

Preparation and properties of the corner-shared double cube $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$ as a derivative of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$

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The heterometallic corner-shared double-cuboidal cluster $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$, with the lead atom common to both cubes, has been prepared for the first time by the reaction of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ with lead shot, which requires up to 1 h to reach completion, and by addition of a solution mix of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ and Pb^{II} to an excess of BH_4^- , when reaction is rapid. The air-sensitive blue-green product has UV/VIS absorbance bands at 387 and 757 nm in 2.0 M HClO_4 . Inductively coupled plasma atomic emission spectroscopy confirmed the Mo:Pb:S ratio as 6:1:8. It was eluted from a cation-exchange column with 4 M Hpts (toluene-*p*-sulfonic acid), but not 2 M Hpts (or 4 M HClO_4), consistent with a high charge, confirmed as 8+ from the 2:1 stoichiometries for the oxidation reactions with *e.g.* $[\text{Co}(\text{dipic})_2]^-$ (dipic = pyridine-2,6-dicarboxylate) or $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, which yield $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$. Kinetic studies on the oxidations with $[\text{Co}(\text{dipic})_2]^-$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ were also carried out as part of an overall appraisal of the reactivity of the heterometallic clusters.

The now extensively studied trinuclear Mo^{IV}_3 incomplete cuboidal cluster $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ (refs. 1 and 2) has the quite remarkable ability of incorporating heterometal atoms M to give $[\text{Mo}_3\text{MS}_4(\text{H}_2\text{O})_9]^{4+}$ ($x = 10$ or 12) and related cuboidal complexes.^{3–5} The present listing (> 14 clusters) extends from Group 6 (Cr)⁶ through Group 15 (Bi)⁷ in the Periodic Table. Heterometallic clusters are also obtained from the Fe_3S_4 incomplete cube present in metalloproteins,^{8–12} and as Fe_3MS_4 analogue clusters,¹³ with *e.g.* M = Fe, Mn, Co, Ni, Zn or Cd. The greater stability and ease of preparation of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ derivatives has resulted in more extensive studies, with a range of single- and double-cube products.^{3,4} Whether a single or double cube is obtained seems to depend on the heterometal atom incorporated and the method of preparation used. With M = Hg, In, Tl, Pb or Bi the corner-shared double cubes (sometimes referred to as sandwich structures) $[\text{Mo}_6\text{MS}_8(\text{H}_2\text{O})_{18}]^{8+}$ are obtained, and are a feature of Main Group metallic elements. Single-cube clusters have been identified only in the case of M = In or Sn. In the present paper we add to this list and describe the preparation and properties of a Pb-containing product reported for the first time.

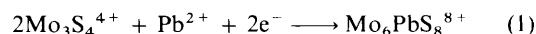
Molybdenum–lead mixed-metal compounds have previously attracted interest, and the stoichiometric compound Mo_6PbS_8 exists as a Chevrel-phase superconductor.¹⁴ Furthermore an all-lead cube $[\text{Pb}_4(\text{OH})_4]^{4+}$,^{15,16} obtained by hydrolysis of perchlorate solutions of Pb^{2+} , was first prepared in the 1960s. The cluster reported in this paper is the first Mo/Pb/S product obtained in aqueous solution.

Experimental

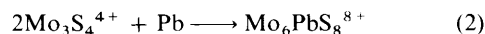
Preparation of Pb-containing cluster

Solutions of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ in 2.0 M Hpts (toluene-*p*-sulfonic acid) or 2.0 M HCl were obtained from the Mo^{V}_2 complex $[\text{Mo}_2(\mu\text{-S})_2\text{O}_2(\text{cys})_2]^{2-}$ [cys = cysteinate(2–)] by BH_4^- reduction as previously described, and purified by Dowex cation-exchange chromatography.^{1,2} Samples in 2.0 M HClO_4 , peak at 603 nm ($\epsilon = 362 \text{ M}^{-1} \text{ cm}^{-1}$ per Mo_3),^{1,2} were prepared by removal of HCl on a vacuum line and taking up the solid in 2.0 M HClO_4 as previously described,^{17,18} thereby obtaining solutions of a sufficiently high concentration. To synthesize the lead cluster two procedures were used. In the first

