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FULL PAPER

Formation (and properties) of palladium derivatives of $[Mo_3Q_4(H_2O)_9]^{4+}$: absence of similar derivatives of $[W_3Q_4(H_2O)_9]^{4+}$ (Q = S, Se)

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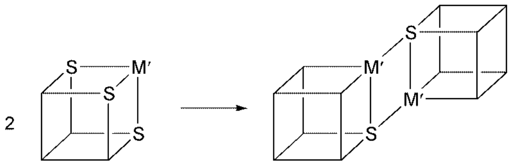
The reaction of Pd black with $[Mo_3Se_4(H_2O)_9]^{4+}$ in 2 M HCl gives the single cube $[Mo_3(PdCl)Se_4(H_2O)_9]^{3+}$, which on removal of Cl^- forms the edge-linked double cube $[\{Mo_3PdSe_4(H_2O)_9\}_2]^{8+}$. No similar reactions of $[W_3S_4(H_2O)_9]^{4+}$ and $[W_3Se_4(H_2O)_9]^{4+}$ are observed, and in no case is Pt black incorporated into the trinuclear species. The crystal structure of $[\{Mo_3PdSe_4(H_2O)_9\}_2](pts)_8\cdot 18H_2O$ has been determined (pts^- = *p*-toluenesulfonate), and is consistent with Mo–Mo and Mo–Pd bonding. Properties of the Pd derivatives of both $[Mo_3Q_4(H_2O)_9]^{4+}$ (Q = S, Se) are considered. No heteroatom transfer is observed on mixing $[Mo_3(PdCl)Se_4(H_2O)_9]^{3+}$ with $[Mo_3S_4\ (H_2O)_9]^{4+}$ as is the case of $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$ with $[Mo_3S_4\ (H_2O)_9]^{4+}$. The single cubes $[Mo_3(PdCl)Q_4\ (H_2O)_9]^{3+}$ (Q = S, Se), react 1 : 1 with $SnCl_3^-$ to give $[Mo_3(PdSnCl_3)Q_4(H_2O)_9]^{3+}$ with Pd–Sn bonding. Formation constants K (25 °C) are $1.15 \times 10^3\ M^{-1}$ (Q = S) and $9.5 \times 10^3\ M^{-1}$ (Q = Se). On mixing the heterometal cubes $[Mo_3PdS_4(H_2O)_{10}]^{4+}$ and $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ in 2 M HCl no Pd–Sn bonding occurs. With $[Pd(H_2O)_4]^{2+}$ and $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ in 2.0 M $HClO_4$, reaction steps $Mo_3SnS_4^{6+} \longrightarrow Mo_3S_4^{4+} + Sn^{II}$, followed by $Sn^{II} + Pd^{II} \longrightarrow Sn^{IV} + Pd^0$ are observed, and Pd^0 is precipitated. Rate constants for the oxidation of $[Mo_3(PdCl)S_4(H_2O)_9]^{4+}$ and $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ with $[Co(dipic)_2]^-$ (dipic = 2,6-pyridinedicarboxylate) are within a factor of 2, indicating no significant change in redox properties. This contrasts with the behaviour of single and corner-shared double cubes *e.g.* M′ = Sn.

Introduction

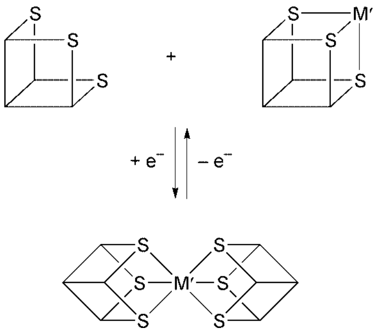
In a recent review behavioural patterns of ≈20 heterometal (M′) cube derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$ were considered,[1] and three different categories A, B and C defined according to the position of M′ in the Periodic Table. The different categories consist of A (Group 6) which have different redox states,[1,2] B (transition metals M′ = Fe, Co, Ni, Pd, Cu),[3–7] and C (Hg and Group 13–15 metals M′ = Ga, In, Ge, Sn, Pb, As, Sb, Bi).[8–19] In the case of B the heterometal is tetrahedrally coordinated, and M′ = Co, Ni, Pd, Cu are known to form edge-linked double cubes, Scheme 1.



Scheme 1

With C however the heterometal is octahedral, and the single to corner-shared double cube interconversion is initiated by a redox change, Scheme 2.

This paper is concerned primarily with palladium incorporation, which in the case of $[Mo_3S_4(H_2O)_{10}]^{4+}$ is known to give a single cube,[6,7] nominally $[Mo_3PdQ_4(H_2O)_9]^{4+}$ but with HCl present $[Mo_3(PdCl)Q_4(H_2O)_9]^{3+}$, where the Cl^- blocks formation of the double cube.[20] The palladium is tetrahedral, and in non-coordinating acids Hpts (*p*-toluenesulfonic acid; $CH_3C_6H_4SO_3H$) and $HClO_4$ the double cube forms as in Scheme 1. The category C single cube $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ is also involved in the present studies. Here the tin is octahedral and Scheme 2 is relevant. X-Ray crystallography has indicated Mo–Mo bonding in all of these cubes.[3–13] However, whereas the Mo–Pd bonds are short in the derivative from $[Mo_3S_4(H_2O)_9]^{4+}$ (consistent with metal–metal bonding),[6] Mo–Sn separations are ≈1 Å longer with no evidence for metal–metal bonding.[13] In keeping with these findings the formalism $Mo_3S_4^{4+}$, Pd^0 and $Mo_3S_4^{4+}$, Sn^{II} has been introduced.[16] Differences in the reactivity of $[M_3Q_4(H_2O)_9]^{4+}$ (M = Mo, W; Q = S, Se) with Pd, and properties of the Pd derivatives are considered in this paper.



