Preparation of heterometallic single cubes $[W_3MS_4(H_2O)_{12}]^{n+}$ (M = In, Ge or Sn) and the first corner-shared double cubes $[W_6SnS_8(H_2O)_{18}]^{8+}$ and $[W_3Mo_3SnS_8(H_2O)_{18}]^{8+}$ as derivatives of $[W_3S_4(H_2O)_9]^{4+}$†

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Conversion of the purple trinuclear W^{IV}_3 incomplete cuboidal cluster $[W_3S_4(H_2O)_9]^{4+}$ into heterometallic single cubes of the kind $[W_3MS_4(H_2O)_{12}]^{n+}$ has been achieved with M = In, Ge or Sn. The indigo blue $[W_3InS_4(H_2O)_{12}]^{5+}$ product was obtained by reaction of $[W_3S_4(H_2O)_9]^{4+}$ with aquaindium(I), or indium metal, or In^{III} in the presence of BH_4^-. Red-brown $[W_3GeS_4(H_2O)_{12}]^{6+}$ was obtained by reaction with GeO, which can also be regarded as addition of Ge^{II}. An alternative route is provided by the reaction with GeO_2 and a reducing agent (here H_3PO_2). Although a crystal structure of $[W_3(SnCl_3)S_4(NCS)_9]^{6-}$ has been reported previously, isolation of the yellow-brown aqua ion $[W_3SnS_4(H_2O)_{12}]^{6+}$ as the chloro product $[W_3(SnCl_3)S_4(H_2O)_9]^{3+}$ by addition of Sn^{II} to $[W_3S_4(H_2O)_9]^{4+}$ in 2 M HCl is described for the first time. The same product was obtained by treating $[W_3S_4(H_2O)_9]^{4+}$ with tin metal. Charges applying to the core of the cube were determined from the stoichiometry of its reaction with $[Fe(H_2O)_6]^{3+}$. In the case of $[Mo_3S_4(H_2O)_9]^{4+}$, reaction with tin metal gave the corner-shared double cube $[Mo_6SnS_8(H_2O)_{18}]^{8+}$. The W_6 analogue was only obtained by the reaction of $[W_3S_4(H_2O)_9]^{4+}$ with $[W_3SnS_4(H_2O)_{12}]^{6+}$ in the presence of a reducing agent (BH_4^-). The corresponding reaction of $[MoSnS_4(H_2O)_{12}]^{6+}$ gave the mixed corner-shared double cube $[W_3Mo_3SnS_8(H_2O)_{18}]^{8+}$. Near-quantitative transfer of the heterometal atom was observed on treating $[W_3InS_4(H_2O)_{12}]^{5+}$ or $[W_3SnS_4(H_2O)_{12}]^{6+}$ with $[Mo_3S_4(H_2O)_9]^{4+}$, indicating a much stronger affinity of the heterometal atom for $[Mo_3S_4(H_2O)_9]^{4+}$.

