distances are 2.76 Å (average of 31 molybdenum structures) and 2.75 Å (average of 3 tungsten structures), respectively (Table 1). This is in keeping with the identical radii for Mo and W brought about by the lanthanide contraction.

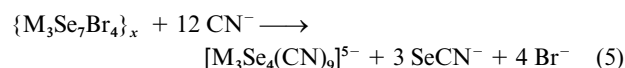
In 1992, Fedin *et al.* reported the preparation and crystal structure of the first $W_3Se_4^{4+}$ complex⁴⁵ $[Me_3NH]_5[W_3Se_4(NCS)_9]$. This preparation involves the reaction of $\{W_3Se_7Br_4\}_x$ with ammonium polysulfide $(NH_4)_2S_x$, treatment with concentrated HCl, and addition of NCS^- and Me_3NH^+ . However, green $[W_3Se_4(H_2O)_9]^{4+}$ is much better prepared in good yield³⁷ by treatment of $\{W_3Se_7Br_4\}_x$ ^{38,46} with H_3PO_2 .

Reduction of an equimolar mixture of ammonium tetrasulfidotungstate(vi), $[NH_4]_2[WS_4]$ and the Mo_2^V -cysteine complex, $Na_2[Mo_2O_2S_2(cys)_2] \cdot 4H_2O$, with $NaBH_4$ gives a mixture of sulfido-bridged clusters from which chromatographic separ-

ation^{47,48} gives the mixed-metal incomplete cubes $[Mo_2WS_4(H_2O)_9]^{4+}$ and $[MoW_2S_4(H_2O)_9]^{4+}$. The aqua coordinated clusters $[Mo_2WS_4(H_2O)_9][pts]_4 \cdot 9H_2O$, $[MoW_2S_4(H_2O)_9][pts]_4 \cdot 9H_2O$ and derivatives $Na_2[MoW_2S_4(Hnta)_3] \cdot 5H_2O$ and $Na_2[Mo_2WS_4(Hnta)_3] \cdot 5H_2O$ have been characterised by X-ray diffraction.⁴⁸ The W and Mo atoms are disordered in the structures of the two aqua ions with M–M distances 2.728(6) and 2.723(6), respectively.

The UV-vis spectrophotometric details for $[Mo_xW_{3-x}S_4(H_2O)_9]^{4+}$ ($x = 0–3$) and $[M_3Se_4(H_2O)_9]^{4+}$ ($M = Mo, W$) are collected in Table 2. The sulfur-bridged species $[Mo_xW_{3-x}S_4(H_2O)_9]^{4+}$ are stable in acidic solution, but the selenium analogues are less stable, giving after 1 week a deposit of red selenium. Solutions of $[M_3Se_4(H_2O)_9]^{4+}$ ($M = Mo, W$) are however more stable under N_2 at $\approx 4^\circ C$, with no spectrophotometric changes observed over ≈ 1 month.

The cyano complexes of the incomplete cubes⁴⁹ $[Mo_3Se_4(CN)_9]^{5-}$ and $[W_3Se_4(CN)_9]^{5-}$ have been prepared by reacting polymeric $\{M_3Se_7Br_4\}_x$ or $[M_3Se_7Br_6]^{2-}$ ($M = Mo, W$) with CN^- , eqn. (5). The crystal structures of $Cs_5[M_3Se_4(CN)_9] \cdot$



$CsCl \cdot 4H_2O$ salts ($M = Mo, W$) are isomorphous. A different feature as compared to the sulfur analogues is the weak dimerization of two trinuclear units giving short $Se \cdots Se$ (≈ 3.5 Å) contacts. This has also been observed for the $[W_3Se_4(NCS)_9]^{5-}$ anion.⁴⁵

While the incomplete cubes $M_3Q_4^{4+}$ ($M = Mo, W; Q = S, Se$) have been prepared by different methods, the preparation of $M_3Te_4^{4+}$ ($M = Mo, W$) using similar procedures has not so far been achieved. In aqueous solution the reaction of CN^- with $\{Mo_3Te_7I_4\}_x$ gives $[Mo_3Te_7(CN)_6]^{2-}$ and not $[Mo_3Te_4(CN)_9]^{5-}$.

2.2 Electrochemical properties

A cyclic voltammogram for $[Mo_3S_4(CN)_9]^{5-}$ has been reported and the reduction potential for the $Mo_3^{IV} + e^- \rightleftharpoons Mo_3^{III}$ - Mo_2^{IV} change reported to be⁵⁰ -1.49 V vs. NHE.

Reduction potentials⁴⁹ for the cyano complexes $[M_3Se_4(CN)_9]^{5-}$ ($M = Mo, W$) associated with the $M_3^{IV} + e^- \rightleftharpoons M_3^{III}$ - M_2^{IV} change of -0.63 (Mo) and -0.97 V (W) vs. NHE indicate that the Mo derivative is more readily reduced.

Cyclic voltammetry⁴⁸ on $[Mo_xW_{3-x}S_4(Hnta)_3]^{3-}$ ($nta^{3-} =$

Table 2 Summary of UV/vis/NIR peak positions for Mo/W chalcogenide-bridged cuboidal clusters as aqua ions

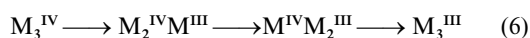
Clusters	Acid	λ/nm ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$)	Ref.
[Mo ₃ S ₄ (H ₂ O) ₉] ⁴⁺	2 M Hpts	366 (5550); 603 (362)	33
	2 M HCl	370 (4995); 616 (326)	33
[Mo ₃ Se ₄ (H ₂ O) ₉] ⁴⁺	2 M Hpts	427 (5820); 646 (595)	33
	2 M HCl	433 (5250); 681 (580)	33
[W ₃ S ₄ (H ₂ O) ₉] ⁴⁺	2 M Hpts	315 (6350); 560 (446)	33
	2 M HCl	317 (6100); 570 (480)	33
[W ₃ Se ₄ (H ₂ O) ₉] ⁴⁺	2 M Hpts	359 (6660); 618 (547)	33
	2 M HCl	360 (6950); 625 (500)	33
[Mo ₂ WS ₄ (H ₂ O) ₉] ⁴⁺	2 M Hpts	340 (4390); 490 (sh) (298); 590 (322)	53
[MoW ₂ S ₄ (H ₂ O) ₉] ⁴⁺	2 M Hpts	325 (5420); 490 (sh) (320); 570 (363)	53
[Mo ₄ S ₄ (H ₂ O) ₁₂] ⁴⁺	2 M HClO ₄	378 (1100)	87
	2 M HCl	375 (1120)	87
[Mo ₄ S ₄ (H ₂ O) ₁₂] ⁵⁺	2 M Hpts	635 (435); 1100 (122)	53
	2 M HCl	330 (sh) (4380); 380 (sh) (1140); 647 (444); 1116 (120)	
[Mo ₄ S ₄ (H ₂ O) ₁₂] ⁶⁺	2 M Hpts	467 (1395); 556 (1280); 935 (295)	78
	2 M HCl	575 (460); 990 (150)	
[Mo ₄ Se ₄ (H ₂ O) ₁₂] ⁵⁺	2 M Hpts	425 (sh) (669); 662 (407); 1188 (117)	53
[Mo ₃ WS ₄ (H ₂ O) ₁₂] ⁵⁺	2 M Hpts	611 (499); 1038 (188)	53
[Mo ₂ W ₂ S ₄ (H ₂ O) ₁₂] ⁵⁺	2 M Hpts	560 (534); 1020 (168)	53
[MoW ₃ S ₄ (H ₂ O) ₁₂] ⁵⁺	2 M Hpts	522 (660); 850 (200)	53
[MoW ₃ Se ₄ (H ₂ O) ₁₂] ⁵⁺	2 M Hpts	514 (sh) (690); 874 (160)	53
[Mo ₇ S ₈ (H ₂ O) ₁₈] ⁸⁺	2 M Hpts	416 (7190); 480 (sh) (9065); 518 (10280); 635 (8860); 950 (4242)	29
[Mo ₇ Se ₈ (H ₂ O) ₁₈] ⁸⁺	2 M Hpts	407 (7200); 579 (9700)	29

Table 3 Reduction potentials^{a,b} vs. NHE for [Mo_{3-x}W_xS₄(H₂O)₉]⁴⁺ ($x = 0-3$)^a in 0.1 M KCl at pH 11.4 with 0.025 M phosphate buffer

Cluster	$E_{1/2}/\text{V}$		
	IV,IV,IV/IV,IV,III	IV,IV,III/IV,III,III	IV,III,III/III,III,III
K ₂ [Mo ₃ S ₄ (Hnta) ₃] \cdot 9H ₂ O	-0.42	-0.86	-1.17 ^c
Na ₂ [Mo ₂ WS ₄ (Hnta) ₃] \cdot 5H ₂ O	-0.51	-1.00	-1.44 ^c
Na ₂ [MoW ₂ S ₄ (Hnta) ₃] \cdot 5H ₂ O	-0.62	-1.18	-1.56 ^c
K ₂ [W ₃ S ₄ (Hnta) ₃] \cdot 10H ₂ O	-0.90	-1.19	-1.66 ^c

^a Values in ref. 48 vs. Ag-AgCl have been converted to the above by addition of 0.222 V. ^b Obtained from sampled dc polarograms. ^c Accompanied by the catalytic hydrogen wave.

nitrotriacetate; $x = 0-3$) incomplete cubes, show three consecutive one-electron reduction steps corresponding to changes in oxidation state which can be written as in eqn. (6).



Reduction potentials vs. NHE for each couple are collected in Table 3. In all cases the [Mo_xW_{3-x}S₄(Hnta)₃]³⁻ clusters ($x = 0-3$) are more readily reduced with increasing number of Mo atoms.

Though mixed-valent reduced species might be generated in this way, only one example [Mo₃S₄Cl₃(dppe)₂(PET₃)] [dppe = 1,2-bis(diphenylphosphino)ethane] has been isolated and structurally characterised.⁵¹ The Mo-Mo bond is elongated to 2.806 Å.

