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FULL PAPER

Formation of Group 14 and 15 heteroatom derivatives of trinuclear $[M_3Se_4(H_2O)_9]^{4+}$ (M = Mo, W) and the decreased reactivity of $[W_3S_4(H_2O)_9]^{4+}$

Rita Hernandez-Molina, Mark R. J. Elsegood, William Clegg and A. G. Sykes*

Department of Chemistry, The University of Newcastle, Newcastle upon Tyne, UK NE1 7RU. E-mail: a.g.sykes@newcastle.ac.uk

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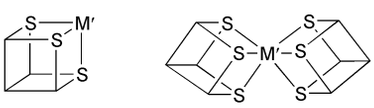
Group 14 and 15 elements (M′ = Pb, As, Sb, Bi), which are known to form corner-shared double cube derivatives $[Mo_6M'S_8(H_2O)_{18}]^{8+}$ of $[Mo_3S_4(H_2O)_9]^{4+}$, are here shown to react with $[M_3Se_4(H_2O)_9]^{4+}$ (M = Mo, W). Using similar procedures, no corresponding derivatives of $[W_3S_4(H_2O)_9]^{4+}$ are obtained. ICP-AES metal analyses on the $[M_3Se_4(H_2O)_9]^{4+}$ products, together with stoichiometries for oxidation with the Co^{III} oxidant $[Co(dipic)_2]^-$, are consistent with corner-shared double cube formulae $[M_6M'Se_8(H_2O)_{18}]^{8+}$. UV-Vis spectra are reported as part of the characterisation, and observations are made on the reactivity of the cubes with O_2. The X-ray crystal structures of $[Mo_3Se_4(H_2O)_9](pts)_4\cdot 10H_2O$, $[W_3Se_4(H_2O)_9](pts)_4\cdot 12H_2O$ and one of the key products $[Mo_6AsSe_8(H_2O)_{18}]$ $(pts)_8\cdot 8H_2O$ have been determined ($pts^- = p$-toluenesulfonate). Whereas differences in reactivity of $[Mo_3Se_4(H_2O)_9]^{4+}$ and $[W_3Se_4(H_2O)_9]^{4+}$ are small, the differences for $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$ are much more marked. In the context of heteroatom incorporation the incomplete cube $[W_3S_4(H_2O)_9]^{4+}$ is by far the least reactive of the four trinuclear clusters.

Introduction

As far as Group 6–15 heteroatom (M′) cube derivatives of $[M_3S_4(H_2O)_9]^{4+}$ (M = Mo, W) are concerned, there are ~20 examples in the case of Mo,[1] but only 6 so far (M′ = Mo, Ni, Cu, In, Ge, Sn) in the case of W.[2–5] The products are either single $[M_3M'S_4(H_2O)_{10\ or\ 12}]^{n+}$ or corner-shared double cube derivatives $[M_6M'S_8(H_2O)_{18}]^{8+}$ as illustrated, with M′ in the latter occupying the nodal position.



The formation of derivatives of the Se-containing incomplete cubes $[M_3Se_4(H_2O)_9]^{4+}$ (M = Mo, W) has not so far been as extensively studied.[6,7] The aim of the present work is to explore the reactions of $[M_3Se_4(H_2O)_9]^{4+}$ (M = Mo, W) with M′ = Pb, As, Sb, Bi. Together with data for M′ = Ge, Sn,[7–10] this provides full coverage of Groups 14 and 15 in the Periodic Table. The reactivity of $[W_3S_4(H_2O)_9]^{4+}$ with these same 4 heteroatoms is also studied, and provides a sharp contrast in behaviour. Reasons for the spread in reactivity of the four incomplete cubes $[M_3Q_4(H_2O)_9]^{4+}$ (M = Mo, W; Q = S, Se) are considered.

Experimental

Preparation of $[Mo_3Se_4(H_2O)_9]^{4+}$

Solutions of yellow-brown $[Mo_3Se_4(H_2O)_9]^{4+}$ were prepared from polymeric $\{Mo_3Se_7Br_4\}_x$ as previously described.[4–7] To obtain the latter Mo (4.0 g), Se (7.44 g), and Br_2 (1.44 mL) were heated in a sealed glass ampoule as previously described.[11,12] The product was powdered and washed with hot EtOH. The brown solid was left to stand in 4.0 M Hpts for 10 h under N_2, and the filtrate treated with PPh_3 in CH_2Cl_2 to convert the $Mo_3Se_7^{4+}$ core to $Mo_3Se_4^{4+}$ by Se abstraction, eqn. (1).[11]

$$Mo_3Se_7^{4+} + 3PPh_3 \rightarrow Mo_3Se_4^{4+} + 3SePPh_3 \quad (1)$$

The mixture was stirred for 3–4 h, when the organic layer was discarded, and the $[Mo_3Se_4(H_2O)_9]^{4+}$ product in the aqueous layer purified by Dowex cation-exchange chromatography as described below. Elution was with 2.0 M HCl or 2.0 M Hpts. Elution in 4 M Hpts (*p*-toluenesulfonic acid, $CH_3C_6H_4SO_3H$; Aldrich) was used to obtain a sample for crystallisation. Details of UV-Vis spectra are included in Table 5 below.

