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Preparation of Two Copper-containing Molybdenum–Tungsten Cuboidal Clusters†

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Two new cuboidal clusters, containing copper, have been developed and studied (using UV–VIS spectroscopy and cyclic voltammetry), thus completing the series $M_nM'_{3-n}CuS_4(aq)^{y+}$, where M = Mo and M′ = W.

The incorporation of elements into $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$ has been well studied.[1–8] In particular, copper has been incorporated into both the Mo[4,9] and the W analogues.[10–12] The clusters produced have cores of $\{Mo_3CuS_4{}^{4+}\}_2$ and $W_3CuS_4{}^{5+}$ by reaction with copper metal.[11,12] A $Mo_3CuS_4{}^{5+}$ core can also be generated using Cu(I).[12]

Two mixed-metal clusters, $[Mo_2WS_4(H_2O)_9]^{4+}$ and $[MoW_2S_4(H_2O)_9]^{4+}$, have been prepared.[13] The incorporation of copper into these clusters has been attempted here. Very low yields of $[MoW_2S_4(H_2O)_9]^{4+}$ have made studies difficult.

Experimental

Preparation of $[Mo_2WS_4(H_2O)_9]^{4+}$ *and* $[MoW_2S_4(H_2O)_9]^{4+}$.—These compounds were prepared as previously.[14] The peaks and extinction coefficients obtained by Shibahara[13] are used with those in the 300–400 nm region obtained by extrapolation.

Cyclic Voltammetry.—Cyclic voltammetry studies were performed in 2.00 M $HClO_4$ at 25.0 °C. An Ag/AgCl reference electrode was used in conjunction with a Pt working electrode and a Pt wire auxiliary electrode.

Results

Both mixed-metal species (*ca.* 1 mM; 2.00 M $HClO_4$) were reacted with copper metal under N_2 for 3–4 h to enable 100% conversion. ϵ values (Table 1) were determined by comparison with the starting material. A colour change of green to yellow-orange (Fig. 1) was obtained with $[Mo_2WS_4(H_2O)_9]^{4+}$; with grey to yellow-green (Fig. 2) for $[MoW_2S_4(H_2O)_9]^{4+}$.

The charge on the derivatives was determined by oxidation to the starting material and $Cu(aq)^{2+}$.

The results obtained for $Mo_2WCuS_4{}^{x+}$ were 1:1 for $[Fe^{3+}]$:$[Mo_2WCuS_4{}^{x+}]$. Determination of the amount of iron(II) ions present in the solution yielded a value of 0.969 ± 0.050:1 for the ratio $[Fe^{2+}]$:$[Mo_2WCuS_4{}^{x+}]$, eqn. (1). For oxidation by $[Co(dipic)_2]^-$ a ratio, of 1.05 ± 0.05:1 was obtained for $[Co^{III}]$:$[Mo_2WCuS_4{}^{x+}]$ consistent with a 5+ charge, eqn. (2).

$$Mo_2WCuS_4{}^{5+} + Fe^{3+} \rightarrow Mo_2WS_4{}^{4+} + Fe^{2+} + Cu^{2+} \qquad (1)$$

$$Mo_2WCuS_4{}^{5+} + Co^{III} \rightarrow Mo_2WS_4{}^{4+} + Co^{II} + Cu^{2+} \qquad (2)$$

Studies on the $MoW_2CuS_4{}^{x+}$ cluster indicated that a ratio of 2:1 for $[Fe^{3+}]$:$[MoW_2CuS_4{}^{x+}]$ was needed indicating a charge of 4+, eqn. (3).

$$MoW_2CuS_4{}^{4+} + 2Fe^{3} \rightarrow MoW_2S_4{}^{4+} + 2Fe^{2+} + Cu^{2+} \qquad (3)$$

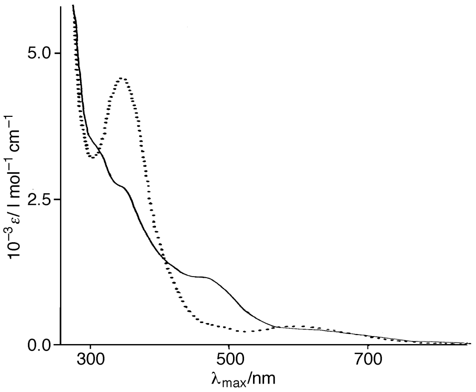

Fig. 1 UV-VIS spectra of $[Mo_2WS_4(H_2O)_9]^{4+}$ (· · · ·) and its copper derivative (—), 2.00 M $HClO_4$, 25.0 °C

Stability.—The cluster assigned as $Mo_2WCuS_4{}^{5+}$ was stable for a minimum of 10 min under nitrogen at room temperature. In air, decomposition occurred to the starting material. Beer's law was obeyed at 340 and 460 nm (25.0 °C).