2.3 Core transformations

Incomplete cubes [M₃Q₄(H₂O)₉]⁴⁺ (M = Mo, W; Q = S, Se) with a vacant metal subsite are the lead-in compounds for a series of heterometallic cuboidal clusters. Thus, 16 different heterometals (Cr,⁵² W,⁵³ Fe,⁵⁴ Co,⁵⁵ Ni,⁵⁶ Pd,⁵⁷ Cu,⁵⁸ Hg,⁵⁹ Ga,⁶⁰ In,⁶¹ Tl,⁶² Sn,⁶³ Pb,⁶⁴ As,⁶⁵ Sb,⁶⁶ Bi⁶⁷), members of Group 6 to Group 15, have been incorporated into [Mo₃S₄(H₂O)₉]⁴⁺. However to date only 6 metals (Ni,⁶⁸ Cu,⁶⁹ In,⁷⁰ Ge,⁷⁰ Sn,^{70,71} Mo⁵³) are known to give heterometallic derivatives of [W₃S₄(H₂O)₉]⁴⁺. This can be attributed to the greater difficulty in reducing W as compared to Mo. Recently incorporation of Sn into the selenide-bridged incomplete cubes [Mo₃Se₄(H₂O)₉]⁴⁺ and [W₃Se₄(H₂O)₉]⁴⁺ has been achieved.^{33,37} There exist three core types to consider, the single cubes Mo₃MS₄ (Fig. 5), edged-

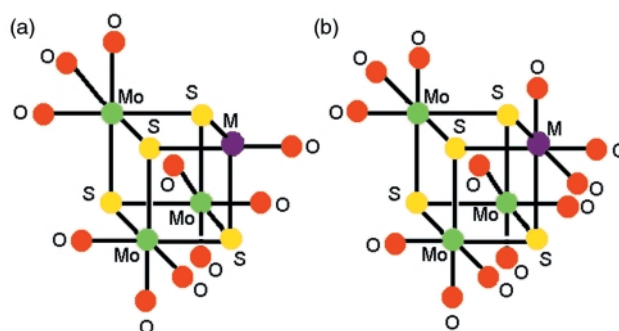


Fig. 5 Structures of the heterometallic single cubes Mo₃MS₄ derived from [Mo₃S₄(H₂O)₉]⁴⁺ with (a) tetrahedral heterometal and (b) octahedral heterometal.

linked double cubes {Mo₃MS₄}₂ (Fig. 6), and corner-shared double cubes {Mo₃S₄}M{S₄Mo₃} (Fig. 7). The corner-shared double-cube structure is most common for main group heterometals, and this product is not obtained with a transition metal except in the case of [Mo₇S₈(H₂O)₁₈]⁸⁺ (M = Mo in Fig. 7). Instead both the Mo₃ and W₃ incomplete cubes give single cubes (M = Cr, W, Fe, Co, Ni, Pd, Cu) or edged-linked double cubes (M = Co, Pd, Cu).

2.4 Kinetics studies

Studies on the substitution of coordinated H₂O of [Mo₃S₄(H₂O)₉]⁴⁺ by NCS⁻ (also Cl⁻ and H₂O) have been reported.^{72,73} The clusters have different types of H₂O ligands, which are one H₂O/Mo *trans* to μ_3 -S (c), and two H₂O's/Mo *trans* to μ -S (d) as

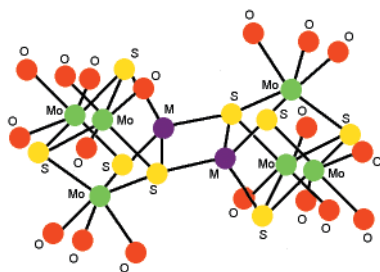


Fig. 6 Structure of the heterometallic edge-linked double cube $\{Mo_3MS_4\}_2$ derived from $[Mo_3S_4(H_2O)_9]^{4+}$.

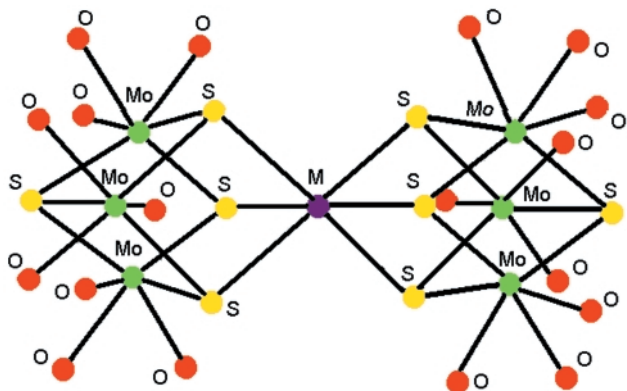


Fig. 7 Structure of the heterometallic corner-shared double cube $\{Mo_3S_4\}M\{Mo_3S_4\}$ derived from $[Mo_3S_4(H_2O)_9]^{4+}$.

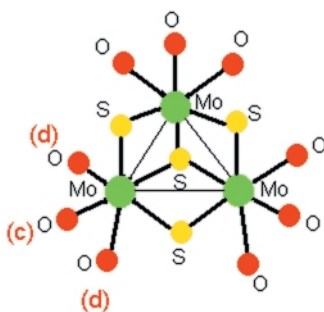


Fig. 8 The structure of $[Mo_3S_4(H_2O)_9]^{4+}$ showing two different types of coordinated H_2O which are *trans* to the core μ_3 -S (c) or μ -S (d).

illustrated in Fig. 8. The d positions are $\approx 10^5$ times more labile than c and the stopped-flow first stage of substitution proceeds by a rate law $a + b[H^+]^{-1}$. The b term is attributable to the presence of the monohydroxo conjugate-base $Mo_3S_4(OH)^{3+}$. Once one of the d H_2O 's has been replaced the conjugate-base mechanism can no longer contribute. NMR studies provide evidence for two additional stages, the slower replacement of the second d- H_2O and the replacement of the c- H_2O .

Chloride substitution⁷⁴ on $[Mo_3S_4(H_2O)_9]^{4+}$ is also biphasic but much less favourable thermodynamically than with NCS^- . Formation constants of $K = 3.24$ (first stage) and $1.85 M^{-1}$ (second stage), have been reported⁷⁴ for Cl^- . With NCS^- the corresponding values are 2300 (first) and $2150 M^{-1}$ (second).⁷²

The same behaviour has been observed for $[W_3S_4(H_2O)_9]^{4+}$,⁷⁴ $[Mo_2WS_4(H_2O)_9]^{4+}$ ⁴⁷ and $[MoW_2S_4(H_2O)_9]^{4+}$.⁴⁷ For $[Mo_2WS_4(H_2O)_9]^{4+}$ and $[MoW_2S_4(H_2O)_9]^{4+}$ statistical factors of 2 and 1, respectively are consistent with a first stage involving substitution at the Mo. In Table 4, rate constants for NCS^- substitution of incomplete cubes $[Mo_xW_{3-x}S_4(H_2O)_9]^{4+}$ ($x = 0-3$) are listed. It can be seen that rate constants for substitution at the Mo and W of the W_2Mo and WMo_2 are little changed and within 50% of values for the homonuclear trinuclear clusters. The X-ray crystallographic studies on NCS^- complexes of Mo and W show a strong preference for N-bonded thiocyanate. An isomerisation process as illustrated in eqn. (7) has however

Table 4 Summary^a of rate and equilibrium constants (25 °C) for the substitution of H_2O by NCS^- at Mo and W in the trinuclear complexes $[Mo_xW_{3-x}S_4(H_2O)_9]^{4+}$ ($x = 1-3$), $[H^+] = 2.00 M$, $I = 2.00 M$ ($HClO_4$)

Cluster	$k_f/M^{-1} s^{-1}$		k_{aq}/s^{-1}		K/M^{-1}	
	Mo	W	Mo	W	Mo	W
$[Mo_3S_4(H_2O)_9]^{4+}$	212 ^b		0.092		2300	
$[W_3S_4(H_2O)_9]^{4+}$ ^c		38		0.025		1520
$[Mo_2WS_4(H_2O)_9]^{4+}$	300		0.10		3000	1040
$[MoW_2S_4(H_2O)_9]^{4+}$	171		0.036		4750	
		39		0.020		1950

^a Values taken from ref. 47. ^b $[NCS^-]$ -dependent and $[H^+]$ -independent second stage assigned as substitution of second d- H_2O gives $k_f = 1.24 M^{-1} s^{-1}$, $k_{aq} = 5.8 \times 10^{-4} s^{-1}$, $K = 1370 M^{-1}$. ^c $[NCS^-]$ -independent second stage assigned as isomerisation of co-ordinated NCS^- , $k_1 = 1.0 \times 10^{-4} s^{-1}$.

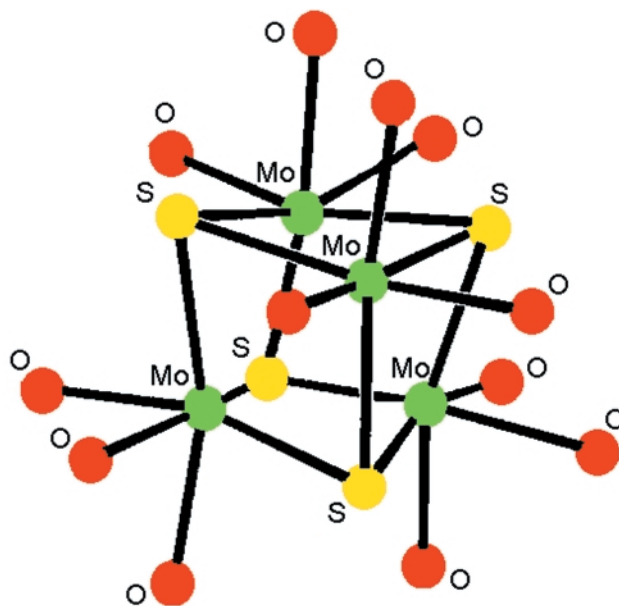
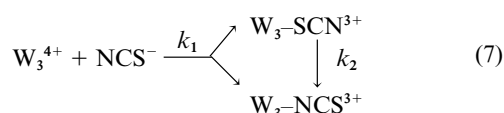


Fig. 9 The structure of the aqua ion $[Mo_4S_4(H_2O)_{12}]^{5+}$.

