Preparation and Aqueous Solution Properties of the Heterometallic Cuboidal Complex $[W_3CuS_4(H_2O)_{10}]^{5+}$ †

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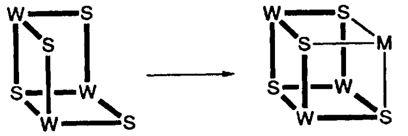
The first heterometallic derivative of the trinuclear W^{IV}_3 incomplete cuboidal cluster $[W_3S_4(H_2O)_9]^{4+}$ has been prepared by reaction with (*i*) Cu metal, and (*ii*) Cu^+ or CuCl(solid). In both cases the product is the cuboidal $[W_3CuS_4(H_2O)_{10}]^{5+}$ ion. The corresponding reactions of $[Mo_3S_4(H_2O)_9]^{4+}$ yield $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ and $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ respectively. The observation that the reaction of $[W_3S_4(H_2O)_9]^{4+}$ with copper yields the 5+ and not the 4+ product suggests that the 4+ cluster is less stable in the tungsten case. Rate constants (25 °C) for the reaction of Cu^+ with $[W_3S_4(H_2O)_9]^{4+}$ (1.82×10^3 M^{-1} s^{-1}) and $[Mo_3S_4(H_2O)_9]^{4+}$ (980 M^{-1} s^{-1}) suggest a similar addition process. The 1:1 stoichiometries for the oxidation of $[W_3CuS_4(H_2O)_{10}]^{5+}$ with $[Co(dipic)_2]^-$ (dipic = pyridine-2,6-dicarboxylate) and $[Fe(H_2O)_6]^{3+}$ giving $[W_3S_4(H_2O)_9]^{4+}$ and Cu^{2+} as products, further support the 5+ overall charge assignment. Rate constants have been determined and mechanisms assigned to these reactions. At 25 °C, I = 2.00 M ($LiClO_4$), the $[Co(dipic)_2]^-$ reaction is outer-sphere with a rate constant of 17.7×10^3 M^{-1} s^{-1}, while outer-sphere $[Fe(H_2O)_6]^{3+}$ (2.68×10^2 M^{-1} s^{-1}) and inner-sphere $[Fe(H_2O)_5(OH)]^{2+}$ (5.0×10^5 M^{-1} s^{-1}) reactions are observed for the Fe^{III} oxidant. Rate constants are of the same order of magnitude to those for the corresponding reactions of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$, suggesting that a common electron-transfer process involving the copper centre may be relevant in both cases.

Recent studies on the preparation, structure and reactivity of heterometallic $Mo_3MS_4{}^{4+}$ and related cuboidal complexes, formed by reacting the trinuclear Mo^{IV}_3 incomplete cuboidal complex $[Mo_3S_4(H_2O)_9]^{4+}$ with metals,[1] or metal ions in the presence of $BH_4{}^-$,[2] equations (1) and (2), have resulted in

$$Mo_3S_4{}^{4+} + M \longrightarrow Mo_3MS_4{}^{4+} \quad (1)$$

$$Mo_3S_4{}^{4+} + M^{2+} + 2e^- \longrightarrow Mo_3MS_4{}^{4+} \quad (2)$$

a rapidly developing area of chalcogenide cluster chemistry.[3] To date clusters with M = Cr,[4] Fe,[5], Co,[6] Ni,[7] Pd,[8] Cu,[9,10] Hg,[11] In,[12,13] Sn[14] or Sb,[15] have been reported. Structures identified are of three main types: (*a*) single cubes (Cr, Fe, Ni, Pd, In or Sn), (*b*) edge-linked double cubes (Co, Pd or Cu) and (*c*) corner-shared double cubes (Hg, In, Sn or Sb), Fig. 1. While in the case of the single cubes early transition metals such as Mo and Cr are octahedrally co-ordinated,[4] the later transition metals Fe, Ni, Pd and Cu have tetrahedral geometries as shown. Evidence for the existence of a series of Mo_3MSe_4 heterometallic clusters from $[Mo_3Se_4(H_2O)_9]^{4+}$ has also been presented.[16] There are, however, no known examples of heterometallic derivatives from $[Mo_3O_4(H_2O)_9]^{4+}$. More significantly no heterometallic derivatives of the now well characterised trinuclear $[W_3S_4(H_2O)_9]^{4+}$ Group 6 analogue of $[Mo_3S_4(H_2O)_9]^{4+}$ have been reported,[17–19,‡] a topic we now address. In the context of reactions (1) and (2) the conversion under investigation can be represented by equation (3).