a solution of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ in 0.50 M Hpts (2 mM, 50 cm^3) containing a 10-fold excess of $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (0.46 g, 20 mM, Sigma) was syphoned onto a ≈ 100 -fold excess of NaBH_4 (0.38 g, 0.20 M) under a nitrogen atmosphere. A vigorous effervescence occurred, and the solution changed from green to blue-green. It was left stirring under N_2 for 30 min, after which the mixture was purified by Dowex 50W-X2 cation-exchange chromatography. All operations were carried out under nitrogen. Using 1–2 M Hpts unreacted $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ was first eluted. The blue-green Pb-containing cluster was then eluted with 4 M Hpts. No elution is observed with 2 M Hpts or 4 M HClO_4 . This is consistent with the stronger complexing of pts^- than ClO_4^- , and high charge on the product demonstrated to be 8+ for the corresponding clusters containing Hg,¹⁹ In,^{20,21} Tl,²² Sn,^{23,24} Sb²⁵ and Bi.⁷ The charge is assumed to be 8+ (confirmed below), which enables the reaction to be expressed as in equation (1).



The second procedure involves the direct interaction of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ (4–5 mM) in 2.0 M Hpts or HClO_4 with a large excess of lead shot (≈ 5 g), under an N_2 atmosphere, and leaving to react for 30–60 min. The lead shot was first cleaned and activated by washing with HClO_4 prior to use. The same colour change is observed for the reaction, (2). This procedure



was preferred as column purification is not required. It was moreover the only method available to us for preparing stock solutions in 2.0 M HClO_4 . However, if stock solutions prepared by reaction (2) are left to stand with an excess of Pb over long periods, a build-up of Pb^{2+} can occur as a result of ingress of O_2 and oxidation back to $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ which recycles. Hydrochloric acid was generally avoided because of the possibility of insoluble PbCl_2 forming. Stock solutions were stored by placing a container within a container, both under nitrogen at 4 °C. Under these conditions less than 10% oxidation was observed in 5 d.

Metal analyses were carried out by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on product freshly eluted from a Dowex column with 2 M HCl. The ratio

Mo:S:Pb obtained was 6.1:8.4:1, consistent with a core structure Mo_6PbS_8 . We have not so far been able to isolate crystals suitable for structure determination.

Solutions of $[\text{Mo}_3\text{S}_3\text{O}(\text{H}_2\text{O})_9]^{4+}$ and $[\text{Mo}_3\text{S}_2\text{O}_2(\text{H}_2\text{O})_9]^{4+}$ were prepared by procedures described.¹

UV/VIS and NIR spectra

The spectrum of the $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$ cluster (ϵ per Mo_6) in 2 M HClO_4 is shown in Fig. 1, alongside that of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ (ϵ per Mo_3). The spectrum varies little in HCl, Hpts and HClO_4 , where peak positions λ/nm ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$) are as listed in Table 1 (ϵ values per Mo_6). The ϵ values were determined by allowing solutions of the lead cube to oxidize with air to $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$, which has accurately known λ/nm ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$ per Mo_3) values of 248 (8219), 366 (5550) and 603 (362) in 2 M HClO_4 .^{1,2} No NIR absorbance was observed up to 1300 nm.

Other reactants

A sample of $\text{NH}_4[\text{Co}^{\text{III}}(\text{dipic})_2]\cdot\text{H}_2\text{O}$, where dipic is pyridine-2,6-dicarboxylate, λ/nm ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$) 510 (630), was prepared as previously described.⁶ Solutions of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ were obtained by column purification of $\text{Fe}(\text{ClO}_4)_3\cdot 6\text{H}_2\text{O}$ (Fluka). The final elution was carried out with 1.0 M HClO_4 . Other reagents used including Hpts (from Aldrich), HCl, HClO_4 and LiClO_4 were of analytical grade purity, and used as supplied.