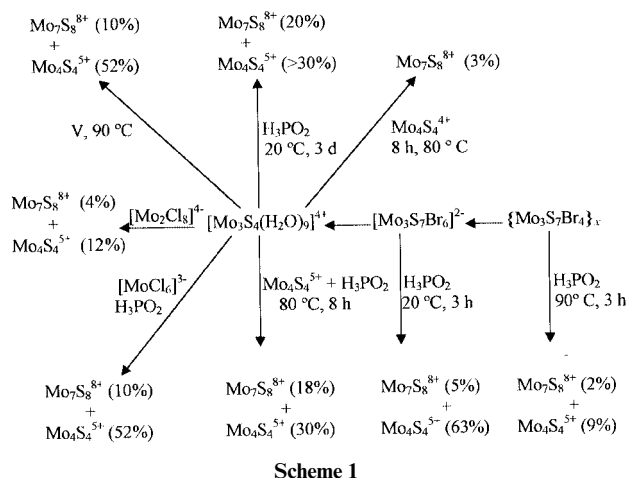


been reported for $[W_3S_4(H_2O)_9]^{4+}$ consistent with intermediate formation of a S-bonded thiocyanate product.

3 Cuboidal clusters with M_4Q_4 cores

3.1 Preparation and structures of aqua ions

Preparative routes for $[Mo_4S_4(H_2O)_{12}]^{5+}$ (Fig. 9) and $[Mo_4Se_4(H_2O)_{12}]^{5+}$ include $NaBH_4$ reduction of the cysteinato Mo_2^V complexes^{15,28} $[Mo_2O_2S_2(cys)_2]^{2-}$ and $[Mo_2O_2Se_2(cys)_2]^{2-}$, respectively. The initial products are air-oxidised in HCl solutions and purified by cation-exchange chromatography. This procedure requires at least one week and yields are variable and $< 20\%$. The mechanism involves a facial linking-up of two $Mo(\mu-Q)_2Mo$ rings in a reduced state (probably Mo^{III}) to generate the cube product. Better yields can be obtained⁵³ by addition of $[Mo_2Cl_8]^{4-}$ to $[Mo_3Q_4(H_2O)_9]^{4+}$ ($Q = S, Se$). Another method yielding both $Mo_4S_4^{5+}$ and $Mo_4Se_4^{4+}$ involves refluxing a mixture of $[Mo(CO)_6]$ and Na_2S in acetic anhydride.^{75,76} Greatly improved methods for the preparation of $[Mo_4S_4(H_2O)_{12}]^{5+}$ alongside $[Mo_7S_8(H_2O)_{18}]^{8+}$ involve the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with different reductants²⁹ (Scheme 1). The best

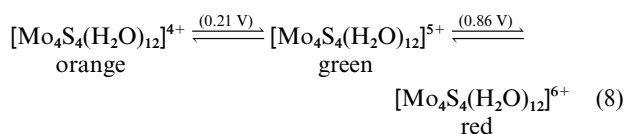


Scheme 1

yields have been obtained by treating $[\text{Mo}_3\text{S}_7\text{Br}_6]^{2-}$ with H_3PO_2 for 3 h which gives $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ (63%) and $[\text{Mo}_7\text{S}_8(\text{H}_2\text{O})_{18}]^{8+}$ (5%). Good yields ($\approx 50\%$) are also obtained by the reaction of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ with vanadium metal. Other methods yielding $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ include the electrolytic reduction²⁸ of $[\text{Mo}_2\text{O}_2\text{S}_2(\text{cys})_2]^{2-}$ in 2 M HCl.

Heating a solution of $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ to 90 °C in air for 12 h results in the loss of one Mo with formation of the Mo_3^{IV} incomplete cube $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$. The $[\text{Mo}_4\text{Se}_4(\text{H}_2\text{O})_{12}]^{5+}$ cube is less stable than the S analogue and at 20 °C decomposes in air to give $[\text{Mo}_3\text{Se}_4(\text{H}_2\text{O})_9]^{4+}$ (half-life 7d). The violet coloured double cube $[\text{Mo}_7\text{S}_8(\text{H}_2\text{O})_{18}]^{8+}$ is rather stable to air oxidation and does not react significantly with O_2 over periods of 1d.

Redox interconversions of trinuclear $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ and heterometallic derivatives of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ are rare. Such changes are however a particularly well established feature of Mo_4Q_4 cubes, have been detected for $[\text{W}_4\text{Q}_4(\text{CN})_{12}]^{7-}$. The $[\text{Mo}_4\text{Q}_4(\text{H}_2\text{O})_{12}]^{5+}$ (Q = S, Se) cubes have a well-defined redox chemistry with two additional oxidation states^{15,77} $[\text{Mo}_4\text{Q}_4(\text{H}_2\text{O})_{12}]^{4+}$ and $[\text{Mo}_4\text{Q}_4(\text{H}_2\text{O})_{12}]^{6+}$. These different states are readily observed in cyclic voltammetry as illustrated in Fig. 10, and can be accessed by chemical redox changes consistent with reaction (8).



The 4+ Mo_4^{III} cube can be prepared by electrochemical reduction of the 5+ $\text{Mo}_3^{\text{III}}\text{Mo}^{\text{IV}}$ cube at a carbon cloth electrode, and by $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ or $[\text{Ru}(\text{NH}_3)_6]^{2+}$ reduction both under N_2 . It has 12 electrons, sufficient for six metal-metal bonds, is very air sensitive and is oxidised by $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ (X = H_2O , F^- , Cl^- , CH_3CO_2^- monitored by conventional methods, and X = Br^- and I^- by stopped-flow). The 6+ $\text{Mo}_2^{\text{III}}\text{Mo}_2^{\text{IV}}$ cube (10 e^-) is prepared⁷⁸ by oxidising the 5+ cube with a limited (2:1) excess of *cis*- $[\text{VO}_2(\text{H}_2\text{O})_4]^+$. Consumption of V^{V} is in excess of stoichiometric amounts since the product has a tendency to fragment due to its high charge and/or low electron count.⁷⁸ The cube is much less stable than the 5+ cube and can be kept for only limited periods under N_2 at ≈ 4 °C. The decomposition products are $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ (major) and $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ (minor).⁷⁸ Treatment of $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ with oxidants also causes degradation with the formation of $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{H}_2\text{O})_6]^{2+}$ (major) and $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ (minor).

The 6+ purple cluster $[\text{Mo}_4\text{S}_4(\text{NCS})_{12}]^{6-}$ is obtained⁷⁶ by addition of 1 M NCS^- to $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ in air and crystallised as $[\text{NH}_4]_6[\text{Mo}_4\text{S}_4(\text{NCS})_{12}] \cdot 10\text{H}_2\text{O}$, therefore coordination of NCS^- to the 5+ cube seems to induce air oxidation. Addi-

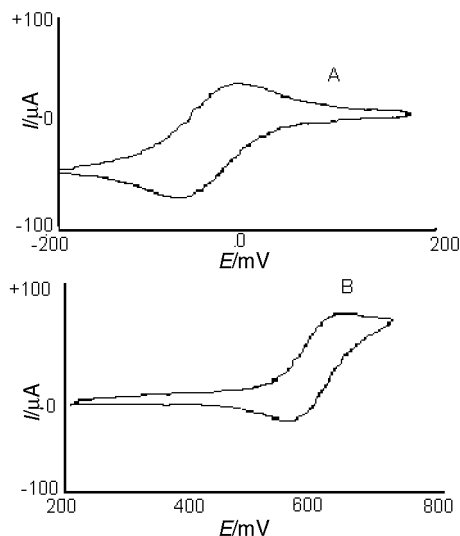


Fig. 10 Cyclic voltammograms of $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ (8 mM) in 2.0 M Hpts, (A) reduction of the 4+ state and (B) oxidation to the 6+ state (ref. 77).

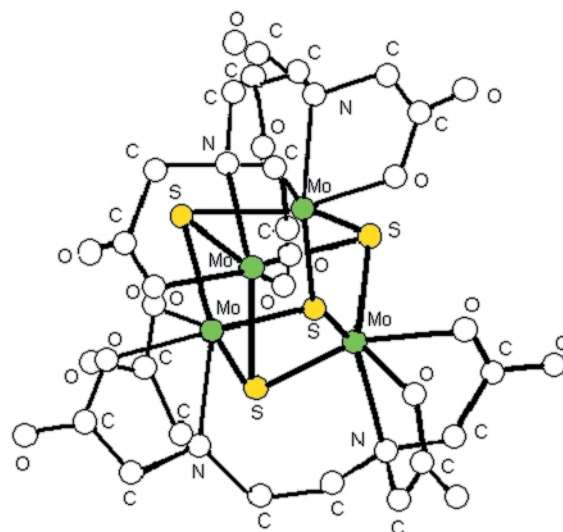


Fig. 11 Structure of the $[\text{Mo}_4\text{S}_4(\text{edta})_2]^{3-}$ anion.