(3)

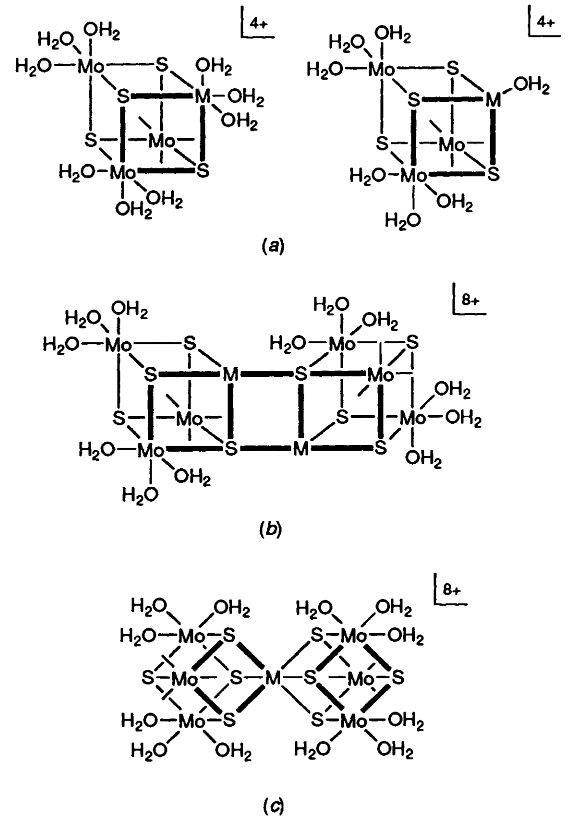


Fig. 1 Structures of Mo_3MS_4 and related cubes where M is a heteroatom: (*a*) single cubes with tetrahedral and octahedral heteroatoms respectively, (*b*) edge-linked double cubes and (*c*) corner-shared double cubes

In only one case, that of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ and $[Mo_3CuS_4(H_2O)_{10}]^{5+}$, have two different oxidation states of the same heterometallic cluster been identified.[10] While the

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

‡ *Note added at proof:* Since this paper was submitted the preparation and characterisation of a W_3SnS_4 cube has been described; A. Müller, V. P. Fedin, E. Diemann, H. Bogge, E. Krickemeyer, D. Sölter, A. M. Guiliani, R. Barbieri and P. Adler, *Inorg. Chem.*, 1994, **33**, 2243.

toluene-*p*-sulfonate (pts$^-$) salt of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ has an edge-linked double cube structure,[9] solutions from a Dowex cation-exchange column are eluted before $[Mo_3S_4(H_2O)_9]^{4+}$ indicating the presence of the 4+ single cube structure. In all other studies the corresponding 5+ state is formed as a transient only in the 2:1 oxidation of $Mo_3MS_4^{4+}$ to $[Mo_3S_4(H_2O)_9]^{4+}$ and the heterometal as the 2+ aqua ion, equation (4).

$$Mo_3MS_4^{4+} - 2e^- \longrightarrow Mo_3S_4^{4+} + M^{2+} \qquad (4)$$

The assignment of oxidation states to individual metal atoms in the heterometallic cubes is not straightforward. For example it is not immediately clear from the chemistry observed, whether in $Mo_3MS_4^{4+}$ (M = Ni or Pd), the heteroatom approximates to the II or zero state. The oxidation state assigned determines any adjustments which have to be made to the charge of the Mo_3 part of the cluster.[8] Although identical structures are observed for a number of $M^V{}_2$ and $M^{IV}{}_3$ (M = Mo or W) complexes, the tungsten complexes are generally much more readily oxidised.[20] It is also more difficult to reduce tungsten to the lower oxidation states. Formation of $W_3MS_4^{4+}$ by BH_4^- reduction of $[W_3S_4(H_2O)_9]^{4+}$ in the presence of M^{2+} may therefore be difficult, and if the existence of W_3MS_4 clusters requires tungsten to have oxidation states < IV it is understandable that such cubes may be less common than in the molybdenum case.

In the present studies it has been found that a new heterometallic Cu-containing cluster can be prepared from $[W_3S_4(H_2O)_9]^{4+}$, and we report herein the characterisation and solution properties of this product.

Experimental

Preparation of $[W_3S_4(H_2O)_9]^{4+}$.—The purple trinuclear $W^{IV}{}_3$ cluster $[W_3S_4(H_2O)_9]^{4+}$ was prepared by a procedure involving reduction of $[NH_4]_2[WS_4]$ with sodium tetrahydroborate, $NaBH_4$ (Aldrich), in 0.5 M HCl as previously described.[18,19,21] The product was purified by Dowex 50W-X2 cation-exchange chromatography. After loading onto the column and washing, elution was with 2.0 M HCl, $HClO_4$ or Hpts as required. Characterisation of $[W_3S_4(H_2O)_9]^{4+}$ was by UV/VIS spectrophotometry; a peak was observed at 563 nm (ε = 446 M^{-1} cm^{-1} per W_3) in 2 M $HClO_4$. Care is required at this stage to exclude other $[W_3O_xS_{4-x}(H_2O)_9]^{4+}$ products.