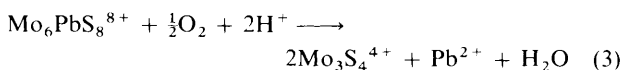
Kinetic studies

These were carried out at $25.0 \pm 0.1^\circ\text{C}$ using perchlorate solutions of $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$, ionic strength 2.00 ± 0.01 M (LiClO_4). Reactions were studied with the oxidant in large >20-fold excess over $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$. All the kinetic runs were performed on a Dionex D-110 stopped-flow spectrophotometer.

Results

Stability of $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$

The cluster is very air sensitive, and rigorous oxygen-free conditions are required for transfers and storage. On exposure to air, with some shaking, decay back to $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ is observed $t_{1/2} \approx 2$ min, equation (3).



Beer's law

On varying the concentration of cluster in 2.00 M HClO_4 within the range 0.05–1.0 mM (using optical cells of different path length), Beer's law was found to be obeyed at all three peak positions 247, 387 and 757 nm, $l = 2.00$ M. It is concluded that a single main species is present in all such solutions.

Complexing with Cl^-

Small changes only are observed in the absorbance spectrum of $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$ on changing the acid from HClO_4 (or Hpts) to HCl, Table 1. Similar shifts have been noted for the incomplete cube $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ in 2.0 M HCl.¹⁸ The effect is assigned to the complexing of Cl^- at the Mo atoms.

Stoichiometry of oxidation reactions

Aliquots of the oxidants $[\text{Co}(\text{dipic})_2]^-$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ (solutions ≈ 20 times more concentrated than those of the cluster) were titrated into solutions of $\text{Mo}_6\text{PbS}_8^{8+}$ in 2 M HClO_4 , and absorbance changes monitored at the cluster peak position at 757 nm. The sole Mo-containing product of

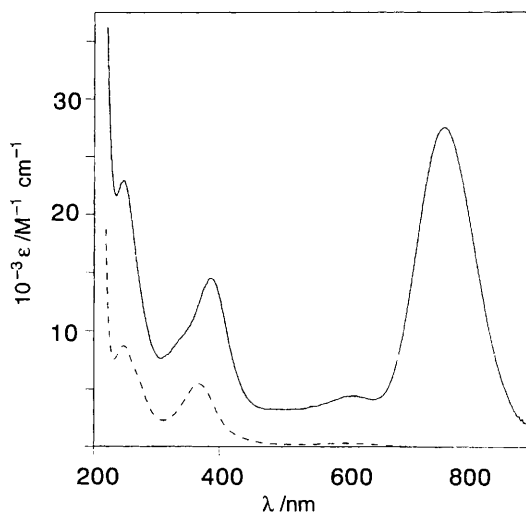


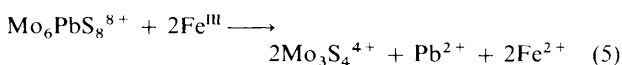
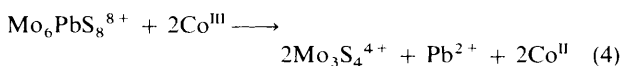
Fig. 1 The UV/VIS spectra (25 °C) of $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$ (—) and $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ (---), ϵ values per Mo_6 and Mo_3 respectively, $l = 2.00$ M (HClO_4)

Table 1 Peak positions λ/nm ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$ per Mo_6) from UV/VIS absorbance spectra of the Mo_6PbS_8 cluster in different acids

| 2 M HClO_4 | 2 M Hpts | 2 M HCl |
|---------------------|-------------------|-----------------|
| 247 (22 068) | 326 (sh) (10 560) | 255 (22 700) |
| 387 (13 955) | 392 (14 590) | 390 (12 800) |
| 612 (sh) (4557) | * | 620 (sh) (3600) |
| 757 (27 300) | 757 (27 300) | 787 (24 100) |

* Not observed.

oxidation was identified spectrophotometrically as $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$. Stoichiometries of 2.11 ± 0.10 (Co) and 1.95 ± 0.07 (Fe) were obtained from six determinations in each case, consistent with equations (4) and (5). To give a balance in



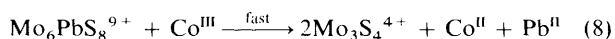
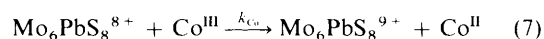
these equations it is concluded that Mo_6PbS_8 has an 8+ charge, and the cluster is therefore assigned a formula $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$, Fig. 2.

