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Preparation and properties of heterometallic cube derivatives $Mo_3M'S_4$ from $[Mo_3S_4(H_2O)_9]^{4+}$ with M′ = Pt, Rh and Re, and $[W_3S_4(H_2O)_9]^{4+}$ analogues

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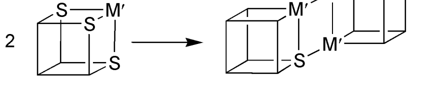
Three heterometallic $Mo_3M'S_4$ derivatives (M′ = Pt, Rh, Re) of the incomplete single-metal depleted cube $[Mo_3S_4(H_2O)_9]^{4+}$ have been prepared by reactions with $[PtCl_4]^{2-}$ (+ H_3PO_2 reductant), $RhCl_3$ and $[Re(CO)_5Br]$, respectively. With $[PtCl_4]^{2-}$, the initial product gives, on standing for 2–3 days, the edge-linked double cube $[\{Mo_3PtS_4(H_2O)_9\}_2]^{8+}$, which is difficult to elute in Dowex cation-exchange chromatography. In the reaction with $RhCl_3$, chloro products, *e.g.* $[Mo_3RhCl_3S_4(H_2O)_9]^{4+}$, precede formation of $[Mo_3RhS_4(H_2O)_{12}]^{7+}$, which is also difficult to elute, and with $[Re(CO)_5Br]$, the product $[Mo_3Re(CO)_3S_4(H_2O)_9]^{5+}$ is obtained. Analyses are consistent with oxidation state assignments Pt^0, Rh^{III} and Re^I, where the reactions proceed by addition of these forms to $[Mo_3S_4(H_2O)_9]^{4+}$. The analyses and X-ray crystal structure of $(Mo_2NH_2)[Mo_3Re(CO)_3S_4(NCS)_4]$ are consistent with the formation of an Mo_3ReS_4 single cube. Yields are high in the first two cases, but much lower in the Re case. Alternative preparations are described in the case of Rh and Re. All three products decay on heating, with reformation of trinuclear $[Mo_3S_4\ (H_2O)_9]^{4+}$, which can be recovered by Dowex chromatography. As compared to heterometallic derivatives so far considered, those with M′ = Pt, Rh, Re are much more substitution (and redox) inert, and are air stable. Analogues from $[W_3S_4(H_2O)_9]^{4+}$ with M′ = Pt, Rh have been prepared using similar procedures.

Introduction

The trinuclear Mo^{IV}_3 incomplete cuboidal cluster $[Mo_3S_4(H_2O)_9]^{4+}$ is able to incorporate a wide range of heteroatoms (M′) from Groups 6 to 15 in the Periodic Table, with formation of $Mo_3M'S_4$ and/or related double cubes.[1,2] In the present work we set out to explore M′ incorporation of the platinum metals Pt, Rh, and of Re, using relatively simple reagents, *i.e.* $[PtCl_4]^{2-}$, $RhCl_3$ and $[Re(CO)_5Br]$. An edge-linked cube is formed in the Pt case, as observed previously with other Group 10 metals Ni and Pd,[3,4] as well as Co and Cu. The reaction is summarised in eqn. (1),[5,6] which shows key atoms only.



(1)

At present the only example of Pt incorporation is with $[Mo_3(PtCl)S_4(dppe)_3Cl_3]$, where dppe is 1,2-bis(diphenylphosphino)ethane, and the Mo_3PtS_4 core has a 4+ charge.[7] Examples of Rh incorporation are with $[Mo_3(RhCp^*)S_4(H_2O)_9]^{4+}$ and $[Mo_3(RhCp^*)S_4(H_2O)_7O]_2^{8+}$,[8] where Cp* is the η^5-pentamethylcyclopentadienide ligand, and the core charge can be assigned as $Mo_3RhS_4^{7+}$. No Re derivative of $[Mo_3S_4(H_2O)_9]^{4+}$ has so far been reported. The reactivity of $[W_3S_4(H_2O)_9]^{4+}$ with M′ = Pt, Rh has also been investigated briefly.

Experimental

Preparation of starting complexes

The green coloured Mo^{IV}_3 incomplete cluster $[Mo_3S_4(H_2O)_9]^{4+}$ was prepared from the Mo^V_2 cysteine complex $[Mo_2O_2(\mu\text{-}S)_2(Cys)_2]^{2-}$,[9] or from polymeric $\{Mo_3S_7Br_4\}_x$,[10] by procedures already described. Purification was by Dowex cation-exchange chromatography, where UV-Vis absorbance peaks λ/nm (ε/M^{-1} cm^{-1} per Mo_3) are 370(4995), 616(326) in 2 M HCl, and 366(5550), 603(362) in 2 M Hpts (*p*-toluenesulfonic acid). Purple coloured $[W_3S_4(H_2O)_9]^{4+}$ was likewise prepared by procedures previously described.[11] UV-Vis absorbance peaks are λ/nm (ε/M^{-1} cm^{-1} per W_3) 317(6100), 570(480) in 2 M HCl; and 315(6350), 560(446) in 2 M Hpts.

Details of the procedures for the preparation of new heterometal-containing clusters are included in the Results section.

