Inorg. Chem. **1994,** *33,* 4283–4289

Preparation and Properties of the Heterometallic Cuboidal Cluster $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ and Comparisons with $[Mo_3CuS_4(H_2O)_{10}]^{4+}$

M. Nasreldin,[†] Yue-Jin Li,[†] Frank E. Mabbs,[‡] and A. Geoffrey Sykes*,[†]

Departments of Chemistry, The University of Newcastle, Newcastle upon Tyne NE1 7RU, U.K., and The University of Manchester, Manchester M13 9PL, U.K.

Received March 23, 1994[®]

A second oxidation state of the Mo_3CuS_4 cuboidal cluster has been prepared for the first time by reacting Cu^+ or solid CuCl with the trinuclear Mo^{IV}_3 incomplete cuboidal cluster $[Mo_3S_4(H_2O)_9]^{4+}$ in aqueous acidic solutions and is here characterized as $[Mo_3CuS_4(H_2O)_{10}]^{5+}$. The previously prepared 4+ cube, which crystallizes from 4 M Hpts (pts^- = *p*-toluenesulfonate) as the edge-linked double cube $[\{Mo_3CuS_4(H_2O)_9\}_2](pts)_8{\cdot}20H_2O$, behaves as a single cube on elution from a cation-exchange resin with HCl or Hpts, and is assigned the corresponding $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ (or related) formula as the dominant species in solutions here studied. Furthermore EPR spectra for $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ in 2 M HCl or 2 M Hpts are similar and provide evidence for an unpaired electron interacting with a single Cu nucleus. An absorption peak in the near-IR at 975 nm for Hpts solutions only may be assigned to the presence of some double cube. At wavelengths in the UV–vis range, 2 M Hpts solutions obey Beer's law, and the expression for complexing with Cl^- gives $K = 3.5 \times 10^3\ M^{-1}$ consistent with the presence of a single cube. At 25 °C kinetic studies on the addition of Cu^+ to $[Mo_3S_4(H_2O)_9]^{4+}$ indicate a $[Cu^+]$-dependent process rate constant of 980 $M^{-1}\ s^{-1}$ at $I = 2.00$ M ($LiClO_4$). Kinetic studies are also reported for the 2:1 hexaaquairon(III) and $[Co(dipic)_2]^-$ (dipic = pyridine-2,6-dicarboxylate) oxidations of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$, which occur in two stages with intermediate formation of $[Mo_3CuS_4(H_2O)]^{5+}$. The second of the rate constants is reproduced in separate studies on $[Mo_3CuS_4(H_2O)_{10}]^{5+}$. Studies on the $[Ru(NH_3)_5(H_2O)]^{2+}$ reduction of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ are also reported. As a result of this work an electron-transfer mechanism is proposed for reactions leading to the Cu^{2+} displacement of M^{2+} from $[Mo_3MS_4(H_2O)_{10}]^{4+}$ cubes; e.g., M = Fe and Ni.

Introduction

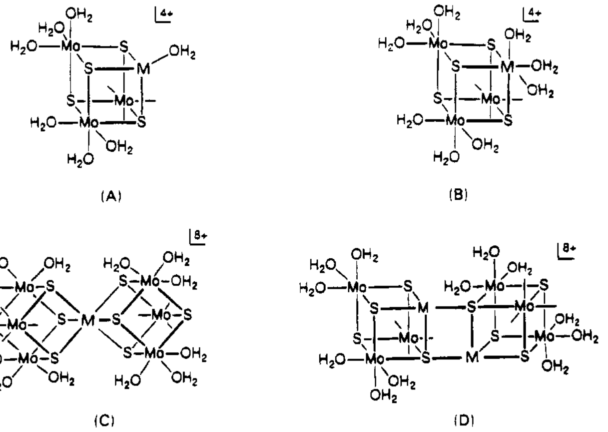


Figure 1. Structures of heterometal cuboidal complexes Mo_3MS_4 as (A) single cube, $[Mo_3MS_4(H_2O)_{10}]^{4+}$, (B) single cube, $[Mo_3MS_4(H_2O)_{12}]^{4+}$, (C) corner-shared double cubes, $[Mo_6MS_4(H_2O)_{18}]^{8+}$, and (D) edge-linked double cube, $[\{Mo_3MS_4(H_2O)_9\}_2]^{8+}$.

The preparation of the trinuclear incomplete cuboidal Mo^{IV}_3 cluster $[Mo_3S_4(H_2O)_9]^{4+}$ is now well documented,[1] and its properties have been the subject of a number of studies.[2,3] A particular interest is the ease with which $[Mo_3S_4(H_2O)_9]^{4+}$ forms heterometallic cuboidal clusters.[4,5] Thus $[Mo_3S_4(H_2O)_9]^{4+}$ reacts with metals (Fe,[6] Co,[7] Ni,[8] Cu,[9] Pd,[10] Sn,[11] Hg,[12] Sb[13]) or metal ions (Sn^{2+}),[11] to give heterometallic (M) incorporated adducts with Mo_3MS_4 cores. Reactions of $[Mo_3S_4(H_2O)_9]^{4+}$ with aqua metal ions, e.g. $[Ni(H_2O)_6]^{2+}$, in the presence of a reductant ($NaBH_4$) have also been explored, when the same Mo_3MS_4 products are obtained.[14] This method has advantages when (as with Ni), the metal reacts only slowly (or is inert) with $[Mo_3S_4(H_2O)_9]^{4+}$. In the reaction with $[Cr(H_2O)_6]^{2+}$, the latter serves also as reductant prior to formation of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$, and no $NaBH_4$ is required.[15] In the $NaBH_4$ procedure intermediate formation of $Mo_3S_4{}^{2+}$ as a transient is a possibility. Reduced forms of the ligated trinuclear core have been implicated in electrochemical studies described.[16] The structures which have been determined are of three main types, Figure 1A–D. These are (A) single cubes (Fe, Ni, Pd), (B) single cubes (Cr, Mo),

---

[†] The University of Newcastle.

[‡] The University of Manchester.

[®] Abstract published in *Advance ACS Abstracts,* August 1, 1994.

(1) See e.g.: Martinez, M.; Ooi, B.-L.; Sykes, A. G. *J. Am. Chem. Soc.* **1987,** *109,* 4615.

(2) Ooi, B.-L.; Sykes, A. G. *Inorg. Chem.* **1989,** *28,* 3799.