Preparation of $[W_3CuS_4(H_2O)_{10}]^{5+}$.—Although most studies were carried out in 2 M $HClO_4$ other acids, 2 M HCl or 2 M Hpts, can also be used. In the first method Cu^+(aq), prepared by quantitative $[Cr(H_2O)_6]^{2+}$ reduction of $[Cu(H_2O)_6]^{2+}$ (see below), was added to $[W_3S_4(H_2O)_9]^{4+}$ in 2 M acid. The reaction gives a purple to green colour change, Fig. 2. A modified procedure involving addition of $[W_3S_4(H_2O)_9]^{4+}$ (20 cm^3, 2 mM) to insoluble copper(I) chloride (0.1 g, Aldrich) was also used, equation (5).

$$[W_3S_4(H_2O)_9]^{4+} + Cu^+ \longrightarrow [W_3CuS_4(H_2O)_{10}]^{5+} \qquad (5)$$

In a second method $[W_3S_4(H_2O)_9]^{4+}$ (20 mM) in 2 M acid was added to copper turnings (≈2 g, BDH), which had been activated by prior immersion in concentrated ≈12 M $HClO_4$ for 15 min. The reaction was allowed to proceed for ≈1 h. Formation of Cu^+ by action of the acid on the metal, or H^+/H_2O oxidation of incipient $[W_3CuS_4(H_2O)_{10}]^{4+}$ is presumably occurring.

The same 5+ product is obtained on reacting $[W_3S_4(H_2O)_9]^{4+}$ with BH_4^- in the presence of Cu^{2+}. Since on addition of BH_4^- to Cu^{2+} the latter is decolourised, the intermediate formation of Cu^+ is able to explain the course of this reaction. The product is air sensitive and rigorous air-free (N_2) conditions are required throughout. Concentrations of the product were determined at 570 nm (ε = 342 M^{-1} cm^{-1} per cube).

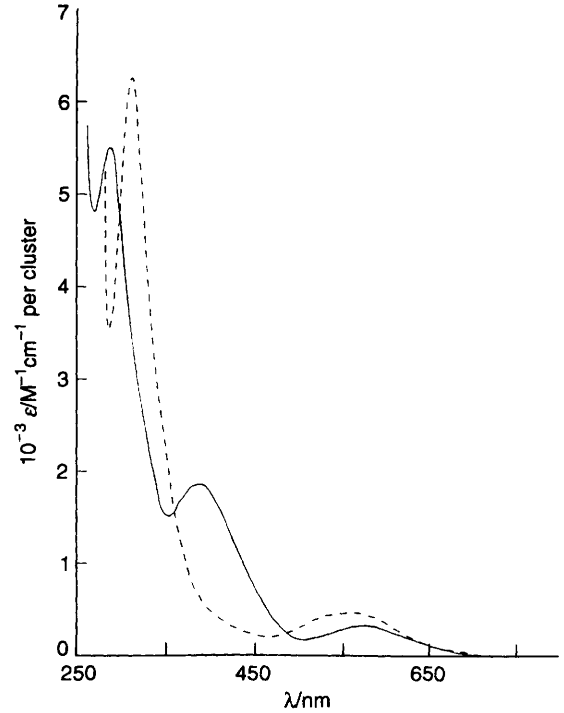

Fig. 2 The UV/VIS absorption spectra of $[W_3CuS_4(H_2O)_{10}]^{5+}$ (——) and $[W_3S_4(H_2O)_9]^{4+}$ (– – –) in 2.0 M $HClO_4$

Other Reagents.—Solutions of Cu^+(aq) were prepared by 1:1 $[Cr(H_2O)_6]^{2+}$ reduction of $[Cu(H_2O)_6]^{2+}$.[22] The $[Cr(H_2O)_6]^{2+}$ was prepared by electrolytic reduction of $[Cr(H_2O)_6]^{3+}$ at a mercury-pool cathode,[23] and the $[Cu(H_2O)_6]^{2+}$ solution was made up from copper(II) perchlorate $[Cu(ClO_4)_2 \cdot 6H_2O$, Aldrich] both in 2.0 M $HClO_4$. Under rigorous air-free conditions > 99% formation of Cu^+(aq) is observed as previously described, equation (6).

$$Cr^{II} + Cu^{II} \longrightarrow Cr^{III} + Cu^{I} \qquad (6)$$

Solutions of ≈2 mM Cu^+(aq) are stable to disproportionation for only limited periods (≈60 min). Equivalent amounts of $[Cr(H_2O)_6]^{3+}$ formed in equation (6), absorption peaks λ/nm (ε/M^{-1} cm^{-1}) at 408 (15.8) 574 (13.3),[24] were present in all subsequent experiments.

A literature method was used to prepare $[NH_4][Co(dipic)_2] \cdot H_2O$, absorption peak at 510 nm (ε = 630 M^{-1} cm^{-1}), dipic^{2-} = pyridine-2,6-dicarboxylate.[25] Solutions of hexaaquairon(III), $[Fe(H_2O)_6]^{3+}$, were purified by loading $Fe(ClO_4)_3 \cdot 6H_2O$ (Fluka) onto a Dowex 50W-X2 cation-exchange column and eluting with 1.0 M $HClO_4$. Lithium perchlorate (Aldrich, Reagent Grade) was recrystallised twice from H_2O. Perchloric acid (70%, BDH AnalaR) was used as supplied.

Analysis and Formula of Product.—The W:Cu ratio of a ≈ 1 mM solution of the W_3CuS_4 cube in 2.0 M Hpts was determined by inductively coupled plasma (ICP) emission spectroscopy at Laporte plc, Widnes, and found to be 3.06:1. A solid sample of the W_3CuS_4 cube was prepared as the pts$^-$ salt by first loading onto a Dowex 50W-X2 column. After washing with 0.50 M Hpts (50 cm^3) and then 1.0 M Hpts (50 cm^3), the cube was eluted with 4.0 M Hpts. After several days at 4 °C under air-free conditions a microcrystalline green solid was filtered off which gave the following elemental analyses: Found (Calc.) C, 23.75 (23.60); H, 2.65 (3.10%).