Other reagents

The strong acid *p*-toluenesulfonic acid (Hpts) was obtained as a white crystalline solid (Aldrich). The reducing agents hypophosphorous acid, H_3PO_2 (50% w/w H_2O solution) and sodium tetrahydroborate, $NaBH_4$, were from Aldrich. Other reagents were of analytical grade purity. Multidentate ligands iminodiacetate (ida), nitrotriacetate (nta), and ethylenediamine-tetra acetate (Na_2H_2edta) were used in some procedures described. Technical grade cylinder carbon monoxide was used.

A sample of $[Re(CO)_5Br]$ was prepared by a procedure modified from that in ref. 12. Rhenium metal powder (0.5 g) was carefully dissolved in hydrogen peroxide. To do this, four 10 mL portions of 30% H_2O_2 were used. After the first addition, it was necessary to allow O_2 evolution to subside, before adding a further portion, *etc.* Care is required to limit over vigorous reaction and spillage. To the product HBr (48% by wt; 100 mL) was added, and the volume reduced on a hotplate to 5 mL. Formic acid (96% by wt; 5 mL) was added and the mixture refluxed for 48 h. White crystals of $[Re(CO)_5Br]$ collected on the lower part of the condenser. The crystals were filtered off, washed with H_2O, and dried in air. Elemental analyses and IR spectra were in good agreement with published data.

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X-Ray crystallography

Data for $(NH_2Me_2)_4[Mo_3Re(CO)_3S_4(NCS)_9]$ were measured on a Bruker AXS SMART CCD diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 160 K. Crystal data: $C_{20}H_{32}Mo_3N_{13}O_3ReS_{13}$, $M = 1393.4$, orthorhombic, space group *Pbca*, $a = 23.1784(11)$, $b = 23.1553(11)$, $c = 43.357(2)$ Å, $U = 23270(2)$ Å^3, $Z = 16$ (2 independent anions and 8 cations in the asymmetric unit), $\mu = 3.21$ mm^{-1}, 91979 measured data, 15211 unique ($R_{int} = 0.18$); R (F, $F^2 > 2\sigma$) = 0.092, wR (F^2, all data) = 0.301, 910 refined parameters and 1284 restraints.

The structure shows a high degree of disorder, and data were very weak. The cluster anions are disordered so that each metal position is statistically occupied by both Mo and Re, and the carbonyl C and O atoms on Re overlap essentially with the N and C atoms of the thiocyanate ligands on Mo. Site occupancy factors were refined for all the metal sites, tied appropriately to those for the S atoms of thiocyanate and restrained to give a total ratio of 3 for Mo : Re. The light atoms of the ligands were assigned as N and C with no attempt to refine mixed N/C and C/O scattering factors or to resolve overlapping sites. Only four out of the eight cation positions could be clearly identified from electron density maps, and even these show high displacement parameters; the remaining cations are presumably highly disordered, together with any solvent molecules present. Similarity restraints were applied to the geometry of all ligands and to the geometry of the refined cations. In view of the nearly equal values of two cell parameters, twinning models were investigated, but none was found to give any improvement. Programs used were Bruker SMART,[13] SAINT[14] and SHELXTL.[15]

CCDC reference number 165093.

See http://www.rsc.org/suppdata/dt/b1/b104755h/ for crystallographic data in CIF or other electronic format.

Results

Preparation and properties of $Mo_3PtS_4^{4+}$

Solid $K_2[PtCl_4]$ (0.68 g) was added to $[Mo_3S_4(H_2O)_9]^{4+}$ (10 mM; 120 mL) in 2 M HCl. The mixture was flushed with N_2 for 30 min (no colour change), and the reductant H_3PO_2 (0.2 mL; 50% w/w aqueous solution) added to initiate reaction. At room temperature a dark brown colour begins to develop within 10 min. To accelerate the process, the mixture was heated to 35–40 °C (more vigorous heating brings about Pt metal formation). The yield is close to 100% with H_3PO_2. With $NaBH_4$ (100-fold excess) high yields of Pt black are observed and only 1–2% of the cube is obtained. The requirement for a strong reductant suggests that the 4+ core $Mo_3PtS_4^{4+}$ is formed (as with M′ = Pd[3,16] and Ni[4,17]), eqn. (2).

$$Mo_3S_4^{4+} + Pt^{II} + 2e^- \longrightarrow Mo_3PtS_4^{4+} \qquad (2)$$

The solution was diluted to 0.5 M in HCl and left to stand for 2–3 days prior to loading on a Dowex 50W-X2 cation-exchange column. Without this further period, most of the product passes straight through the column. Only on standing does slow substitution at the Pt occur to give the 8+ edge-linked double cube. After loading, the column was washed successively with *ca.* 100 mL amounts of 0.5 and 1.0 M HCl. With 2.0 M HCl, unreacted $[Mo_3S_4(H_2O)_9]^{4+}$ was eluted before a brown solution of the Pt product. The latter was obtained as a more concentrated solution using 3–4 M HCl. Attempts to elute with 4.0 M Hpts gave only very dilute solutions, which suggests that an 8+ edge-linked double cube is formed, eqn. (3), which is inert to

$$2Mo_3PtS_4^{4+} \longrightarrow \{Mo_3PtS_4\}_2^{8+} \qquad (3)$$

single cube re-formation. The solutions were too dilute to obtain crystals.