(3) Richens, D. T.; Pittet, P.-A.; Merbach, A. E.; Humanes, M.; Lamprecht, G. J.; Ooi, B.-L.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1993,** 2305.

(4) Shibahara, T. *Adv. Inorg. Chem.* **1991,** *37,* 143–173.

(5) Holm, R. H. *Adv. Inorg. Chem.* **1992,** *38,* 1–71.

(6) Shibahara, T.; Akashi, H.; Kuroya, H. *J. Am. Chem. Soc.* **1986,** *108,* 1342.

(7) Shibahara, T.; Akashi, H.; Yamasaki, M.; Hashimoto, K. *Chem. Lett.* **1991,** 689.

(8) Shibahara, T.; Yamasaki, M.; Akashi, H.; Katayama, T. *Inorg. Chem.* **1991,** *30,* 2693.

(9) Shibahara, T.; Akashi, H.; Kuroya, H. *J. Am. Chem. Soc.* **1988,** *110,* 3313.

(10) (a) Murata, T.; Gao, H.; Mizobe, Y.; Nakano, F.; Motomura, S.; Tanase, T.; Yano, S.; Hidai, M. *J. Am. Chem. Soc.* **1992,** *114,* 8287. (b) Murata, T.; Mizobe, Y.; Gao, H.; Ishii, Y.; Wakabayashi, T.; Nakano, F.; Tanase, T.; Yano, S.; Hidai, M.; Echizen, I.; Nanikawa, H.; Motomura, S. *J. Am. Chem. Soc.* **1994,** *116,* 3389.

(11) Akashi, H.; Shibahara, T. *Inorg. Chem.* **1989,** *28,* 2906.

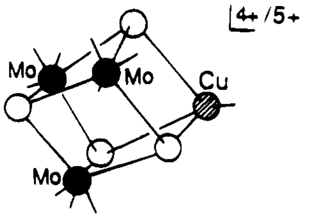
(12) Shibahara, T.; Akashi, H.; Yamasaki, M.; Hashimoto, K. *Chem. Lett.* **1991,** 689.

(13) Shibahara, T.; Hashimoto, K.; Sakane, G. Abstracts for the Fifth International Conference on Bioinorganic Chemistry, Oxford, U.K. *J. Inorg. Biochem.* **1991,** *43,* 280.

0020-1669/94/1333-4283$04.50/0

(C) corner-shared double cubes (Sn, Hg, Sb), and (D) edge-linked double cubes (Co, Cu, Pd). In the case of the $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ single cube, the Cr is octahedrally coordinated. The chemistry observed illustrates a high reactivity at the vacant sub-site of the trinuclear ion $[Mo_3S_4(H_2O)_9]^{4+}$, which has three μ-sulfido groups. To date only one oxidation state has been identified for each heterometallic structure, and reaction with O_2 or other oxidants results in the re-formation of $[Mo_3S_4(H_2O)_9]^{4+}$.

In this paper we report the preparation and properties of a second oxidation state of the Mo_3CuS_4 cube as an aqua ion of 5+ charge. Comparisons with the 4+ ion are made.



The structure of $[Mo_3CuS_4\{S_2P(OC_2H_5)\}_3(I)(CH_3CO_2)(HCON(CH_3)_2)]$, which contains an Mo_3CuS_4 core of 5+ charge and has a tetrahedrally coordinated Cu, has been determined.[17] However no route to the corresponding aqua ion, $[Mo_3CuS_4(H_2O)_{10}]^{5+}$, has so far been reported. The $Mo_3CuS_4^{4+}$ cube, previously described by Shibahara and colleagues,[9] crystallizes from 4 M Hpts (*p*-toluenesulfonic acid) solutions as an edge-linked double cube, $[\{Mo_3CuS_4(H_2O)_9\}_2](pts)_8\cdot 20H_2O$, in which two Mo_3CuS_4 clusters are joined together as in Figure 1D.[9] X-ray crystal structures of two other heterometallic cubes, Mo_3MS_4 (M = Co, Pd), have also indicated the existence of edge-linked double cubes, $[\{Mo_3CoS_4(H_2O)_9\}_2](pts)_8\cdot 18H_2O$,[7] and $[\{Mo_3PdS_4(H_2O)_9\}_2](pts)_8\cdot 24H_2O$.[10] All three of these clusters are very strongly held on Dowex 50W-X2 cation-exchange columns, and require ≥4 M Hpts for their elution consistent with the presence of 8+ species. In the case of the Co-containing cube, elution from Dowex columns with HCl or Hpts occurs after $[Mo_3S_4(H_2O)_9]^{4+}$, consistent with retention of the double cube in solution.[18] In contrast, elution of the Cu containing 4+ cube occurs before $[Mo_3S_4(H_2O)_9]^{4+}$. A number of approaches are adopted, including EPR and UV–vis spectra and stability constant and kinetic experiments, in order to comment further on the existence of single and/or double cube structures in solution.

Solution properties of other heterometallic clusters $Mo_3MS_4^{4+}$, with M = Fe, Ni, and Cr, have been reported previously.[14,15,19] These studies have included investigations on anion complexing at the heterometallic atom as well as redox studies. In the case of the $[Fe(H_2O)_6]^{3+}$ and $[Co(dipic)_2]^-$ oxidations of for example $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ the reactions conform to the stoichiometric equations (1) and (2). The rate

$$Mo_3NiS_4^{4+} + 2Fe(III) \rightarrow Mo_3S_4^{4+} + Ni(II) + 2Fe(II) \quad (1)$$

$$Mo_3NiS_4^{4+} + 2Co(III) \rightarrow Mo_3S_4^{4+} + Ni(II) + 2Co(II) \quad (2)$$

$$Mo_3NiS_4^{4+} + Fe(III) \rightarrow Mo_3NiS_4^{5+} + Fe^{2+} \quad (3)$$

$$Mo_3NiS_4^{5+} + Fe(III) \xrightarrow{\text{fast}} Mo_3S_4^{4+} + Ni^{2+} + Fe^{2+} \quad (4)$$

laws are consistent with a two-stage mechanism, e.g. (3) and (4). Similar behavior is observed in other cases.[15,19] It has not however been possible in studies to date to detect the intermediate $Mo_3MS_4^{5+}$ by spectrophotometry or other means. In the redox studies of $Mo_3CuS_4^{4+}$ here described, an important difference is the detection and isolation of the intermediate 5+ cube.