A $W_3CuS_4^{5+}$ cuboidal cluster has been characterised previously by X-ray crystallography as the compound $[W_3CuS_4(\mu\text{-}O_2CMe)\{S_2P(OEt)_2\}_3I(py)]$ (py = pyridine).[26] The copper in this compound has a distorted-tetrahedral geometry, and is attached to three core μ_3-sulfido and one terminal iodo group. The structure is therefore as in the second example of Fig. 1(*a*). No direct conversion to the corresponding 5+ cluster with aqua terminal ligands as in this work has yet been achieved.

In the case of the $W_3CuS_4{}^{5+}$ aqua cube at concentrations in the range (0.2–1.8) × 10^{-3} M in 2.0 M $HClO_4$, Beer's law was found to be applicable at 384 and 570 nm. Thus no UV/VIS spectrophotometric evidence was obtained for an equilibrium involving dimerisation to give an edge-linked double cube. Because of the increased charge to 5+ a double cube may have greater difficulty in forming. Even with $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ the double cube does not appear to be the dominant form in aqueous acidic solutions.[10]

Stability and UV/VIS Spectrum.—Immediate colour changes are obtained on exposure of $[W_3CuS_4(H_2O)_{10}]^{5+}$ to air, when purple $[W_3S_4(H_2O)_9]^{4+}$ is re-formed, Fig. 2. The changes observed are consistent with equation (7). Since absorption

$$4W_3CuS_4{}^{5+} + O_2 + 4H^+ \longrightarrow 4W_3S_4{}^{4+} + 4Cu^{2+} + 2H_2O \quad (7)$$

coefficients (ε) for $[W_3S_4(H_2O)_9]^{4+}$ are known this reaction provides the means of determining the ε values for $[W_3CuS_4(H_2O)_{10}]^{5+}$. These were confirmed by addition of $[W_3S_4(H_2O)_9]^{4+}$ to a large (> 100-fold) excess of copper turnings. The reaction was allowed to proceed until no further absorbance changes were observed (≈1 h), when the UV/VIS spectrum was recorded. Peak positions λ/nm (ε/M^{-1} cm^{-1} per cluster) are 288 (5500), 384 (1940) and 570 (342). Absorption coefficients using the ICP analysis results were in good agreement with the above values. The UV/VIS spectra of $[W_3CuS_4(H_2O)_{10}]^{5+}$ and $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ exhibit similar features, Fig. 3.

Stoichiometry of Oxidation Processes.—Two reactions with $[Co(dipic)_2]^-$ and $[Fe(H_2O)_6]^{3+}$ were studied in detail. With $[Co(dipic)_2]^-$ as oxidant the stoichiometry was determined by the addition of aliquots of $[W_3CuS_4(H_2O)_{10}]^{5+}$ to $[Co(dipic)_2]^-$ in 2.0 M $HClO_4$ in a spectrophotometer cell and monitoring the decrease in absorbance at 510 nm (ε = 630 M^{-1} cm^{-1}). Measurements indicated a 0.96 (±0.1):1 stoichiometry (average of three determinations), equation (8).

$$W_3CuS_4{}^{5+} + Co^{III} \longrightarrow W_3S_4{}^{4+} + Cu^{II} + Co^{II} \quad (8)$$

With $[Fe(H_2O)_6]^{3+}$ as the oxidant the $[Fe(H_2O)_6]^{2+}$ produced was determined by two methods. The first involved complexation of $[Fe(H_2O)_6]^{2+}$ by 4,7-diphenyl-1,10-phenanthroline (here abbreviated to dpphen, commercially known as bathophen).[27] The pH of product solutions was adjusted to ≈2 using 10% ammonium dihydrogen phosphate and glacial acetic acid, followed by the addition of a large (≈100 fold) excess of ligand. The complex $[Fe(dpphen)_3]^{2+}$ was extracted with isopentyl acetate, and determined at 535 nm (ε = 17 850 M^{-1} cm^{-1}). Measurements indicated a 1.04 (±0.09):1 stoichiometry (average of three determinations), equation (9).

$$W_3CuS_4{}^{5+} + Fe^{III} \longrightarrow W_3S_4{}^{4+} + Cu^{II} + Fe^{II} \quad (9)$$

An alternative procedure which involved mixing solutions of Fe^{III} and $[W_3CuS_4(H_2O)_{10}]^{5+}$ in different molar ratios and monitoring changes in the UV/VIS absorbance spectra gave measurements consistent with the above.

Kinetic Studies.—All runs were carried out at 25.0 ± 0.1 °C, *I* = 2.00 ± 0.01 M ($LiClO_4$), and monitored on a Dionex D-110 stopped-flow spectrophotometer. The reaction of $[W_3S_4(H_2O)_9]^{4+}$ with $Cu^+(aq)$ was studied at 384 nm, with check runs at 570 nm, $[Cu^+]$ in > 10-fold excess. The oxidations of $[W_3CuS_4(H_2O)_{10}]^{5+}$ with $[Co(dipic)_2]^-$ and $[Fe(H_2O)_6]^{3+}$ were monitored at 384 nm with the oxidant in > 10-fold excess.