tion of concentrated aqueous ammonia to the 5+ cube $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ also induces a change in the oxidation state of the molybdenum since the 4+ cube $[\text{Mo}_4\text{S}_4(\text{NH}_3)_{12}]^{4+}$ is obtained. The crystal structure of this product was determined as $[\text{Mo}_4\text{S}_4(\text{NH}_3)_{12}]\text{Cl}_4 \cdot 7\text{H}_2\text{O}$.⁷⁹ The best method of preparing the edta^{4-} coordinated cubes is by reduction⁷⁹ of the molybdenum(v) dimer $[\text{Mo}_2\text{O}_2\text{S}_2(\text{edta})]^{2-}$ with NaBH_4 , followed by air oxidation and chromatographic separation to give the mixed-valence cluster $[\text{Mo}_4\text{S}_4(\text{edta})_2]^{3-}$ (Fig. 11). A cyclic voltammogram indicated two quasi-reversible one-electron waves. The oxidised and reduced forms $[\text{Mo}_4\text{S}_4(\text{edta})_2]^{n-}$ ($n = 4, 2$) have also been isolated and the structures determined. The oxidised form $\text{Na}_2[\text{Mo}_4\text{S}_4(\text{edta})_2] \cdot 6\text{H}_2\text{O}$ was prepared by the oxidation of $\text{Na}_3[\text{Mo}_4\text{S}_4(\text{edta})_2] \cdot 10\text{H}_2\text{O}$ with bromine water. The reduced form $[\text{Mo}_4\text{S}_4(\text{edta})_2]^{4-}$ was obtained by the reduction of $[\text{Mo}_4\text{S}_4(\text{edta})_2]^{3-}$ with NaBH_4 under N_2 . The Mo-Mo distances become longer as the clusters are more oxidised⁷⁹ (Table 5). The $[\text{Mo}_4\text{Se}_4(\text{edta})_2]^{3-}$ was prepared by reaction of $[\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{edta})]^{2-}$ with NaBH_4 followed by Dowex purification.⁸⁰ The replacement of aqua by edta ligands does not affect significantly the structure which is analogous to that of $[\text{Mo}_4\text{S}_4(\text{edta})_2]^{3-}$. UV-vis spectra for the clusters $[\text{Mo}_4\text{Se}_4(\text{edta})_2]^{2-/3-/4-}$ are shown in Fig. 12. Crystal structures (Table 5) of the 4+ ion and $\text{Mg}_2[\text{Mo}_4\text{S}_4(\text{edta})_2] \cdot 20\text{H}_2\text{O}$, and the 5+ cubes $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}][\text{pts}]_5 \cdot 14\text{H}_2\text{O}$ (Fig. 9) and $\text{Ca}_{1.5}[\text{Mo}_4\text{S}_4(\text{edta})_2] \cdot$

Table 5 Structural parameters (Å) for cuboidal complexes with M_4Q_4 cores ($M = Mo, W; Q = S, Se, Te$)

Cluster	M–M	M– μ_3 -S	M–L	Ref.
$[NH_4]_6[Mo_4S_4(NCS)_{12}] \cdot 10H_2O$	2.791(1) ^a 2.869(1) ^a			11
$[Mo_4S_4(H_2O)_{12}][pts]_5 \cdot 14H_2O$	2.802(18)	2.349(4)	2.188(11), O	11
$[Mo_4S_4(NH_3)_{12}]Cl_4 \cdot 7H_2O$	2.797(7)	2.370(5)	2.336(15), N	11
$K_8[Mo_4S_4(CN)_{12}] \cdot 4H_2O$	2.854(1)	2.381(1)	2.190(1), C	11
$Na_2[Mo_4S_4(edta)_2] \cdot 6.5H_2O$	2.761(28) ^b 2.860(14) ^b	2.355(24)	2.273(14), N 2.095(11), O	11
$Ca_{1.5}[Mo_4S_4(edta)_2] \cdot 13H_2O$	2.780(19) ^c 2.863(25) ^c	2.356(6)	2.289(8), N 2.141(9), O	11
$Mg_2[Mo_4S_4(edta)_2] \cdot 22H_2O$	2.783(11)	2.355(4)	2.279(3), N 2.179(16), O	11
$[Mo_4S_4(C_5H_4Pr^i)_4][I_3]_2$	2.805(21) ^c 2.885(19) ^c	2.343(2)	2.331(6), Cp	11
$[Mo_7S_8(H_2O)_{18}][pts]_8 \cdot 18H_2O$	2.770(4) ^d 3.046(18) ^d	2.334(13) ^e 2.452(9) ^e	2.178(18), O	11
$[Mo_4Se_4(H_2O)_{12}][pts]_5 \cdot 14H_2O$	2.866(4)	2.480(4)	2.199	15
$[MoW_3S_4(H_2O)_{12}][pts]_5 \cdot Hpts \cdot 16H_2O$	2.797(4)	2.361(1)	2.147(3)	53
$[Me_2NH_2]_6[MoW_3S_4(NCS)_{12}] \cdot 0.5H_2O$	2.840(1)	2.356(4)	2.09(2)	53
$Na_{2.5}H_{0.5}[Mo_4Se_4(edta)_2] \cdot 10H_2O$	2.848(2)	2.479	2.289(11), N 2.156(10), O	80
$KCs_8[W_4S_4(CN)_{12}] \cdot CH_3OH \cdot 2H_2O$	2.845(1)	2.394(3)	2.18(1), C	2
$K_6[W_4Se_4(CN)_{12}] \cdot 6H_2O$	2.884(2)	2.506(3)	2.13(2), C	2
$K_6[W_4Te_4(CN)_{12}] \cdot 5H_2O$	2.962(2)	2.686(2)	2.15(3), C	2
$Cs_8[Mo_4Te_4(CN)_{12}] \cdot 2H_2O$	2.966(7)	2.678(6)	2.15(1), C	2
$K_7[Mo_4Te_4(CN)_{12}] \cdot 12H_2O$	2.992(1)	2.674(8)	2.16(1), C	2

^a Three short and three long distances. ^b Two short and four long distances. ^c Four short and two long distances. ^d Three short and three long distances per half of the core. ^e Nine short and three long distances per half of the core.

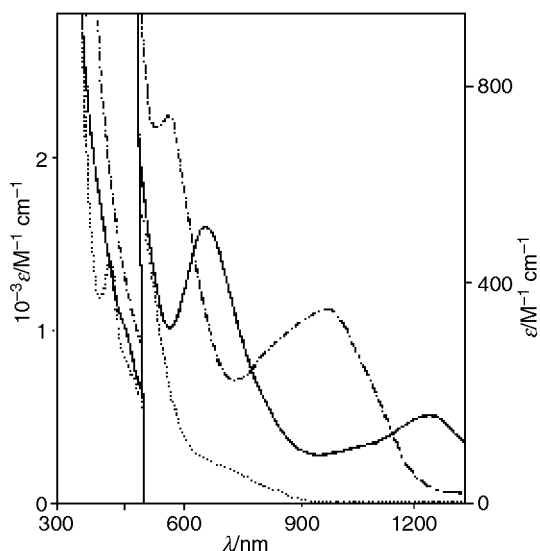


Fig. 12 UV-vis spectra for $[Mo_4Se_4(edta)_2]^{3-}$ (—), $[Mo_4Se_4(edta)_2]^{4-}$ (---) and $[Mo_4Se_4(edta)_2]^{5+}$ (···) in water as examples of variation for 4+, 5+ and 6+ core charges (ref. 80).

$13H_2O$ ⁷⁹ as well as the 6+ cube $[Mo_4S_4(C_5H_4Pr^i)_4][I_3]_2$ containing a singly-substituted cyclopentadienyl ligand,⁸¹ have also been reported.

The structure of the selenide-bridged cube $[Mo_4Se_4(H_2O)_{12}][pts]_5 \cdot 14H_2O$ has been determined.¹⁵ The mean Mo–Mo distance 2.866 Å compares with 2.802 Å observed for $Mo_4S_4^{5+}$ (Table 5). This is explained by the difference in the ionic radii of S^{2-} and Se^{2-} , the latter pushing the Mo further apart. The four Mo atoms have 11 electrons, one less than is required to give six Mo–Mo bonds. The $Mo_4S_4^{5+}$ and $Mo_4Se_4^{5+}$ mixed-valent cores give EPR spectra (Fig. 13) with no evidence of hyperfine structure in support of localised structures.^{74,80}

The mixed-metal cuboidal clusters⁵³ $[Mo_3WS_4(H_2O)_{12}]^{5+}$, $[Mo_2W_2S_4(H_2O)_{12}]^{5+}$, $[MoW_3S_4(H_2O)_{12}]^{5+}$, and the Se analogue $[MoW_3Se_4(H_2O)_{12}]^{5+}$, have been obtained from the trinuclear incomplete clusters $[Mo_2WS_4(H_2O)_9]^{4+}$, $[MoW_2S_4(H_2O)_9]^{4+}$, $[W_3S_4(H_2O)_9]^{4+}$ and $[W_3Se_4(H_2O)_9]^{4+}$, respectively, by reaction

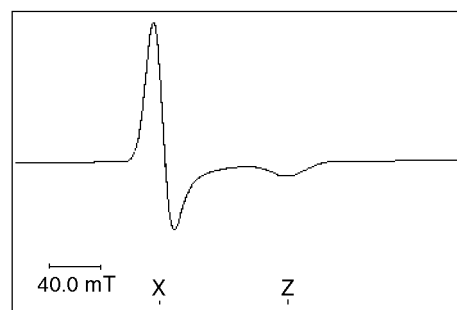


Fig. 13 EPR spectrum of $[Mo_4S_4(H_2O)_{12}]^{5+}$ (2 mM) in 2.0 M Hpts, at 3.8 K, with microwave frequency 9.25 GHz, power 20 mW, and gain 1.25×10^{-3} (ref. 87).

with $[Mo_2Cl_8]^{4-}$. Yields were close to 100%, where the M_3^{IV} reactant undergoes reductive addition with Mo_2^{II} , eqn. (9).



