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Preparation and properties of the corner-shared double cube $[Mo_6PbS_8(H_2O)_{18}]^{8+}$ as a derivative of $[Mo_3S_4(H_2O)_9]^{4+}$

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The heterometallic corner-shared double-cuboidal cluster $[Mo_6PbS_8(H_2O)_{18}]^{8+}$, with the lead atom common to both cubes, has been prepared for the first time by the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with lead shot, which requires up to 1 h to reach completion, and by addition of a solution mix of $[Mo_3S_4(H_2O)_9]^{4+}$ 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.* $[Co(dipic)_2]^-$ (dipic = pyridine-2,6-dicarboxylate) or $[Fe(H_2O)_6]^{3+}$, which yield $[Mo_3S_4(H_2O)_9]^{4+}$. Kinetic studies on the oxidations with $[Co(dipic)_2]^-$ and $[Fe(H_2O)_6]^{3+}$ 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 $[Mo_3S_4(H_2O)_9]^{4+}$ (refs. 1 and 2) has the quite remarkable ability of incorporating heterometal atoms M to give $[Mo_3MS_4(H_2O)_x]^{4+}$ (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 $[Mo_3S_4(H_2O)_9]^{4+}$ 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) $[Mo_6MS_8(H_2O)_{18}]^{8+}$ 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 $[Pb_4(OH)_4]^{4+}$,[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 $[Mo_3S_4(H_2O)_9]^{4+}$ in 2.0 M Hpts (toluene-*p*-sulfonic acid) or 2.0 M HCl were obtained from the Mo^V_2 complex $[Mo_2(\mu\text{-}S)_2O_2(cys)_2]^{2-}$ [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 (ε = 362 M^{-1} 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 $[Mo_3S_4(H_2O)_9]^{4+}$ in 0.50 M Hpts (2 mM, 50 cm^3) containing a 10-fold excess of $Pb(ClO_4)_2 \cdot 3H_2O$ (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 $[Mo_3S_4(H_2O)_9]^{4+}$ 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] Sb[25] and Bi.[7] The charge is assumed to be 8+ (confirmed below), which enables the reaction to be expressed as in equation (1).

$$2Mo_3S_4^{4+} + Pb^{2+} + 2e^- \longrightarrow Mo_6PbS_8^{8+} \qquad (1)$$

The second procedure involves the direct interaction of $[Mo_3S_4(H_2O)_9]^{4+}$ (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

$$2Mo_3S_4^{4+} + Pb \longrightarrow Mo_6PbS_8^{8+} \qquad (2)$$

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 $[Mo_3S_4(H_2O)_9]^{4+}$ 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 $[Mo_3S_3O(H_2O)_9]^{4+}$ and $[Mo_3S_2O_2(H_2O)_9]^{4+}$ were prepared by procedures described.[1]

UV/VIS and NIR spectra

The spectrum of the $[Mo_6PbS_8(H_2O)_{18}]^{8+}$ cluster (ε per Mo_6) in 2 M $HClO_4$ is shown in Fig. 1, alongside that of $[Mo_3S_4(H_2O)_9]^{4+}$ (ε per Mo_3). The spectrum varies little in HCl, Hpts and $HClO_4$, where peak positions λ/nm (ε/M^{-1} 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 $[Mo_3S_4(H_2O)_9]^{4+}$, which has accurately known λ/nm (ε/M^{-1} 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 $NH_4[Co^{III}(dipic)_2]\cdot H_2O$, where dipic is pyridine-2,6-dicarboxylate, λ/nm (ε/M^{-1} cm^{-1}) 510 (630), was prepared as previously described.[6] Solutions of $[Fe(H_2O)_6]^{3+}$ were obtained by column purification of $Fe(ClO_4)_3\cdot 6H_2O$ (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 ± 0.1 °C using perchlorate solutions of $[Mo_6PbS_8(H_2O)_{18}]^{8+}$, ionic strength 2.00 ± 0.01 M ($LiClO_4$). Reactions were studied with the oxidant in large >20-fold excess over $[Mo_6PbS_8(H_2O)_{18}]^{8+}$. All the kinetic runs were performed on a Dionex D-110 stopped-flow spectrophotometer.