Preparation of $[W_3Se_4(H_2O)_9]^{4+}$

To polymeric $\{W_3Se_7Br_4\}_x$ (5 g), prepared by a procedure similar to that for the Mo analogue, HCl (11.3 M; 20 mL) and the reductant H_3PO_2 (5 mL, 1:1 w/w solution in H_2O) were added,[13] and the mixture heated at 90 °C under N_2 for 12–15 h. The green colour of $[W_3Se_4(H_2O)_9]^{4+}$ formed, and the H_2Se which was evolved was absorbed in alkali (*CAUTION: use fumehood!*), eqn. (2).

$$W_3Se_7Br_4 + 3H_3PO_2 + 3H_2O \rightarrow W_3Se_4^{4+} + 3H_2Se + 3H_3PO_3 + 4Br^- \quad (2)$$

The green solution was filtered and purified by cation-exchange chromatography. A sample eluted in 4.0 M Hpts was left to crystallise. Details of UV-Vis spectra are included in Table 5 below.

Preparation of $[W_3S_4(H_2O)_9]^{4+}$

A procedure as described previously was used.[10]

Cation-ion exchange chromatography

Purification of derivatives was carried out by loading 0.5 M HCl (or 0.5 M Hpts) solutions onto an ice-cooled Dowex 50W–X2 cation-exchange resin column (Sigma Chemicals; 200–400 dry mesh size), typically 15 × 1.5 cm. The columns were washed

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Table 1 Crystallographic data

Compound	$[Mo_3Se_4(H_2O)_9]$ $(pts)_4 \cdot 10H_2O$	$[W_3Se_4(H_2O)_9]$ $(pts)_4 \cdot 12H_2O$	$[Mo_6AsSe_8(H_2O)_{18}]$ $(pts)_8 \cdot 8H_2O$
Formula	$C_{28}H_{66}Mo_3O_{31}S_4Se_4$	$C_{28}H_{70}O_{33}S_4Se_4W_3$	$C_{56}H_{108}AsMo_6O_{50}S_8Se_8$
Formula weight	1630.7	1930.5	3120.1
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	13.8860(19)	11.9215(7)	12.3516(11)
b/Å	13.8899(19)	15.4869(7)	34.072(3)
c/Å	17.180(2)	16.9541(8)	11.9253(11)
α/°	99.535(2)	101.655(2)	
β/°	102.458(2)	96.056(2)	92.645(4)
γ/°	117.597(2)	109.195(2)	
U/Å^3	2729.0(6)	2844.8(2)	5013.4(8)
Z	2	2	2
Data collected, unique	17886, 9356	25158, 13149	43190, 11896
R_{int}	0.076	0.035	0.059
Parameters	747	895	666
R, R_w[a]	0.071, 0.178	0.045, 0.111	0.036, 0.076
diff. map extremes/e Å^{-3}	+3.14, −1.44	+5.29, −2.44	+1.20, −0.87

[a] R on F values for data with $F^2 > 2\sigma$; R_w on all unique F^2 values.

in turn with 100 mL volumes of first 0.5 M, and then 1.0 M HCl, and elution was carried out with 2.0 M HCl. Alternatively for Hpts solutions, further washing was with 2.0 M Hpts followed by elution with 4.0 M Hpts. Any remaining trinuclear reactant was eluted by 1.0 M HCl or 2.0 M Hpts. All crystallisation procedures were with the most concentrated fractions of solutions eluted by 4.0 M Hpts.

X-Ray crystallography

Crystal data are given in Table 1. All data were collected at a temperature T of 160 K. Methods were as described previously.[7] Residual electron density peaks suggest some possible minor disorder in the metal–selenium framework for the incomplete single cube structures, but this was not resolved. Two-fold disorder was resolved and refined, with restraints in displacement parameters and geometry (similarity and planarity), for most of the anions in these two structures. H atoms were included only for the anions and were not located for coordinated or uncoordinated water molecules. The uncoordinated water molecules in the W-containing structure are also disordered and the total water content is approximate; it may well be variable in samples of these materials, though it appears to be reasonably well defined in the Mo_3Se_4 structure. The value of 12 is used here for the purpose of calculating derived results such as density. The double-cube structure showed no disorder; all H atoms were located in difference maps and were included in the refinement.

CCDC reference numbers 158608–158610.

See http://www.rsc.org/suppdata/dt/b1/b101399h/ for crystallographic files in CIF or other electronic format.

Results

Preparation of $[Mo_3Se_4(H_2O)_9]^{4+}$ derivatives

For Pb incorporation a solution of $[Mo_3Se_4(H_2O)_9]^{4+}$ (4.2 mM; 15 mL) in 2.0 M Hpts was added to Pb shot (4 g; Aldrich; 1–3 mm mesh size) under N_2. The solution turned a dark green within 2–3 min, and after standing overnight was diluted to 0.5 M Hpts for purification by Dowex cation-exchange chromatography. The preparation is summarised by eqn. (3).

$$2Mo_3Se_4^{4+} + Pb \rightarrow Mo_6PbSe_8^{8+} \quad (3)$$

After loading the column was washed with ~100 mL amounts of 0.50 M, 1.0 M and 2.0 M Hpts. Elution was with 2.0 M HCl or 4.0 M Hpts.