Whereas some 15 heterometallic cube derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$ are now known,[1,2] the only derivatives of $[W_3S_4(H_2O)_9]^{4+}$ so far reported are $[W_3CuS_4(H_2O)_{10}]^{5+}$,[3] $[W_3NiS_4(H_2O)_{10}]^{4+}$,[4] and the anionic complex $[NMe_2H_2]_6[W_3(SnCl_3)S_4(NCS)_9]\cdot0.5H_2O$.[5] From this it might appear that reaction routes available in the case of $[Mo_3S_4(H_2O)_9]^{4+}$ are not as readily accessed with $[W_3S_4(H_2O)_9]^{4+}$. We set out further to explore heterometallic incorporation into $[W_3S_4(H_2O)_9]^{4+}$ with emphasis on Main Group metals, a number of which have been incorporated in recent studies with $[Mo_3S_4(H_2O)_9]^{4+}$.[6-8] Some differences are already apparent, notably in the reaction of Cu with $[W_3S_4(H_2O)_9]^{4+}$ which gives the heterometallic product $[W_3CuS_4(H_2O)_{10}]^{5+}$,[3] whereas $[Mo_3S_4(H_2O)_9]^{4+}$ gives the 4+ product $[Mo_3CuS_4(H_2O)_{10}]^{4+}$.[9,10] Although not the most common preparative route, addition reactions of Cu^I, In^I and Sn^{II} to $[Mo_3S_4(H_2O)_9]^{4+}$ giving $[Mo_3CuS_4(H_2O)_{10}]^{5+}$,[10] $[Mo_3InS_4(H_2O)_{10}]^{5+}$,[6] and $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ respectively have been observed.[8] Addition appears to be an effective route in the present studies with $[W_3S_4(H_2O)_9]^{4+}$ (M = In^I, Ge^{II} or Sn^{II}). We also report the preparation of the first corner-shared double cubes $[W_6SnS_8(H_2O)_{18}]^{8+}$ and $[W_3Mo_3SnS_8(H_2O)_{18}]^{8+}$ using the recently identified[6,8] redox-induced combination of single cubes in this case $[W_3SnS_4(H_2O)_{12}]^{6+}$ and $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ with $[W_3S_4(H_2O)_9]^{4+}$.

Experimental

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

Two procedures were used to prepare the purple trinuclear W^{IV}_3 cluster $[W_3S_4(H_2O)_9]^{4+}$. The first involved reduction of ammonium tetrasulfidotungstate(VI), $[NH_4]_2[WS_4]$, with sodium tetrahydroborate, $Na[BH_4]$ (Aldrich), in 0.5 M HCl as previously described.[11-13] The product was purified by Dowex 50W-X2 cation-exchange chromatography. Elution was with different 2.0 M acids as required, generally in the present studies with 2.0 M HCl. The product has UV/VIS peaks at λ/nm (ε/M^{-1} cm^{-1} per W_3) 317 (6100) and 570 (480) in HCl, and 315 (8650) and 560 (546) in Hpts (toluene-*p*-sulfonic acid). The second procedure involved boiling $[NH_4]_2[W_3S_4(S_4)_3(NH_3)_3]\cdot H_2O$ (1 g) in concentrated HCl (10 cm^3) for 20 min.[14] The resulting $[W_3S_4(H_2O)_9]^{4+}$ solution was filtered and rota-evaporated to dryness (reduced pressure). The solid was taken up in 2.0 M HCl, diluted to 0.30 M HCl, and purified by Dowex 50W-X2 chromatography as above.

Preparation of $[W_3InS_4(H_2O)_{12}]^{5+}$

Three methods were used.

Method A. A solution of 0.1 mM In^I in 0.02 M perchloric acid was prepared by anodic oxidation of an indium-wire electrode (1.6 mm diameter; Specpure, Johnson Matthey Ltd.) as previously described.[15] On addition to $[W_3S_4(H_2O)_9]^{4+}$ the formation of a strong indigo blue colour was observed. Since In^I reacts with H^+[15] it is important to keep the H^+ of stock solutions of In^I as low as possible.

Method B. To a solution of $[W_3S_4(H_2O)_9]^{4+}$ in 2.0 M Hpts (50 cm^3, 1.78 mM), three pieces of indium wire (each ≈1 cm long) were added. The reaction under air-free conditions gives the same blue solution in 3 d. Alternatively it is possible to accelerate the reaction by heating at 60 °C, when the reaction is complete in ≈30 min (yield ≈95%).

Method C. A mixture of $[W_3S_4(H_2O)_9]^{4+}$ (5 cm^3, 10 mM) in 0.50 M HCl and an In solution (1 cm^3) obtained by dissolving In metal (0.5 g) in 4 M HCl (10 cm^3) was syphoned onto $Na[BH_4]$ (0.4 g) in a round-bottomed flask under rigorous air-free conditions. A change from purple to blue was observed. After standing for 12 h the solution was diluted and loaded onto

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† *Non-SI unit employed:* M = mol dm^{-3}.

a Dowex 50W-X2 cation-exchange column, and washed with 0.50 M HCl. With 1.0 M HCl the $[W_3InS_4(H_2O)_{12}]^{5+}$ product was eluted as a single band ($\approx$91% yield) then $[W_3S_4(H_2O)_9]^{4+}$ ($\approx$4%). From the elution behaviour some chloride complexing at the In is apparent. Elution with 2.0 M Hpts was also carried out.