The four metal atoms in the 5+ product have an average oxidation state of 3.25. UV-vis spectra of these mixed-cubes are shown in Fig. 14. The reaction of $[W_3MoS_4(H_2O)_{12}]^{5+}$ in 2 M HCl with 1 M NCS^- in air gives the 6+ cube $[MoW_3S_4(NCS)_{12}]^{6-}$. The structures of the 5+ and 6+ state products $[MoW_3S_4(H_2O)_{12}][pts]_5 \cdot Hpts \cdot 16H_2O$ and $[Me_2NH_2]_6[MoW_3S_4(NCS)_{12}] \cdot 0.5H_2O$, respectively have been determined.⁵³ Three terminal ligands (H_2O or NCS^-) are coordinated on each metal, and the Mo and W atoms are randomly orientated in both structures. The M–M bond distances for the aqua complexes range from 2.7052(4) to 2.8793(3) Å and for the thiocyanato complexes from 2.8314(14) to 2.8494(13) Å. The NCS^- ligands are N-bonded. Air oxidation, or oxidation with $[Fe(H_2O)_6]^{3+}$, of $[Mo_xW_{4-x}S_4(H_2O)_{12}]^{5+}$ cubes ($x = 1-3$) gives first the 6+ cube which fragments in a process involving exclusively loss of W, e.g. eqn. (10).



This provides an alternative route for the syntheses of mixed-metal depleted cubes $[Mo_xW_{3-x}S_4(H_2O)_9]^{4+}$. Details of UV/vis/

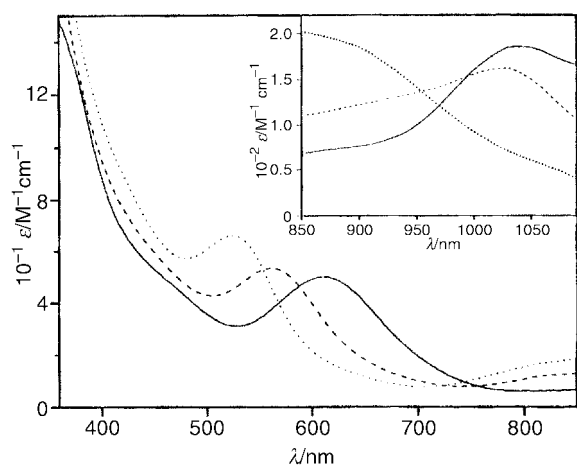


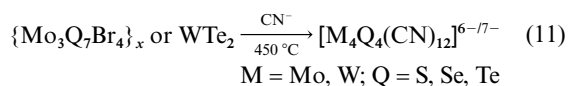
Fig. 14 The UV-vis/NIR spectra of $[\text{Mo}_3\text{WS}_4(\text{H}_2\text{O})_{12}]^{5+}$ (—), $[\text{Mo}_2\text{W}_2\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ (-----) and $[\text{MoW}_3\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ (···) in 2.0 M Hpts (ref. 53).

NIR peak position of different 5+ cubes are shown in Table 2. The wavelength trends observed for the $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$, $[\text{Mo}_3\text{WS}_4(\text{H}_2\text{O})_{12}]^{5+}$, $[\text{Mo}_2\text{W}_2\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ and $[\text{MoW}_3\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ indicate shifts to higher energy transitions with increasing number of W atoms.

3.2 Preparation of cyano complexes

Cuboidal clusters not so far mentioned with $\text{W}_4\text{S}_4^{6+}$, $\text{W}_4\text{Se}_4^{6+}$, $\text{W}_4\text{Te}_4^{6+}$, $\text{Mo}_4\text{Te}_4^{6+}$ and $\text{Mo}_4\text{S}_4^{6+}$ cores have been prepared² as cyano complexes $[\text{M}_4\text{Q}_4(\text{CN})_{12}]^{6-}$ or $[\text{M}_4\text{Q}_4(\text{CN})_{12}]^{7-}$. The reaction route involves high-temperature reaction of the corresponding polymeric chain compounds $\{\text{W}_3\text{S}_7\text{Br}_4\}_x$, $\{\text{W}_3\text{Se}_7\text{Br}_4\}_x$ or $\{\text{Mo}_3\text{Te}_7\text{I}_4\}_x$, with KCN and crystallization from aqueous solution. In these reactions abstraction of S or Se from the bridging $\mu\text{-S}_2$ (or $\mu\text{-Se}_2$) ligands of the starting compounds occurs.³⁰ In contrast, no similar abstraction is observed in the reaction of $\{\text{Mo}_3\text{Te}_7\text{I}_4\}_x$ with aqueous CN^- , and instead the triangular $[\text{Mo}_3\text{Te}_7(\text{CN})_6]^{2-}$ complex is obtained in high yield.⁸² The number of telluride-containing clusters remains small.

Crystals of the telluride complexes Mo_4Te_4 and W_4Te_4 were obtained in high yields (>80%) by the high-temperature reaction of $\{\text{Mo}_3\text{Te}_7\text{I}_4\}_x$ or WTe_2 with CN^- at 450 °C and further recrystallization from aqueous solution. The higher charge on the W_4Q_4 (Q = S, Se, Te) clusters is consistent with the greater difficulty in reducing W to its lower oxidation states. The preparative route is indicated in eqn. (11).



Oxidation of the $\text{Mo}_4\text{Te}_4^{5+}$ product with Br_2 at room temperature gives the $\text{Mo}_4\text{Te}_4^{6+}$ analogue. These clusters are stable in air in aqueous solutions (pH = 2–10) at 95 °C with no tendency to lose core atoms.

The structures of $[\text{M}_4\text{Q}_4(\text{CN})_{12}]^{6-7-}$ (Fig. 15) are similar (M = Mo, W; Q = S, Se, Te). The metal and chalcogen atoms form a distorted cube and each metal is coordinated by three CN^- groups. The M–Q bond distances vary regularly in the sequence $\text{W–S} < \text{W–Se} < \text{W–Te}$ (Table 5). Note that the W–W bond distances, and volume of the W_4 tetrahedron decrease systematically from W_4Te_4 to W_4Se_4 and W_4S_4 . NMR studies on the ⁷⁷Se, ¹²⁵Te and ¹⁸³W isotopes provide further evidence of four equivalent W atoms each coordinated by three μ_3 chalcogenide atoms in diamagnetic $[\text{W}_4\text{Q}_4(\text{CN})_{12}]^{6-}$. Red shifts in the UV-vis spectra are observed in going from S to Te and from Mo to W.

In addition crystal structures of cuboidal $[\text{W}_4\text{S}_4\{\text{S}_2\text{P}(\text{OEt})_2\}_6]$, $[\text{W}_4\text{S}_4(\text{CN})_{12}]^{6-}$ (both 6+ cubes) and the W_4^{V} *p*-tolylimido cube $[\text{W}_4\text{S}_4(\text{toIN})_4\{\text{S}_2\text{P}(\text{OEt})_2\}_4]$ have been reported.^{83–85}

Table 6 Reduction potentials E° vs. NHE (20 °C) for M_4Q_4 cubes (E_1° for 6+/5+ couples; E_2° for 5+/4+ couples)

	E_1°/mV	E_2°/mV	Ref.
$[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$	860	210 ^a	53
$[\text{Mo}_3\text{WS}_4(\text{H}_2\text{O})_{12}]^{5+}$	673	6 ^a	53
$[\text{Mo}_2\text{W}_2\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$	422	–248 ^a	53
$[\text{MoW}_3\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$	258	–395 ^a	53
$[\text{Mo}_4\text{Se}_4(\text{H}_2\text{O})_{12}]^{5+}$	792	193 ^a	53
$[\text{MoW}_3\text{Se}_4(\text{H}_2\text{O})_{12}]^{5+}$	214	–410 ^a	53
$[\text{Mo}_4\text{Te}_4(\text{CN})_{12}]^{6-}$	810	–30 ^b	2
$[\text{W}_4\text{Te}_4(\text{CN})_{12}]^{6-}$	559	–397 ^b	2
$[\text{W}_4\text{Se}_4(\text{CN})_{12}]^{6-}$	694	–343 ^b	2
$[\text{W}_4\text{S}_4(\text{CN})_{12}]^{6-}$	769	–299 ^b	2

^a 2 M Hpts. ^b Aqueous solution (0.10 M Na_2SO_4).

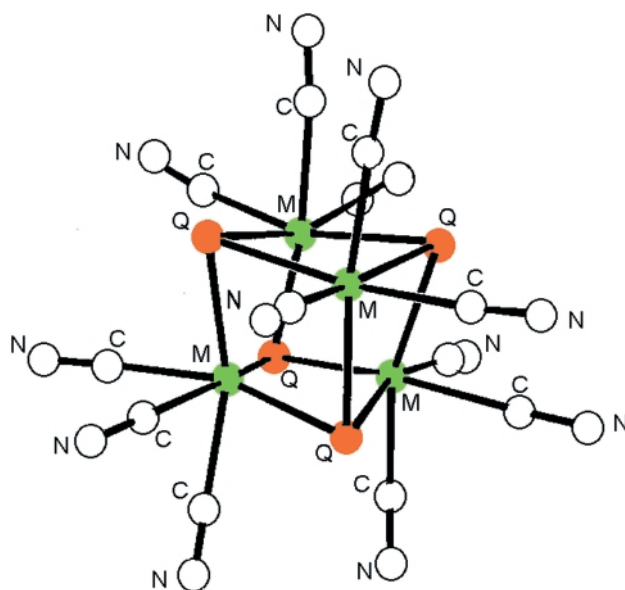


Fig. 15 The structures of $[\text{M}_4\text{Q}_4(\text{CN})_{12}]^{6-}$ (M = Mo, W; Q = S, Se, Te).

However no preparation of $[\text{W}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{n+}$ ($n = 4, 5, 6$) has yet been achieved. In view of the greater difficulty in reducing W compared to Mo, $\text{W}_4\text{S}_4^{6+}$ is the most likely oxidation state to be generated. The synthesis of $\beta\text{-}[\text{W}_4\text{S}_4(\mu\text{-dtp})_2(\text{dtp})_4]$ and $\alpha\text{-}[\text{W}_4\text{S}_4(\mu\text{-dtp})_3(\text{dtp})_3]$ cubes [dtp = $\text{S}_2\text{P}(\text{OEt})_2$], from $[\text{W}(\text{CO})_6]$ and $\text{Na}_2[\text{W}_4\text{O}_{12}]$ in the presence of $\text{P}_2\text{S}_5/\text{EtOH}$, and from $\text{K}_2[\text{W}_2\text{Cl}_6]$ respectively, have been described.⁸⁶ The Mo_4S_4 and Mo_4OS_3 cubes as dtp complexes⁸⁶ have been prepared from $\text{MoCl}_3 \cdot 3\text{H}_2\text{O}$ and $[\text{Mo}(\text{CO})_6]$.