In the case of arsenic $[Mo_3Se_4(H_2O)_9]^{4+}$ (4–6 mM; 18 mL) in 2.0 M HCl was added to a solution of Na_2HAsO_4 (0.15 g), and the mixture degassed by bubbling N_2 for 15 min. Hypophosphorous acid, H_3PO_2 (0.2 mL; 10% w/w solution, Aldrich) was added and the mixture heated at ~70 °C. The solution became green within 5 min, and after 1 h the mixture was diluted to 0.5 M HCl and loaded on to an ice-cooled Dowex column. The preparation is summarised by eqn. (4).

$$2Mo_3Se_4^{4+} + As^{V} + 5e^- \rightarrow Mo_6AsSe_8^{8+} \quad (4)$$

Washing was with Hpts or HCl acids, amounts as indicated above. Elution was with 4.0 M Hpts (green product), or 3.0 M HCl brown. Crystals suitable for X-ray studies were obtained from 4.0 M Hpts solutions at 4 °C.

Incorporation of antimony was achieved by adding a solution of $[Mo_3Se_4(H_2O)_9]^{4+}$ (4.5 mM; 14 mL) in 1.0 M HCl to Sb shot (4 g; Aldrich) under N_2. A colour change to dark green was observed within a few minutes, and the solution was diluted to 0.5 M HCl for Dowex cation-exchange purification. The reaction occurs by eqn. (5).

$$2Mo_3Se_4^{4+} + Sb \rightarrow Mo_6SbSe_8^{8+} \quad (5)$$

Column purification was as above. Elution with 4.0 M Hpts gave a dark-green solution.

A bismuth derivative was obtained from $[Mo_3Se_4(H_2O)_9]^{4+}$ (4.1 mM; 10 mL) in 2.0 M HCl by addition of bismuth(III) citrate (0.1 g; Sigma), and H_3PO_2 (0.3 mL; 10% w/w solution) under N_2. The mixture was stirred for 30 min at ~70 °C. A colour change to dark green took place within a few minutes. After dilution to 0.5 M HCl column purification was carried out. The reaction is summarised by eqn. (6).

$$2Mo_3Se_4^{4+} + Bi^{III} + 3e^- \rightarrow Mo_6BiSe_8^{8+} \quad (6)$$

Eluted solutions were green (4.0 M Hpts), and brown (3.0 M HCl).

Preparation of $[W_3Se_4(H_2O)_9]^{4+}$ derivatives

For the Pb derivative $[W_3Se_4(H_2O)_9]^{4+}$ (7 mM; 20 mL) in 2.0 M Hpts was added to Pb shot (6 g) under N_2. The colour of the solution turned dark red after 1 h, and was left overnight prior to dilution to 0.5 M Hpts and cation-exchange purification. Eluted solutions were wine-red.

An arsenic derivative was obtained by adding hypophosphorous acid H_3PO_2 (50% w/w solution) to a solution of $[W_3Se_4(H_2O)_9]^{4+}$ (8 mM; 10 mL) with sodium arsenite, $NaAsO_2$ (0.2 g), in 2.0 M HCl under N_2. The mixture was heated to

Table 2 Results of analyses by ICP-AES, and stoichiometry determination with $[Co(dipic)_2]^-$ as oxidant

Cluster	ICP-AES Analyses		Mol of Co^{III} per double cube
$[Mo_6PbSe_8(H_2O)_{18}]^{8+}$	Mo:Pb	6.0:1.09	2:1
$[W_6PbSe_8(H_2O)_{18}]^{8+}$	W:Pb	6.0:1.02	
$[Mo_6AsSe_8(H_2O)_{18}]^{8+}$	Mo:As	6.0::1.02	3:1
$[W_6AsSe_8(H_2O)_{18}]^{8+}$	W:As	6.0:0.93	
$[Mo_6SbSe_8(H_2O)_{18}]^{8+}$	Mo:Sb	6.0:0.98	3:1
$[W_6SbSe_8(H_2O)_{18}]^{8+}$			3:1
$[Mo_6BiSe_8(H_2O)_{18}]^{8+}$	Mo:Bi	6.0:0.91 [a]	
$[W_6BiSe_8(H_2O)_{18}]^{8+}$	W:Bi	6.0:1.02	

[a] Mo : Bi : Se determined as 6.0 : 0.91 : 8.9.

~80 °C for 1 h. A colour change to blue-green occurred after ~30 min. The solution was diluted ×4 and loaded onto a Dowex column for purification. Eluted solutions were blue-green.

Solutions of $[W_3Se_4(H_2O)_9]^{4+}$ react with $SbCl_3$ to give a yellow-brown adduct believed to be the single cube $[W_3(SbCl_3)Se_4(H_2O)_9]^{4+}$. The same product is observed with Sb shot. No Dowex purification of the product was possible as a copious white precipitate of a white hydrolysed form of Sb is obtained. The procedure was modified to include a reductant. Thus to a solution of $[W_3Se_4(H_2O)_9]^{4+}$ (10 mL; 8 mM) in 2 M HCl, $SbCl_3$ (40 mg) and a drop of H_3PO_2 (50% w/w solution) were added. An immediate change to brown-yellow occurred, and on heating to 70 °C under N_2 for 30 min a colour change to green-blue was observed. This was diluted to 0.5 M HCl and loaded onto the Dowex column. After washing with 0.5 M and then 1.0 M HCl, a green-blue solution of $[W_6SbSe_8(H_2O)_{18}]^{8+}$ was eluted.