Scheme 2

Experimental

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

Solutions of yellow-brown $[Mo_3Se_4(H_2O)_9]^{4+}$ (5 mM), in 2 M HCl, were prepared as described previously from $(Ph_4P)_2[Mo_3Se_7Br_6]$.[21,22] A sample of the latter was powdered, washed

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with hot EtOH and the brown solid left to stand in 4 M Hpts (*p*-toluenesulfonic acid; Aldrich) for 10 h under N_2. The filtrate was then treated with PPh_3 in dichloromethane to convert $Se_7 \longrightarrow Se_4$ by Se abstraction,[23] and the two phase reaction stirred for 3–4 h. After discarding the organic layer, $[Mo_3Se_4(H_2O)_9]^{4+}$ in the aqueous layer was purified by Dowex 50W–X2 cation-exchange chromatography. In the present case yellow-brown $[Mo_3Se_4(H_2O)_9]^{4+}$ was eluted with 2M HCl, UV-Vis peak positions λ/nm (ε/M^{-1} cm^{-1} per Mo_3) at 433(5250), 681(580).

Preparation of $[Mo_3S_4(H_2O)_9]^{4+}$

The procedure from polymeric $\{Mo_3S_7Br_4\}_x$ *via* water soluble $(Et_4N)_2[Mo_3S_7Br_6]$, was used.[24] In 2 M HCl UV-Vis peak positio ns λ/nm (ε/M^{-1} cm^{-1} per Mo_3) for green $[Mo_3S_4(H_2O)_9]^{4+}$ are at 370(4995) and 616(326).[14]

Preparation of $[W_3S_4(H_2O)_9]^{4+}$ and $[W_3Se_4(H_2O)_9]^{4+}$

Solutions in 2 M HCl were obtained as previously described.[14,25] UV-Vis peak positions were for purple $[W_3S_4(H_2O)_9]^{4+}$ 317(6100) and 570(480), and for green $[W_3Se_4(H_2O)_9]^{4+}$ 360(7500) and 625(400).

Preparation of Pd black

Palladium black was freshly prepared by reduction of a solution of $PdCl_2$ (0.05 M; Johnson Matthey) in 1 M HCl with hydrazine hydrochloride.[20]

Preparation of $[Mo_3(PdCl)Se_4(H_2O)_9]^{3+}$

Conversion of $[Mo_3Se_4(H_2O)_9]^{4+}$ (5 mM in 2 M HCl) was achieved by adding a large excess of Pd black (Pd : Mo_3 of 50 : 1), and heating the mixture under N_2 with stirring for 6–10 h at ≈70 °C. Excess Pd was filtered off, and the product purified by Dowex 50W–X2 cation-exchange chromatography. The solution was loaded after diluting to 0.5 M HCl. The column was washed with 100 mL amounts of first 0.50 M followed by 1.0 M HCl, when blue $[Mo_3(PdCl)Se_4(H_2O)_9]^{3+}$ separated from unreacted $[Mo_3Se_4(H_2O)_9]^{4+}$. Elution of the 3+ product was achieved with 2.0 M HCl. Yields were 85–95% based on the conversion of $[Mo_3Se_4(H_2O)_9]^{4+}$, and concentrations of $[Mo_3(PdCl)Se_4(H_2O)_9]^{3+}$ were in the range 5–12 mM in 2.0 M HCl.

Preparation of $[\{Mo_3PdSe_4(H_2O)_9\}_2]^{8+}$

A solution of $[Mo_3(PdCl)Se_4(H_2O)_9]^{3+}$ (1 mL; 5 mM) was dried *in vacuo* at room temperature. Aqueous Hpts (4 mL; 1 M) was added, and the dark-blue solution kept at ambient temperature for 7 days. Dark crystals of $[\{Mo_3PdSe_4(H_2O)_9\}_2](pts)_8\cdot18H_2O$ were filtered off in good yield.

Conversion of $[Mo_3S_4(H_2O)_9]^{4+}$ to Pd products

As previously,[20] a large excess of Pd black was added to $[Mo_3S_4(H_2O)_9]^{4+}$ (0.01 M) in 2 M HCl, and the mixture stirred under N_2 for 3–4 days. Excess Pd was filtered off, and the blue-green filtrate purified by Dowex 50W–X2 chromatography. On washing with first 0.5 M HCl and then 1.0 M HCl the blue coloured $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ separated from green unreacted $[Mo_3S_4(H_2O)_9]^{4+}$. Elution was with 2.0 M HCl. Typical yields were 70–80% based on the conversion of $[Mo_3S_4(H_2O)_9]^{4+}$. UV-Vis peaks were at 450(1013) and 580(1382), (ε's per Mo_3).[20] Conversion to the dimer $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ was achieved by re-loading a solution of $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ in 0.3 M HCl onto a Dowex column, washing with 0.5, 1.0 and 2.0 M Hpts, and eluting the 8+ dimer with 4 M Hpts. UV-Vis peaks were at 456(1155) and 572(1393) (ε's per Mo_3).[20] A similar procedure was used to prepare the double cube in 4 M $HClO_4$.