Results

Stability of $[Mo_6PbS_8(H_2O)_{18}]^{8+}$

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 $[Mo_3S_4(H_2O)_9]^{4+}$ is observed $t_{\frac{1}{2}} \approx 2$ min, equation (3).

$$Mo_6PbS_8{}^{8+} + \tfrac{1}{2}O_2 + 2H^+ \longrightarrow 2Mo_3S_4{}^{4+} + Pb^{2+} + H_2O \quad (3)$$

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, $I = 2.00$ 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 $[Mo_6PbS_8(H_2O)_{18}]^{8+}$ on changing the acid from $HClO_4$ (or Hpts) to HCl, Table 1. Similar shifts have been noted for the incomplete cube $[Mo_3S_4(H_2O)_9]^{4+}$ 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 $[Co(dipic)_2]^-$ and $[Fe(H_2O)_6]^{3+}$ (solutions ≈20 times more concentrated than those of the cluster) were titrated into solutions of $Mo_6PbS_8{}^{8+}$ in 2 M $HClO_4$, and absorbance changes monitored at the cluster peak position at 757 nm. The sole Mo-containing product of oxidation was identified spectrophotometrically as $[Mo_3S_4(H_2O)_9]^{4+}$. 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

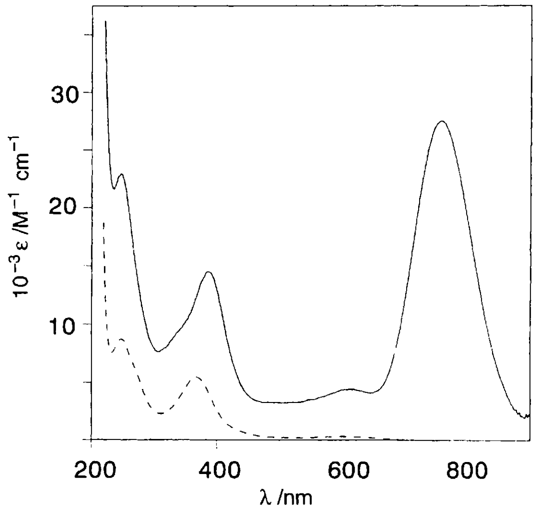

Fig. 1 The UV/VIS spectra (25 °C) of $[Mo_6PbS_8(H_2O)_{18}]^{8+}$ (——) and $[Mo_3S_4(H_2O)_9]^{4+}$ (– – – –), ε values per Mo_6 and Mo_3 respectively, $I = 2.00$ M ($HClO_4$)

Table 1 Peak positions λ/nm (ε/M^{-1} 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.

$$Mo_6PbS_8{}^{8+} + 2Co^{III} \longrightarrow 2Mo_3S_4{}^{4+} + Pb^{2+} + 2Co^{II} \quad (4)$$

$$Mo_6PbS_8{}^{8+} + 2Fe^{III} \longrightarrow 2Mo_3S_4{}^{4+} + Pb^{2+} + 2Fe^{2+} \quad (5)$$

these equations it is concluded that Mo_6PbS_8 has an 8+ charge, and the cluster is therefore assigned a formula $[Mo_6PbS_8(H_2O)_{18}]^{8+}$, Fig. 2.

Kinetics of oxidation of $[Mo_6PbS_8(H_2O)_{18}]^{8+}$ with $[Co(dipic)_2]^-$

The conversion of $[Mo_6PbS_8(H_2O)_{18}]^{8+}$ into $[Mo_3S_4(H_2O)_9]^{4+}$, equation (4), was monitored at 757 nm. First-order rate constants k_{obs} were determined by the stopped-flow method, with the oxidant $[Co(dipic)_2]^-$ in ⩾20-fold excess over $[Mo_6PbS_8(H_2O)_{18}]^{8+}$. A linear dependence of k_{obs} on $[Co(dipic)_2{}^-]$ is observed, Fig. 3, consistent with the rate law (6). No dependence of rate constants on $[H^+]$ in the range

$$-d[Mo_6PbS_8{}^{8+}]/dt = k_{Co}[Mo_6PbS_8{}^{8+}][Co(dipic)_2{}^-] \quad (6)$$

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

$$Mo_6PbS_8{}^{8+} + Co^{III} \xrightarrow{k_{Co}} Mo_6PbS_8{}^{9+} + Co^{II} \quad (7)$$

$$Mo_6PbS_8{}^{9+} + Co^{III} \xrightarrow{\text{fast}} 2Mo_3S_4{}^{4+} + Co^{II} + Pb^{II} \quad (8)$$