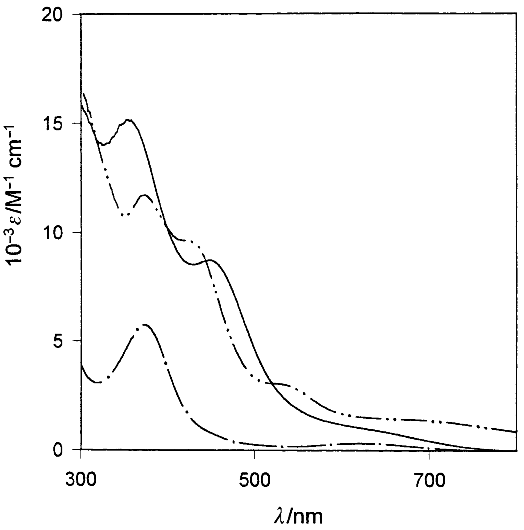

Fig. 1 UV-Vis spectra of $Mo_3PtS_4^{4+}$ (—), $Mo_3RhS_4^{7+}$ (—··—), alongside $[Mo_3S_4(H_2O)_9]^{4+}$ (—•—) in 2 M HCl (ε values per Mo_3).

Solutions in HCl are stable in air with only 3–5% decay to $[Mo_3S_4(H_2O)_9]^{4+}$ in a week. Heating 2–4 M HCl solutions in air on a steam bath (*ca.* 90 °C) for 3–4 h brings about decomposition to green $[Mo_3S_4(H_2O)_9]^{4+}$ and Pt^{II}, eqn. (4).

$$Mo_3PtS_4^{4+} + \tfrac{1}{2}O_2 + 2H^+ \rightarrow Mo_3S_4^{4+} + Pt^{II} + H_2O \quad (4)$$

The $[Mo_3S_4(H_2O)_9]^{4+}$ was determined from the visible range absorbance, and the Pt^{II} by addition of a large (*ca.* 100-fold) excess of $SnCl_2{\cdot}2H_2O$ in 3–5 M HCl after oxidation of the $Mo_3S_4^{4+}$ with HNO_3. Any Pt^{IV} formed in eqn. (4) is reduced by Sn^{II}. The Pt^{II} gives yellow coloured products with as many as five mol of $SnCl_3^-$ coordinating to give $[Pt(SnCl_3)_5]^{3-}$, which can be determined from the absorbance at 400 nm.[18] The procedure was standardised using $K_2[PtCl_4]$ solutions of known HCl concentration in the presence of Mo^{VI}. A ratio $Mo_3S_4^{4+} : Pt^{II}$ of 1.1 : 1.0 was obtained in support of the formula $Mo_3PtS_4^{4+}$. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) gave Mo : Pt : S ratios of 3.0 : 0.78 : 3.5. Analyses therefore exclude the possibility of the 6 : 1 ratio Mo : Pt corner-shared double cube.

The UV-Vis spectrum of $Mo_3PtS_4^{4+}$ in 2–4 M HCl gives peak positions λ/nm (ε/M^{-1} cm^{-1} per Mo_3) at 361(15600) and 452(9040), with other peaks at 207 and 223 nm, Fig. 1. A 2 M HCl solution was evaporated to dryness by vacuum line techniques, and dissolved in 0.5 M $HClO_4$ to give a 0.50×10^{-4} M solution with a UV-Vis spectrum showing peaks at λ/nm (ε/M^{-1} cm^{-1} per MO_3) 236sh(17100), 297(16240), 346(14240), 443(8820). The latter approach also gives a solution in 4.0 M Hpts. No suitable crystals were, however, obtained in this or other procedures involving addition of cyanide, which gave $[Mo_3S_4(CN)_9]^{5-}$, or with the multidentate ligands ida, nta and edta.

Consistent with the low reactivity of $Mo_3PtS_4^{4+}$ with O_2, the one-equivalent oxidants $[Co(dipic)_2]^-$ (362 mV), $[Fe(H_2O)_6]^{3+}$ (770 mV), $[V(O)_2(H_2O)_4]^+$ (1.0 V) give little or no reaction with the $Mo_3PtS_4^{4+}$ core.

On bubbling CO through solutions of $Mo_3PtS_4^{4+}$ in 3.0 M HCl or 4.0 M Hpts, no UV-Vis changes were observed within 10 min at *ca.* 20 °C. On heating to 60 °C for 20 min, the only UV-Vis changes observed corresponded to the formation of $[Mo_3S_4(H_2O)_9]^{4+}$. These experiments suggest that the 8+ edge-linked double cube formed in eqn. (3) is retained in 2 M HCl solutions, with the Pt unavailable for CO complexation.