The derivative $MoW_2CuS_4{}^{4+}$, was found to be stable under nitrogen for several hours at room temperature. The lifetime increased in the presence of the metal, at 4.0 °C. Beer's law was obeyed at 410 nm at 25 °C.

Cyclic Voltammetry.—$Mo_2WCuS_4{}^{5+}$. When a solution of $Mo_2WCuS_4{}^{5+}$ (1 mM) was reduced in 2.00 M $HClO_4$, a transient species appeared to occur. On scanning from 0.9 to 0.0 V at 50 mV s^{-1}, a non-reversible reduction wave was observed at *ca.* 0.5 V (0.72 V *vs.* SHE), Fig. 3a, consistent with the reduction of the 5+ species to 4 +, and the latter then decomposing, eqn. (4)

$$Mo_2WCuS_4{}^{5+} + e^- \rightarrow [Mo_2WCuS_4{}^{4+}]^\ddagger$$

$$[Mo_2WCuS_4{}^{4+}]^\ddagger \rightarrow Mo_2WS_4{}^{4+} + Cu \qquad (4)$$

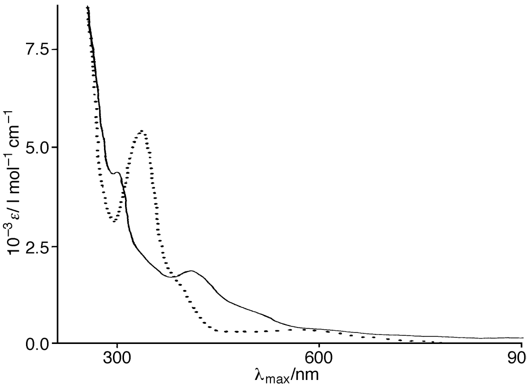

Fig. 2 UV-VIS spectra of $[MoW_2S_4(H_2O)_9]^{4+}$ (· · · ·) and its copper derivative (—), 2.00 M $HClO_4$, 25.0 °C

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Table 1 Values of λ_{max} and ϵ in 2.00 M $HClO_4$, 25 °C

Cluster	λ_{max}/nm (ϵ/l mol^{-1} cm^{-1} per cluster)			
$Mo_2WS_4(aq)^{4+}$		340 (4390)	490(sh) (298)	590 (322)
$Mo_2WCuS_4(aq)^{5+}$	310(sh) (3176)	340(sh) (2616)	460(sh) (1108)	610(sh) (263)
$MoW_2S_4(aq)^{4+}$	325 (5420)		490 (320)	570 (363)
$MoW_2CuS_4(aq)^{4+}$	298 (4527)	410 (1927)	500(sh) (874)	

If the scan rate was decreased to 5 mV s^{-1}, a second process was observed at 0.12 V (0.34 V *vs.* SHE), presumably the oxidation of one end-product (Fig. 3b). If the scanning was then begun at –0.3 V, *i.e.* beginning with the reduced form of the copper derivative, this oxidation can be seen to be non-reversible (Fig. 3c). The potential and relative height of this oxidation wave (*ca.* two-fold greater than the reduction wave) indicates possibly a two-electron oxidation, perhaps that of Cu^0 to Cu^{II} ($Cu^{2+}/Cu^0 = 0.34$ V), the non-reversibility being due to the dispersion into the bulk solution of the Cu^{II} so reducing the concentration at the electrode to negligible. This would indicate a lifetime of 14–92 s for the transient '4 + ' species (based on various scan rates) under air-free conditions.

$MoW_2CuS_4{}^{4+}$.—When a solution of $MoW_2CuS_4{}^{4+}$ (< 1 mM) was oxidised and then reduced by scanning from 0 to 0.65 V and back, a quasi-reversible process was observed with E_{pa} ($= E_{ox}$) = 0.393 V and E_{pc} ($= E_{red}$) = 0.279 V. This process has been assigned to a one-electron oxidation of the 4+ species to a 5+ core, and its subsequent reduction. Low concentrations made resolution difficult.