Experimental Section

Preparation of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$. The procedure here used involves the addition of a solution of 3 mM $[Mo_3S_4(H_2O)_9]^{4+}$ in 2 M HCl (25 mL) to solid copper(I) chloride (0.1 g, Aldrich), under rigorous O_2-free conditions and allowing the reaction to proceed for 1 h.

$$[Mo_3S_4(H_2O)_9]^{4+} + Cu^+ \rightarrow [Mo_3CuS_4(H_2O)_{10}]^{5+} \quad (5)$$

Purification was by ice-cooled O_2-free Dowex 50W-X2 cation-exchange column chromatography (20 cm × 1 cm diameter). The solution was first Millipore filtered (8 μm pore size) to remove any solid CuCl, diluted four times, and loaded onto the column. Red $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ was eluted with 4 M Hpts as a separate band after any $[Mo_3S_4(H_2O)_9]^{4+}$. Metal analyses were carried out by inductively coupled plasma (ICP) atomic emission spectroscopy and gave a Mo:Cu ratio of 2.88 ± 0.14:1 (three determinations).

The $\epsilon/M^{-1}\ cm^{-1}$ values for the UV–vis spectrum were determined by air oxidation of the cube. In such experiments two products only were separated using Dowex chromatography, blue Cu^{2+} (eluted with 0.5 M Hpts), and green $[Mo_3S_4(H_2O)_9]^{4+}$ (eluted with 2.0 M Hpts). Since the yield of the latter can be quantified from its known spectrum ($\epsilon = 362\ M^{-1}\ cm^{-1}$ per Mo_3 at 603 nm)[2,3] the absorption coefficients (ϵ) for $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ could be determined. The spectrum of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ in 2 M Hpts, λ/nm ($\epsilon/M^{-1}\ cm^{-1}$ per cube) 328 (5130), 365(sh) (1930), 472 (2200), 623(sh) (299), is shown alongside that of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$, in Figure 2. The same 5+ product was obtained under homogeneous solution conditions when a solution of Cu^+ generated as described below in (8) was added to $[Mo_3S_4(H_2O)_9]^{4+}$ in 2.0 M $HClO_4$ (eq 5). Repeated attempts to obtain crystals from, e.g., 4 M Hpts solutions gave on standing the air-oxidized product $[Mo_3S_4(H_2O)_9](pts)_4\cdot 9H_2O$.

Preparation of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$. Rigorous O_2-free conditions are required. Copper turnings (~2 g, BDH) were added to a solution of $[Mo_3S_4(H_2O)_9]^{4+}$ (20 mL of 2 mM) in 2.0 M $HClO_4$, and the reaction was allowed to proceed for 2 h.[9]

$$[Mo_3S_4(H_2O)_9]^{4+} + Cu \rightarrow [Mo_3CuS_4(H_2O)_{10}]^{4+} \quad (6)$$

The copper turnings were activated by pretreating with concentrated $HClO_4$, followed by washing with 2 M $HClO_4$. The product was used without further purification. A second method involved the addition of $[Mo_3S_4(H_2O)_9]^{4+}$ in 0.5 M HCl (50 mL of 2 mM), together with a 10-fold excess of $CuCl_2\cdot 2H_2O$ (0.17 g, BDH AnalaR), to a 100-fold excess of sodium borohydride, $NaBH_4$ (Aldrich). A brisk effervescence accompanied by a change in color from green to brown was observed.

$$[Mo_3S_4(H_2O)_9]^{4+} + Cu^{2+} \xrightarrow{BH_4^-} [Mo_3CuS_4(H_2O)_{10}]^{4+} \quad (7)$$

Since BH_4^- also reduces Cu^{2+}, different reaction pathways are possible in this procedure. Any $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ produced will be reduced by BH_4^- to the 4+ cluster. After the product mixture was loaded onto an O_2-free Dowex 50W-X2 cation-exchange column (25 × 1.5 cm

---

(14) Dimmock, P. W.; Lamprecht, G. J.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 955.

(15) Routledge, C. A.; Humanes, M.; Li, Y.-J.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1994**, 1275.

(16) Shibahara, T.; Yamasaki, M.; Watase, T.; Ichimura, A. *Inorg. Chem.* **1994**, *33*, 292.

(17) Xinato, W.; Shaofeng, L.; Lianyong, Z.; Qjangin, W.; Jiaxi, L. *Inorg. Chim. Acta* **1987**, *133*, 39.

(18) Dimmock, P. W., Saysell, D. M., Sykes, A. G., *Inorg. Chim. Acta*, in press.

(19) Dimmock, P. W.; Dickson, D. P. E.; Sykes, A. G. *Inorg. Chem.* **1990**, *29*, 5120.

(20) Shibahara, T.; Asano, T.; Sakane, G. *Polyhedron* **1991**, *10*, 2351.

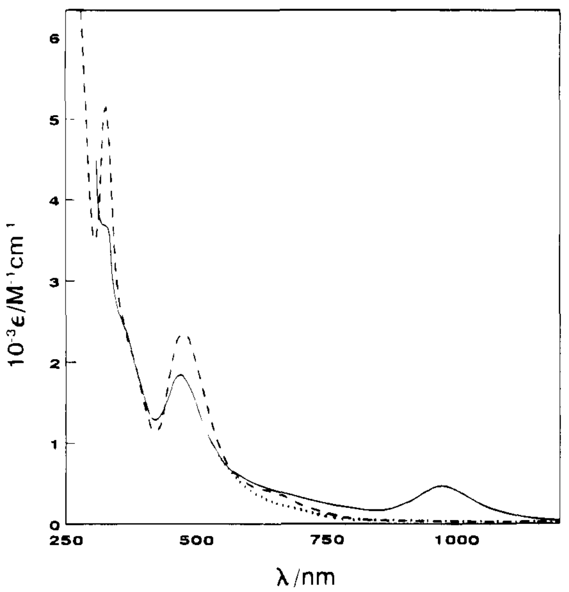


Figure 2. UV–vis–nearIR Spectra of heterometallic cuboidal complexes $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ in 2M Hpts (—), 2M $HClO_4$ (•••) where different, and $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ (---) in 2.0 M Hpts, ε's per cube.

diameter) and washed with 0.5 M HCl, a band of red-brown $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ was eluted prior to green $[Mo_3S_4(H_2O)_9]^{4+}$ using 1 M HCl.