To obtain a Bi derivative bismuth citrate (0.2 g) and H_3PO_2 (0.5 mL; 50% w/w solution) were added to $[W_3Se_4(H_2O)_9]^{4+}$ (4.4 mM; 21 mL) in 2.0 M HCl under N_2. The mixture was heated to ~60 °C for ~1 h (colour change to blue-green after 15 min), and diluted ×4 for Dowex purification.

Reactions of $[W_3S_4(H_2O)_9]^{4+}$

Using procedures as above no Pb, As, Sb or Bi derivatives were obtained.

Elemental analyses

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses were carried out on 2.0 M HCl solutions, and results (Table 2) indicate 6:1 ratios of Mo/W to heteroatom, consistent with corner-shared double cube formation.

Stoichiometry of $[Co(dipic)_2]^-$ oxidation

Reactions of cube products (~1.0×10^{-4} M) with the Co^{III} oxidant $[Co(dipic)_2]^-$ ($E^{o\prime}$ 362 mV *vs.* nhe), dipic = pyridine-2,6-dicarboxylate, were studied under rigorously air-free conditions. Solutions of $NH_4[Co(dipic)_2]\cdot H_2O$ (~1.7 mM), peak at 510 nm ($\varepsilon = 630\ M^{-1}\ cm^{-1}$), were titrated into the cube solution. Reactions studied were fast. The Group 14 heteroatom Pb gave a 2:1 stoichiometry as in eqn. (7),

$$Mo_6PbSe_8^{8+} + 2Co^{III} \rightarrow 2Mo_3Se_4^{4+} + Pb^{II} + 2Co^{II} \quad (7)$$

and Group 15 heteroatoms 3:1 stoichiometries as in eqn. (8).

$$Mo_6M'Se_8^{8+} + 3Co^{III} \rightarrow 2Mo_3Se_4^{4+} + M'^{III} + 3Co^{II} \quad (8)$$

Amounts of Co^{III} consumed gave a ±3% spread of the values indicated in Table 2.

X-Ray crystal structures

Although the two incomplete single cube cations have essentially the same structure, their pts^- salts are not isomorphous and they may have different and variable amounts of uncoordinated water in their crystal structures. Selected interatomic distances for these and for the arsenic-containing double cube are given in Table 3. The incomplete cubes have the familiar structure with one vacant corner and with short M–M distances indicative of direct bonding interactions, leading to acute angles at the bridging Se atoms. Fig. 1 shows the Mo-containing cation, and the W-containing cation is essentially identical. The As-containing double cube structure is shown in Fig. 2. It is crystallographically centrosymmetric with an essentially regular octahedral arrangement of Se atoms around the central As atom. The short Mo–Mo distances and acute angles observed in the incomplete cube cation are retained when the double cube is formed, with only minor changes. The lack of disorder in this structure has enabled location of all the hydrogen atoms. The aqua ligands, uncoordinated water molecules and pts^- anions engage in a network of hydrogen bonds. Such hydrogen bonding is also present in the other structures, evidenced by many relatively short O···O distances even in the absence of known hydrogen atom positions.

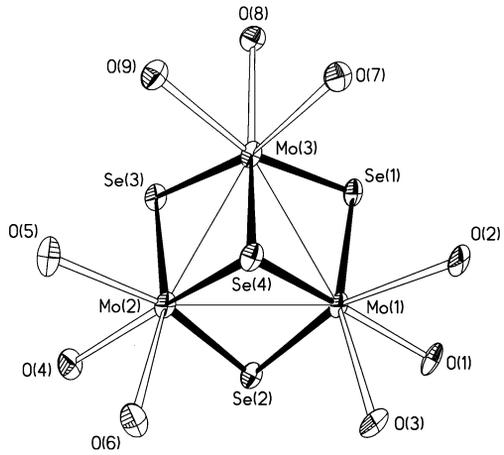

Fig. 1 View of the incomplete cube $[Mo_3Se_4(H_2O)_9]^{4+}$ with 50% probability ellipsoids. The structure of $[W_3Se_4(H_2O)_9]^{4+}$ is essentially the same.

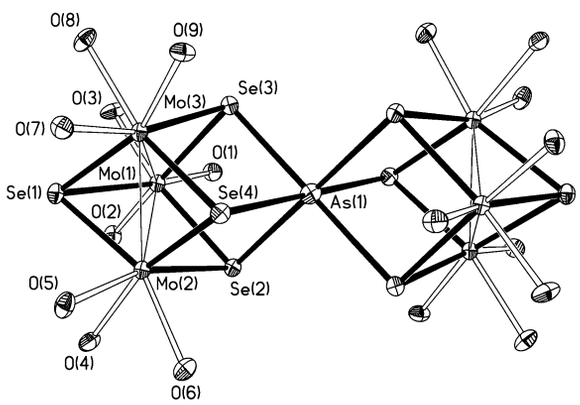

Fig. 2 View of the corner-shared double cube $[Mo_6AsSe_8(H_2O)_{18}]^{8+}$ with 50% probability ellipsoids and labelling of unique atoms.

UV-Vis Spectra

These were recorded in (a) 2.0 M HCl solutions, when there is Cl^- coordination of the Mo/W atoms present in the cube; and (b) 2.0 M Hpts, when there is less tendency of pts^- to coordinate the Group 6 metals. Details of spectra are listed in Table 5 (later). UV-Vis spectra for $[Mo_3Se_4(H_2O)_9]^{4+}$ derivatives in 2.0 M HCl are shown in Fig. 3, and those for $[W_3Se_4(H_2O)_9]^{4+}$ in Fig. 4. The similarity of the UV-Vis spectrum of the green-blue product obtained from the reaction of $[W_3Se_4(H_2O)_9]^{4+}$ with Sb, Fig. 4, supports a corner-shared double cube assignment $[W_6SbSe_8(H_2O)_{18}]^{8+}$.