Finally, the product was reacted with 1,2-bis(diphenylphosphine)ethane (dppe) to give $[Mo_3(PtCl)_4(dppe)_3Cl_3]$,[7] the X-ray crystal structure of which has been determined. The

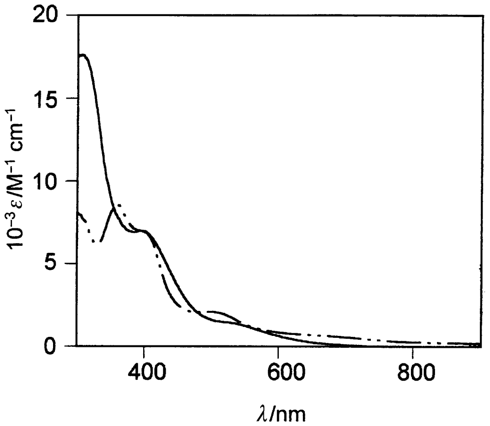

Fig. 2 UV-Vis spectra of $W_3PtS_4^{4+}$ (—) and $W_3RhS_4^{7+}$ (—··—) in 2 M HCl (ε values per W_3).

product was identified by elemental analyses and ^{31}P NMR spectra.

Preparation of $W_3PtS_4^{4+}$

The same procedure was used with H_3PO_2 as reductant. Elution of a brown product from a Dowex 50W-X2 resin was again with 3–4 M HCl. The UV-Vis spectrum in 3 M HCl gave peak positions λ/nm (ε/M^{-1} cm^{-1} per Mo_3) at 306(17600), 396(6990), Fig. 2. ICP-AES analyses gave a W : Pt ratio of 3.0 : 0.8 consistent with the core structure $W_3PtS_4^{4+}$. Dowex cation-exchange behaviour was similar to that of $Mo_3PtS_4^{4+}$, indicating formation of an edge-linked dimer $[\{W_3PtS_4(H_2O)_9\}_2]^{8+}$, which is also known to form in the case of $W_3NiS_4^{4+}$. [4]

Preparation and properties of the $Mo_3RhS_4^{7+}$

A solution of $RhCl_3$ (five-fold excess) and $[Mo_3S_4(H_2O)_9]^{4+}$ in 4.0 M HCl (1 mM; 15 mL) was heated in air on a hotplate for 3 h. Within 20 min, a colour change to brown commenced. The final solution was diluted to 0.5 M HCl and loaded onto a Dowex 50W-X2 cation-exchange column, washed with *ca.* 100 mL amounts of 0.5 M HCl (to remove any $[RhCl_6]^{3-}$ as a pink solution), and then 1.0 M HCl (to remove unreacted $[Mo_3S_4(H_2O)_9]^{4+}$). No reductant was used and the $Mo_3(RhCl_3)S_4^{4+}$ core was formed in an addition process [eqn. (5)].

$$Mo_3S_4^{4+} + RhCl_3 \longrightarrow Mo_3(RhCl_3)S_4^{4+} \qquad (5)$$

Elution with 2 M HCl gave a brown solution and behaviour characteristic of the 4+ ion $[Mo_3(RhCl_3)S_4(H_2O)_9]^{4+}$. Increasing the time of the reaction or addition of ethanol (which catalyses reactions of Rh^{III}) did not affect the yield, which was up to 80%.

A second procedure requires air-free (N_2) conditions. A sample of blue–green $[Rh_2(O_2CCH_3)_4]$ was first prepared as previously described.[19] A sample of $[Rh_2(O_2CCH_3)_4]$ (5.4 mg) was dissolved in 2 M HCl with heating, and $[Mo_3S_4(H_2O)_9]^{4+}$ in 2 M Hpts (2.75 mM; 10 mL) added. The resultant mixture was kept on a hotplate for 6 h, whereupon the colour gradually became brown. After dilution to 0.5 M in Hpts, the solution was loaded onto a Dowex 50W-X2 cation-exchange column. Any black precipitate was removed by filtration prior to loading on the column. After washing and removal of unwanted fractions with 0.5–1 M HCl, a brown product was eluted with 2 M HCl. Yields of 20–40% were obtained from five repeat experiments. The product has the same UV-Vis spectrum as in the first procedure, and complexing by Cl^- gives $[Mo_3(RhCl_3)S_4(H_2O)_9]^{4+}$ as the dominant product.

Elemental analysis by ICP-AES gave an Mo : Rh ratio of 3.0 : 1.0. On heating, $[Mo_3S_4(H_2O)_9]^{4+}$ reforms slowly as the only detectable Mo product, and since the UV-Vis peak positions are well known, such a procedure provides the means of determining absorption coefficients. Hence, in 2 M HCl, peak positions λ/nm (ε/M^{-1} cm^{-1} per Mo_3) are 260(sh), 291(sh), 370 (1.17×10^4), 422(9700), 533(2730), 670(sh) (*ca.* 1250), Fig. 1.

The $Mo_3(RhCl_3)S_4^{4+}$ cluster equilibrated in 0.5 M HCl was loaded onto a Dowex column. The dark band which formed could not be eluted with 4 M Hpts and the aqua form $[Mo_3RhS_4(H_2O)_{12}]^{7+}$ is believed to be present under these conditions. A solution of $Mo_3(RhCl_3)S_4^{4+}$ in 0.5 M HCl was evaporated to dryness (vacuum line), and then dissolved in 4 M Hpts. No crystals formed on leaving the solution to stand at 4 °C. With excess NCS^-, formation of $[Mo_3S_4(NCS)_9]^{5-}$ (or related) is observed, and the multidentate ligands ida, nta and edta gave green $Mo_3S_4^{4+}$products. No satisfactory crystallisation procedure was identified.