Treatment of Data.—Stopped-flow rate constants were evaluated using exponential fitting programs supplied by On-Line Instrument Systems (Bogart, Georgia). An unweighted least-squares program was used to determine the rate constants (and standard deviations) from linear fits.

Results

Addition of Cu^+ *to* $[W_3S_4(H_2O)_9]^{4+}$.—A uniphasic process was observed in studies at $[H^+]$ = 1.90 M, *I* = 2.00 M. First-order rate constants, k_{obs} Table 1, give a linear dependence on $[Cu^+(aq)]$, Fig. 4, from which the second-order rate constant k_{Cu} = (1.82 ± 0.02) × 10^3 M^{-1} s^{-1} was obtained.

Oxidation of $[W_3CuS_4(H_2O)_{10}]^{5+}$ *with* $[Co(dipic)_2]^-$.—First-order rate constants, k_{obs} Table 2, exhibit a linear dependence on $[Co(dipic)_2{}^-]$, Fig. 5, and no dependence on $[H^+]$ in the range 0.50–1.80 M. The second-order rate constant (25 °C) obtained is k_{Co} = (17.7 ± 0.2) × 10^3 M^{-1} s^{-1}.

Oxidation of $[W_3CuS_4(H_2O)_{10}]^{5+}$ *with* $[Fe(H_2O)_6]^{3+}$.—This reaction is also uniphasic yielding rate constants k_{obs}, Table 3. A linear dependence on $[Fe^{III}]$ is observed from which the second-order rate constant k_{Fe} is obtained, equation (10).

$$-d[W_3CuS_4{}^{4+}]/dt = k_{Fe}[W_3CuS_4{}^{5+}][Fe^{III}] \quad (10)$$

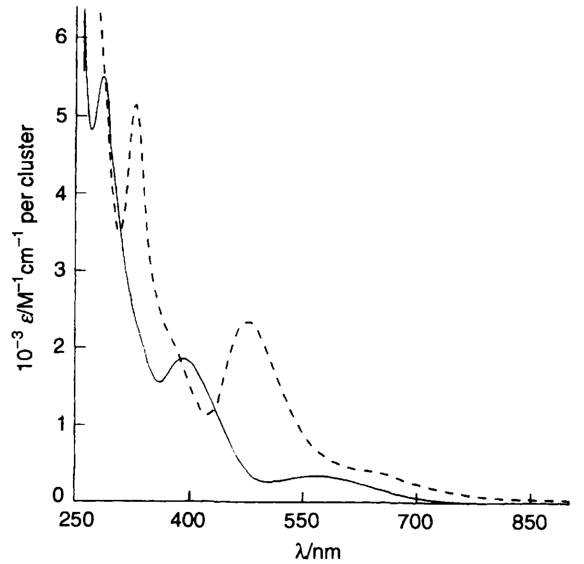

Fig. 3 Comparison of the UV/VIS absorption spectra for $[W_3CuS_4(H_2O)_{10}]^{5+}$ (——) and $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ (- - -) in 2.0 M $HClO_4$

Table 1 The variation of first-order rate constants, k_{obs} (26 °C), for the reaction of $Cu^+(aq)$ with $[W_3S_4(H_2O)_9]^{4+}$ (5 × 10^{-5} M) at $[H^+]$ = 1.90 M, *I* = 2.00 M ($LiClO_4$)

$10^3[Cu^+]$/M	k_{obs}/s^{-1}
0.53	0.85
0.78	1.40
1.00	1.83
1.50	2.75
2.00	3.6

Table 2 The dependence of first-order rate constants, k_{obs} (25 °C), for the $[Co(dipic)_2]^-$ oxidation of $[W_3CuS_4(H_2O)_{10}]^{5+}$, (0.50–1.00) × 10^{-4} M, on oxidant concentration and $[H^+]$, I = 2.00 M ($LiClO_4$)

$[H^+]$/M	$10^3[Co^{III}]$/M	k_{obs}/s^{-1}
1.80	0.50	8.1
	1.25	19.3
	2.00	38.0
1.00	0.50	7.5
	1.00	16.8
	1.40	24.6
	1.70	30.0
	2.00	36.0
0.50	0.50	7.0
	1.25	20.6
	2.00	35.0