Stock solutions were stored under N_2 at 4 °C. Under these conditions 10% oxidation to $[W_3S_4(H_2O)_9]^{4+}$ was observed in 10 d. With slow bubbling of air through solutions there is 50% decay in 10 min.

Preparation of GeO

A slightly modified version of a literature procedure was used.[16] Germanium powder (Aldrich; 100 mesh, 99.99%) was first washed in 4.0 M HCl–water, and then dissolved in a solution of KOH (1 g) in water (20 cm^3) with 20% H_2O_2 (2 cm^3) added. Hydrochloric acid (200 cm^3, 11.3 M) and 50% hypophosphorous acid H_3PO_2 (Aldrich; 15 cm^3) were added. The solution was refluxed at 100 °C for 6 h under N_2. After cooling an excess of NH_3 was added to precipitate GeO. The yellow precipitate was filtered off under N_2, washed and dried. Yield 1.75 g.

Preparation of $[W_3GeS_4(H_2O)_{12}]^{6+}$

Two methods were used.

Method A. A sample of GeO was first prepared by the above procedure. A solution of $[W_3S_4(H_2O)_9]^{4+}$ (5 cm^3, 18.7 mM) in 2.0 M HCl was added to GeO (0.20 g) under air-free conditions. An immediate change to red-brown $[W_3GeS_4(H_2O)_{12}]^{6+}$ was observed. The product was diluted to 0.50 M HCl, loaded onto a Dowex 50W-X2 cation-exchange column, washed with 0.50 and 1.0 M HCl, and eluted with 2.0 M HCl (or acid as required). No remaining $[W_3S_4(H_2O)_9]^{4+}$ was observed.

Method B. A mixture of $[W_3S_4(H_2O)_9]^{4+}$ (2 cm^3, 21 mM) in 1.0 M HCl, a 5% solution of GeO_2 (Avocado UK Chemicals Ltd., 99.98%) in 11.3 M HCl (1 cm^3), and a 45% solution of H_3PO_2 (0.4 cm^3) was heated for 10 min at $\approx$60 °C. The red-brown product was purified by column chromatography as above.

Solutions could be stored for 2–3 weeks under N_2 at 4 °C. After 12 h in air the UV/VIS spectrum gave only peaks of $[W_3S_4(H_2O)_9]^{4+}$, which could be separated (92% yield) by Dowex chromatography.

Preparation of $[W_3SnS_4(H_2O)_{12}]^{6+}$

Two methods were used.

Method A. A solution of $[W_3S_4(H_2O)_9]^{4+}$ (5 cm^3, 20 mM) in 2.0 M HCl was added to $SnCl_2{\cdot}2H_2O$ (0.2 g) under air-free conditions. The yellow-brown solution was diluted to 0.50 M HCl and loaded onto a Dowex 50W-X2 cation-exchange column. The column was washed with 0.50 and 1.0 M HCl, and $[W_3SnS_4(H_2O)_{12}]^{6+}$ eluted with 2.0 M HCl as the chloro complex $[W_3(SnCl_3)S_4(H_2O)_9]^{3+}$. No remaining $[W_3S_4(H_2O)_9]^{4+}$ was detected. Attempts to elute $[W_3SnS_4(H_2O)_{12}]^{6+}$ in 2–3 M Hpts at 0 °C gave $[W_3S_4(H_2O)_9]^{4+}$ as the only product.

Method B. A solution of $[W_3S_4(H_2O)_9]^{4+}$ (2 cm^3, 20 mM) in 2.0 M HCl was added to tin shot (activated by washing with 2.0 M HCl and water) under air-free conditions. Colour changes to a yellow-brown solution were complete in $\approx$6 h. Chromatographic purification was as above. No violet $[W_3S_4(H_2O)_9]^{4+}$ band was observed.