The UV–vis–near IR spectrum of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ was determined by adding $[Mo_3S_4(H_2O)_9]^{4+}$ of known concentration in 2 M Hpts to a large (>100-fold) excess of copper turnings. The reaction was allowed to proceed for 4 h, after which time no further change in absorbance was observed. the ε's values were again determined by air oxidation of Dowex-purified $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ to $[Mo_3S_4(H_2O)_9]^{4+}$ and Cu^{2+}. The spectrum in 2 M Hpts, Figure 2, gives λ/nm (ϵ/M^{-1} cm^{-1} per cube) 325 (3700), 363 (sh) (2480), 470 (1870), and 975 (473).

Other Reagents. Solutions of the aqua Cu^+ ions for kinetic studies[21] were obtained by reacting a solution of $[Cr(H_2O)_6]^{2+}$, prepared by the electrolytic reduction of $[Cr(H_2O)_6]^{3+}$ perchlorate in 2.0 M perchloric acid,[21] with excess $[Cu(H_2O)_6]^{2+}$ under rigorous air-free conditions (eq 8). The reaction proceeds to ~99% completion. The time required was

$$Cr(II) + Cu(II) \rightarrow Cr(III) + Cu(I) \qquad (8)$$

calculated from known rate constants.[21] The concentration of Cu^+ was obtained from that of Cr^{2+} which had been measured spectrophotometrically.[22] Solutions of hexaaqua Fe(III) ($E^{\circ\prime}$ = 0.77 V) were obtained from a Dowex 50W-X2 cation-exchange column, loaded with $Fe(ClO_4)_3 \cdot 6H_2O$ (Fluka), by elution with 1.0 M $HClO_4$. A sample of lithium *p*-toluenesulfonate (Li(pts)) was prepared by neutralization of 4 M Hpts with lithium carbonate (BDH, Reagent Grade) followed by crystallization twice from H_2O. Lithium perchlorate (Aldrich, Reagent Grade) was recrystallized twice from water. Acids were HCl and $HClO_4$ (both BDH, AnalaR) and *p*-toluenesulfonic acid (Aldrich), all of which were used without further purification. The complex $NH_4[Co(dipic)_2]$ ($E^{\circ\prime}$ = 0.75 V), dipic = pyridine-2,6-dicarboxylate or dipicolinate, was prepared as previously, and its purity confirmed from the UV–vis peak at 510 nm (ε = 630 M^{-1} cm^{-1}).[23] A sample of the one-electron reductant $[Ru(NH_3)_5H_2O)]^{2+}$ ($E^{\circ\prime}$ = 0.08 V) was obtained as described in the literature.[24] The latter reagent requires an argon inert atmosphere. All studies involving the cubes were under rigorous air-free conditions using high purity gas (N_2 or Ar), rubber seals for containment, Teflon tubing, and Hamilton glass (micro) or Atlas nylon syringes for transfers.

Stability of the $[Mo_3CuS_4(H_2O)_{10}]^{4+/5+}$ Clusters. Both clusters react rapidly with O_2, (9) and (10). From preliminary stopped-flow

$$2Mo_3CuS_4^{\ 4+} + O_2 + 4H^+ \rightarrow 2Mo_3S_4^{\ 4+} + 2Cu^{2+} + 2H_2O \qquad (9)$$

$$4Mo_3CuS_4^{\ 5+} + O_2 + 4H^+ \rightarrow 4Mo_3S_4^{\ 4+} + 4Cu^{2+} + 2H_2O \qquad (10)$$

studies (25 °C) with O_2 in > 10-fold excess, both the 4+ and 5+ cubes react in more than one step, and $t_{1/2}$ for the slower stages are ~0.25 s at $[O_2]$ = 0.5 mM and $[H^+]$ = I = 2.0 M.

When the concentration of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ is varied over the range 0.05–0.45 mM in 2.0 M Hpts, Beer's law is obeyed at the peak positions 325 nm (±4%) and 470 nm (±7%). Similar experiments with $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ at concentrations 0.05–0.46 mM in 2.0 M Hpts, at 327 nm (±3%) and 473 nm (±6%) are also consistent with Beer's law. There is therefore no spectrophotometric evidence in either case for an equilibrium between single and double cubes, assuming the latter have different absorbances at these two wavelengths.

However solutions of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ in 2.0 M Hpts also give an absorbance at 975 nm, Figure 2. When 2.0 M Hpts is replaced with 2.0 M HCl or 2.0 M $HClO_4$, this peak disappears. At 975 nm in 2.0 M Hpts solutions, a nonlinear Beer's law dependence is observed, consistent with a dimerization process. At 325 and 470 nm (see above), the absorption appears to be independent of the molecularity. It is concluded that pts^- induces dimer formation possibly by outer-sphere complexation (consistent with the X-ray crystal structure), and this gives rise to the 975-nm absorption band.

Stoichiometries. The $[Fe(H_2O)_6]^{2+}$ formed in the $[Fe(H_2O)_6]^{3+}$ oxidations of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ and $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ was determined by complexing with 4,7-diphenyl-1,10-phenanthroline (here abbreviated to bathophen).[25] The procedure requires a large ~100-fold excess of ligand and the adjustment of pH to ~2 by addition of 10% ammonium dihydrogen phosphate and glacial acetic acid. The complex $[Fe(bathophen)_3]^{2+}$ was extracted with isoamyl acetate, and determined at 535 nm (ε = 17 850 M^{-1} cm^{-1}). Measurements indicated ratios 1.94 ± 01:1 and 0.96 ± 0.08:1 (three determinations) of Fe^{2+} produced per cube and stoichiometries for the 4+ and 5+ clusters as in (11) and (12). An alternative titration procedure which involved

$$Mo_3CuS_4^{\ 4+} + 2Fe(III) \rightarrow Mo_3S_4^{\ 4+} + Cu^{2+} + 2Fe(II) \qquad (11)$$

$$Mo_3CuS_4^{\ 5+} + Fe(III) \rightarrow Mo_3S_4^{\ 4+} + Cu^{2+} + Fe(II) \qquad (12)$$

adding different molar ratios of hexaaqua Fe(III) to $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ and $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ and monitoring the decrease in absorbance at 470 nm was also used. These measurements gave the same stoichiometries as indicated in (11) and (12).

Similar stoichiometries were determined for the reactions of the 4+ and 5+ cubes with $[Co(dipic)_2]^-$ as oxidant.