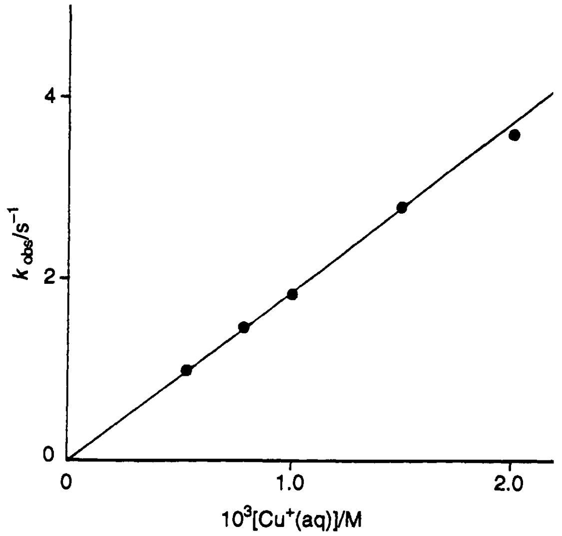

Fig. 4 The variation of first-order rate constants, k_{obs} (25 °C), for the reaction of $Cu^+(aq)$ with $[W_3S_4(H_2O)_9]^{4+}$ (5 × 10^{-5} M), $[H^+]$ = 1.90 M, I = 2.00 M ($LiClO_4$)

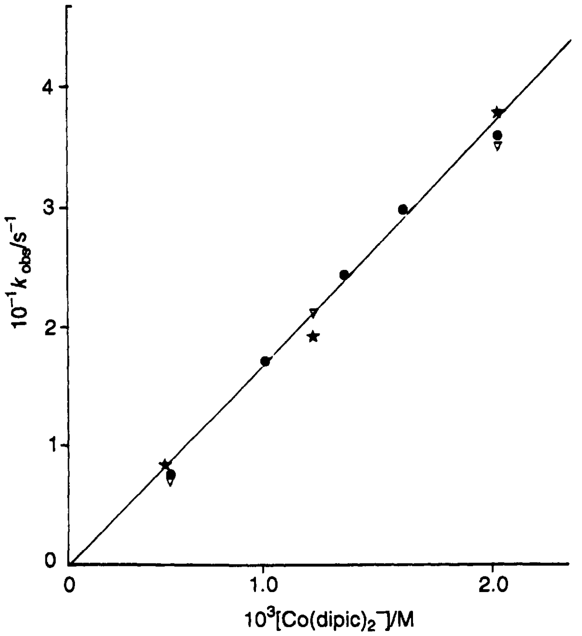

Fig. 5 The dependence of first-order rate constants, k_{obs} (25 °C), for the $[Co(dipic)_2]^-$ oxidation of $[W_3CuS_4(H_2O)_{10}]^{5+}$; $[H^+]$ = 1.80 (*), 1.00 (●) and 0.50 M (∇) $HClO_4$; I = 2.00 M ($LiClO_4$)

Table 3 The dependence of first-order rate constants, k_{obs} (25 °C), for the $[Fe(H_2O)_6]^{3-}$ oxidation of $[W_3CuS_4(H_2O)_{10}]^{5+}$, (0.50–1.00) × 10^{-4} M, on oxidant concentration and $[H^+]$, I = 2.00 M ($LiClO_4$)

$[H^+]$/M	$10^3[Fe^{III}]$/M	k_{obs}/s^{-1}
1.90	2.0	0.99
	4.0	1.86
	6.0	2.90
	8.0	3.9
	10.0	4.9
1.40	2.5	1.50
	5.0	3.1
	7.5	4.9
	10.0	6.3
1.00	2.0	1.58
	4.0	3.4
	6.0	5.1
	8.0	6.3
	10.0	7.8
0.70	5.0	5.0
	7.5	7.2
	10.0	9.8
0.50	2.5	3.3
	5.0	6.5
	7.5	9.5
	9.0	11.1

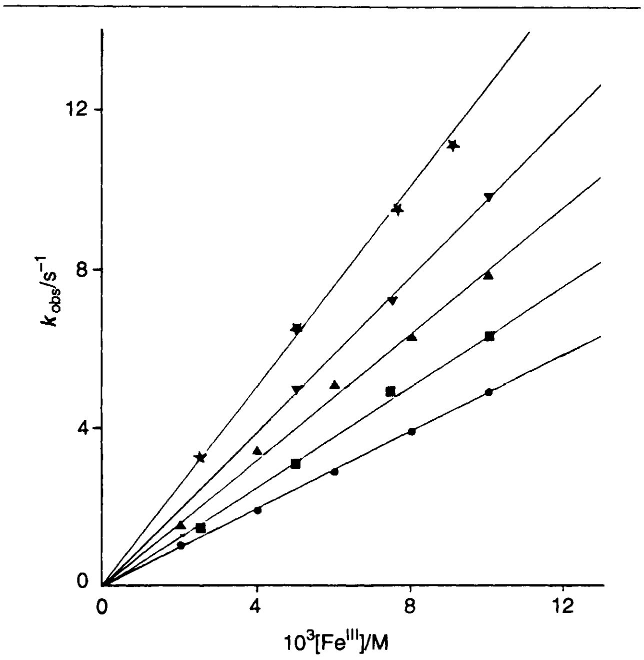

Fig. 6 The dependence of first-order rate constants, k_{obs} (25 °C), for the $[Fe(H_2O)_6]^{3+}$ oxidation of $[W_3CuS_4(H_2O)_{10}]^{5+}$; $[H^+]$ = 1.90 (●), 1.40 (■), 1.00 (▲), 0.70 (▼) and 0.50 M (*) $HClO_4$; I = 2.00 M ($LiClO_4$)