With slow bubbling of air through solutions of the product in 2.0 M HCl there is 20% decay in 10 min.

Preparation of $[W_6SnS_8(H_2O)_{18}]^{8+}$

A mixture of $[W_3SnS_4(H_2O)_{12}]^{6+}$ (10 cm^3, 2.0 mM) and $[W_3S_4(H_2O)_9]^{4+}$ (11.1 cm^3, 1.8 mM), both in 1 M HCl, was syphoned onto $Na[BH_4]$ (0.4 g) under rigorous air-free conditions. A change to purple-red occurred. After standing for 30 min the solution was diluted to 0.50 M HCl and loaded onto a Dowex 50W-X2 cation-exchange column at 0 °C, and washed with 0.50 and then 1.0 M HCl. Elution of yellow-brown $[W_3SnS_4(H_2O)_{12}]^{6+}$ ($\approx$2%) and then purple $[W_3S_4(H_2O)_9]^{4+}$ ($\approx$1%) took place with 2.0 M HCl. Purple-red $[W_6SnS_8(H_2O)_{18}]^{8+}$ was eluted in 3.0 M HCl.

Stock solutions were stored by a procedure involving placing a container within a container both under N_2 at 4 °C. Under these conditions 10% decay was observed in 2 d. With slow bubbling of air through solutions 100% decay was observed in 2 min. The products of decomposition are $[W_3SnS_4(H_2O)_{12}]^{6+}$ and $[W_3S_4(H_2O)_9]^{4+}$ in a 1:1 ratio.

Preparation of $[W_3Mo_3SnS_8(H_2O)_{18}]^{8+}$

A yellow-green solution of $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ was first prepared as described.[9] A mixture of $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ (10 cm^3, 1.33 mM) and $[W_3S_4(H_2O)_9]^{4+}$ (9.43 cm^3, 1.41 mM) both in 2.0 M HCl was syphoned onto $Na[BH_4]$ (0.4 g) under air-free conditions. The colour changed to red-purple, and the product was separated by cation-exchange chromatography as in the previous section. Elution of the red-purple product was carried out with 2.0 M HCl or 4.0 M Hpts. The final product was more red in appearance than $[W_6SnS_8(H_2O)_{18}]^{8+}$.

Stock solutions were stored under N_2 at 4 °C. Under these conditions 10% oxidation was observed in 2 d. With slow bubbling of air through solutions there is 25% decay in 5 min.

Heteroatom transfer reactions

On mixing $[Mo_3S_4(H_2O)_9]^{4+}$ (2.8 cm^3, 3.75 mM) and $[W_3SnS_4(H_2O)_{12}]^{6+}$ (5.0 cm^3, 2.10 mM) in 2.0 M HCl the colour began to change almost immediately. Column separation of the products gave only $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ and $[W_3S_4(H_2O)_9]^{4+}$ as products. Similarly on mixing $[Mo_3S_4(H_2O)_9]^{4+}$ (2.4 cm^3, 1.7 mM) with $[W_3InS_4(H_2O)_{12}]^{5+}$ (1.0 cm^3, 4.1 mM) the UV/VIS spectrum obtained corresponded to a mixture of $[Mo_3InS_4(H_2O)_{12}]^{5+}$ and $[W_3S_4(H_2O)_9]^{4+}$. Yields 95 ± 5%.

Other attempted preparations

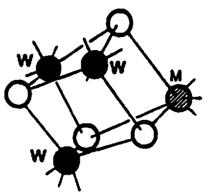
Whereas a solution of $[Mo_3S_4(H_2O)_9]^{4+}$ and Ga^{III} in 1.0 M HCl gives with $Na[BH_4]$ the single cube $[Mo_3GaS_4(H_2O)_{12}]^{5+}$,[7] no similar reaction was observed with $[W_3S_4(H_2O)_9]^{4+}$.