Qualitative bonding schemes have been developed for incomplete cuboidal clusters Mo_3S_4 and for homometallic cubes M_4S_4 .¹³

3.3 Electrochemical studies

Electrochemical studies on $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$,¹⁵ $[\text{Mo}_4\text{Se}_4(\text{H}_2\text{O})_{12}]^{5+}$,¹⁶ and $[\text{Mo}_x\text{W}_{4-x}\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ ($x = 1\text{--}3$)⁵³ indicate two reversible redox processes. Reduction potentials E° vs. NHE for the 6+/5+ and 5+/4+ couples are collected in Table 6. Values for the $[\text{W}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+/5+}$ and $[\text{W}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+/4+}$ couples can be estimated by extrapolation as 39 mV and –627 mV, respectively (Fig. 16). The reduction potentials show systematic trends to more negative values the more tungsten atoms are incorporated.

Cyclic voltammograms of the 5+ cube $[\text{Mo}_4\text{Se}_4(\text{edta})_2]^{3-}$ have shown the existence of quasi-reversible one-electron reduction and oxidation.⁸⁰ Reduction potentials for the couples (5+/4+) $[\text{Mo}_4\text{Se}_4(\text{edta})_2]^{3-/4-}$ and (6+/5+) $[\text{Mo}_4\text{Se}_4(\text{edta})_2]^{2-/3-}$ are –0.040 and 0.65 V, respectively. The replacement of S by Se in Mo_4Q_4 cubes causes a shift in the reduction potentials to less-positive values for the aqua ions 5+/4+ (20 mV) and 6+/5+ (70

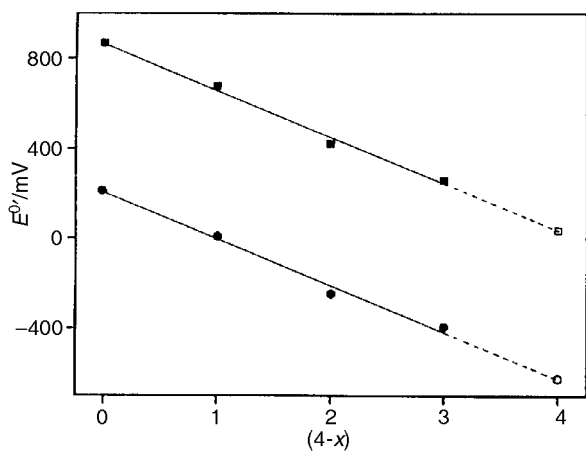


Fig. 16 The variation of reduction potentials vs. NHE ($\approx 20^\circ\text{C}$), $E_1^{\circ'}$ for $[\text{Mo}_x\text{W}_{4-x}\text{S}_4(\text{H}_2\text{O})_{12}]^{6+/5+}$ and $[\text{Mo}_x\text{W}_{4-x}\text{S}_4(\text{H}_2\text{O})_{12}]^{5+/4+}$ couples ($x = 1-3$), from cyclic voltammetry in 2.0 M Hpts together with values for the corresponding Mo_4S_4 ($x = 4$) couples. The open circles are extrapolated values for the W_4S_4 ($x = 0$) cubes which have not so far been isolated (ref. 53).

mV) (Table 6), whereas with edta as ligand little change was detected. Compared to analogous Mo–S clusters, Mo–Se clusters exhibit identical structures but with longer bond lengths, red-shifted UV-vis absorption bands, and in the case of the cuboidal aqua complexes less-positive reduction potentials (Tables 2 and 6).

Cyclic voltammetry has shown that the cyano clusters with the M_4Q_4 ($\text{M} = \text{Mo}, \text{W}; \text{Q} = \text{S}, \text{Se}, \text{Te}$) cubes are capable of existing in three oxidation states ranging from the most oxidised ($n = 6, 10 e^-$) to the most reduced form ($n = 4, 12 e^-$). The oxidation potentials decrease on going from S to Te, thus making the 6+ state more stable, and decreasing the stability of the 4+ state, as with the W_3MoQ_4 aqua ions ($\text{Q} = \text{S}, \text{Se}$).⁵³ In M_4Q_4 ($\text{M} = \text{Mo}, \text{W}; \text{Q} = \text{S}, \text{Se}, \text{Te}$) cubes the 4+/5+ couple is reversible while the 6+/5+ is quasi-reversible. This difference was attributed to removing one electron from the 5+ species, which is accompanied by a greater distortion of the M_4 skeleton than for removal of one electron from the 4+ species. Thus in the highly distorted core in $[\text{W}_4\text{Te}_4(\text{CN})_{12}]^{6-}$, the longest and shortest W–W distances differ by 0.215 Å, whereas for the much less distorted 5+ cube $[\text{Mo}_4\text{Te}_4(\text{CN})_{12}]^{7-}$, the difference is only 0.03 Å.

3.4 Kinetics studies

All the core sulfides in the Mo_4S_4 cube are $\mu_3\text{-S}$, and coordinated waters are all *trans* to $\mu_3\text{-S}$ (c type). Substitution reactions are slow. The reactions of the 4+ and 5+ cubes are independent of $[\text{H}^+]$ in the range 0.4–2.0 M studied. Reactions with NCS^- give relatively large absorbance changes and are the easiest to monitor.

For NCS^- substitution on $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{4+}$,⁸⁷ which has four identical Mo^{III} , the first stage of reaction gives equilibrium kinetics $k_{\text{eq}} = k_{\text{f}}[\text{NCS}^-]/4 + k_{\text{b}}$, with NCS^- in >10-fold excess. The second stage (independent of $[\text{NCS}^-]$) is assigned to isomerisation of Mo–SCN to the more stable Mo–NCS form, $k_{\text{isom}} = 3.6 \times 10^{-5} \text{ s}^{-1}$. Rate constants for the first stage with the cube in excess differ from those with NCS^- in excess by the statistical factor of 4, corresponding to the number of equivalent Mo's, and the forward and back rate constants are $k_{\text{f}} = 1.95 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{b}} = 1.44 \times 10^{-3} \text{ s}^{-1}$.

Substitution⁸⁷ on $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ is slower and has two concurrent $[\text{NCS}^-]$ dependent reactions. For the first stage a statistical factor of 3 applies, and the rate constant k_{f1} ($0.116 \text{ M}^{-1} \text{ s}^{-1}$) is assigned as substitution at each of the three Mo^{III} s. For the second stage there is no statistical factor, and $k_{\text{f2}} = 0.0166 \text{ M}^{-1} \text{ s}^{-1}$ is assigned to reaction at the single Mo^{IV} .

Table 7 Summary^a of rate and equilibrium constants (25°C) for NCS^- substitution of a single H_2O on $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{n+}$ ($n = 4-6$) or $[\text{Mo}_7\text{S}_8(\text{H}_2\text{O})_{18}]^{8+}$, and assignments for substitution

Cluster	Assignment	$k_{\text{f}}/\text{M}^{-1} \text{ s}^{-1}$	$k_{\text{aq}}/\text{s}^{-1}$	K/M^{-1}
$[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{4+}$	Mo^{III}	1.95	1.44×10^{-3}	1300
$[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$	Mo^{III}	0.116	4.3×10^{-3}	2700
	Mo^{IV}	0.0166	5.0×10^{-6}	3300
$[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$	$\text{Mo}^{\text{III}}\text{Mo}^{\text{IV}}$	13.3	2.53×10^{-3}	5220
	Conjugate-base path	$\text{Mo}^{\text{III}}\text{Mo}^{\text{IV}}$	5.1	1.08×10^{-3}
$[\text{Mo}_7\text{S}_8(\text{H}_2\text{O})_{18}]^{8+}$	Not made	0.173	2.0×10^{-4}	870
	Not made	0.079	2.2×10^{-4}	360

^a Values taken from ref. 29.

There is therefore evidence for an electron distribution which approximates to $\text{Mo}_3^{\text{III}}\text{Mo}^{\text{IV}}$. Rapid formation of the outer-sphere adduct, which is sensitive to charge on the nearby Mo is a possible explanation, leading to the discrimination observed. The $\text{Mo}_3^{\text{IV}}\text{Mo}^{\text{IV}}$ non-equivalence could not however be detected in NMR experiments,⁸⁰ and intracube electron-exchange is rapid. To summarise the present position would be that outer-sphere complexation is faster than intracube electron exchange. No isomerisation step was detected in the case of the 5+ cube. No $[\text{H}^+]$ dependence was observed for both the 5+ and 4+ cubes with $[\text{H}^+]$ as low as 0.4 M. Substitution with Cl^- is thermodynamically $\approx 10^3$ less favourable, and absorbance changes are much smaller, and as a consequence only one stage was detected. By analogy with NCS^- the reaction is assigned to substitution at the Mo^{IV} .

The substitution⁷⁸ of H_2O by NCS^- on $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$ shows different features as compared to that on 4+ and 5+ cubes. The reaction is monophasic whereas the 4+ and 5+ cubes give biphasic kinetics. Substitution on the 6+ cube is up to $\approx 10^3$ faster than that for the 4+ and 5+ cubes. Whereas the latter do not exhibit $[\text{H}^+]^{-1}$ dependences, in the case of 6+ cube a dependence of the kind $k_{\text{f}} = a + b[\text{H}^+]^{-1}$ (with $a = 13.3 \text{ M}^{-1} \text{ s}^{-1}$, $b = 5.1 \text{ s}^{-1}$) is observed for $[\text{H}^+]$ in the range, thus implicating a conjugate-base form $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{11}(\text{OH})]^{5+}$. These observations and the statistical factor of 2 suggest that the cube behaves as two identical delocalised $\text{Mo}^{\text{III}}\text{Mo}^{\text{IV}}$ pairs as in high-potential Fe_4S_4 clusters.⁸⁸ The higher overall charge and smaller electron population ($10 e^-$) are contributing factors to the faster reaction of the 6+ cube. A summary of rate constants for NCS^- substitution on $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{n+}$ ($n = 4, 5, 6$) is shown in Table 7.