Kinetics of oxidation of $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$ with $[\text{Co}(\text{dipic})_2]^-$

The conversion of $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$ into $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$, equation (4), was monitored at 757 nm. First-order rate constants k_{obs} were determined by the stopped-flow method, with the oxidant $[\text{Co}(\text{dipic})_2]^-$ in ≥ 20 -fold excess over $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$. A linear dependence of k_{obs} on $[\text{Co}(\text{dipic})_2]^-$ is observed, Fig. 3, consistent with the rate law (6). No dependence of rate constants on $[\text{H}^+]$ in the range

$$-d[\text{Mo}_6\text{PbS}_8^{8+}]/dt = k_{\text{Co}}[\text{Mo}_6\text{PbS}_8^{8+}][\text{Co}(\text{dipic})_2^-] \quad (6)$$

0.50–2.00 M is observed, $l = 2.00$ M (LiClO_4), Fig. 3. From the slope $k_{\text{Co}} = (2.76 \pm 0.05) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. A reaction sequence (7), (8) is consistent with the behaviour observed, where the 9+



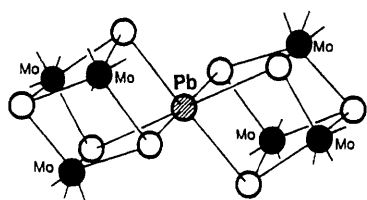


Fig. 2 Structure of $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$ in solution

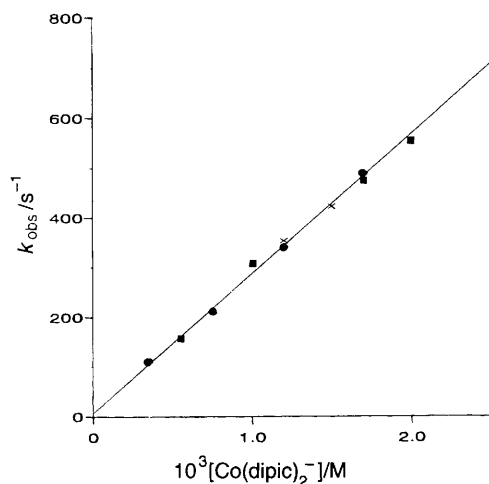


Fig. 3 Dependence of first-order rate constants k_{obs} (25 °C) for the oxidation of $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$ with $[\text{Co}(\text{dipic})_2]^-$, $[\text{H}^+] = 2.00$ (■), 1.00 (×) and 0.50 M (●). $I = 2.00$ M (LiClO_4)

product is a transient species, not so far characterized. Reaction (8) can occur by fast oxidation to a 10+ product which then undergoes decay, or alternatively by dissociation of the 9+ product to give a fragment which oxidizes rapidly.

Kinetics of oxidation of $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$ with $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

The reaction summarized by equation (5) was monitored by stopped-flow spectrophotometry at 757 nm. Pseudo-first-order behaviour is again observed, and rate constants (k_{obs}) with the oxidant in large excess are as listed in Table 2. A linear dependence of k_{obs} on $[\text{Fe}^{\text{III}}]$ is observed at each $[\text{H}^+]$. The reaction is therefore first order in the concentrations of each reactant, (9). On varying $[\text{H}^+]$ in the range 0.50–2.00 M a linear

$$-d[\text{Mo}_6\text{PbS}_8^{8+}]/dt = k_{\text{Fe}}[\text{Mo}_6\text{PbS}_8^{8+}][\text{Fe}^{\text{III}}] \quad (9)$$

dependence of k_{Fe} on $[\text{H}^+]^{-1}$, (10), is found, Fig. 4. From a plot

$$k_{\text{Fe}} = k_a + k'_b[\text{H}^+]^{-1} \quad (10)$$

of k_{Fe} against $[\text{H}^+]^{-1}$ the intercept yields k_a ($1430 \pm 60 \text{ M}^{-1} \text{ s}^{-1}$) and slope k'_b ($820 \pm 50 \text{ s}^{-1}$). The reaction sequence is similar to (7) and (8), with $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ (k_a) and $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ (k_b) contributing to the rate-determining first stage (7).