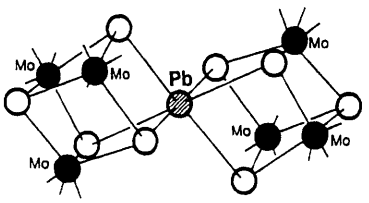

Fig. 2 Structure of $[Mo_6PbS_8(H_2O)_{18}]^{8+}$ in solution

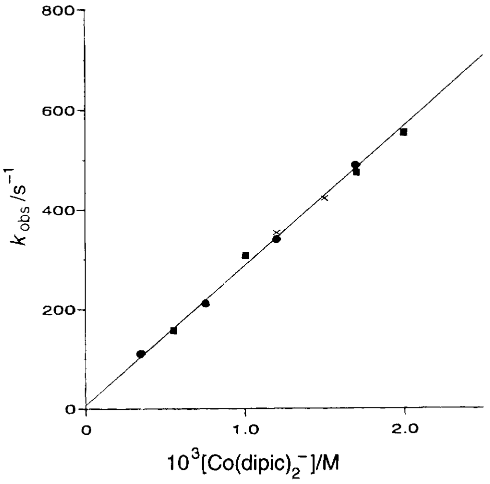

Fig. 3 Dependence of first-order rate constants k_{obs} (25 °C) for the oxidation of $[Mo_6PbS_8(H_2O)_{18}]^{8+}$ with $[Co(dipic)_2]^-$, $[H^+]$ = 2.00 (■), 1.00 (×) and 0.50 M (●), I = 2.00 M ($LiClO_4$)

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 $[Mo_6PbS_8(H_2O)_{18}]^{8+}$ with $[Fe(H_2O)_6]^{3+}$

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 $[Fe^{III}]$ is observed at each $[H^+]$. The reaction is therefore first order in the concentrations of each reactant, (9). On varying $[H^+]$ in the range 0.50–2.00 M a linear

$$-d[Mo_6PbS_8{}^{8+}]/dt = k_{Fe}[Mo_6PbS_8{}^{8+}][Fe^{III}] \qquad (9)$$

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

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

of k_{Fe} against $[H^+]^{-1}$ the intercept yields k_a (1430 ± 60 M^{-1} s^{-1}) and slope k'_b (820 ± 50 s^{-1}). The reaction sequence is similar to (7) and (8), with $[Fe(H_2O)_6]^{3+}$ (k_a) and $[Fe(H_2O)_5(OH)]^{2+}$ (k_b) contributing to the rate-determining first stage (7).

Discussion

The corner-shared double-cube $[Mo_6PbS_8(H_2O)_{18}]^{8+}$ 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 $[Co(dipic)_2]^-$ and $[Fe(H_2O)_6]^{3+}$, equations (4) and (5), with $[Mo_3S_4(H_2O)_9]^{4+}$ 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] Sb[25] and Bi.[7] Those of Hg,[19] In,[20,26] Sn,[23] and Sb[25] 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 $[Mo_7S_8(H_2O)_{18}]^{8+}$,[27] which is the only case at present in which a transition metal occupies the nodal position.

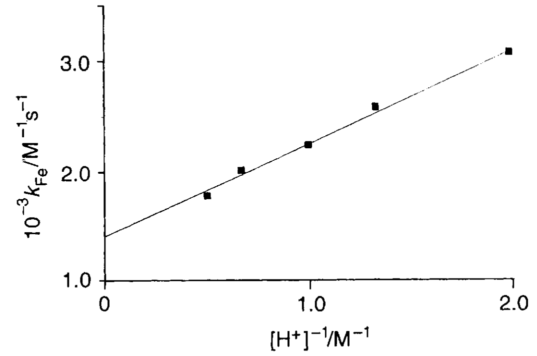

Fig. 4 Dependence of second-order rate constants k_{Fe} (25 °C) on $[H^+]^{-1}$ for the $[Fe(H_2O)_6]^{3+}$ oxidation of $[Mo_6PbS_8(H_2O)_{18}]^{8+}$, I = 2.00 M ($LiClO_4$)

Table 2 The variation of rate constants k_{obs} (25 °C) for the oxidation of $[Mo_6PbS_8(H_2O)_{18}]^{8+}$, (4–8) × 10^{-6} M, by $[Fe(H_2O)_6]^{3+}$, I = 2.00 M ($LiClO_4$)

$[H^+]$/M	$[Fe^{III}]$/mM	k_{obs}/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	0.50	1.51
	1.00	3.1
	1.50	4.5
	2.00	6.1