The substitution of H_2O by NCS^- on $[\text{Mo}_4\text{Se}_4(\text{H}_2\text{O})_{12}]^{5+}$ indicates a faster substitution at both the Mo^{III} ($\approx 1.5 \text{ M}^{-1} \text{ s}^{-1}$) and Mo^{IV} ($\approx 0.11 \text{ M}^{-1} \text{ s}^{-1}$) centres.⁸⁹

4 Corner-shared M_7Q_8 clusters

4.1 Preparation and structure

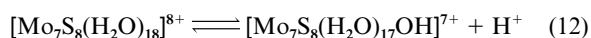
The corner-shared double cube $[\text{Mo}_7\text{S}_8(\text{H}_2\text{O})_{18}]^{8+}$ ($\text{M} = \text{Mo}$ in Fig. 7) was first prepared by reduction of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ with Mg ,⁹⁰ however the yield was low. Much improved methods using different reductants (Scheme 1) have been described,²⁹ the most successful of which involves treating $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ with the reducing agent H_3PO_2 (yield $\approx 20\%$). A breaking down and reassembly of Mo_3S_4 explains the formation of $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ and $[\text{Mo}_7\text{S}_8(\text{H}_2\text{O})_{18}]^{8+}$. The latter has been isolated as the pts^- salt and structurally characterised.⁹⁰ Two Mo_3S_4 cores are bridged by a nodal molybdenum atom which lies on a center of symmetry, and constitutes the only example of corner-shared double cube with a transition metal (Mo) at the nodal position. The distances between the nodal Mo and other Mo atoms (3.026–3.060 Å) are longer than the other Mo–Mo distances (2.766–2.773 Å). Strong absorptions in the vis/NIR region are ascribed to charge-transfer transitions (Table 2).

The preparation of the selenium analogue of the corner-shared double cube $[\text{Mo}_7\text{Se}_8(\text{H}_2\text{O})_{18}]^{8+}$ has also been reported.²⁹ It was accessed by reaction of polymeric $\{\text{Mo}_3\text{Se}_7\text{Br}_4\}_x$ with concentrated HCl and H_3PO_2 . Chromatographic purification of the reaction mixture gave two bands identified as $[\text{Mo}_4\text{Se}_4(\text{H}_2\text{O})_{12}]^{5+}$ and $[\text{Mo}_7\text{Se}_8(\text{H}_2\text{O})_{18}]^{8+}$. The latter is less stable in air than the S analogue, and decays in several days in 4 M HCl.

In the cation-exchange chromatography carried out to isolate $[\text{MoW}_3\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ and $[\text{MoW}_3\text{Se}_4(\text{H}_2\text{O})_{12}]^{5+}$ small amounts of a violet more highly charged product believed to be the corner-shared double cubes $[\text{MoW}_6\text{S}_8(\text{H}_2\text{O})_{18}]^{8+}$ and $[\text{MoW}_6\text{Se}_8(\text{H}_2\text{O})_{18}]^{8+}$ were obtained.

4.2 Kinetic studies

Substitution kinetics²⁹ of water by NCS^- on the double cube $[\text{Mo}_7\text{S}_8(\text{H}_2\text{O})_{18}]^{8+}$ shows that the latter has a substitution inertness comparable to $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$. The 4+ and 6+ single cubes substitute one or two orders of magnitude faster, respectively. Formation (k_f) and aquation (k_{aq}) rate constants for $[\text{Mo}_7\text{S}_8(\text{H}_2\text{O})_{18}]^{8+}$ exhibit dependences on $[\text{H}^+]$ of the kind $a + b[\text{H}^+]^{-1}$. The 6+ but not the 4+ and 5+ single cubes exhibit a similar dependence on $[\text{H}^+]^{-1}$ in keeping with the greater acidity of water ligands on the 6+ and 8+ cubes, eqn. (12).

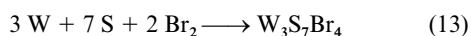


Formation of a hydroxo conjugate-base form labilises water coordinated to the same Mo. An isomerization step was also observed for $[\text{Mo}_7\text{S}_8(\text{H}_2\text{O})_{18}]^{8+}$ similar to NCS^- substitution on $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{4+}$ and $[\text{W}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$. The isomerization is assigned to intermediate formation of the metastable S-bonded $\text{Mo}_7\text{S}_8(\text{SCN})$ alongside $\text{Mo}_7\text{S}_8(\text{NCS})$. Second-order kinetics were observed for $[\text{Co}(\text{dipic})_2]^-$ (H_2dipic = pyridine-2,6-dicarboxylic acid) oxidation of $[\text{Mo}_7\text{S}_8(\text{H}_2\text{O})_{18}]^{8+}$ with the rate constant $0.31 \text{ M}^{-1} \text{ s}^{-1}$ independent of $[\text{H}^+]$ consistent with an outer-sphere mechanism.

5 Chalcogenide-rich clusters with the M_3Q_7 core

5.1 Preparation and structures

Polymeric compounds^{31,32} $\{\text{M}_3\text{Q}_7\text{X}_4\}_x$ ($\text{M} = \text{Mo}, \text{W}$; $\text{Q} = \text{S}, \text{Se}$; $\text{X} = \text{Cl}, \text{Br}$) have been prepared by high-temperature reaction ($\approx 450^\circ\text{C}$) of the elements in a sealed tube for ≈ 50 h, e.g. eqn. (13) for the preparation of $\{\text{W}_3\text{S}_7\text{Br}_4\}_x$.



The crystal structures of $\{\text{Mo}_3\text{S}_7\text{Cl}_4\}_x$ (Fig. 4) and $\{\text{W}_3\text{S}_7\text{Br}_4\}_x$ have been reported,^{91,92} and are isostructural. They consist of $\text{M}_3(\mu_3\text{-S})(\mu\text{-S}_2)_3$ units bridged by four halide atoms forming an extended zig-zag chain. The $\text{M}_3(\mu_3\text{-Q})(\mu\text{-Q}_2)_3$ type compounds have a triangle of M_3 atoms capped by a $\mu_3\text{-Q}$ ligand, each M-M edge being bridged by a Q_2^{2-} ligand. The ligands $\mu\text{-Q}_2$ have one chalcogen atom in axial position and another in equatorial position with respect to the M_3 plane. Thus three of them lie in the M_3 plane (equatorial Q_e atoms) and the other three occupy the side of the M_3 opposite $\mu_3\text{-Q}$ (axial Q_a).

Heating these polymeric compounds in a melt of phosphonium salts (Ph_4PCl , Ph_4PBr) cleaves the bromine bridged chain to give the compound $[\text{PPh}_4]_2[\text{M}_3\text{Q}_7\text{Br}_6]$ with discrete $[\text{M}_3\text{Q}_7\text{Br}_6]^{2-}$ units (Fig. 2). Reactions of phosphines with the chalcogenide-rich clusters $\text{M}_3\text{Q}_7^{4+}$ ($\text{M} = \text{Mo}, \text{W}$; $\text{Q} = \text{S}, \text{Se}$) give abstraction of three chalcogen atoms at equatorial positions³² with M_3Q_4 as products. The mixed-chalcogen $\text{M}_3\text{S}_4\text{Se}_3^{4+}$ complexes containing a $\mu\text{-SSe}$ ligand have been reported.^{93,94} They form in a chalcogen transfer reaction between $[\text{M}_3\text{S}_7\text{X}_6]^{2-}$ and PPh_3Se in CH_3CN . The stereochemistry of the reaction has been determined by isotopic substitution (using ^{34}S), and by X-ray structure determination of $[\text{Ph}_3\text{PEt}]_2[\text{Mo}_3\text{S}_4\text{Se}_3\text{Cl}_6]$ when the

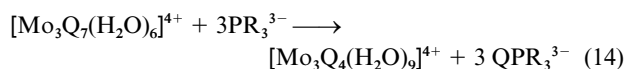
equatorial S-atoms are seen to be replaced.^{93,94} Several other $\text{Mo}_3\text{S}_4\text{Se}_3^{4+}$ complexes have been reported.^{95,96}

The polymeric $\{\text{M}_3\text{Q}_7\text{X}_4\}_x$ compounds are appropriate starting materials for the preparation of clusters containing $\text{M}_3\text{-}(\mu_3\text{-S})(\mu_2\text{-S}_2)_3^{4+}$, $\text{M}_3(\mu_3\text{-Se})(\mu_2\text{-Se}_2)_3^{4+}$, $\text{M}_3(\mu_3\text{-S})(\mu_2\text{-SSe})_3^{4+}$, $\text{M}_3\text{-}(\mu_3\text{-S})(\mu_2\text{-S})_3^{4+}$ and $\text{M}_3(\mu_3\text{-Se})(\mu_2\text{-Se})_3^{4+}$ cores.^{30,31,93,94} The chalcogenide-rich aqua clusters³⁰ Mo_3^{IV} clusters $[\text{Mo}_3\text{Q}_7(\text{H}_2\text{O})_6]^{4+}$ ($\text{Q} = \text{S}, \text{Se}$) are obtained from polymeric chain compounds $\{\text{Mo}_3\text{Q}_7\text{Br}_4\}_x$ via $[\text{Mo}_3\text{Q}_7\text{Br}_6]^{2-}$. The $\{\text{Mo}_3\text{Q}_7\text{Br}_4\}_x$ is melted with PPh_4Br under N_2 and converted into $[\text{Mo}_3\text{Q}_7\text{Br}_6]^{2-}$, aquation of the latter in 4 M Hpts followed by cation-exchange purification led to the elution of aqua ions $[\text{Mo}_3\text{Q}_7(\text{H}_2\text{O})_6]^{4+}$ as a single band with 2 M Hpts. Acidic solutions of $[\text{Mo}_3\text{S}_7(\text{H}_2\text{O})_6]^{4+}$ are stable for several weeks under N_2 but in air give 10% decay in 12 h. The Se analogue $[\text{Mo}_3\text{Se}_7(\text{H}_2\text{O})_6]^{4+}$ is less stable in air. $[\text{Mo}_3\text{Q}_7(\text{H}_2\text{O})_6]^{4+}$ can be converted into $[\text{Mo}_3\text{Q}_4(\text{H}_2\text{O})_9]^{4+}$ by chalcogenide abstraction with PPh_3 . The $[\text{W}_3\text{Q}_7(\text{H}_2\text{O})_6]^{4+}$ clusters can be prepared by the same procedure.⁴⁹