Discussion

The corner-shared double-cube $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$ structure, Fig. 2, is deduced for the blue-green product obtained in these studies. Thus ICP-AES analyses indicate a Mo:Pb:S ratio of 6:1:8. In addition Dowex cation-exchange chromatography experiments, with elution using 4.0 M Hpts (but not 2.0 M Hpts or 4.0 M HClO_4), are consistent with a high charge. The charge is confirmed as 8+ from the 2:1 stoichiometries observed for the reactions with $[\text{Co}(\text{dipic})_2]^-$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, equations (4) and (5), with $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$

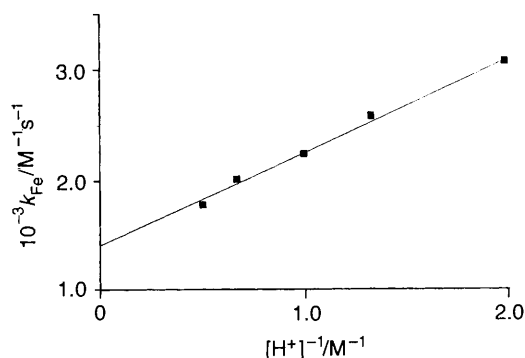


Fig. 4 Dependence of second-order rate constants k_{Fe} (25 °C) on $[\text{H}^+]^{-1}$ for the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ oxidation of $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$, $I = 2.00$ M (LiClO_4)

Table 2 The variation of rate constants k_{obs} (25 °C) for the oxidation of $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$, $(4-8) \times 10^{-6}$ M, by $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $I = 2.00$ M (LiClO_4)

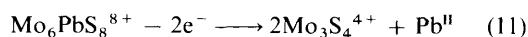
| $[\text{H}^+]/\text{M}$ | $[\text{Fe}^{\text{III}}]/\text{mM}$ | $k_{\text{obs}}/\text{s}^{-1}$ |
|-------------------------|--------------------------------------|--------------------------------|
| 2.00 | 0.50 | 1.00 |
| | 1.00 | 1.90 |
| | 1.50 | 2.56 |
| | 2.00 | 3.7 |
| | 2.50 | 4.4 |
| 1.50 | 0.50 | 1.10 |
| | 1.00 | 2.06 |
| | 1.50 | 3.00 |
| | 2.00 | 4.0 |
| | 2.50 | 5.1 |
| 1.00 | 0.50 | 1.30 |
| | 1.00 | 2.46 |
| | 1.50 | 3.6 |
| | 2.00 | 4.6 |
| | 2.50 | 5.8 |
| 0.75 | 0.50 | 1.40 |
| | 1.50 | 4.0 |
| | 2.00 | 5.1 |
| | 0.50 | 1.51 |
| | 1.00 | 3.1 |
| 0.50 | 1.50 | 4.5 |
| | 2.00 | 6.1 |

the only Mo-containing product. Moreover a single species is indicated from the conformity to Beer's law at three different wavelengths using a 20-fold variation in cluster concentration. There are now seven clusters of this type, the others incorporating Hg,¹⁹ In,^{20,21} Tl,²² Sn,^{23,24} Sb²⁵ and Bi.⁷ Those of Hg,¹⁹ In,^{20,26} Sn,²³ and Sb²⁵ have been characterized by X-ray crystallography. This type of structure appears to be by far the most favoured by Main Group heterometal atoms. Another example is provided by $[\text{Mo}_7\text{S}_8(\text{H}_2\text{O})_{18}]^{8+}$,²⁷ which is the only case at present in which a transition metal occupies the nodal position.