On varying $[H^+]$ within the range 0.50–1.90 M, Fig. 6, k_{Fe} shows a dependence on $[H^+]^{-1}$, Table 4, equation (11). The

$$k_{Fe} = a + b[H^+]^{-1} \qquad (11)$$

dependence illustrated in Fig. 7 implicates reaction paths involving $[Fe(H_2O)_6]^{3+}$ (*a*), and $[Fe(H_2O)_5(OH)]^{2+}$ (*b*), where a = (2.68 ± 0.04) × 10^2 M^{-1} s^{-1} and b = (5.0 ± 0.3) × 10^2 s^{-1}. At 25 °C the acid dissociation process (12) is

$$[Fe(H_2O)_6]^{3+} \xrightleftharpoons{K_a} [Fe(H_2O)_5(OH)]^{2+} + H^+ \qquad (12)$$

known to have K_a = 1.0 × 10^{-3} M, I = 2.0 M ($NaClO_4$),[28] which allows the second-order rate constant b' for the reaction

Table 4 Second-order rate constants, k_{Fe} (25 °C), for the oxidation of $[W_3CuS_4(H_2O)_{10}]^{5+}$ with $[Fe(H_2O)_6]^{3+}$, $I = 2.00$ M ($LiClO_4$)

$[H^+]$/M	$k_{Fe}/M^{-1} s^{-1}$
1.90	490 ± 20
1.40	650 ± 30
1.00	800 ± 70
0.70	980 ± 30
0.50	1260 ± 60

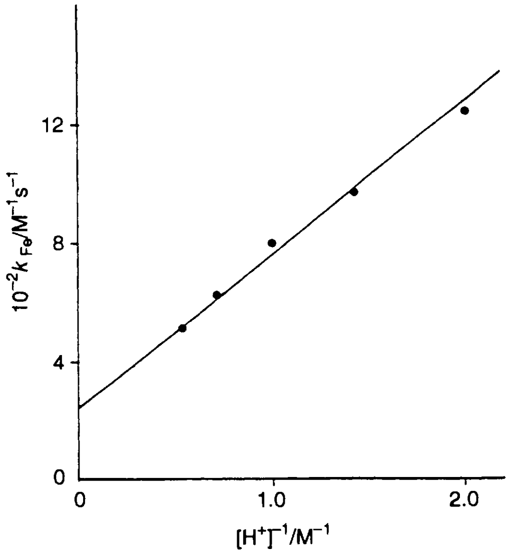

Fig. 7 The linear dependence of second-order rate constants, k_{Fe} (25 °C), on $[H^+]^{-1}$ for the $[Fe(H_2O)_6]^{3+}$ oxidation of $[W_3CuS_4(H_2O)_{10}]^{5+}$ at $I = 2.00$ M ($LiClO_4$)

of $[Fe(H_2O)_5(OH)]^{2+}$ ($= b/K_a$) to be determined as 5.0 × 10^5 $M^{-1} s^{-1}$.

Discussion

Recent work including quantitative redox studies, together with UV/VIS and EPR spectroscopic investigations, has confirmed the existence of two oxidation states for the Mo_3CuS_4 cluster, namely $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ and $[Mo_3CuS_4(H_2O)_{10}]^{5+}$.[10] Both are obtained from $[Mo_3S_4(H_2O)_9]^{4+}$, the 4+ cube by reaction with Cu metal, and the 5+ cube by reaction with Cu^I. The structural characterisation of $[W_3CuS_4(\mu\text{-}O_2CMe)\{S_2P(OEt)_2\}_3I(py)]$ has indicated the existence of the cuboidal $W_3CuS_4{}^{5+}$ core with a tetrahedrally co-ordinated copper subsite. The same 5+ core has been obtained as an aqua ion in this work by reacting $[W_3S_4(H_2O)_9]^{4+}$ with Cu^+(aq) or solid CuCl. Surprisingly, the reaction of $[W_3S_4(H_2O)_9]^{4+}$ with Cu metal also gives $[W_3CuS_4(H_2O)_{10}]^{5+}$ with no evidence for the existence of $[W_3CuS_4(H_2O)_{10}]^{4+}$ as a stable entity.

Formation of the 5+ product on reacting $[W_3S_4(H_2O)_9]^{4+}$ with Cu metal suggests an instability of incipient $[W_3CuS_4(H_2O)_{10}]^{4+}$ in the presence of H^+ and/or H_2O, or the presence of some Cu^+ which reacts directly with $[W_3S_4(H_2O)_9]^{4+}$. However, the formation of Cu^+ from the interaction of Cu metal with dilute acid in the absence of air is not normally observed, and prior activation of the Cu with concentrated acid is expected to remove any surface oxide. The high reactivity/instability of the 4+ product can be understood in terms of a quantitative bonding model proposed by Harris.[29] Thus the metal-based electrons on $[W_3CuS_4(H_2O)_{10}]^{5+}$ total 16, all of which occupy bonding or non-bonding orbitals. The additional electron which has to be included for the 4+ analogue occupies an anti-bonding orbital, hence there is a greater potential reactivity. Whereas in the molybdenum case both the 4+ and 5+ cubes are obtained, with tungsten the relative stability of the 5d level appears to favour immediate conversion of the 4+ ion to the 5+ state.