Conversion of $[Mo_3S_4(H_2O)_9]^{4+}$ to $[Mo_3SnS_4(H_2O)_{12}]^{6+}$

As described,[8] a 2-fold excess of Sn^{II} in 0.5 M Hpts was added to $[Mo_3S_4(H_2O)_9]^{4+}$ (≈5 mM) in 2.0 M Hpts, both solutions air-free (N_2).[13] An immediate change to green-yellow was observed, eqn. (1).

$$Mo_3S_4^{\,4+} + Sn^{II} \longrightarrow Mo_3SnS_4^{\,6+} \qquad (1)$$

The product diluted to 0.5 M Hpts was loaded onto a Dowex 50W–X2 column, washed with 100 mL amounts of 0.5, 1.0 and 2.0 M ($HClO_4$ or HCl as required). The $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ was eluted with 3.0 M $HClO_4$ (3 H_2O's coordinated to Sn), or as $[Mo_3(SnCl_3)S_4(H_2O)_9]^{3+}$ with 2.0 M HCl. The products have UV-Vis peaks at 331(10010), 382(≈2900) in 2.0 M $HClO_4$, and 356(14030), 424(8260) in 2.0 M HCl.[13]

Reactions with $SnCl_3^-$

A fresh sealed sample of $SnCl_2\cdot2H_2O$ (Aldrich) was standardised by redox titration and shown to be free of Sn^{IV}. Solutions in 2.0 M HCl give trigonal pyramidal $SnCl_3^-$, which has a lone-pair of electrons and shows little tendency to form $SnCl_4^{2-}$.[26] Titrations of $[Mo_3(PdCl)Q_4(H_2O)_9]^{3+}$ in 2.0 M HCl were carried out by making up solutions at different $SnCl_3^-$ concentrations, and measuring UV-Vis absorbance changes. The reactions giving $[Mo_3(PdSnCl_3)S_4(H_2O)_9]^{3+}$ (orange), and $[Mo_3(PdSnCl_3)Se_4(H_2O)_9]^{3+}$ (pink) are fast.

Other reagents

A solution of $[Pd(H_2O)_4]^{2+}$ was obtained by first dissolving Pd metal in fuming nitric acid, followed by repeated evaporation with the addition of 70% $HClO_4$.[27–29] Concentrations of pale yellow $[Pd(H_2O)_4]^{2+}$ were obtained from the absorbance at 380 nm (ε = 83 M^{-1} cm^{-1}). Platinum black was from Johnson-Matthey. Commercially available samples of CO and acetylene (C_2H_2) were used. A crystalline sample of the Co^{III} oxidant $(NH_4)[Co(dipic)_2]$ (dipic = 2,6-pyridinedicarboxylate), peak at 510 nm (ε = 83 M^{-1} cm^{-1}), was prepared as previously (Co^{III}/Co^{II} reduction potential 362 mV *vs.* NHE).[14]

Crystallographic studies for $[\{Mo_3PdSe_4(H_2O)_9\}_2](pts)_8\cdot18H_2O$

Crystal data for: $C_{56}H_{128}Mo_6O_{60}Pd_2S_8Se_8$, $M = 3438.2$, triclinic, space group $P\bar{1}$, $a = 11.6971(11)$, $b = 14.9372(15)$, $c = 16.4307(16)$ Å, $\alpha = 77.380(2)$, $\beta = 84.506(3)$, $\gamma = 82.822(2)°$, $U = 2772.5(5)$ Å^3, $T = 160(2)$ K, $Z = 1$; $R(F, F^2 > 2\sigma) = 0.038$, $R_w(F^2$, all data) = 0.103 for 12534 unique absorption-corrected data (20783 measured, $R_{int} = 0.029$) and 672 parameters, final difference map between +1.19 and −1.81 e Å^{-3}. Orientational disorder was resolved and refined for one pts^- anion, with restraints on geometry and displacement parameters. Constrained H atoms were included on the anions, but none were located for the coordinated or uncoordinated H_2O.

CCDC reference number 158154.

See http://www.rsc.org/suppdata/dt/b1/b106522j/ for crystallographic data in CIF or other electronic format.

Results

Characterisation of Pd products from $[Mo_3Se_4(H_2O)_9]^{4+}$

The single $[Mo_3(PdCl)Se_4(H_2O)_9]^{3+}$ and double cubes $[\{Mo_3PdSe_4(H_2O)_9\}_2]^{8+}$ are clearly distinguished by their Dowex cation-exchange column behaviour. The two forms are quantitatively interconverted. Unlike the vast majority of heterometallic derivatives,[1] both cubes are air stable over long periods (≥ 4 weeks). Inductively coupled plasma atomic emission spectroscopy gave for the single cube in 1 M HCl a Mo : Pd : Se ratio of 3.10 : 1.00 : 3.93, and no changes are observed on conversion to the double cube. UV-Vis spectra are shown in