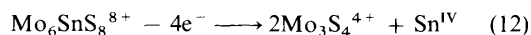
The double-cube $[\text{Mo}_6\text{InS}_8(\text{H}_2\text{O})_{18}]^{8+}$ [λ/nm ($\epsilon/\text{M}^{-1} \text{ cm}^{-1}$) 488 (6650) and 794 (648) (ϵ per Mo_6)] has only recently been prepared by reduction of a mixture of the single cube $[\text{Mo}_3\text{InS}_4(\text{H}_2\text{O})_{12}]^{5+}$ and $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ with BH_4^- or H_3PO_2 .²¹ The product cannot be column purified due to a quite rapid reaction with H^+ . However in related chemistry the incomplete cube $[\text{Mo}_3\text{S}_3\text{O}(\text{H}_2\text{O})_9]^{4+}$, with one μ -sulfido core atom replaced by μ -oxo, has been shown to react with indium metal to give the corner-shared double cube $[(\text{H}_2\text{O})_9\text{Mo}_3\text{S}_3\text{OInOS}_3\text{Mo}_3(\text{H}_2\text{O})_9]^{8+}$, which has been characterized by X-ray crystallography.²⁰ No evidence was found in the present studies for any reaction of lead with the oxosulfido clusters $[\text{Mo}_3\text{S}_3\text{O}(\text{H}_2\text{O})_9]^{4+}$ and $[\text{Mo}_3\text{S}_2\text{O}_2(\text{H}_2\text{O})_9]^{4+}$, containing one μ -oxo and two μ -oxo core atoms respectively. The

indium derivative of $[\text{Mo}_3\text{S}_3\text{O}(\text{H}_2\text{O})_9]^{4+}$ therefore remains an isolated example. More generally it is not clear why the Mo_6 heterometallic clusters should be $8+$, and why the heterometal should occupy the nodal position. These are features which require further clarification.

The oxidations of $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$ with $[\text{Co}(\text{dipic})_2]^-$ and hexaaqua iron(III) give 1:2 stoichiometries, equations (4) and (5). Two moles of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_6]^{4+}$ are formed and no other stable oxidation state is identified. Equation (11)



summarizes the half-reaction. When the cluster $[\text{Mo}_6\text{SnS}_8(\text{H}_2\text{O})_{18}]^{8+}$ is oxidized (Sn also Group 14)²⁴ the single-cube cluster $[\text{Mo}_3\text{SnS}_4(\text{H}_2\text{O})_{12}]^{6+}$ is formed as a two-equivalent product prior to further oxidation to $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$

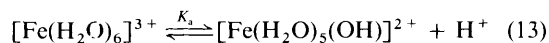


The corresponding half-reaction (12), differs therefore from (11) in the oxidation state of the heterometallic product.

Only two single-cube clusters $[\text{Mo}_3\text{InS}_4(\text{H}_2\text{O})_{12}]^{5+}$ and $[\text{Mo}_3\text{SnS}_4(\text{H}_2\text{O})_{12}]^{6+}$ of the Main Group metals have so far been isolated. Both have been characterized by X-ray crystallography.^{24,26} The existence of single and corner-shared double cubes for these 5p metals may relate to the redox properties of $\text{In}^{\text{I}}-\text{In}^{\text{III}}$ and $\text{Sn}^{\text{II}}-\text{Sn}^{\text{IV}}$. In the latter case an assignment of these states to the double (Sn^{II}) and single (Sn^{IV}) cubes respectively has been suggested, consistent with the redox behaviour observed. No evidence has been obtained for the single cube Mo_3PbS_4 as a stable form, and Pb as a heterometal appears therefore to behave like Hg, Tl and Bi (6p series).

There is no marked influence of 2.0 M HCl on the UV/VIS spectrum of $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$. This contrasts with the behaviour observed for $[\text{Mo}_6\text{BiS}_8(\text{H}_2\text{O})_{18}]^{8+}$, which gives a strong association ($K > 40 \text{ M}^{-1}$), and an appreciable change in colour assigned to the complexing of one chloride at the Bi atom.⁷ In the case of $[\text{Mo}_6\text{SnS}_8(\text{H}_2\text{O})_{18}]^{8+}$ it is known that chloride interacts with the Sn and induces dissociation to $[\text{Mo}_3(\text{SnCl}_3)\text{S}_4(\text{H}_2\text{O})_9]^{3+}$.²⁴ The high affinity of Sn for Cl^- in the single cube ($K > 10^2 \text{ M}^{-3}$) has been noted.