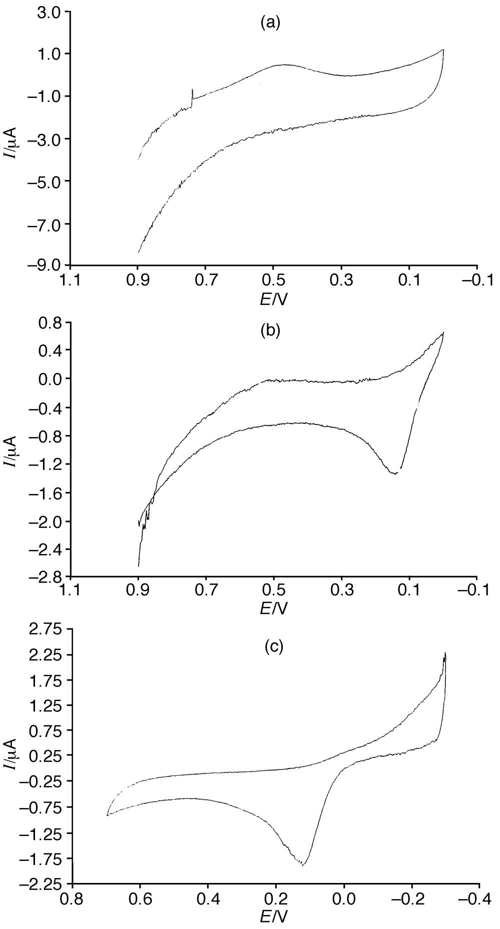

Fig. 3 Cyclic voltammograms obtained for $Mo_2WCuS_4(aq)^{5+}$ (1 mM) in 2.00 M $HClO_4$, at room temperature (*ca.* 18 °C):
(a) on scanning from 0.9 to 0.0 V (and back) at 50 mV s^{-1};
(b) on scanning from 0.9 to 0.0 V (and back) at 5 mV s^{-1};
(c) on scanning from –0.3 to 0.7 V (and back) at 5 mV s^{-1}

Discussion

Only copper and tin have been incorporated into both $[Mo_3S_4(H_2O)_9]^{4+}$ [1,4] and $[W_3S_4(H_2O)_9]^{4+}$ [12] clusters forming ($[\{Mo_3CuS_4\}_2(H_2O)_{18}]^{8+}$ [4] and $[W_3CuS_4(H_2O)_{10}]^{5+}$ [12] with copper metal. It has been shown that Cu^+ can form $Mo_3CuS_4(aq)^{5+}$.[12] Here new complexes have been prepared completing the first cuboidal cluster series.

A 5+ core was obtained with $[Mo_2WS_4(H_2O)_9]^{4+}$ and a 4+ core (or possibly 8+ if double cuboidal) with $[MoW_2S_4(H_2O)_9]^{4+}$. This anomalous result indicates that the heterometal in the minority in the trinuclear cluster appears to control the charge on the cuboidal core. The compounds do follow a general colour pattern: Mo_3CuS_4(aq), red-orange; Mo_2CuS_4(aq), orange-yellow; MoW_2CuS_4(aq), yellow-green; W_3CuS_4(aq), green.

By comparison, $MoW_2CuS_4(aq)^{4+}$ would be expected to be an edge-shared double cuboidal structure ($\{Mo_3CuS_4(aq)^{4+}\}_2$ [4]), whilst $Mo_2WCuS_4(aq)^{5+}$ would be expected to be a single cuboidal cluster.

The electrochemical studies indicate that the reduced 4+ species of $Mo_2WCuS_4(aq)^{5+}$ does not appear stable, whilst the oxidised '5+' species obtained from $MoW_2CuS_4(aq)^{4+}$ does. This indicates that a similar chemistry may occur in the latter as in $Mo_3CuS_4(aq)^{4+}$ when a 5+ core can be isolated in the oxidation reaction. The stabilisation of this new '5+' species is, however, more likely to be due to the species being '$\{MoW_2CuS_4\}_2(aq)^{9+}$' rather than the monomeric 5+ cuboidal cluster. A double cuboidal structure would be expected to tolerate the loss of an electron better than a single cuboidal species.

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