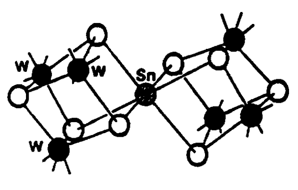
Oxidant

A 0.5 M solution of iron(III) chloride hexahydrate (BDH, Analar) in 2.0 M HCl was used in redox/stoichiometry experiments.

Metal analyses

A Unicam 701 inductively coupled plasma atomic emission spectrometer was used. Solutions in 1–2 M HCl give better results than those in Hpts, which can give erroneous results.





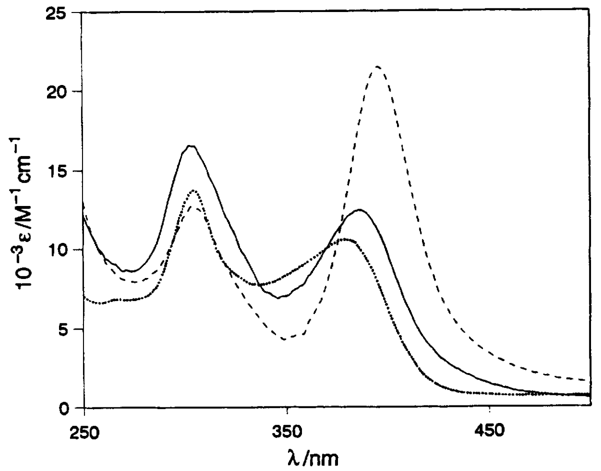


Fig. 1 The UV/VIS spectra of single-cube derivatives of $[W_3S_4(H_2O)_9]^{4+}$, $[W_3InS_4(H_2O)_{12}]^{5+}$ (. . .) in 1 M HCl, $[W_3GeS_4(H_2O)_{12}]^{6+}$ (——) and $[W_3SnS_4(H_2O)_{12}]^{6+}$ (– – –) in 2.0 M HCl

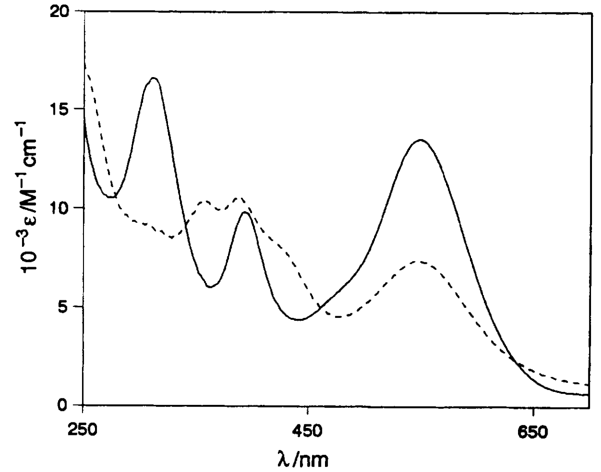


Fig. 2 The UV/VIS spectra of corner-shared double-cube clusters $[W_6SnS_8(H_2O)_{18}]^{8+}$ (——) and $[W_3Mo_3SnS_8(H_2O)_{18}]^{8+}$ (– – –) in 2.0 M HCl

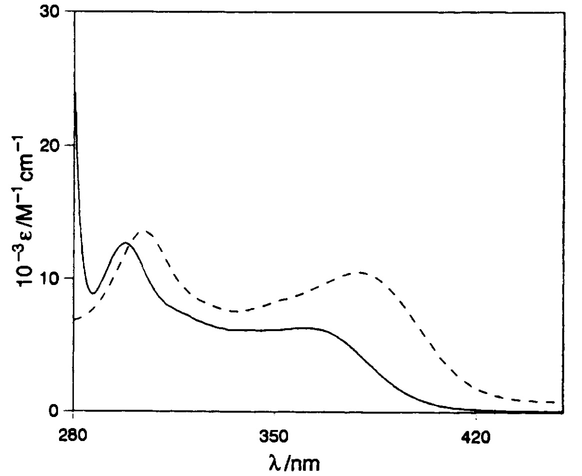


Fig. 3 Comparison of UV/VIS spectra of $[W_3InS_4(H_2O)_{12}]^{5+}$ in 2.0 M Hpts (——) and 2.0 M HCl (– – –)