The absence of an $[\text{H}^+]$ dependence for the $[\text{Co}(\text{dipic})_2]^-$ oxidation of $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$ is as observed for other clusters,^{4,28} and the mechanism is outer sphere. Likewise the k_a and k_b terms determined in the case of the iron(III) oxidation (10) are assigned to the reactions of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ respectively, where K_a (25 °C) for the acid-dissociation process (13) is $1.0 \times 10^{-3} \text{ M}$ at $I = 2.00 \text{ M}$



(NaClO_4).²⁹ The k_a term ($1430 \text{ M}^{-1} \text{ s}^{-1}$) corresponds to an outer-sphere process, and k_b ($=k_b'/K_a$) to the reaction of $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ with $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$ ($8.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$). The rate constant enhancement in the latter case is attributed to an inner-sphere process, with a hydroxo-bridge between Fe and Mo (or Pb) in the activated complex $\{\text{Mo}_6\text{S}_8\text{Pb}(\text{OH})\text{Fe}(\text{H}_2\text{O})_5\}^{10+}$ assisting the electron-transfer process.

The lead cluster is very oxygen sensitive, like many other heterometallic clusters obtained from $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$, and in particular the corner-shared clusters. This is of interest in view of the sheltered position of the heterometal atom, and the expected substitution inertness of the Mo atoms.³⁰ The reaction of $[\text{Mo}_3\text{FeS}_4(\text{H}_2\text{O})_{10}]^{4+}$ with oxygen has been studied in some detail,³¹ and an intermediate formulated as $[\text{Mo}_3\text{FeS}_4(\text{O}_2)]^{4+}$ detected. Addition of oxygen at the lead in the protected nodal position of the double cube is less likely to occur, and an outer-

sphere mechanism is therefore suggested. Outer-sphere reactions of O_2 have been observed previously.^{32,34}

All the corner-shared double clusters have intense UV bands in the range 320–390 nm, and a second intense band at higher wavelengths. In the case of $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$ such a peak is observed at 757 nm, with the unusually high ϵ associated with a charge-transfer process. By analogy with $[\text{Mo}_6\text{SnS}_8(\text{H}_2\text{O})_{18}]^{8+}$ the oxidation state of Pb is most likely II. Shibahara *et al.*¹⁹ have suggested an assignment Hg^0 in the $[\text{Mo}_6\text{HgS}_8(\text{H}_2\text{O})_{18}]^{8+}$ cluster, which has very long Hg–S bond lengths of $\approx 2.84 \text{ \AA}$. Owing to the sensitivity of the In- and Tl-containing clusters to H^+ oxidation,^{21,22} an oxidation state I assignment to these heterometal atoms is favoured. Different oxidation levels of the Mo_3S_4 component are implicated by such variations in oxidation state of the heterometal atom.

Recent work has revealed that $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ in 2 M HCl will interact with lead metal to form $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{4+}$,³⁵ with no incorporation of lead. The mechanism of this reaction is not clear to us, and certainly merits further investigation.

To summarize, lead has been incorporated into $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ for the first time to give $[\text{Mo}_6\text{PbS}_8(\text{H}_2\text{O})_{18}]^{8+}$. Heterometallic corner-shared double-cube clusters of this type have now been prepared for $M = \text{Hg}, \text{In}, \text{Tl}, \text{Sn}, \text{Pb}, \text{Sb}$ or Bi , and are a particular feature of Main Group metals. No evidence has been obtained for a single cube analogous to $[\text{Mo}_3\text{SnS}_4(\text{H}_2\text{O})_{12}]^{6+}$. Whilst the cluster has the same empirical formula as the Chevrel-phase superconductor Mo_6PbS_8 , the latter has a quite different structure with eight S atoms in a cube containing an Mo_6 unit, *i.e.* with a Mo at the centre of each face of the cube.¹⁶ The Pb atoms intercalate between Mo_6S_8 units in this structure.

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