The mixed-chalcogenide $[\text{Mo}_3\text{S}_4\text{Se}_3(\text{H}_2\text{O})_6]^{4+}$ was obtained from $[\text{Et}_4\text{N}]_2[\text{Mo}_3\text{S}_4\text{Se}_3\text{Br}_6]$ (or Cl for Br) as described. The $[\text{Mo}_3\text{S}_4\text{Se}_3(\text{H}_2\text{O})_6]^{4+}$ cluster has one $\mu_3\text{-S}^{2-}$ and three $\mu\text{-SSe}^{2-}$ core ligands. Reaction of $[\text{Mo}_3\text{S}_4\text{Se}_3(\text{H}_2\text{O})_6]^{4+}$ in aqueous solution with PPh_3 (in chloroform) gives $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ in a fast reaction. The same Se abstraction was observed on elution of $[\text{Mo}_3\text{S}_4\text{Se}_3(\text{H}_2\text{O})_6]^{4+}$ from a cation-exchange column with CN^- . The equatorial Se atoms of the three $\mu\text{-SSe}^{2-}$ groups are removed with formation of the $\text{Mo}_3\text{S}_4^{4+}$ core. No Te abstraction of $[\text{Mo}_3\text{Te}_7(\text{CN})_6]^{2-}$ with PR_3^{3-} or CN^- is observed probably due to the weakness of P=Te bonds and the extreme instability of TeCN^- .

5.2 Kinetic studies

Uniphase kinetics studies³⁰ on the reaction of $[\text{Mo}_3\text{Q}_7(\text{H}_2\text{O})_6]^{4+}$ ($\text{Q} = \text{S}, \text{Se}$) with water soluble phosphine PR_3^{3-} [eqn. (14)] gave $\approx 10^3$ faster abstraction rate constants for S than Se.



An unusual $[\text{H}^+]$ dependence of the type $k_a = k_1[\text{H}^+] + k_{-1}[\text{H}^+]^{-1}$ was obtained, which is explained by the involvement of protonated $\mu\text{-Q}_2^{2-}$ (k_1), and a conjugate-base (of coordinated H_2O) form (k_{-1}), eqn. (14). Rate constants for Se abstraction from $[\text{Mo}_3\text{S}_4\text{Se}_3(\text{H}_2\text{O})_6]^{4+}$ are 10 times faster than for S abstraction from $[\text{Mo}_3\text{S}_7(\text{H}_2\text{O})_6]^{4+}$.

Substitution of H_2O on $[\text{Mo}_3\text{S}_7(\text{H}_2\text{O})_6]^{4+}$ and $[\text{Mo}_3\text{Se}_7(\text{H}_2\text{O})_6]^{4+}$ with Cl^- and Br^- are independent of $[\text{H}^+]$ in the range 0.5–2.0 M. The reactions are uniphase and assigned as substitution on H_2O *cis* to $\mu_3\text{-Q}^{2-}$ at each Mo. Formation rate constants for Cl^- are surprisingly 2×10^6 times slower than for the reaction of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ with Cl^- , indicating that Cl^- is a much less effective nucleophile for the chalcogenide-rich clusters. This is attributed to the high electron density on the $\mu\text{-Q}_2^{2-}$ ligands of $[\text{Mo}_3\text{Q}_7(\text{H}_2\text{O})_6]^{4+}$, which is in part delocalised onto the metals and appears to inhibit interaction with incoming nucleophiles.

6 Other recent examples and future trends

A niobium⁹⁷ cluster $[\text{Nb}_4(\mu_4\text{-O})(\mu_3\text{-Te})_4(\text{CN})_{12}]^{6-}$ has recently been prepared by high-temperature reaction of NbTe_4 with KCN at 450°C and recrystallization from aqueous solution. The cluster was isolated as $\text{K}_6[\text{Nb}_4\text{OTe}_4(\text{CN})_{12}] \cdot \text{K}_2\text{CO}_3 \cdot \text{KOH} \cdot 8\text{H}_2\text{O}$ and characterised by X-ray crystallography. An unusual feature is the oxo ion at the centre of the cube, which is the first example of this kind.⁹⁷ Such interstitial atoms are believed to stabilise clusters containing Group 3 and 4 metals which are electron deficient.⁹⁸ The Nb_4Te_4 cube is similar to those in $[\text{M}_4\text{Q}_4(\text{CN})_{12}]^{n-}$ ($\text{M} = \text{Mo}, \text{W}, \text{Re}$; $\text{Q} = \text{S}, \text{Se}, \text{Te}$),^{2,85,99} with the metal and chalcogen atoms forming a distorted cube

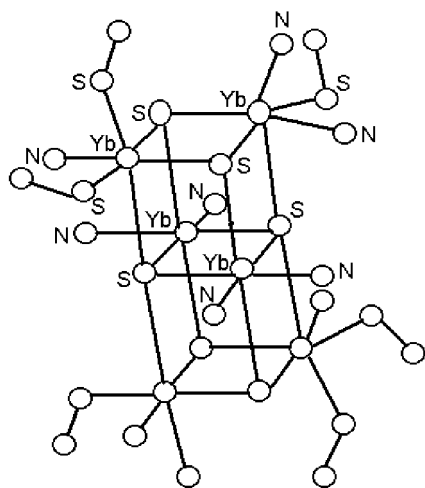


Fig. 17 The structure of the face-shared double cube $[Yb_6S_6(SPh)_6(py)_{10}]$.

surrounded by 12 terminal CN ligands. The Nb–Nb distance (average 3.20 Å) is longer than in other compounds having a Nb–Nb single bond.¹⁰⁰ The only other example of a niobium cube so far reported is $[Nb_4Se_4I_4]$.¹⁰¹

The first lanthanide cluster having a Yb_4Se_4 core has been prepared recently,¹⁰² and the crystal structure of $[Yb_4Se_4(SePh)_4(py)_8]$ determined. The procedure involves reduction of elemental Se by $Yb(SePh)_2(py)_4$ in pyridine. Also in the lanthanide area a new structural type¹⁰² of formula $[Yb_6S_6(SPh)_6(py)_{10}]$ consisting of two face-shared cubes has been reported (Fig. 17). This is an interesting development which could open up a new area of chalcogenide-bridged clusters incorporating f-block metals.

Clusters having Mo_6 cores and intercluster Mo–S bonds are obtained by high-temperature solid state reactions. The Saito group has for example prepared the molecular analogue, $Mo_6S_8(PEt_3)_6$, by reductive coupling of two Mo_3S_4 incomplete cuboidal clusters. The reaction involves reduction of $[Mo_3S_4Cl_4(PEt_3)_4(MeOH)]$ with Mg.¹⁰³ Similarly, $W_6S_8(PEt_3)_6$ has been prepared despite the non-existence of such a Chevrel structure for tungsten.¹⁰⁴ Analogous Se compounds have also been described. Thus incomplete cuboidal clusters of the M_3Y_4 type are lead-in compounds for higher nuclearity Mo and W clusters. Even more highly condensed clusters (Mo_9 and Mo_{12}) exist in the solid state, featuring in all cases the Mo_3 incomplete cube unit. Molecular analogues should likewise be accessible by reductive condensation of M_3S_4 clusters. The M_3Y_4 clusters can be regarded as building blocks for these structures as well as molecular models of Chevrel structures.

Assemblage of the M_3Y_4 incomplete cuboidal clusters into octahedral and (possibly) fused Mo_6 octahedral clusters is only one way of organising the triangular M_3 units of the trinuclear clusters into larger units. The reaction sequence $M_3Y_4 + M_4Y_4 \rightarrow M_7Y_8$ shows that a metal atom in one cube can be incorporated into a vacant metal position of M_3Y_4 . Also in Chevrel Mo_6S_8 octahedral clusters are linked together by a heterometal atoms (e.g. Ag, Sn, Pb, Zn) in intercluster position.¹⁰⁵ There are no obvious reasons why oligomeric, polymeric or cyclic aggregates cannot be synthesised based on this principle. A recent example¹⁰⁶ of the latter is the paper describing the structure of a Eu(III) tyrosine complex $[Eu_{15}(Cl)(\mu_3-Tyr)_{10}(\mu_3-OH)_{20}(\mu-H_2O)_5(OH)_{12}(H_2O)_8][ClO_4]_2 \cdot 56H_2O$, where five Eu_4O_4 cuboidal units are joined together *via* nodal Eu atoms to form a “wheel” at the centre of which is a chloride.

A further new type of double cube structure¹⁰⁷ consisting of two $[Mo_3PbOS_3]^{6+}$ single cubes linked by two bridging oxo ligands has been reported for $(\{[Mo_3PbOS_3]O\}_2)^{8+}$.

In conclusion, although the cube is a very fundamental crystallographic unit, it is only recently that relatively simple

molecular cube units have been isolated, and their solution chemistry studied. The Group 6 Mo, W chalcogenide structures provide an extensive contribution at the forefront of such studies.

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