Unlike the aqua ion $[Mo_3S_4(H_2O)_9]^{4+}$, the cyano and $Hnta^{2-}$ complexes $[Mo_3S_4(CN)_9]^{5-}$ and $[Mo_3S_4(Hnta)_3]^{2-}$ (H_3nta = nitrilotriacetic acid) can be reduced to products in which the average molybdenum oxidation state is less than IV.[30-32] In previous studies on the heterometallic clusters $Mo_3MS_4{}^{4+}$ it has been suggested that the oxidation states of the molybdenum atoms may be less than IV. A number of contradictions result when more detailed assignments are attempted. Thus in the case of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$, X-ray photo electron spectroscopy (XPS) experiments seem to favour a Cu^I assignment,[9] whereas EPR studies provide evidence for an unpaired electron interacting with the Cu nucleus.[10] The conflicting evidence here does not help in the assignment of oxidation states to the molybdenum atoms. The difficulty in reducing trinuclear $W^{IV}{}_3$[32] indicates a possible preference for a Cu^I assignment in $[W_3CuS_4(H_2O)_{10}]^{5+}$. Similar features in the UV/VIS spectra of $[W_3CuS_4(H_2O)_{10}]^{5+}$ and $[W_3S_4(H_2O)_9]^{4+}$, Fig. 2, suggest that both may have a $W^{IV}{}_3$ component, and a $Mo^{IV}{}_3$ assignment may likewise apply in the case of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$, Fig. 3. The implication that the 5+ ions may have a Cu^I component, while in the $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ cube the Cu^{II} component is present with the molybdenum atoms in the $Mo^{III}{}_2Mo^{IV}$ (3.33) state, would be an interesting if somewhat unexpected outcome. There has been considerable discussion of the question of oxidation assignments in the case of the $Fe_4S_4{}^{3+}$ core structures.[33]

Addition of Cu^+(aq) to $[W_3S_4(H_2O)_9]^{4+}$ is fast and kinetic studies require the stopped-flow method. A uniphasic reaction exhibiting a $[Cu^+]$ dependence is observed. The same step has been identified in the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$.[10] Since Cu^+ has a high affinity for S^{2-},[34] this is assigned as Cu^+ attachment to one of the three $\mu\text{-}S^{2-}$ core ligands. The second-order rate constant in the tungsten case (18.2 × 10^3 $M^{-1} s^{-1}$) is comparable to that for molybdenum (980 $M^{-1} s^{-1}$). Once the initial Cu–S bond is formed subsequent re-orientation and attachment to the other μ-S core atoms is presumably rapid. In the molybdenum case a second $[Cu^+]$-independent kinetic step is observed.[10]

The conversion of $[W_3CuS_4(H_2O)_{10}]^{5+}$ to $[W_3S_4(H_2O)_9]^{4+}$ and Cu^{2+} requires the release of one electron, as has been confirmed in the stoichiometry determinations with $[Co(dipic)_2]^-$ and $[Fe(H_2O)_6]^{3+}$ as oxidants, equation (13). This provides

$$W_3CuS_4{}^{5+} - e^- \longrightarrow W_3S_4{}^{4+} + Cu^{2+} \quad (13)$$

additional evidence that the W_3CuS_4 cube is indeed 5+. A single rate-determining step, first-order in each reactant, is observed with both oxidants. The $[Co(dipic)_2]^-$ reaction is assigned as outer-sphere, with inner-sphere bridging difficult to envisage. There is moreover no $[H^+]$ dependence, in keeping with previous studies on this oxidant.[2,35,36] On the other hand the oxidation with Fe^{III} exhibits an $[H^+]^{-1}$ dependence, equation (14). Values of a and b are 268 $M^{-1} s^{-1}$ and 500 s^{-1}, and

$$k_{Fe} = a + b[H^+]^{-1} \quad (14)$$

the ratio $a:b$ is consistent with outer-sphere and inner-sphere mechanisms respectively. Thus if the acid dissociation constant for $[Fe(H_2O)_6]^{3+}$, $K_a = 1.0 \times 10^{-3}$ M^{-1} at 25 °C, $I = 2.0$ M ($NaClO_4$),[28] is taken into consideration, the second-order rate constant $b' = 5.0 \times 10^5$ $M^{-1} s^{-1}$ exhibits a 10^3 enhancement factor over a, which is as expected for an OH^- inner-sphere bridged activated complex.[37] Since the copper is likely to be labile, it is not clear how the inner-sphere activated complex assembles, and whether this is by substitution of Fe(OH) into the Cu or of a Cu ligand into the Fe co-ordination sphere. In the latter case the Fe(OH) conjugate base will further labilise the Fe^{III}-co-ordinated H_2O ligands.

Rate constants *a* and *b* for the reaction with $[Fe(H_2O)_6]^{3+}$ are not too different from the values 720 M^{-1} s^{-1} and 2380 s^{-1} respectively for the corresponding reaction of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$. Again the numerical similarity of these rate constants for *a* and *b* respectively suggests that the oxidation-state assignments Cu^I and M^{IV}_3 (M = W or Mo) may be appropriate.

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