Complexing of Anions to $[Mo_3CuS_4(H_2O)_{10}]^{4+}$. The equilibrium constant for the 1:1 complexing of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ with chloride, (13),was determined from spectrophotometric changes at 975 nm. The

$$[Mo_3CuS_4(H_2O)_{10}]^{4+} + Cl^- \overset{K}{\rightleftharpoons} [Mo_3CuS_4(H_2O)_9Cl]^{3+} + H_2O \qquad (13)$$

4+ cube was in 2.00 M Hpts, and Cl^- was added (as HCl) to concentrations in the range (0–7.0) × 10^{-3} M, while maintaining I = 2.00 M (Hpts). Absorbance changes give a good fit to (14), where A_0,

$$\frac{1}{(A_0 - A_{Cl})} = \frac{1}{K(A_0 - A_\infty)}\frac{1}{[Cl^-]} + \frac{1}{(A_0 - A_\infty)} \qquad (14)$$

A_{Cl} and A_∞ are respectively the absorbance readings with no Cl^-, $[Cl^-]$ as selected, and $[Cl^-]$ such that there is complete formation of the chloro complex. The ratio of slope to intercept of a graph of $[A_0 - A_{Cl}]^{-1}$ vs $[Cl]^{-1}$, Figure 3, gives K = (3.5 ± 0.1) × 10^3 M^{-1}. Stopped-flow studies at 450 nm indicate that the reaction is complete in <3 ms. The linearity in Figure 3 requires that the single cube and not the edge-

---

[21] Shaw, K.; Espenson, J. H. *Inorg. Chem.* **1968**, *8*, 1619.

[22] Ooi, B.-L.; Sharp, C.; Sykes, A. G. *J. Am. Chem. Soc.* **1989**, *111*, 125.

[23] Mauk, A. G.; Coyle, C. L.; Bordignon, E.; Gray, H. B. *J. Am. Chem. Soc.* **1979**, *101*, 5054.

[24] Isied, S. S.; Taube, H. *Inorg. Chem.* **1976**, *15*, 3070.

[25] Clark, L. J. *Anal. Chem.* **1962**, *34*, 348.

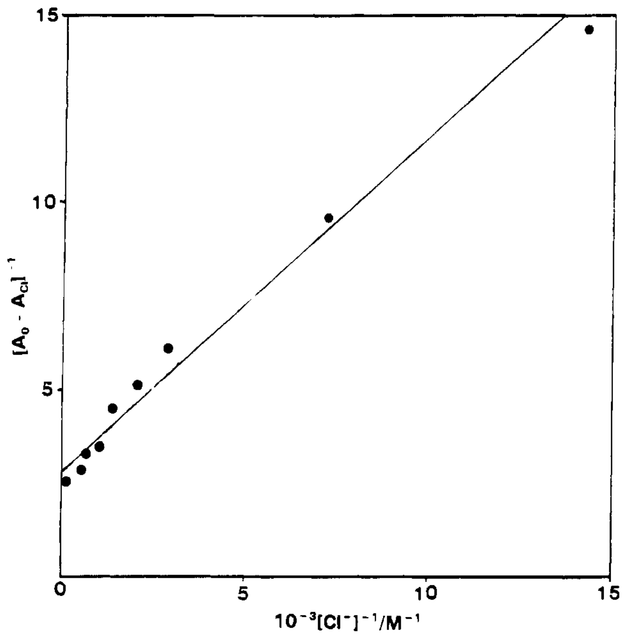


Figure 3. Determination of the formation equilibrium constant *K* (25 °C) for the 1:1 Cl^- complexing at the Cu of the heterometallic cuboidal complex $[Mo_3CuS_4(H_2O)_{12}]^{4+}$ (1.0 mM), from absorbance changes at 975 nm and I = 2.00 M (Hpts).

linked double cube is the dominant form of the $Mo_3CuS_4^{4+}$ present in these solutions.

Spectrophotometric changes were also observed at 975 nm on addition of $HClO_4$ to $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ in 2.00 M Hpts. Using an expression similar to (14), an equilibrium constant $K = 2.07 \pm 0.08$ M^{-1} was obtained, corresponding to pts^- complexing with the cube. No $HClO_4$ oxidation of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ is observed. Thus a solution of air-free 1 mM $[Mo_3CuS_4(H_2O)_{10}{}^{4+}]$ in 0.68 M $HClO_4$, adjusted to I = 2.00 M (Hpts), gave no change in spectrum over 24 h.

Kinetic Studies. These were carried out on a Dionex D-110 stopped-flow spectrophotometer, and were under rigorous air-free conditions at 25.0 ± 0.1 °C, with I adjusted to 2.00 ± 0.01 M ($LiClO_4$) unless stated. The addition of Cu^+ to $[Mo_3S_4(H_2O)_9]^{4+}$ to give $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ was monitored at 470 nm, with the concentration of Cu^+ in >10-fold excess. Likewise the hexaaqua iron(III) and $[Co(dipic)_2]^-$ oxidations of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ and $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ were with the oxidant in >10-fold excess. Solutions of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ were eluted from a Dowex 50W-X2 column with 4.0 M Hpts. The kinetics were monitored at 470 nm, $\Delta\epsilon$ = 1870 and 2200 M^{-1} cm^{-1} respectively for the 4+ and 5+ ions. The $[Ru(NH_3)_5H_2O]^{2+}$ reduction of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ (under Ar) with the reductant in >10-fold excess, was monitored at 600 nm. All rate constants were evaluated using exponential fitting programmes supplied by On-Line Instruments Systems (OLIS, Bogart, GA).

Solutions for EPR Studies. Solutions of red-brown $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ in 2 M HCl were obtained by adding $[Mo_3S_4(H_2O)_9]^{4+}$ (1 mM) in 2.0 M HCl to copper turnings and allowing the reaction to proceed for ~5 min. The $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ product (with some Cl^- complexing) was used without further purification. In 2 M Hpts the reaction requires a longer time of ~2 h. Because some air oxidation occurs and Cu^{2+} is formed an alternative method was used to prepare the 2 M Hpts solutions. This involved the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with copper turnings in 1.0 M HCl for ~1 h. The resultant solution was then diluted to ~0.5 M HCl and loaded onto a Dowex 50W-X2 ion-exchange column (15 cm × 1.2 cm). Elution was with 4.0 M Hpts.

Solutions of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ were obtained by reacting solid CuCl with $[Mo_3S_4(H_2O)_9]^{4+}$ in 0.5 M Hpts. The product was Millipore filtered and loaded onto a Dowex column. Elution of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ was with 4.0 M Hpts.

Solutions of aqua copper(II) were prepared by dissolving $CuCl_2$ in 2.0 M HCl, and $CuCO_3{\cdot}Cu(OH)_2$ in 2.0 M Hpts.