Results and Discussion

Preparative procedures for three heterometallic (M = In, Ge or Sn) single-cube derivatives of $[W_3S_4(H_2O)_9]^{4+}$, characterised as $[W_3InS_4(H_2O)_{12}]^{5+}$, $[W_3GeS_4(H_2O)_{12}]^{6+}$ and $[W_3SnS_4(H_2O)_{12}]^{6+}$ or related in 2 M HCl, are described for the first time. The first corner-shared double-cube derivative of $[W_3S_4(H_2O)_9]^{4+}$ assigned as $[W_6SnS_8(H_2O)_{18}]^{8+}$ has also been isolated. Different cube structure types have been established previously in the corresponding $[Mo_3S_4(H_2O)_{19}]^{4+}$ chemistry. Structures relevant to the present studies are as illustrated.

Table 1 Results of metal analyses by ICP-AES, and stoichiometry determination with aquairon(III) as oxidant

Cluster	ICP-AES Analysis	Moles of Fe^{III} consumed
$[W_3InS_4(H_2O)_{12}]^{5+}$	W:In 3.0:0.95	2.05
$[W_3GeS_4(H_2O)_{12}]^{6+}$	W:Ge 3.0:0.97	2.10
$[W_3SnS_4(H_2O)_{12}]^{6+}$	W:Sn 3.0:0.94	*a*
$[W_6SnS_8(H_2O)_{18}]^{8+}$	W:Sn 6.0:1.2	4.20
$[W_3Mo_3SnS_8(H_2O)_{18}]^{8+}$	Mo:W:Sn 3.0:2.94:1.12	*b*

[a] The crystal structure of $[NMe_2H_2]_6[W_3(SnCl_3)S_4(NCS)_9]\cdot 0.5H_2O$ is consistent with a 6+ charge, ref. 5. [b] The crystal structure of $[NMe_2H_2]_6[Mo_3(SnCl_3)S_4(NCS)_9]\cdot 5H_2O$ has been reported, ref. 8.

Table 2 Peak positions in UV/VIS spectra of heterometallic single and corner-shared double cube derivatives of $[W_3S_4(H_2O)_9]^{4+}$ in 2 M HCl except as stated

Cluster	λ/nm (ε/M^{-1} cm^{-1})
$[W_3InS_4(H_2O)_{12}]^{5+}$ [a]	304 (13 600), 379 (10 500), 590 (1500)
$[W_3InS_4(H_2O)_{12}]^{5+}$ [b]	298 (13 000), 362 (6010), 591 (900)
$[W_3GeS_4(H_2O)_{12}]^{6+}$ [a]	303 (16 300), 386 (12 600)
$[W_3SnS_4(H_2O)_{12}]^{6+}$ [a]	303 (12 800), 396 (21 200)
$[W_6SnS_8(H_2O)_{18}]^{8+}$ [c]	311 (16 600), 393 (9800), 548 (13 500)
$[W_3Mo_3SnS_8(H_2O)_{18}]^{8+}$ [d]	355 (10 400), 389 (10 600), 548 (7400)

[a] ε per W_3. [b] Acid 2.0 M Hpts. [c] ε per W_6. [d] ε per W_3Mo_3.

The same procedures have been applied to characterise the heterometallic derivatives of $[W_3S_4(H_2O)_9]^{4+}$ as used for $[Mo_3S_4(H_2O)_9]^{4+}$.[1,8] Dowex cation-exchange chromatography differentiates between the lower-charged single cubes and higher-charged double cubes. The differences in charge are greater using HCl for elution, since Cl complexes to the heterometal of the single cubes. Complexing of Cl^- to W (and Mo) is much weaker.[13,17] Thus with $[Cl^-] \approx 0.1$ M it has been established that $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ is present as $[Mo_3(SnCl_3)S_4(H_2O)_9]^{3+}$, and it is clear that $[W_3(SnCl_3)S_4(H_2O)_9]^{3+}$ also readily forms.[5] It is moreover a stabilising influence, since $[W_3SnS_4(H_2O)_{12}]^{6+}$ cannot be eluted from Dowex cation-exchange columns with 2.0 M Hpts when $[W_3S_4(H_2O)_9]^{4+}$ reforms.