Table 1 Selected distances (Å) and angles (°) in the cation

Pd(1)–Se(1)	2.4442(6)	Pd(1)–Se(2)	2.4399(6)
Pd(1)–Se(3)	2.5673(6)	Pd(1)–Se(3′)	2.5350(6)
Mo(1)–Se(1)	2.4748(6)	Mo(1)–Se(2)	2.4686(6)
Mo(1)–Se(4)	2.4584(6)	Mo(2)–Se(2)	2.4475(6)
Mo(2)–Se(3)	2.4857(6)	Mo(2)–Se(4)	2.4706(6)
Mo(3)–Se(1)	2.4525(6)	Mo(3)–Se(3)	2.4745(6)
Mo(3)–Se(4)	2.4626(6)	Mo(1)–Mo(2)	2.7953(6)
Mo(1)–Mo(3)	2.8650(6)	Mo(2)–Mo(3)	2.8182(6)
Pd(1)–Mo(1)	2.7459(6)	Pd(1)–Mo(2)	2.8556(6)
Pd(1)–Mo(3)	2.8166(5)		
Se(3)–Pd(1)–Se(3′)	114.811(17)	Se–Pd–Se	104.16(2)–114.811(17)
Pd–Se–Mo	67.862(18)–71.506(18) (within cubes)	Se–Mo–Se	104.14(2)–109.19(2)
Mo–Se–Mo	69.096(18)–71.210(19)		

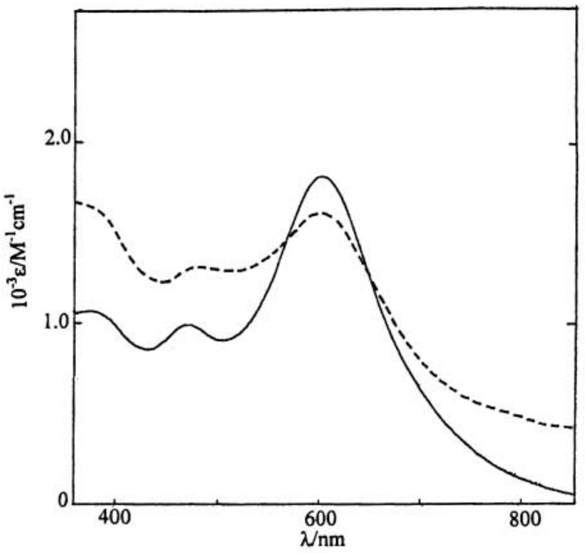

Fig. 1 UV-Vis spectra (ε's per Mo_3) for single cube $[Mo_3(PdCl)Se_4(H_2O)_9]^{3+}$ (—) in 2.0 M HCl, and the edge-linked double cube $[\{Mo_3PdSe_4(H_2O)_9\}_2]^{8+}$ (- - -) in 0.5 M Hpts.

Fig. 1, peak positions λ/nm (ε/M^{-1} cm^{-1} per Mo_3) for the single cube (blue), 390sh(1013), 475(1005), 611(1823), and for the double cube (darker blue), 390sh(1575), 485(1315), 606(1635), based on ICP determinations. The two colours are clearly distinguishable.

Crystallographic study

The dimeric edge-linked cation has crystallographic inversion symmetry. Principal geometrical results are shown in Table 1, with the cation structure displayed in Fig. 2. The Pd–Se bonds in the central four-membered ring are about 0.1 Å longer than the others within the $PdMo_3Se_4$ cubes. These cubes have a typical distorted structure, with acute angles at Se and short metal–metal distances indicative of some direct bonding interaction. The aqua ligands, uncoordinated water molecules and pts$^-$ anions engage in a complex three-dimensional hydrogen-bonding network, as shown by many O—O distances in the range 2.6–2.8 Å.

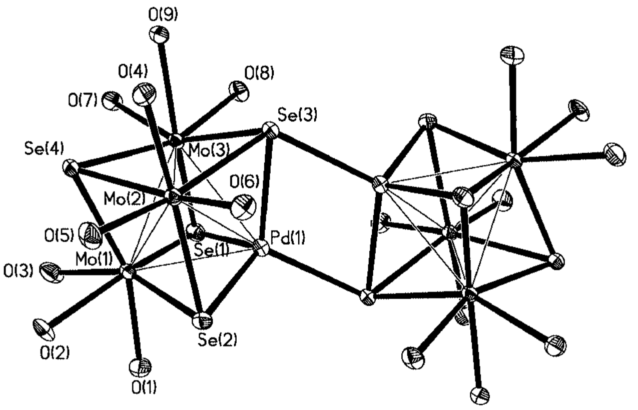

Fig. 2 View of the cation edge-shared double cube $[\{Mo_3PdSe_4(H_2O)_9\}_2]^{8+}$ with 50% probability ellipsoids and atomic labelling for the unique atoms.

$[W_3Q_4(H_2O)_9]^{4+}$ (Q = S, Se) with Pd black

To $[W_3Q_4(H_2O)_9]^{4+}$ solutions (4 mL; 2 mM) in 2.0 M HCl, palladium black (20 mg amounts) was added. More extreme conditions were used, including 6 h at 150 °C a sealed tube. No UV-Vis changes were observed, and it is concluded that no reaction occurs.