EPR Measurements. EPR spectra were obtained on frozen and fluid solutions at X-band frequencies over the temperature range 4.2–300 K using a Varian E112 spectrometer at the University of Manchester. Cooling was by an Oxford Instruments ESR 9 cryostat using either liquid helium or liquid nitrogen as the refrigerant. Solutions of $Mo_3CuS_4^{4+}$ in 2.0 M HCl containing 10% glycerol gave no spectra above *ca.* 100 K. At 77 K the spectrum is dominated by what appears to be a spectrum from an $S = {}^1/_2$ system, with the unpaired electron interacting with a *single* copper nucleus, see Figure 4A. The spectrum is axial with a small *g*-value anisotropy: $g_{\parallel} = 1.94$, $A_{\parallel} = 2.8$ mT, and $g_{\perp} = 1.91$. This signal persists down to 4.2 K, and no other signals were observed in the magnetic field range 0–2 T. A similar spectrum, Figure 4B, was obtained for $Mo_3CuS_4^{4+}$ in 2.0 M Hpts at 77 K.

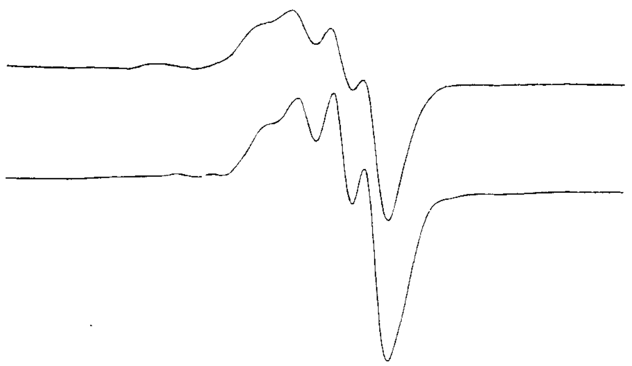


Figure 4. EPR spectra at 77 K of the $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ cuboidal complex in (A) 2.0 M HCl (upper spectrum) and (B) 2.0 M Hpts (lower spectrum). Conditions: scan range, 500 G; field set (center of scan), 3400 G (10^4 G = 1 T); microwave frequency, 9.250 GHz for (A) and 9.248 GHz for (B); microwave power, 20 mW.

The similarity of EPR spectra in 2.0 M HCl and Hpts, Figure 4, suggests that the same species are dominant in both solutions. The hyperfine splitting patterns in the spectra are compatible with a single cube containing one unpaired electron; hence the formula $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ is used. However, the *g*- and *A*-values, especially the *g*-values, are unusually low compared with monomeric copper(II) species. For any of the d-orbitals as the ground state, *g*-values greater than 2.0023 would be expected.[26] Although tetrahedral copper(II) complexes do have small values for $A_{\parallel}$, each of the three principal *g*-values are greater than 2.0023. For example $[CuCl_4]^{2-}$, with D_{2d} point symmetry, has $g_{11} = 2.083$, $g_{22} = 2.103$, and $g_{33} = 2.446$.[27] The closest examples to the present case are the sulfur ligated Type 1 copper proteins plastocyanin, stellacyanin, and azurin. These proteins have g_{11} and g_{22} values in the range 2.02–2.08, while g_{33} is in the range 2.23–2.29.[28] These comparisons strongly suggest that, in the ground state, the unpaired electron is delocalised over the cube rather than localized on the copper, either as copper(I), which would be EPR silent, or as copper(II).

Air oxidation of $Mo_3CuS_4^{4+}$ in HCl solution gave an EPR spectrum which was identical to that obtained from $CuCl_2$ in 2M HCl, while in Hpts solution the spectrum was identical to that obtained by dissolving $CuCO_3{\cdot}Cu(OH)_2$ in 2 M Hpts. These observations are consistent with the release of monomeric Cu(II) from the cube upon air oxidation.

Solutions of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$, generated as above, were also examined. Although this cube has an even number of electrons, two signals were always observed, Figure 5. The predominant signal is the same as that which we obtained for $CuCO_3{\cdot}Cu(OH)_2$ dissolved in 2 M Hpts, and from the oxidation of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$. This is

---

(26) Mabbs, F. E.; Collison, D. *Electron Paramagnetic Resonance of d Transition Metal Compounds*; Elsevier: Amsterdam, 1992; pp 394–408.

(27) Sharnoff, M. *J. Chem. Phys.* **1965**, *42*, 3383.

(28) Blumberg, W. E.; Peisach, J. *J. Biochem. Biophys. Acta* **1966**, *126*, 269. Brill, A. S.; Bryce, G. F.; Maria, H. J. *Biochem. Biophys. Acta* **1968**, *154*, 342. Malmstrom, B. G.; Reinhammar, B.; Vanngard, T. *Biochem. Biophys. Acta* **1970**, *205*, 48. Malkin, R.; Malmstrom, B. G. *Adv. Enzymol.* **1970**, *33*, 177. Fee, J. A. *Struct. Bonding (Berlin)* **1975**, *23*, 1. Gray, H. B.; Solomon, E. I. In *Copper Proteins*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1980; pp 1–39. Penfield, K. W.; Gray, R. R.; Himmelwright, R. S.; Eickman, N. C.; Norris, A.; Freeman, H. C.; Solomon, E. I., *J. Am. Chem. Soc.* **1981**, *103*, 4382.

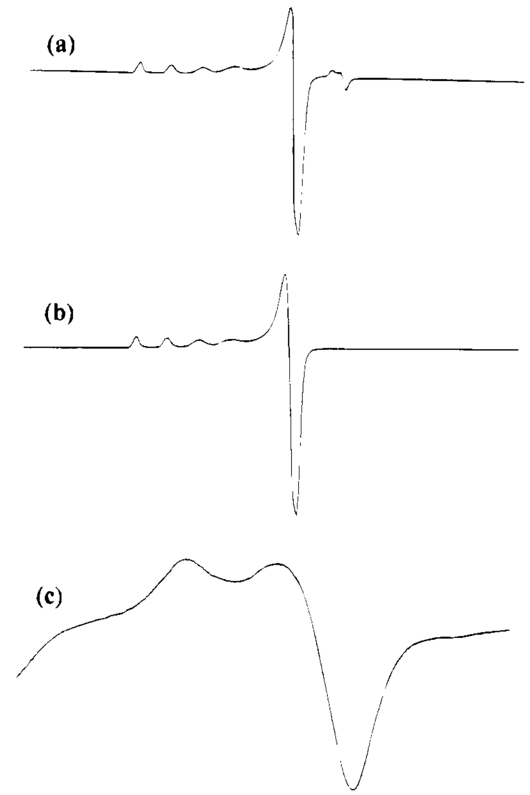


Figure 5. EPR spectrum at 77 K of the putative $\{Mo_3CuS_4\}^{5+}$ in 2 M Hpts (a), an expansion of the minor signal (b), and the spectrum after air oxidation (c). Conditions for parts a and c: scan range, 2000 G; field set (center of scan), 3100 G. Conditions for part b scan range, 200 G; field set (center of scan), 3350 G. For each spectrum the microwave frequency was 9.253 GHz, and the microwave power was 20 mW.