Metal analyses by inductively coupled plasma atomic emission spectroscopy (ICP-AES) for the heterometallic derivatives of $[W_3S_4(H_2O)_9]^{4+}$ are listed in Table 1. The 3:1 W to heterometal ratios indicate single cubes, and 6:1 ratios (or 3:3:1 in the case of the W/Mo product) corner-shared double cubes. Solutions of the heterometallic products undergo air oxidation, with $[W_3S_4(H_2O)_9]^{4+}$ a product in all cases. With aquairon(III) as oxidant the single cubes give 2:1 stoichiometries, enabling the charge on the heterometallic cube to be designated as in equations (1)–(3). Similarly for the corner-shared double cube a 4:1 stoichiometry is observed, equation (4), and in the case of the W_3Mo_3 double cube reaction (5) holds.

$$W_3InS_4{}^{5+} + 2Fe^{III} \longrightarrow W_3S_4{}^{4+} + In^{III} + 2Fe^{II} \quad (1)$$

$$W_3GeS_4{}^{6+} + 2Fe^{III} \longrightarrow W_3S_4{}^{4+} + Ge^{IV} + 2Fe^{II} \quad (2)$$

$$W_3SnS_4{}^{6+} + 2Fe^{III} \longrightarrow W_3S_4{}^{4+} + Sn^{IV} + 2Fe^{II} \quad (3)$$

$$W_6SnS_8{}^{8+} + 4Fe^{III} \longrightarrow 2W_3S_4{}^{4+} + Sn^{IV} + 4Fe^{II} \quad (4)$$

$$W_3Mo_3SnS_8{}^{8+} + 4Fe^{III} \longrightarrow W_3S_4{}^{4+} + Mo_3S_4{}^{4+} + Sn^{IV} + 4Fe^{III} \quad (5)$$

The UV/VIS spectra of the single cubes $[W_3InS_4(H_2O)_{12}]^{5+}$, $[W_3GeS_4(H_2O)_{12}]^{6+}$, $[W_3SnS_4(H_2O)_{12}]^{6+}$, and the double cubes $[W_6SnS_8(H_2O)_{18}]^{8+}$ and $[W_3Mo_3SnS_8(H_2O)_{18}]^{8+}$, are illustrated in Figs. 1 and 2, with details as listed in Table 2. The $[W_3InS_4(H_2O)_{12}]^{5+}$ spectrum has an additional peak at 590 nm not shown in Fig. 1 which is responsible for the blue colour. The effect of Cl^- complexing to the heterometal atom is illustrated for $[W_3InS_4(H_2O)_{12}]^{5+}$ in Fig. 3, with shifts similar to those illustrated in earlier work for $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ in 2.0 M HCl and 2.0 M Hpts as well as 2.0 M $HClO_4$.[8]

Addition reactions of In^I, Ge^{II} (as GeO), and Sn^{II} to $[W_3S_4(H_2O)_9]^{4+}$ constitute a preparative route, equations (6)–(8), to be considered alongside the earlier example of copper(I)