Reactivity of $[Mo_3(PdCl)Se_4(H_2O)_9]^{3+}$ with CO and C_2H_2

As in the case of the μ-S analogue there is a fast reaction on bubbling CO through 10^{-3} M cube solutions in 1 M HCl.[6,30] Within 5 min the colour changed from blue to yellow. The UV-Vis spectrum has a peak at 441 nm and 483 nm (sh). The IR (Nujol) spectrum gives a terminal carbonyl CO stretching frequency of 2080 cm^{-1}, eqn. (2).

$$Mo_3(PdCl)Se_4^{3+} + CO \longrightarrow Mo_3(PdCO)Se_4^{4+} + Cl^- \quad (2)$$

The reaction is reversed by passing Ar through the solution when the blue colour returns. The reaction of $[Mo_3(PdCl)Se_4(H_2O)_9]^{3+}$ with C_2H_2 was studied by the same procedure, eqn. (3),

$$Mo_3(PdCl)Se_4^{3+} + C_2H_2 \longrightarrow Mo_3(PdC_2H_2)Se_4^{4+} + Cl^- \quad (3)$$

but required much longer (≈10 h). The solution becomes red, with UV-Vis peaks at 452 nm and 488 nm (sh). The cubes $[Mo_3M'S_4(H_2O)_{10}]^{4+}$ (M′ = Co, Ni, Pd having 9 or 10 metal electrons) are able to bind CO,[30] and the 1,4,7-triazacyclononane (tacn) complex $[Mo_3(PdCO)S_4(tacn)_3]^{4+}$ has been characterised by X-ray crystallography.[6] The Pd cube also reacts with alkene and alkyne molecules and the products are well characterised.[6]

Titration of $[Mo_3(PdCl)Q_4(H_2O)_9]^{3+}$ (Q = S, Se) with $SnCl_3^-$

Orange/pink colours respectively attributed to the formation of $[Mo_3(PdSnCl_3)S_4(H_2O)_9]^{3+}$ and $[Mo_3(PdSnCl_3)Se_4(H_2O)_9]^{3+}$ are observed, *e.g.* Fig. 3. No reduction of $Mo_3PdS_4^{4+}$ is apparent and none occurs with H_3PO_2 or $NaBH_4$, both stronger reducing agents than $SnCl_3^-$. No reactions of $SnCl_3^-$ with other Mo cubes have been observed.[1] The reaction with $SnCl_3^-$ is reversible, and titrations with $SnCl_3^-$ give evidence for a 1 : 1 reaction. Thus equilibrium constants *K* defined in eqn. (4),

$$Mo_3(PdCl)Q_4^{3+} + SnCl_3^- \rightleftharpoons Mo_3(PdSnCl_3)Q_4^{3+} + Cl^- \quad (4)$$

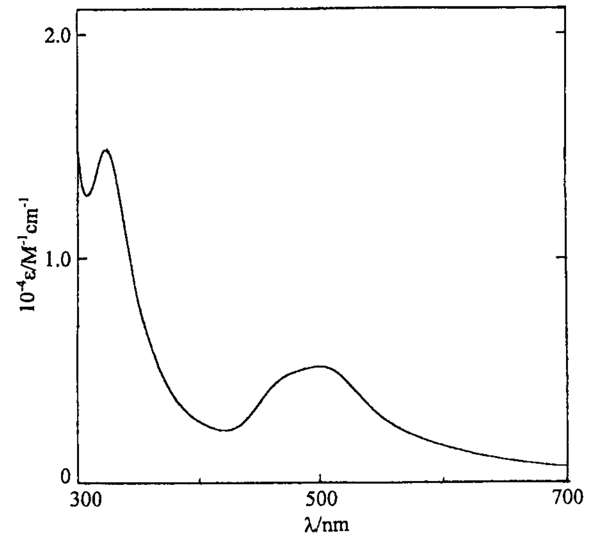

Fig. 3 The UV-Vis spectrum of $[Mo_3(PdSnCl_3)Se_4(H_2O)_9]^{3+}$ in 2 M HCl.

were determined from absorbance changes at 499 nm with $[Mo_3(PdCl)Q_4(H_2O)_9]^{3+}$ ($\approx 7.0 \times 10^{-5}$ M), and $SnCl_3^-$ varied in the range $(3.7–100) \times 10^{-4}$ M. Both reactant solutions were air-free and in 2.0 M HCl. For eqn. (4) the expression (5) can be derived,

$$\frac{\varepsilon_0 - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_{Sn}} = \frac{1}{K[SnCl_3^-]} + 1 \qquad (5)$$

where ε_0, ε_∞ and ε_{Sn} are absorption coefficients for the cube with no $SnCl_3^-$ present, for the product with $SnCl_3^-$ attached, and with $[SnCl_3^-]$ a variable. At 25 °C, $I = 2.00$ M (HCl), graphs of $(\varepsilon_0 - \varepsilon_\infty)/(\varepsilon_0 - \varepsilon_{Sn})$ against $[SnCl_3^-]^{-1}$, Fig. 4, give $K = 1.15(4) \times 10^3$ M^{-1} for $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$, and $9.5(1) \times 10^3$ M^{-1} for $[Mo_3(PdCl)Se_4(H_2O)_9]^{3+}$.

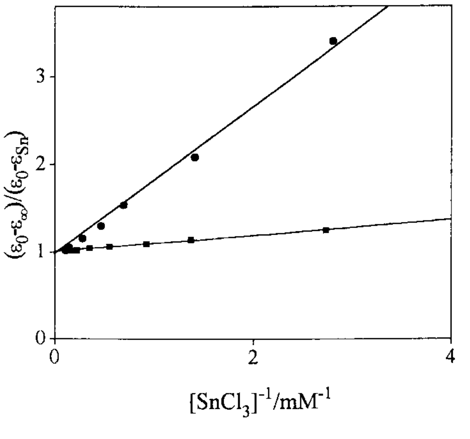

Fig. 4 Determination of formation constants K for the titration of 7.0×10^{-5} M $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ (●) and $[Mo_3(PdCl)Se_4(H_2O)_9]^{3+}$ (■) with $[SnCl_3^-]$ according to eqn. (4).