Table 3 Selected interatomic distances (Å)

$[Mo_3Se_4(H_2O)_9](pts)_4 \cdot 10H_2O$			
Mo(1)–Se(1)	2.3920(17)	Mo(1)–Se(2)	2.3840(18)
Mo(1)–Se(4)	2.4754(18)	Mo(2)–Se(2)	2.3929(19)
Mo(2)–Se(3)	2.4050(18)	Mo(2)–Se(4)	2.4518(17)
Mo(3)–Se(1)	2.3919(19)	Mo(3)–Se(3)	2.4048(17)
Mo(3)–Se(4)	2.4462(17)	Mo(1)–Mo(2)	2.8055(17)
Mo(1)–Mo(3)	2.7910(17)	Mo(2)–Mo(3)	2.7816(16)
Mo–O	2.168(9)–2.262(8)		
$[W_3Se_4(H_2O)_9](pts)_4 \cdot 12H_2O$			
W(1)–Se(1)	2.4664(8)	W(1)–Se(2)	2.4161(8)
W(1)–Se(4)	2.4095(8)	W(2)–Se(1)	2.4673(9)
W(2)–Se(2)	2.4255(8)	W(2)–Se(3)	2.4045(9)
W(3)–Se(1)	2.4843(10)	W(3)–Se(3)	2.4130(10)
W(4)–Se(4)	2.4201(8)	W(1)–W(2)	2.7661(5)
W(1)–W(3)	2.7708(5)	W(2)–W(3)	2.7540(5)
W–O	2.155(6)–2.295(6)		
$[Mo_6AsSe_8(H_2O)_{18}](pts)_8 \cdot 8H_2O$			
Mo(1)–Se(1)	2.4619(6)	Mo(1)–Se(2)	2.4549(5)
Mo(1)–Se(3)	2.4579(6)	Mo(2)–Se(1)	2.4719(6)
Mo(2)–Se(2)	2.4590(6)	Mo(2)–Se(4)	2.4641(5)
Mo(3)–Se(1)	2.4659(6)	Mo(3)–Se(3)	2.4607(6)
Mo(3)–Se(4)	2.4591(6)	Mo(1)–Mo(2)	2.7370(5)
Mo(1)–Mo(3)	2.7917(5)	Mo(2)–Mo(3)	2.7686(5)
Mo–O	2.147(3)–2.211(3)	As(1)–Se(2)	2.5843(4)
As(1)–Se(3)	2.5803(4)	As(1)–Se(4)	2.6293(5)

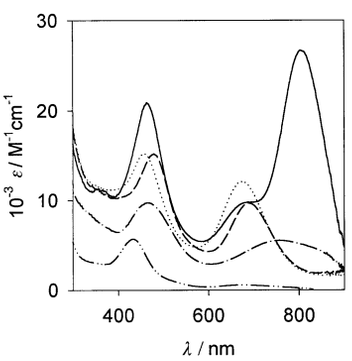

Fig. 3 UV-Vis spectra of $[Mo_6PbSe_8(H_2O)_{18}]^{8+}$ (—), $[Mo_6AsSe_8(H_2O)_{18}]^{18+}$ (– – –), $[Mo_6SbSe_8(H_2O)_{18}]^{8+}$ (·····), $[Mo_6BiSe_8(H_2O)_{18}]^{8+}$ (—·—), alongside that of $[Mo_3Se_4(H_2O)_9]^{4+}$ (—··—), all in 2.0 M HCl acid.

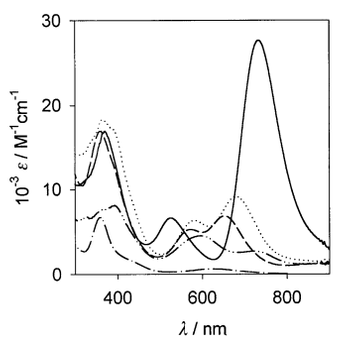

Fig. 4 UV-Vis spectra of $[W_6PbSe_8(H_2O)_{18}]^{8+}$ (—), $[W_6AsSe_8(H_2O)_{18}]^{8+}$ (·····) $[W_6SbSe_8(H_2O)_{18}]^{8+}$ (– – –), $[W_6BiSe_8(H_2O)_{18}]^{8+}$ (—··—), alongside that of $[W_3Se_4(H_2O)_9]^{4+}$ (–·–), all in 2.0 M HCl acid.

Stability in air

On exposing 2.0 M HCl solutions to air in an open 1 cm^2 cross-section optical cell with some shaking 100% decay was observed *e.g.* $[Mo_6PbSe_8(H_2O)_{18}]^{8+}$ (12 min), $[W_6PbSe_8(H_2O)_{18}]^{8+}$ (5 min), $[Mo_6SbSe_8(H_2O)_{18}]^{8+}$ (10 min), $[W_6BiSe_8(H_2O)_{18}]^{8+}$ (3–4 min). The reactions can be summarised by eqn. (9) for Pb (M = Mo, W),

$$2M_6PbSe_8^{8+} + O_2 + 4H^+ \rightarrow 4M_3Se_4^{4+} + 2Pb^{II} + 2H_2O \quad (9)$$

and by eqn. (10) for the Group 15 heteroatoms.

$$4M_6M'Se_8^{8+} + 3O_2 + 12H^+ \rightarrow 8M_3Se_4^{4+} + 4M'^{III} + 6H_2O \quad (10)$$

Solutions containing $[Mo_6AsSe_8(H_2O)_{18}]^{8+}$ were the most stable (2% decay in 10 min), and crystallisation was possible. The product obtained from $[W_3Se_4(H_2O)_9]^{4+}$ and Sb showed high air sensitivity.