Table 1. Rate Constants (25 °C) for the Biphasic Reaction of Aqua–Cu^+ with $[Mo_3S_4(H_2O)_9]^{4+}$ (8×10^{-5} M) at $[H^+] = 1.90$ M and $I = 2.00$ M ($LiClO_4$)

$10^3[Cu^+]$/M	$k_{1\mathrm{obs}}^{\mathrm{Cu}}/s^{-1}$	$k_{2\mathrm{obs}}^{\mathrm{Cu}}/s^{-1}$
0.83	15.2	0.85
1.02	14.9	1.08
1.52	16.2	1.41
2.03	14.6	2.07

consistent with release of copper(II) from the cluster. The minor signal is axially symmetric with $g_\parallel \approx g_\perp \approx 1.95$, but with no hyperfine structure. This minor signal, which disappears completely upon air oxidation, Figure 5, is different in both form and magnetic field positions from that of the signal from $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ in 2 M Hpts. The assignment of this signal is uncertain. It has the form expected from a system with one unpaired electron, which makes it unlikely that it is from $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ which has an even number of electrons.

Treatment of Kinetic Data. An unweighted least-square treatment was carried out for all rate law fits.

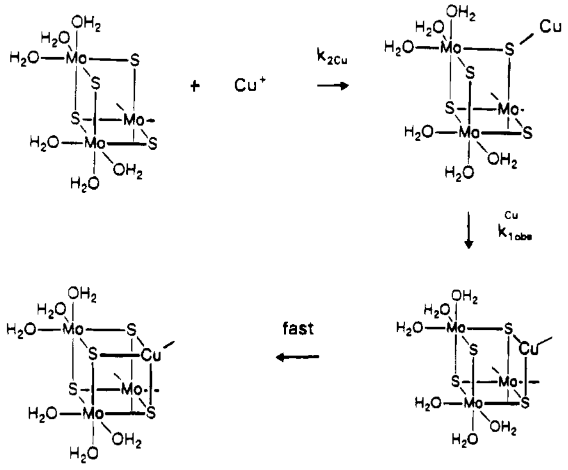
Results

Existence of $Mo_3CuS_4^{4+}$ and $Mo_3CuS_4^{5+}$ Cubes. UV–vis spectra, Figure 2, along with stoichiometry measurements with $[Fe(H_2O)_6]^{3+}$ as oxidant (Experimental Section), provide substantial support for two oxidation states. Also Beer's law plots, stability constant measurements (with Cl^-), and the EPR studies provide substantial evidence for the 4+ state single cube as the dominant form in both 2 M HCl and 2 M Hpts solutions. Relevant crystal structures are referred to,[9,17] and formulas $[MoCuS_4(H_2O)_{10}]^{4+}$ and $[MoCuS_4(H_2O)_{10}]^{5+}$ are assumed to apply.

Table 2. Variation of Rate Constants (25 °C) for the Hexaaquairon(III) Oxidation of $[Mo_3CuS_4(H_2O)]^{4+}$ (1×10^{-4} M) at different $[H^+]$ and $I = 2.00$ M ($LiClO_4$)

$[H^+]$/M	$10^3[Fe(III)]$/M	$k_{1\mathrm{obs}}^{\mathrm{Fe}}/s^{-1}$	$k_{2\mathrm{obs}}^{\mathrm{Fe}}/s^{-1}$
1.80	1.92	8.7	2.90
	2.88	13.1	4.2
	5.8	26.1	8.6
	8.6	36.0	12.3
1.40	1.92	10.1	3.8
	2.88	15.5	5.7
	4.8	24.1	9.2
	6.7	35.5	12.6
1.00	0.96	7.9	2.6
	2.88	19.6	7.5
	4.8	29.9	12.1
	6.7	41.9	14.8
0.70	0.96	9.3	3.6
	1.92	17.7	7.2
	3.84	33.4	13.9
0.50	0.96	12.8	4.4
	1.92	21.7	9.1
	2.88	33.9	13.9

Kinetics of the Addition of Cu^+ to $[Mo_3S_4(H_2O)_9]^{4+}$. Absorbance changes indicate two stopped-flow stages for the reaction of Cu^+ with $[Mo_3S_4(H_2O)_9]^{4+}$ to give $[Mo_3CuS_4(H_2O)_{10}]^{5+}$. Rate constants $k_{1\mathrm{obs}}^{\mathrm{Cu}}$ and $k_{2\mathrm{obs}}^{\mathrm{Cu}}$ are listed in Table 1, for $[H^+] = 1.90$ M and $I = 2.00$ M ($LiClO_4$). Rate constants $k_{2\mathrm{obs}}^{\mathrm{Cu}}$ show a linear dependence on $[Cu^+]$, the slope of which gives 980 ± 100 M^{-1} s^{-1}. The intercept is small, 0.04 ± 0.14 s^{-1}, and is probably not meaningful. The $k_{1\mathrm{obs}}^{\mathrm{Cu}}$ step is independent of $[Cu^+]$ and gives a rate constant 15.2 ± 1.0 s^{-1}. The behavior observed suggests a mechanism involving complexation of Cu^+ to one of the three μ-sulfido ligands, followed by attachment to the other two to give the $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ product (eq 15). Since Cu(I) is required to participate in the first-stage, it is concluded that the two kinetic steps are observed in reverse order.