Reaction of $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ with $[Pd(H_2O)_4]^{2+}$

Both reactants were prepared in 2.0 M $HClO_4$ to avoid effects due to Cl^- complexing. The tin cube (5.0×10^{-5} M) was mixed with an excess of $[Pd(H_2O)_4]^{2+}$ (1.0×10^{-3} M). UV-Vis scan spectra, and absorbance changes at 330 nm were monitored for 10–15 min, Fig. 5. At this wavelength absorption coefficients (ε) for $[Mo_3SnS_4(H_2O)_{12}]^{6+}$, $[Mo_3S_4(H_2O)_9]^{4+}$ and $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ are approximately 10 : 3 : 1. Accordingly the absorbance changes, Fig. 5, are explained by the conversion of $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ to $[Mo_3S_4(H_2O)_9]^{4+}$, with the subsequent increases brought about by the precipitation of Pd metal. Under these stoichiometric conditions there is no evidence for formation of $[Mo_3PdS_4(H_2O)_{10}]^{4+}$. With $A_\infty = 0.22$ the first phase gives a plot of $\ln(A_\infty - A_t)$ *vs.* time, which is linear to ≈80% conversion (inset), rate constant $k = 1.27 \times 10^{-2}$ s^{-1}.

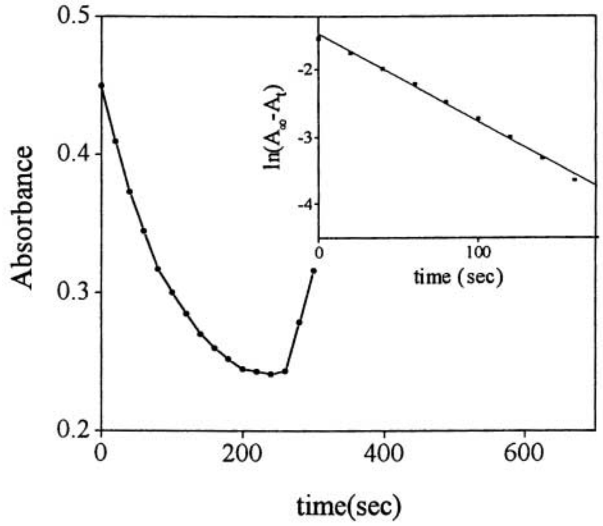

Fig. 5 Absorbance changes at 330 nm in 3 mL optical cell (1 cm path length) for the reaction of $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ (5.0×10^{-5} M) with $[Pd(H_2O)_4]^{2+}$ (1.0×10^{-3} M) in 2.0 M $HClO_4$ at 25 °C. The first phase corresponds to the Pd^{II} induced decay of $[Mo_3SnS_4(H_2O)_{12}]^{6+}$, and the second phase to the precipitation of Pd metal.

Reaction of $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ with $[Mo_3PdS_4(H_2O)_{10}]^{4+}$

The two cubes present in 2.0 M HCl as $[Mo_3(SnCl_3)S_4(H_2O)_9]^{3+}$ and $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ were mixed (both 5.0×10^{-5} M). No UV-Vis absorbance changes were observed over 8 h, and no Sn–Pd interaction is apparent.

Reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with $[Mo_3(PdCl)Se_4(H_2O)_9]^{4+}$

To $[Mo_3S_4(H_2O)_9]^{4+}$ solution (1 mL, 10 mM) in 2 M HCl a solution of $[Mo_3(PdCl)Se_4(H_2O)_9]^{4+}$ in 2 M HCl (1 mL, 10 mM) was added. The reaction mixture was heated (90–100 °C) for 4 h in Ar. Trinuclear and cuboidal clusters were separated on a Dowex column. UV-Vis spectra indicate no Pd transfer from the Se to S containing cluster.

Reactions with $[Co(dipic)_2]^-$ as oxidant

Studies were with $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ and $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ made up to $I = 2.00$ M (LiCl) and 2.00 M (Lipts) respectively. The stoichiometries were confirmed as 1.97(11) : 1 per mole and 4.14(20) : 1 from UV-Vis spectrophotometry (510 nm), eqn. (6) and (7).

$$Mo_3PdS_4 + 2Co^{III} \longrightarrow Mo_3S_4^{4+} + Pd^{II} + 2Co^{II} \qquad (6)$$

$$\{Mo_3PdS_4\}_2^{8+} + 4Co^{III} \longrightarrow 2Mo_3S_4^{4+} + 2Pd^{II} + 4Co^{II} \qquad (7)$$

Both reactions are slow. For kinetic studies the oxidant was in 20-fold excess, and formation of $[Mo_3S_4(H_2O)_9]^{4+}$ was monitored at 370 nm. From first-order plots of $\ln(A_\infty - A_t)$ *vs.* time rate constants k_{obs} (25 °C) are obtained. These give a first-order dependence on $[Co(dipic)_2^-]$, Fig. 6, with no dependence on $[H^+] = 0.50–2.00$ M. The first redox stage is therefore rate determining. No intermediates are observed, and no evidence was obtained to suggest that other redox states such as $Mo_3PdS_4^{5+}$ are stable. Second-order rate constants are 0.075(2) M^{-1} s^{-1} for $[Mo_3(PdCl)S_4(H_2O)_9]^{4+}$ and 0.045(2) M^{-1} s^{-1} for $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$. These are within a factor of ×2 of each