Discussion

Procedures for the preparation and characterisation of M′ = Pb, As, Sb, Bi derivatives of the Se containing incomplete cubes $[M_3Se_4(H_2O)_9]^{4+}$ (M = Mo, W) are described in this paper. To prepare the Pb and Sb derivatives small size metal shot or powder was used as the source of M′. With M′ = As, Bi, the preferred route involved treatment of $[M_3Se_4(H_2O)_9]^{4+}$ with an M'^{III} salt and reductant (H_3PO_2). The same procedures as in earlier work were used to characterise the double cubes.[10] With one exception, that of $[W_3Se_4(H_2O)_9]^{4+}$ with $SbCl_3$, no single cubes were detected and corner-shared double cubes only were observed. The single cubes with $Mo_3PbS_4^{6+}$ and $Mo_3BiS_4^{7+}$ cores have been isolated previously as the dithiophosphate (dtp) complexes $[Mo_3(PbI_3)S_4(dtp)_3(py)_3]$ and $[Mo_3(BiI_3)S_4(\mu\text{-}CH_3CO_2)(dtp)_3(py)] \cdot (CH_3)_2O$, but there is no evidence as yet for the corresponding aqua ions.[14] The brown-yellow coloured product obtained on reacting $[W_3Se_4(H_2O)_9]^{4+}$ in 2.0 M HCl with $SbCl_3$ or by reaction with Sb in 2.0 M HCl is believed to be the single cube $[W_3(SbCl_3)Se_4(H_2O)_9]^{4+}$. The behaviour is similar therefore to that observed for the two Group 14 elements Ge^{II},[9] and Sn^{II},[10] with $[W_3Q_4(H_2O)_9]^{4+}$ (Q = S, Se), eqn. (11)

$$M_3Q_4^{4+} + M'^{II} \rightarrow M_3M'Q_4^{6+} \quad (11)$$

and in the case of Sb gives the single cube, eqn. (12).

$$W_3Se_4^{4+} + Sb^{III} \rightarrow W_3SbSe_4^{7+} \quad (12)$$

Double-cube formation follows with a second mol of $[W_3Q_4(H_2O)_9]^{4+}$ and H_3PO_2 as reductant, in a reductive addition process, eqn. (13).

$$W_3SbSe_4^{7+} + W_3Se_4^{4+} + 3e^- \rightarrow W_6SbSe_8^{8+} \quad (13)$$

Table 4 Summary of average bond lengths (Å) for incomplete cubes and corresponding As double cubes with Se and S as chalcogenide

	Mo–Mo	Mo–As	Mo–μ-Q	Mo–μ_3-Q	As–Q
$[Mo_3Se_4(H_2O)_9]^{4+}$	2.793(10)		2.395(4)	2.458(3)	
$[Mo_6AsSe_8(H_2O)_{18}]^{8+}$	2.766(22)		2.459(3)	2.467(4)	2.598(22)
$[Mo_3S_4(H_2O)_9]^{4+}$ [a]	2.732(7)		2.286(6)	2.332(4)	
$[Mo_6AsS_8(H_2O)_{18}]^{8+}$ [b]	2.716(26)	3.554	2.339(3)	2.341(1)	2.456(24)

[a] Ref. 22. [b] Ref. 16.

Table 5 Summary of UV-Vis spectra of corner-shared double cube derivatives of $[Mo_3Se_4(H_2O)_9]^{4+}$ and $[W_3Se_4(H_2O)_9]^{4+}$

Cluster	Solution	λ/nm (ε/M^{-1} cm^{-1})
$[Mo_3Se_4(H_2O)_9]^{4+}$	2.0 M HCl	433(5250); 681(580)
	2.0 M Hpts	427(5820); 646(595)
$[W_3Se_4(H_2O)_9]^{4+}$	2.0 M HCl	360(6950); 625(500)
	2.0 M Hpts	359(6660); 618(547)
$[W_3S_4(H_2O)_9]^{4+}$	2.0 M HCl	317(6100); 570(480)
	2.0 M Hpts	315(6350); 560(446)
$[Mo_6PbSe_8(H_2O)_{18}]^{8+}$	2.0 M HCl	358(9980); 464(19060); 680sh(8500); 804(24800)
	2.0 M Hpts	354(9636); 453(17260); 785(18940)
$[W_6PbSe_8(H_2O)_{18}]^{8+}$	2.0 M HCl	371(16890); 525(6615); 734(27630)
$[Mo_6AsSe_8(H_2O)_{18}]^{8+}$	2.0 M HCl	330sh; 479(15170); 686(9460)
	2.0 M Hpts	459(15150); 671(9406)
$[W_6AsSe_8(H_2O)_{18}]^{8+}$	2.0 M HCl	360(17000); 581(6400); 680(9130)
	2.0 M Hpts	377(15590); 556(5280); 663(7480)
$[Mo_6SbSe_8(H_2O)_{18}]^{8+}$	2.0 M HCl	458(15200); 675(12060)
	2.0 M Hpts	441(12760); 675(8825)
$[W_6SbSe_8(H_2O)_{18}]^{8+}$	2.0 M HCl	361(16930); 573(5263); 653(6860)
$[Mo_6BiSe_8(H_2O)_{18}]^{8+}$	2.0 M HCl	464(15110); 735(7396); 845sh(~7500)
	2.0 M Hpts	447(12830); 736(7120); 800sh(~7000)
$[W_6BiSe_8(H_2O)_{18}]^{8+}$	2.0 M HCl	393(8140); 597(4510); 727(2700)
	2.0 M Hpts	360(16160) 581(8244); 706(5407)