$$W_3S_4{}^{4+} + In^I \longrightarrow W_3InS_4{}^{5+} \qquad (6)$$

$$W_3S_4{}^{4+} + Ge^{II} \longrightarrow W_3GeS_4{}^{6+} \qquad (7)$$

$$W_3S_4{}^{4+} + Sn^{II} \longrightarrow W_3SnS_4{}^{6+} \qquad (8)$$

addition, equation (9).[10] The reactions of $[W_3S_4(H_2O)_9]^{4+}$

$$W_3S_4{}^{4+} + Cu^I \longrightarrow W_3CuS_4{}^{5+} \qquad (9)$$

with the metals In and Sn (and also with Cu[3]) give the same single-cube products as in equations (6), (8) and (9). The reactions are however difficult to express as single stoichiometric equations and further mechanistic information is required. One possibility is that unstable 4+ adducts of $[W_3S_4(H_2O)_9]^{4+}$ are first formed, $W_3MS_4{}^{4+}$, which react further with the H^+ present. Thus it has recently been shown that $Mo_6TlS_8{}^{8+}$ as well as In-containing single and double cubes react with H^+ liberating H_2.[1,6,18] In contrast to the reaction of Sn with $[W_3S_4(H_2O)_9]^{4+}$, that with $[Mo_3S_4(H_2O)_9]^{4+}$ gives the corner-shared double cube, equation (10).[19] The $W_6SnS_8{}^{8+}$

$$2Mo_3S_4{}^{4+} + Sn \longrightarrow Mo_6SnS_8{}^{8+} \qquad (10)$$

double cube has been prepared by an alternative route, see equation (12) below. The reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with copper metal gives the 4+ single cube,[10] which has been isolated as an edge-linked double cube, equation (11).[9] The only

$$2Mo_3S_4{}^{4+} + 2Cu \longrightarrow 2Mo_3CuS_4{}^{4+} \rightleftharpoons \{Mo_3CuS_4\}_2{}^{8+} \qquad (11)$$

other heterometallic derivative of $[W_3S_4(H_2O)_9]^{4+}$ is obtained by reaction with nickel metal. The 4+ product $[W_3NiS_4(H_2O)_{10}]^{4+}$ differs from $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ in forming an edge-linked double cube $[\{W_3NiS_4(H_2O)_9\}_2]^{8+}$.[4] The greater difficulty in reducing the $W^{IV}{}_3$ trinuclear unit as compared to $Mo^{IV}{}_3$ explains some of these differences.

Alternative procedures used to obtain the single-cube derivatives of $[W_3S_4(H_2O)_9]^{4+}$ involve the addition of In^{III} + $BH_4{}^-$ and GeO_2 + H_3PO_2. These can be explained by *in situ* generation of In^I and Ge^{II} respectively, which react as in (6) and (7). The use of H_3PO_2 instead of $BH_4{}^-$ as a reducing agent in this chemistry has a number of advantages and is being further explored.

The two corner-shared double cubes $[W_6SnS_8(H_2O)_{18}]^{8+}$ and $[W_3Mo_3SnS_8(H_2O)_{18}]^{8+}$ were both prepared by redox-induced addition of $[W_3S_4(H_2O)_9]^{4+}$ to the single cubes as in equations (12) and (13). In these reactions reduction of the single cube most likely initiates reaction.[1,8]

$$W_3SnS_4{}^{6+} + W_3S_4{}^{4+} + 2e^- \longrightarrow W_6SnS_8{}^{8+} \qquad (12)$$

$$Mo_3SnS_4{}^{6+} + W_3S_4{}^{4+} + 2e^- \longrightarrow W_3Mo_3SnS_8{}^{8+} \qquad (13)$$

Finally the occurrence of tin transfer in reaction (14), with no corresponding UV/VIS changes for $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ with $[W_3S_4(H_2O)_9]^{4+}$, suggests a greater affinity of $[Mo_3S_4(H_2O)_9]^{4+}$ for Sn^{II}. A possible mechanism involves dissociation *via* equation (15) and subsequent reaction of

$$W_3SnS_4{}^{6+} + Mo_3S_4{}^{4+} \longrightarrow W_3S_4{}^{4+} + Mo_3SnS_4{}^{6+} \qquad (14)$$

$$W_3SnS_4{}^{6+} \rightleftharpoons W_3S_4{}^{4+} + Sn^{II} \qquad (15)$$

$[Mo_3S_4(H_2O)_9]^{4+}$ with Sn^{II}. The reaction of $[W_3S_4(H_2O)_9]^{4+}$ (0.10 mM) with Sn^{II} (1.0 mM) in 2.0 M HCl or 2.0 M Hpts was too fast to monitor by the stopped-flow method at 25 °C.

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