The $Mo_3(RhCl_3)S_4$ cube gave no reaction with a 10-fold excess of $[Co(dipic)_2]^-$ in 2 M HCl. Over *ca.* 30 min the $[Co(dipic)_2]^-$ absorbance decayed, but that of Mo_3RhS_4 remained unchanged. No reaction was observed on bubbling CO through a 2 M HCl solution for 40 min, with and without heating to 50 °C.

Preparation of $W_3RhS_4^{7+}$

A brown coloured derivative was prepared in the same way as for the $Mo_3RhS_4^{7+}$ core from $[W_3S_4(H_2O)_9]^{4+}$. The UV-Vis spectrum in 3 M HCl gave peak positions λ/nm (ε/M^{-1} cm^{-1} per W_3) at 359(8600) and 497(2080), Fig. 2. ICP-AES analyses gave a W : Rh ratio of W : Rh or 3.0 : 0.93, consistent with $W_3RhS_4^{7+}$.

Preparation and properties of $Mo_3ReS_4^{5+}$

A 10 : 1 solution of $[Re(CO)_5Br]$ and $[Mo_3S_4(H_2O)_9]^{4+}$ (20 mL; 5 mM) was taken to dryness, and concentrated HCO_2H and HCl (50 : 1 by volume) added. The mixture was refluxed for 48h (oil bath). The resulting brown solution was cooled down, evaporated to dryness (vacuum line), and re-dissolved in 4 M HCl. After diluting to 0.2–0.3 M HCl, this was loaded onto Dowex 50W-X2 cation-exchange resin. Washing was with 100 mL amounts of 0.5 M and 1 M HCl, the latter eluting any unreacted $[Mo_3S_4(H_2O)_9]^{4+}$. A brown solution eluted with 2 M HCl, and was purified using the same column procedure. Yields 5–8%. A higher 5+ charge was ascribed to this product from its Dowex cation-exchange column behaviour. ICP-AES gave a ratio Mo : Re : S of 3.00 : 0.94 : 4.11. A Dowex columned solution of the Re cube was taken to dryness (vacuum line), and the IR spectrum of the solid recorded. This gave absorption bands at 1904, 1947 and 2016 cm^{-1} consistent with three CO ligands attached to the Re, and a formula of $[Mo_3Re(CO)_3S_4(H_2O)_9]^{5+}$. No change in the UV-Vis spectrum was observed after passing N_2 through a 2 M HCl solution for 3 days at *ca.* 20 °C, indicating that the CO remains strongly bonded to the Re. No corresponding derivative was obtained on treating $[W_3S_4(H_2O)_9]^{4+}$ with $[Re(CO)_5Br]$.

In 2 M HCl, the UV-Vis spectrum gives peak positions λ/nm (ε/M^{-1} cm^{-1} per Mo_3) at 248 (1.56×10^4), 287 (1.13×10^4), 380(3500), 452(1345), Fig. 3. Solutions of the $[Mo_3Re(CO)_3S_4(H_2O)_9]^{5+}$ in 2 M HCl can be kept in air for several weeks without decomposition. When air is passed through a solution of the cube at 90 °C, the UV-Vis spectrum begins to change after 2 h, and after >8 h quantitative formation of green $[Mo_3S_4(H_2O)_9]^{4+}$ was observed, and could be separated by column chromatography.

A sample of the $Mo_3ReS_4^{5+}$ cube in 2 M HCl was taken to dryness (vacuum line) giving *ca.* 0.3 g of brown solid. This was re-dissolved in 2 M HCl (5 mL), to which solid K^+NCS^- (0.5 g) and Me_2NH_2Cl (0.2 g) were added. The solution turned grad-

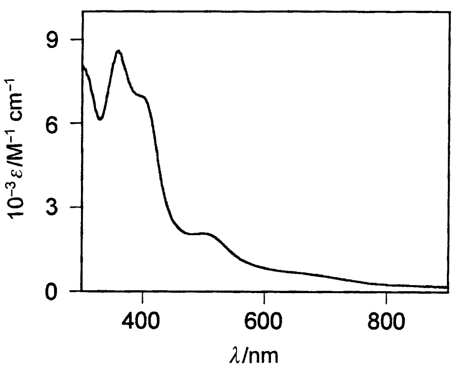

Fig. 3 UV-Vis spectrum of $[Mo_3Re(CO)_3S_4(H_2O)_9]^{5+}$ in 2 M HCl (ε values per Mo_3).

ually to a purple–brown colour. After one day at 4 °C dark crystals of $(Me_2NH_2)_4[Mo_3Re(CO)_3(NCS)_9]$ were obtained. Analyses: Calc. for $C_{20}H_{32}N_{13}S_{13}O_3Mo_3Re$: C, 29.7; H, 2.8; N, 13.0; S, 29.7%. Found: C, 29.3; H, 2.6; N, 13.9; S, 29.3%. The structure from X-ray crystallography is given below.