The observations with Ge, Sn, and now Sb, leave open the possibility that conditions for the formation of Pb, As, Bi single cube derivatives will eventually be identified. The reactivity of $[M_3Se_4(H_2O)_9]^{4+}$ (M = Mo, W) with M′ = Pb, As, Sb, Bi reagents is similar to that of $[Mo_3S_4(H_2O)_9]^{4+}$,[15–18] but quite different from that of $[W_3S_4(H_2O)_9]^{4+}$, where no evidence for single or double cube formation is obtained. Likewise no heteroatom incorporation occurs on treatment of $[W_3S_4(H_2O)_9]^{4+}$ with M′ = Fe, Co, Pd, Hg reagents.[19–21]

A summary of bond lengths obtained in the three X-ray diffraction studies is given in Table 3. The structures of isomorphous products $Cs_5[M_3Se_4(CN)_9]\cdot CsCl\cdot 4H_2O$ (M = Mo, W),[12] and of $(NMe_4)_5[Mo_3Se_4(NCS)_5]$[6] have been determined previously, and give M–M (2.829 and 2.817 Å), M–μ-Se (2.393 and 2.409 Å), and M–μ_3-Se (2.458 and 2.452 Å) respectively. The bimolecular units in the latter all have short chalcogenide Se···Se contacts averaging ~3.5 Å, which is a feature not observed in the $[Mo_3S_4(H_2O)_9]^{4+}$ structure.[22] The Mo–Se bonds are longer than the Mo–S bonds by amounts corresponding to differences in ionic radii $Se^{2-} > S^{2-}$ of 0.14 Å. Structures of the aqua ions $[M_3Se_4(H_2O)_9](pts)_4\cdot xH_2O$ (M = Mo, W; x = 10–12) are also essentially the same in their pts^- salts, and have similar M–M and M–Se bond lengths, Table 4. The Se···Se contacts 3.209–3.393 Å for the Mo complex and 3.450–3.561 Å for the W complex are again consistent with a weak dimerisation.

The structure of the double cube $[Mo_6AsSe_8(H_2O)_{18}](pts)_8\cdot 8H_2O$ has been determined, and bond lengths Mo–Mo, Mo–Se, Mo–As, As–Se are also listed in Table 4. Of the ten corner-shared $[Mo_6M'S_8(H_2O)_{18}]^{8+}$ derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$ so far identified (M′ = Mo, Hg, In, Tl, Ge, Sn, Pb, As, Sb, Bi),[1] X-ray structures have been determined for M′ = Mo,[23] Hg,[20,24] Ge,[9] Sn,[7,8,25] As,[16] Sb.[17] An 8+ charge is apparent in all cases, see also ref. 16. This is unusual since the heteroatoms M′ are from different Groups in the Periodic Table, and might be expected to have different oxidation states. To account for the behaviour observed the formulation $(Mo_3S_4^{4+})_2M'^0$, with retention of the trinuclear units, has been suggested.[16] The same 8+ charge applies to $[W_3S_4(H_2O)_9]^{4+}$ derivatives,[10] and to those with Se as the chalcogenide.[7] Moreover, with all post-transition M′ heteroatoms, there is evidence for M–M but no M–M′ bonding. The colours of the double cubes are different from those of the incomplete cubes, but UV-Vis spectra (Table 5) suggest some peak positions in common consistent with the formulation $(M_3Se_4^{4+})_2M'^0$. Similar colours for *e.g.* M′ = As, Sb, Bi derivatives of $[Mo_3Se_4(H_2O)_9]^{4+}$ (green) and $[W_3S_4(H_2O)_9]^{4+}$ (blue-green) are also apparent, Fig. 3 and 4.

Table 6 summarises the formation of single (S) and double (D) cube derivatives of the four trinuclear incomplete cubes $[M_3Q_4(H_2O)_9]^{4+}$ (M = Mo, W; Q = S, Se) with heteroatoms from Groups 12–15. All 10 heteroatoms so far studied react with $[Mo_3S_4(H_2O)_9]^{4+}$, but only 3 with $[W_3S_4(H_2O)_9]^{4+}$. A fuller picture now emerges of the reactivity of $[Mo_3Se_4(H_2O)_9]^{4+}$ with heteroatoms incorporated using Fe wire (~4 h),[6] Cu metal (~1 h),[6] as well as M′ = Hg,[20,24] In,[26] Ge,[9] Sn,[7] and in the present studies Pb, As, Sb, Bi (10 out of 10 so far). A similar reactivity is observed for $[W_3Se_4(H_2O)_9]^{4+}$ with M′ = Mo,[2] Hg,[20] In,[26] Ge,[9] Sn,[7] Pb, As, Bi (8 out of 8). The reactivity of $[W_3S_4(H_2O)_9]^{4+}$ on the other hand is less, with only 6 known examples M′ = Mo,[2] Ni,[3] Cu,[4] In,[10] Ge,[9] Sn.[10] Examples in which there is no reaction of $[W_3S_4(H_2O)_9]^{4+}$ include M′ = Fe,[19] Co,[19] Pd,[21] Hg,[20] and now Pb, As, Sb, Bi.