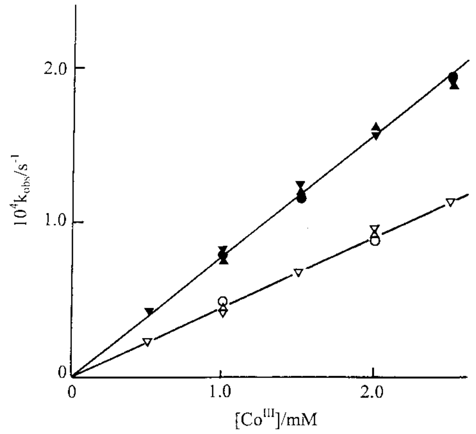

Fig. 6 The dependence of first-order rate constants k_{obs} (25 °C) on [Co(dipic)$_2$$^-$] (reactant in excess), for the oxidation of [$Mo_3(PdCl)S_4(H_2O)_9$]$^{3+}$, I made up to 2.0 M (LiCl) (upper line), and [{$Mo_3PdS_4(H_2O)_9$}$_2$]$^{8+}$ in 2.0 M (Lipts) (lower line); [H^+] = 0.50 M (●, ○), 1.00 M (▲, △), 2.00 M (▼, ▽). Concentrations of cube (3–5) × 10^{-5} M.

other, which can be accounted for by electrostatics and the effect of different anions present.

Discussion

In this work it has been shown that palladium derivatives of [$Mo_3Se_4(H_2O)_9$]$^{4+}$ can be prepared as single [$Mo_3(PdCl)Se_4(H_2O)_9$]$^{3+}$ and double [{$Mo_3PdSe_4H_2O)_9$}$_2$]$^{8+}$ cubes. The structure of the double cube has been determined by X-ray crystallography, and an edge-linked interaction of two single cube units demonstrated. The Mo–Se bonds (2.448–2.486 Å) are bigger than Mo–S bonds (2.331–2.355 Å) in [{$Mo_3PdS_4(H_2O)_9$}$_2$]$^{8+}$,[7] by an amount close to the difference in radius of Se^{2-} and S^{2-}. The four-membered ring Pd_2Se_2 is ≈4% bigger than the Pd_2S_2 ring. Both CO and C_2H_2 displace Cl^- at the palladium of the single cube, which has been assigned as tetrahedral Pd^0 (d^{10}).[6,31] The products have been characterised by UV-Vis and IR spectra. Commercially available Pt-black does not similarly react with any of the trinuclear clusters used in the present studies.

No reaction is observed on addition of Pd-black to [$W_3Q_4(H_2O)_9$]$^{4+}$ (Q = S, Se). At present there are only about one-third as many heterometallic derivatives of [$W_3S_4(H_2O)_9$]$^{4+}$ as [$Mo_3S_4(H_2O)_9$]$^{4+}$, and notably no [$W_3S_4(H_2O)_9$]$^{4+}$ derivatives are observed with M′ = Fe, Co, Hg.[1] It is well known that tungsten has a marked preference for forming the higher oxidation states, with the lower states more strongly reducing than in the case of molybdenum. Interaction of [$W_3S_4(H_2O)_9$]$^{4+}$ with a low oxidation state heterometal is not therefore as favourable as in the case of [$Mo_3S_4(H_2O)_9$]$^{4+}$.[32] Normally [$W_3Se_4(H_2O)_9$]$^{4+}$ behaves similarly to [$Mo_3Se_4(H_2O)_9$]$^{4+}$, but here an order of reactivity reads $Mo_3S_4^{4+} \approx Mo_3Se_4^{4+} > W_3Se_4^{4+} \approx W_3S_4^{4+}$. With M′ = Sn it has been found that [$W_3Se_4(H_2O)_9$]$^{4+}$ has more affinity for the heteroatom than [$W_3S_4(H_2O)_9$]$^{4+}$,[14] and an order $Mo_3S_4^{4+} > Mo_3Se_4^{4+} > W_3Se_4^{4+} > W_3S_4^{4+}$ is observed. There are no reduction potentials for the trinuclear species, but for the cubes [$Mo_4S_4(H_2O)_{12}$]$^{n+}$ (n = 4, 5, 6) the 6+/5+ and 5+/4+ couples have reduction potentials of 860 and 210 mV respectively.[33] From an extrapolation of reduction potentials for [$Mo_xW_{4-x}S_4(H_2O)_{12}$]$^{5+}$ (x = 1–4) values of 39 and −627 mV have been estimated for the [$W_4S_4(H_2O)_{12}$]$^{n+}$ 6+/5+ and 5+/4+ couples respectively.[34] These are 821 and 833 mV more reducing than the corresponding [$Mo_4S_4(H_2O)_{12}$]$^{n+}$ cubes, which indicates the magnitude of W *vs.* Mo effects possible.