In an alternative procedure for the preparation of $Mo_3ReS_4^{5+}$, a sample of $(NH_4)_2[Mo_2S_4Br_8]$ was first prepared from $(NH_4)_2[Mo_2S_{12}]$ using an excess of liquid Br_2 in an inert organic solvent (CH_3CN).[20] The mixture was stirred at room temperature until all the black $(NH_4)_2[Mo_2S_{12}]$ had changed into orange $(NH_4)_2[Mo_2S_4Br_8]$. On completion of the reaction, the solid was filtered off and dried *in vacuo*. The solid obtained is air stable over several months. A sample of $K_2[ReCl_6]$ was prepared from $NH_4[ReO_4]$.[21] Amounts of $(NH_4)_2[Mo_2S_4Br_8]$ (0.46 g) and $K_2[ReCl_6]$ (0.18 g) were mixed with conc. HCl (20 mL). The mixture was brought to boiling and zinc granules (*ca.* 1 g) were added. After all the zinc had been consumed, the resultant solution was diluted 1 : 2 with H_2O and filtered from a copious brown precipitate. The solution was further evaporated to dryness on a rotavap, dissolved in 0.5 M HCl and then loaded onto a Dowex 50W-X2 cation-exchange column. A blue solution of $[Re_2Cl_8]^{2-}$ (identified by its UV-Vis spectrum),[22] formed by Zn reduction of $[ReCl_6]^{2-}$ was not retained. After washing with 0.5 M HCl, unreacted $[Mo_3S_4(H_2O)_9]^{4+}$ was eluted with 1 M HCl. Finally, a brown product was eluted with 2 M HCl. This was collected, diluted to 0.5 M HCl, and recolumned using Dowex chromatography as a single brown band. Yield 3%.

Elemental analysis by ICP gave Mo : Re of 3.0 : 1.15. The UV-Vis spectrum gave peak positions λ/nm at 207(7.1), 269(4.8), 370sh(1.5), 467(1.0), relative absorbance values in brackets. The product appears to be related to $[Mo_3Re(CO)_3S_4(H_2O)_9]^{5+}$, and a possible formula is $[Mo_3ReS_4(H_2O)_{12}]^{5+}$. Some chloro complexation of the Re (Cl^- for H_2O) is possible.

Crystal structure

The crystal structure for $(NH_2Me_2)_4[Mo_3Re(CO)_3S_4(NCS)_9]$ shows the expected M_4S_4 single cube core structure, Fig. 4. There are two independent cations in the structure. Unfortunately, there is a high degree of disorder, with Re distributed unequally over all four metal sites of each cation. Similar disorder has been observed in the $W_3MoS_4^{5+/6+}$ clusters.[23] This means the carbonyl and thiocyanate ligands are also scrambled in the average structure observed, precluding a free refinement and meaningful analysis of the ligand geometry. The results, requiring many restraints on geometry and atomic displacement parameters, are consistent with the proposed cation formulation, but do not provide an independent proof of the composition. However, analytical data and relatively straightforward synthesis leave little doubt as to the identity of the product. Extensive disorder is also observed in the cations.

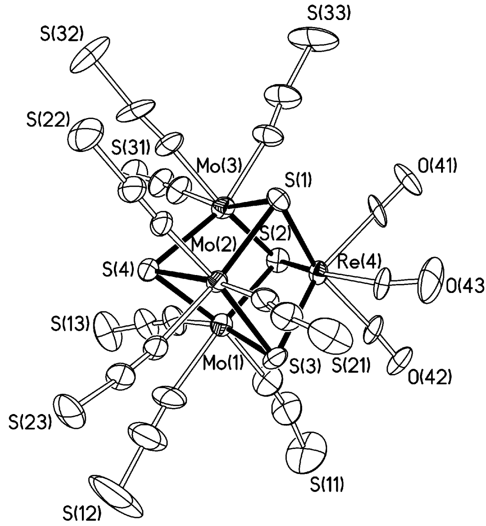

Fig. 4 One of the two independent anions of $(NH_2Me_2)_4$-$[Mo_3Re(CO)_3S_4(NCS)_9]$ with 20% displacement ellipsoids. All atoms within each ligand have the same number, which is shown only for the S atoms of NCS^- and O atoms of CO.

Discussion

Heterometal Pt, Rh, Re-containing cube derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$ have been prepared in this work. The reaction of the strong reductant H_3PO_2 with $[PtCl_4]^{2-}$ results in incipient formation of Pt^0, which reacts with $[Mo_3S_4(H_2O)_9]^{4+}$ to give the $Mo_3PtS_4^{4+}$ core. The reaction is similar to that of Pd^0 (Pd black) with $[Mo_3S_4(H_2O)_9]^{4+}$.[3,16] No reaction is observed however with Pt black.[24] Attempts to load the product obtained after *ca.* 30 min onto Dowex cation-exchange resin were unsuccessful, suggesting that a lower charged Cl^- complexed single cube is present in 2 M HCl. On leaving to stand for 2–3 days in 0.5 M HCl, aquation of the Cl^- occurs, and all observations point to the formation of the edge-linked double cube $[\{Mo_3PtS_4(H_2O)_9\}_2]^{8+}$. No reductant was used with $RhCl_3$, which gives the $Mo_3(RhCl_3)S_4^{4+}$ adduct, and subsequently (in 0.5 M HCl) aquates to give $[Mo_3RhS_4(H_2O)_{12}]^{7+}$ or a related product. The inability to elute the Pt and Rh products from a Dowex column using 4 M Hpts is consistent with the presence of highly-charged species, one the 8+ edge-linked Pt-containing double cube, and the other the single cube $[Mo_3RhS_4(H_2O)_{12}]^{7+}$.