The observation that $[W_3S_4(H_2O)_9]^{4+}$ is much less reactive than the three other trinuclear clusters is most likely attributable to the redox properties of $M_3Q_4^{4+}$ (M = Mo, W; Q = S, Se). It is well known that W is more difficult to reduce than Mo,[27,28] and this observation appears to hold also for the chalcogenide clusters.[2,29] As MO calculations have shown the HOMO are predominantly 4d (Mo) or 5d (W) in character, which means that transfer of electron density upon heterometal incorporation (formally M'^0) is more favourable for Mo than W. However, as the same calculations show, it is the chalcogen which receives the extra negative charge.[30] As the electronegativity of S is greater than of Se, the resulting order of stability of the double cubes should be $Mo_6M'S_8 > Mo_6M'Se_8$ (which

Table 6 Summary of single (S) and corner-shared double cube (D) derivatives obtained from incomplete cubes $[M_3Q_4(H_2O)_9]^{4+}$ (M = Mo, W; Q = S, Se)

Heteroatom	$Mo_3S_4^{4+}$	$W_3S_4^{4+}$	$Mo_3Se_4^{4+}$	$W_3Se_4^{4+}$
Hg	D	No reaction	D	D
Ga	S	Not studied	Not studied	Not studied
In	S, D	S [a]	S [a]	S [a]
Tl	D	Not studied	Not studied	Not studied
Ge	S, D	S, D	S, D	S [a]
Sn	S, D	S, D	S, D	S, D
Pb	D	No reaction	D	D
As	D	No reaction	D	D
Sb	D	No reaction	D	D, S [b]
Bi	D	No reaction	D	D

[a] Existence of double cube not investigated. [b] A brown-yellow product is observed.

is what is observed). The opposite order is observed however for W with $W_6M'Se_8 > W_6M'S_8$. The mixing of metal and chalcogen AO in the HOMO is probably greater for Se than for S, and this lowers the energy of the HOMO sufficiently to compensate for the decrease in electronegativity for S as compared to Se. The net result is that the $W_3S_4^{4+}$ core does not bind readily to the transition metals or to those metals to the right-hand side of the Periodic Table in zero oxidation state. The ability of $[Mo_3S_4(H_2O)_9]^{4+}$ to interact with Cu metal and with Cu^{I} to give $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ and $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ respectively is of interest in this context.[31] With $[W_3S_4(H_2O)_9]^{4+}$ both reactions give $[W_3CuS_4(H_2O)_{10}]^{5+}$,[4] and $[W_3CuS_4(H_2O)_{10}]^{4+}$ (if it forms) undergoes spontaneous conversion to the 5+ cluster. A further example is provided by the binding of ethylene to the Ni of $[W_3NiS_4(H_2O)_{10}]^{4+}$ and related mixed Mo/W analogues.[3] The tungsten has less electron density than Mo, and ^{1}H NMR indicates a higher electron density on the H-atoms of the ethylene in the tungsten containing clusters. In the case of the Se clusters the softer Se^{2-} group is a dominant feature, and the properties of $[M_3Se_4(H_2O)_9]^{4+}$ (M = Mo, W) are much more alike.

As far as the magnetism of the cubes is concerned, the Group 15 containing double cubes have an odd number of electrons and are paramagnetic. In the case of Group 14 a molecular orbital treatment has been considered for $[Mo_6SnS_8(H_2O)_{18}]^{8+}$.[30] This shows that four electrons from the Sn are located in two MOs (HOMO and SHOMO *i.e.* the second highest OMO) of symmetry a_{1u} and a_{1g}. Because these orbitals are non-degenerate the Group 14 double cubes must be diamagnetic (2 and 2 populations in each). Group 13 containing double cubes have one electron less (they are paramagnetic and less stable), and the Group 15 cubes an odd electron in the LUMO (again they are less stable). This therefore agrees well with the higher stability of the Group 14 double cubes (in particular Ge and Sn).

To summarise, the work described illustrates a similar ability of $[M_3Se_4(H_2O)_9]^{4+}$ (M = Mo, W) to that of $[Mo_3S_4(H_2O)_9]^{4+}$ in forming heteroatom (M′) cubes with Pb, As, Sb and Bi. Corner-shared double cubes $[M_6M'Se_8(H_2O)_{18}]^{8+}$ are obtained with no evidence for single cube formation except in the case of Sb (M = W). However no similar reactivity of $[W_3S_4(H_2O)_9]^{4+}$ is observed, and here there is an unexpected diversity in behaviour. The latter is rationalised by considering electron-shifts in the case of $[W_3S_4(H_2O)_9]^{4+}$ which are more extreme than those for the two $[M_3Se_4(H_2O)_9]^{4+}$ clusters and $Mo_3S_4(H_2O)_9]^{4+}$.

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