Platinum-group metals are known to react with $SnCl_3^-$, to give metal–metal bonded products, the $SnCl_3^-$ remaining in the Sn^{II} state. A particularly well studied example is square-planar $PtCl_4^{2-}$ with $SnCl_3^-$, when complexing can proceed through to [$Pt(SnCl_3)_5$]$^{3-}$.[35] Other examples of $SnCl_3^-$ coordination to zero oxidation state platinum have been reported. Although there are fewer examples with palladium, $SnCl_3^-$ is known to react with [$Pd(H_2O)_4$]$^{2+}$.[36] In all such reactions the $SnCl_3^-$ behaves as a strong π-acceptor, with the tin lone electron pair σ-bonding to the palladium. Formation constants K (25 °C) for the reaction of $SnCl_3^-$ with [$Mo_3(PdCl)S_4(H_2O)_9$]$^{3+}$ and [$Mo_3(PdCl)Se_4(H_2O)_9$]$^{3+}$,[4] have been determined as 1.15 × 10^3 M^{-1} and 9.5 × 10^3 M^{-1} respectively. Stronger bonding is apparent in the interaction of the soft donor $SnCl_3^-$ with Mo_3PdSe_4 than Mo_3PdS_4.

There is no evidence from the X-ray structure of [$Mo_3(SnCl_3)S_4(NCS)_9$]$^{6-}$ for an electron lone pair on the Sn^{II} (which is six-coordinate),[13] and no Sn–Pd bonding occurs on addition of [$Pd(H_2O)_4$]$^{2+}$ to [$Mo_3SnS_4(H_2O)_{12}$]$^{6+}$ (in 2.0 M $HClO_4$), or on mixing the two cubes [$Mo_3(PdCl)S_4(H_2O)_9$]$^{3+}$ and [$Mo_3(SnCl_3)S_4(H_2O)_9$]$^{3+}$ (in 2.0 M HCl). In the former case slow (2–3 h) UV-Vis absorbance changes are consistent with dissociation, eqn. (8),

$$Mo_3SnS_4^{6+} \rightleftharpoons Mo_3S_4^{4+} + Sn^{II} \qquad (8)$$

followed by Sn^{II} reduction of Pd^{II}, eqn. (9).

$$Sn^{II} + Pd^{II} \rightleftharpoons Sn^{IV} + Pd^0 \qquad (9)$$

The subsequent increases in absorbance are explained by the aggregation and precipitation of Pd^0. Relevant reduction potentials (*vs.* NHE; acidic solutions) are $Sn^{IV} + 2e^- = Sn^{II}$ (0.150 V), and $Sn^{II} + 2e^- = Sn$ (white) (0.136 V).[37] The reduction potential of the $Pd^{2+} + 2e^- = Pd^0$ couple in 4 M perchloric acid is 0.98 V.[29]

The redox reactivity of edge-linked double cubes and related single cubes have not previously been compared. An advantage in the present case is that the Pd cubes react slowly with O_2 making such studies more straightforward. Rate constants have been determined with [$Co(dipic)_2$]$^-$ as oxidant. The reactions of [$Mo_3(PdCl)S_4(H_2O)_9$]$^{3+}$ and [{$Mo_3PdS_4(H_2O)_9$}$_2$]$^{8+}$ are among the slowest of those so far observed. No significance is attached to the 2-fold difference in rate constants in view of the different conditions (2 M HCl and 2 M Hpts) used. Therefore the redox reactivity of the edge-linked double cubes is similar to that of the corresponding single cubes. In contrast different heteroatom oxidation states are observed for the single and corner-shared double cubes.[1]

To summarise, the formation of Pd heterometal derivatives with [$Mo_3Q_4(H_2O)_9$]$^{4+}$ (Q = S, Se), is in marked contrast to the behaviour of [$W_3Q_4(H_2O)_9$]$^{4+}$, illustrating a major change in reactivity on replacing Mo by W. With Sn^{II},[14] the order of reactivity is $Mo_3S_4^{4+} > Mo_3Se_4^{4+} > W_3Se_4^{4+} > W_3S_4^{4+}$, whereas with Hg^0 a break in reactivity is observed between [$W_3Se_4(H_2O)_9$]$^{4+}$ (reactive) and [$W_3S_4(H_2O)_9$]$^{4+}$ (non-reactive).[8] Consistent with Mo–Pd metal–metal bonding, there is no Pd transfer from [$Mo_3(PdCl)Se_4(H_2O)_9$]$^{3+}$ to trinuclear [$Mo_3S_4(H_2O)_9$]$^{4+}$. This is in sharp contrast to the behaviour of [$Mo_3(SnCl_3)Se_4(H_2O)_9$]$^{6+}$ with [$Mo_3S_4(H_2O)_9$]$^{4+}$ when Sn^{II} transfer is observed.[14] The electron pair on $SnCl_3^-$ is an essential part of its bonding to the Pd of [$Mo_3(PdCl)Q_4(H_2O)_9$]$^{4+}$, as is the π-back bonding of Pd⟶Sn. No Pd–Sn bonding is however observed on mixing [$Mo_3SnS_4(H_2O)_{12}$]$^{6+}$ with either [$Pd(H_2O)_4$]$^{2+}$ or [$Mo_3PdS_4(H_2O)_{10}$]$^{4+}$. Formation constants K for the reaction of $SnCl_3^-$ with $Mo_3PdQ_4^{4+}$ indicate an 8-fold more favourable reaction with Q = Se than S.

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