Both products are however eluted with ≥ 3 M HCl. In the Pt case Cl^- complexing to the Mo's occurs. In the Rh case, Cl^- complexation at the Mo and Rh atoms is likely. Both the single core components have been identified previously in the X-ray crystal structures of $[Mo_3(PtCl)S_4(dppe)_3]Cl_3$,[7] and $[Mo_3(Rh\text{-}Cp^*)S_4(H_2O)_9]^{4+}$.[8] The Pt single cube can be written as $Mo_3S_4^{4+}$, Pt^0 consistent with tetrahedral Pt^0. The ability to form an edge-linked double cube is similar to that observed for the d^{10} heterometals (Pd, Ni) in $Mo_3PdS_4^{4+}$ and $W_3NiS_4^{4+}$.[4,5] From the properties observed, the Pt^0 is more inert than Pd^0,[25] and the Pt double cube appears to persist in 2 M HCl. The Rh-containing single cube can be written as $Mo_3S_4^{4+}$, Rh^{III} with d^6 Rh^{III} expected to be substitution inert.[26,27] The three μ_3-sulfido core ligands do not give an obvious labilisation of the Pt^0 or Rh^{III}, see also the discussion in ref. 28. No reaction of CO with the Pt^0 of $Mo_3PtS_4^{4+}$ in 3.0 M HCl is observed. From studies on carbonyl and phosphine binary complexes it has been noted that in transition metal triads (*e.g.* Ni^0, Pd^0, Pt^0), the second-row element reacts the faster.[29] This appears to be the case here also with an order Pd > Ni > Pt applying. Thus the reaction of $Mo_3PdS_4^{4+}$ with CO is fast to give $Mo_3(PdCO)S_4^{4+}$, $k = 1.1 \times 10^5$ M^{-1} s^{-1},[16] while that of $Mo_3NiS_4^{4+}$ is slower, $k = 0.66$ M^{-1} s^{-1},[17] and no reaction is detected with $Mo_3PtS_4^{4+}$. Neither is any reaction of CO with Rh^{III} observed. As a result, the potential of Pt and Rh to bind organic moieties (as with Pd and Ni), and serve as centres for catalytic changes is much less.

The Re-containing cube $Mo_3ReS_4^{5+}$ has been synthesised for the first time, and likewise exhibits substitution and redox inert properties. On treating the parent compound $[Mo_3Re(CO)_3S_4(H_2O)_9]^{5+}$ with 1 M NCS^-, the latter coordinates to the Mo's, but whether it displaces the 3CO's was at first uncertain. However, elemental analyses on the product indicate a formula $(Me_2NH_2)_4[Mo_3Re(CO)_3(NCS)_9]$ with the CO's retained. The X-ray structure is shown in Fig. 4.

The stability of Group 10 (Ni, Pd, Pt) cubes with tetrahedral M′ sites, and of Group 9 octahedral Rh^{III} can be explained by the electron counts of 60 which are exactly as required to fill all the bonding orbitals. In the case of the odd electron clusters $Mo_3CuS_4^{4+}$ (61e) and $Mo_3CoS_4^{4+}$ (59e), both are highly reactive, and dimerisation with formation of M′–M′ bonds occurs.[5,6] The Cu^+ adduct $Mo_3CuS_4^{5+}$ (60e) has also been prepared,[30,31] but here the Cu^+ is less likely to form M′–M′ bonds. A stable cube structure $Mo_3ReS_4^{5+}$ (60e) incorporating an octahedral Re^I is therefore perfectly reasonable.

In spite of the reluctance of $[W_3S_4(H_2O)_9]^{4+}$ to form heterometallic derivatives, it is possible with Pt and Rh to prepare analogues of those from $[Mo_3S_4(H_2O)_9]^{4+}$ using the same procedures. From studies carried out similar structures are indicated. With the inclusion of Pt and Rh eight derivatives of $[W_3S_4(H_2O)_9]^{4+}$ are now known to form (Mo, Rh, Ni, Pt, Cu, In, Ge, Sn). The greater reluctance of $[W_3S_4(H_2O)_9]^{4+}$ to form heterometal adducts has already been discussed.[32]

In conclusion, derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$ have been prepared by addition of Pt^0 (d^{10}), Rh^{III} (d^6) and Re^I (d^6) to give the edge-linked double cube $[\{Mo_3PtS_4(H_2O)_9\}_2]^{8+}$, and double cubes $[Mo_3RhS_4(H_2O)_{12}]^{7+}$ and $[Mo_3(Re(CO)_3)S_4(H_2O)_9]^{5+}$. In the case of the Pt and Rh derivatives the formulae are consistent with previous studies, with the important difference that aqua ligands are present. The tendency of the Pt double cube to reform the single cube with different ligands, *e.g.* CO, is much less than in the case of the Pd analogue. The studies described indicate substitution and redox inert properties in all three cases. Whereas the Pt^0 assignment is consistent with existing Group 10 Ni^0 and Pd^0 studies, the Rh^{III} (d^6) oxidation state with high overall charge of $Mo_3RhS_4^{7+}$ is a novel feature. In the Re case, an $Mo_3ReS_4^{5+}$ structure, and Re^I (d^6) state provide the most reasonable assignment. In all three cases, it is possible to recover $[Mo_3S_4(H_2O)_9]^{4+}$ by heating, which is consistent with representations $Mo_3S_4^{4+}$,Pt^0; $Mo_3S_4^{4+}$,Rh^{III} and $Mo_3S_4^{4+}$,Re^I.[10]