The double-cube $[Mo_6InS_8(H_2O)_{18}]^{8+}$ [λ/nm (ε/M^{-1} 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 $[Mo_3InS_4(H_2O)_{12}]^{5+}$ and $[Mo_3S_4(H_2O)_9]^{4+}$ 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 $[Mo_3S_3O(H_2O)_9]^{4+}$, 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 $[(H_2O)_9Mo_3S_3OInOS_3Mo_3(H_2O)_9]^{8+}$, 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 $[Mo_3S_3O(H_2O)_9]^{4+}$ and $[Mo_3S_2O_2(H_2O)_9]^{4+}$, containing one μ-oxo and two μ-oxo core atoms respectively. The indium derivative of $[Mo_3S_3O(H_2O)_9]^{4+}$ 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 $[Mo_6PbS_8(H_2O)_{18}]^{8+}$ with $[Co(dipic)_2]^-$ and hexaaqua iron(III) give 1:2 stoichiometries, equations (4) and (5). Two moles of $[Mo_3S_4(H_2O)_9]^{4+}$ are formed and no other stable oxidation state is identified. Equation (11)

$$Mo_6PbS_8{}^{8+} - 2e^- \longrightarrow 2Mo_3S_4{}^{4+} + Pb^{II} \qquad (11)$$

summarizes the half-reaction. When the cluster $[Mo_6SnS_8(H_2O)_{18}]^{8+}$ is oxidized (Sn also Group 14)[24] the single-cube cluster $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ is formed as a two-equivalent product prior to further oxidation to $[Mo_3S_4(H_2O)_9]^{4+}$

$$Mo_6SnS_8{}^{8+} - 4e^- \longrightarrow 2Mo_3S_4{}^{4+} + Sn^{IV} \qquad (12)$$

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

Only two single-cube clusters $[Mo_3InS_4(H_2O)_{12}]^{5+}$ and $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ 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 In^{I}–In^{III} and Sn^{II}–Sn^{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 $[Mo_6PbS_8(H_2O)_{18}]^{8+}$. This contrasts with the behaviour observed for $[Mo_6BiS_8(H_2O)_{18}]^{8+}$, which gives a strong association ($K > 40$ M^{-1}), and an appreciable change in colour assigned to the complexing of one chloride at the Bi atom.[7] In the case of $[Mo_6SnS_8(H_2O)_{18}]^{8+}$ it is known that chloride interacts with the Sn and induces dissociation to $[Mo_3(SnCl_3)S_4(H_2O)_9]^{3+}$.[24] The high affinity of Sn for Cl^- in the single cube ($K > 10^2$ M^{-1}) has been noted.

The absence of an $[H^+]$ dependence for the $[Co(dipic)_2]^-$ oxidation of $[Mo_6PbS_8(H_2O)_{18}]^{8+}$ 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 $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_5(OH)]^{2+}$ respectively, where K_a (25 °C) for the acid-dissociation process (13) is 1.0×10^{-3} M at $I = 2.00$ M

$$[Fe(H_2O)_6]^{3+} \overset{K_a}{\rightleftharpoons} [Fe(H_2O)_5(OH)]^{2+} + H^+ \qquad (13)$$

($NaClO_4$).[29] The k_a term (1430 M^{-1} s^{-1}) corresponds to an outer-sphere process, and k_b ($=k_b'/K_a$) to the reaction of $[Fe(H_2O)_5(OH)]^{2+}$ with $[Mo_6PbS_8(H_2O)_{18}]^{8+}$ (8.2×10^5 M^{-1} 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 $\{Mo_6S_8Pb(OH)Fe(H_2O)_5\}^{10+}$ assisting the electron-transfer process.

The lead cluster is very oxygen sensitive, like many other heterometallic clusters obtained from $[Mo_3S_4(H_2O)_9]^{4+}$, 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 $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ with oxygen has been studied in some detail,[31] and an intermediate formulated as $[Mo_3FeS_4(O_2)]^{4+}$ 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 $[Mo_6PbS_8(H_2O)_{18}]^{8+}$ such a peak is observed at 757 nm, with the unusually high ε associated with a charge-transfer process. By analogy with $[Mo_6SnS_8(H_2O)_{18}]^{8+}$ the oxidation state of Pb is most likely II. Shibahara *et al.*[19] have suggested an assignment Hg^0 in the $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ cluster, which has very long Hg–S bond lengths of ≈2.84 Å. 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 $[Mo_3S_4(H_2O)_9]^{4+}$ in 2 M HCl will interact with lead metal to form $[Mo_4S_4(H_2O)_{12}]^{4+}$,[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 $[Mo_3S_4(H_2O)_9]^{4+}$ for the first time to give $[Mo_6PbS_8(H_2O)_{18}]^{8+}$. Heterometallic corner-shared double-cube clusters of this type have now been prepared for M = Hg, In, Tl, Sn, Pb, Sb or Bi, and are a particular feature of Main Group metals. No evidence has been obtained for a single cube analogous to $[Mo_3SnS_4(H_2O)_{12}]^{6+}$. 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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