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References

1 (*a*) R. Hernandez-Molina, M. N. Sokolov and A. G. Sykes, *Acc. Chem. Res.*, 2001, **34**, 223; (*b*) D. M. Saysell, M. N. Sokolov and A. G. Sykes, in *Sulfur Coordinated Transition Metal Complexes*, ACS Symp. Ser. No. 653, ed. K. Matsumoto and E. I. Stiefel, American Chemical Society, Washington D.C., 1996, pp. 216–224.
2 T. Shibahara, *Adv. Inorg. Chem.*, 1991, **37**, 143.
3 T. Murata, Y. Mizobe, H. Gao, Y. Ishii, T. Wakabayashi, F. Nakano, T. Tanase, S. Yano, M. Hidai, I. Echizen, H. Namikawa and S. Motomura, *J. Am. Chem. Soc.*, 1994, **116**, 3389.
4 T. Shibahara, G. Sakane, M. Maeyama, H. Kobashi, T. Yamamoto and T. Watase, *Inorg. Chim. Acta*, 1996, **251**, 207.
5 T. Shibahara, H. Akashi, M. Yamasaki and K. Hashimoto, *Chem. Lett.*, 1991, 689.
6 T. Shibahara, H. Akashi and H. Kuroya, *J. Am. Chem. Soc.*, 1988, **110**, 3313.
7 D. Masai, Y. Ishii and M. Hidai, *48th Japanese Conference on Coordination Chemistry*, Kochi, Japan, 1998, abstract 3A306.
8 (*a*) H. Akashi and T. Shibahara, *Abstracts to the 30th ICCC*, Kyoto, Japan, 1994, p. 175; (*b*) H. Akashi, A. Nakano and T. Shibahara, *XVIIth IUCr Congress*, Glasgow, UK, 1999, abstract P07.07.041.
9 M. Martinez, B.-L. Ooi and A. G. Sykes, *J. Am. Chem. Soc.*, 1987, **109**, 4615.
10 M. N. Sokolov, N. Coichev, H. D. Moya, R. Hernandez-Molina, C. D. Borman and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1997, 1863.
11 V. P. Fedin, M. N. Sokolov and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1996, 44089.
12 R. Colton and J. Knapp, *Aust. J. Chem.*, 1971, 9.
13 SMART, Program for X-Ray Diffraction Data Collection, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1998.
14 SAINT, Program for Area Detector Absorption Correction, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1994.
15 G. M. Sheldrick, SHELXTL, Program for Crystal Structure Determination, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1994.
16 D. M. Saysell, G. J. Lamprecht, J. Darkwa and A. G. Sykes, *Inorg. Chem.*, 1996, **35**, 5531.
17 D. M. Saysell, C. D. Borman, C.-H. Kwak and A. G. Sykes, *Inorg. Chem.*, 1996, **35**, 173.
18 See *e.g.: Analytical Chemistry of the Elements – Platinum Metals*, J. Wiley & Sons, New York, 1975, p. 339.
19 G. A. Rempel, P. Legzdins, H. Smith and G. Wilkinson, *Inorg. Synth.*, 1972, **13**, 90.
20 V. P. Fedin, Y. Mironov and V. Fedorov, *Zh. Neorg. Khim*, 1989, **34**, 2984.
21 G. W. Watt and R. J. Thompson, *Inorg. Synth.*, 1963, **7**, 189.
22 F. A. Cotton, N. F. Curtis, B. F. G. Johnson and W. R. Robinson, *Inorg. Chem.*, 1965, **4**, 326.
23 I. J. McLean, R. Hernandez-Molina, M. N. Sokolov, M.-S. Seo, A. V. Virovets, M. R. J. Elsegood, W. Clegg and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1998, 2557.
24 V. P. Fedin, M.-S. Seo, D. M. Saysell, D. N. Dybtsev, M. R. J. Elsegood, W. Clegg and A. G. Sykes, to be published.
25 R. Hernandez-Molina and A. G. Sykes, *Coord. Chem. Rev.*, 1999, **187**, 291.
26 S. F. Lincoln and A. E. Merbach, *Adv. Inorg. Chem.*, 1995, **42**, 3.
27 G. Laurenczy, I. Rapaport, D. Zbinden and A. E. Merbach, *Magn. Reson. Chem.*, 1991, **29**, 545.
28 C. A. Routledge, M. Humanes, Y.-J. Li and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1994, 1275.
29 F. Basolo, *Polyhedron*, 1990, **9**, 1503.
30 M. Nasreldin, Y.-J. Li, F. E. Mabbs and A. G. Sykes, *Inorg. Chem.*, 1994, **33**, 4283.
31 H. Akashi and T. Shibahara, *Inorg. Chim. Acta*, 2000, **572**, 300.
32 R. Hernandez-Molina, M. R. J. Elsegood, W. Clegg and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 2001, 2173.