(15)

Oxidation of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ with Hexaaquairon(III). The oxidant was present in >10-fold excess. The reaction is biphasic yielding first-order rate constants $k_{1\mathrm{obs}}^{\mathrm{Fe}}$ and $k_{2\mathrm{obs}}^{\mathrm{Fe}}$, Table 2. Both rate constants give linear dependencies on [Fe(III)] yielding second-order rate constants $k_{1\mathrm{Fe}}$ and $k_{2\mathrm{Fe}}$. The reaction sequence can therefore be written as in (16) and (17).

$$Mo_3CuS_4^{4+} + Fe(III) \xrightarrow{k_{1\mathrm{Fe}}} Mo_3CuS_4^{5+} + Fe(II) \quad (16)$$

$$Mo_3CuS_4^{5+} + Fe(III) \xrightarrow{k_{2\mathrm{Fe}}} Mo_3CuS_4^{4+} + Cu(II) + Fe(II) \quad (17)$$

Table 3. Summary of Second-Order Rate Constants k_{1Fe} and k_{2Fe} for the First and Second Stages of the Oxidation of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ with Hexaaquairon(III) at I = 2.00 M ($LiClO_4$)

$[H^+]$/M	$10^{-3}k_{1Fe}$/M^{-1} s^{-1}	$10^{-3}k_{2Fe}$/M^{-1} s^{-1}
1.80	4.2	1.42
1.40	5.2	1.87
1.00	5.9	2.24
0.70	8.6	3.6
0.50	11.5	4.8

Table 4. First-Order Rate Constants (25 °C) for the Hexaaquairon(III) oxidation of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ and $[Mo_3CuS_4(H_2O)_{10}]^{5+}$, Both 1 × 10^{-4} M, at $[H^+]$ = 1.80 M (1.70 M ClO_4^- + 0.10 M pts^-) and I = 2.00 M ($LiClO_4$), Where Reactions of the 4+ Cube (a) Are Biphasic (k^{Fe}_{1obs} and k^{Fe}_{2obs}) and Those of the 5+ Cube (b) Are Monophasic (k^{Fe}_{2obs})

(a) Biphasic Reactions

10^3[Fe(III)]/M	k^{Fe}_{1obs}/s^{-1}	k^{Fe}_{2obs}/s^{-1}
0.96	7.4	2.63
2.88	24.5	8.2
4.80	42.2	13.3
6.40	57.2	19.0

(b) Monophasic Reactions

10^3[Fe(III)]/M	k^{Fe}_{2obs}/s^{-1}	10^3[Fe(III)]/M	k^{Fe}_{2obs}/s^{-1}
1.44	4.0	4.80	14.0
2.88	9.1	6.40	17.3

Table 5. Rate Constants (25 °C) for the Biphasic $[Co(dipic)_2]^-$ Oxidation of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ (2.5 × 10^{-5} M) in 2.00 M $HClO_4$ Solutions at I = 2.00 M

10^4[Co(III)]/M	k^{Co}_{1obs}/s^{-1}	k^{Co}_{2obs}/s^{-1}
5.0	33	18
7.4	52	24
10.0	62	31
12.5	79	39
15.0	94	48

When $[H^+]$ is varied within the range 0.50–1.80 M, Table 3, the dependencies (18) and (19) are observed. These give a_1 =

$$k_{1Fe} = a_1 + b_1[H^+]^{-1} \tag{18}$$

$$k_{2Fe} = a_2 + b_2[H^+]^{-1} \tag{19}$$

(1.33 ± 0.33) × 10^3 M^{-1} s^{-1}, b_1 = (5.1 ± 0.3) × 10^3 s^{-1}, a_2 = (0.72 ± 0.16) × 10^3 M^{-1} s^{-1}, and b_2 = (2.38 ± 0.13) × 10^3 s^{-1}.

The rate constants k^{Fe}_{1obs} and k^{Fe}_{2obs} were also determined with 0.10 M Hpts as a component of solutions to enable comparisons with the $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ studies. Values of k^{Fe}_{1obs} and k^{Fe}_{2obs} with $[H^+]$ = 1.80 M (made up of 1.70 M ClO_4^- and 0.10 M pts^-) at varying [Fe(III)] are listed in Table 4.

Oxidation of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ with Hexaaquairon(III). Stock solutions of the 5+ cube were in Hpts, and reactant solutions were made up therefore with $[H^+]$ = 1.80 M (consisting of 1.70 M $HClO_4$ + 0.10 M Hpts) and I = 2.00 M. The reaction is uniphasic, Table 4, and first-order rate constants k^{Fe}_{2obs} give a linear dependence on [Fe(III)]. Moreover the points obtained overlay those for the second stage of the $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ reaction. Under these conditions, from the combined data, k_{2Fe} = (2.86 ± 0.15) × 10^3 M^{-1} s^{-1}.

Oxidation of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ with $[Co(dipic)_2]^-$. As in the Fe(III) oxidation the reaction with >10-fold excess of $[Co(dipic)_2]^-$ gives two stages of reaction. First-order rate constants k^{Co}_{1obs} and k^{Co}_{2obs} are listed in Table 5. No $[H^+]$ dependence is observed. At 25 °C, k_{1Co} = (5.9 ± 0.3) × 10^4 M^{-1} s^{-1}, and k_{2Co} = (3.0 ± 0.1) × 10^4 M^{-1} s^{-1}, at I = 2.00 M ($LiClO_4$).

Table 6. First-Order Rate Constants k^{Ru}_{obs} (25 °C) for the $[Ru(NH_3)_5H_2O]^{2+}$ Reduction of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ (4.2 × 10^{-5} M) at I = 2.00 M (Li(pts))

$[H^+]$/M	10^3[Ru(II)]/M	$10^2k^{Ru}_{obs}$/s^{-1}
2.0	0.63	1.30
	0.92	1.62
	1.05	2.11
	1.25	2.30
	1.47	2.89
1.0	0.66	1.50
	0.96	2.15
	1.24	2.70
0.5	0.46	1.04
	0.69	1.56
	0.92	1.89
	1.16	2.36

Reduction of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ with $[Ru(NH_3)_5H_2O]^{2+}$. Studies were with $[Ru(NH_3)_5(H_2O)]^{2+}$ in >10-fold excess of the cluster. The reaction is uniphasic, consistent with (20). First-order rate constants k^{Ru}_{obs}, Table 6, give a linear dependence on $[Ru(NH_3)_5(H_2O)^{2+}]$, and are independent of $[H^+]$ in the range 0.50–2.00 M. At 25 °C the second-order rate constant is k_{Ru} = 19.0 ± 2.2 M^{-1} s^{-1}.

$$\mathrm{Ru(II)} + \mathrm{Mo_3CuS_4}^{5+} \rightarrow \mathrm{Ru(III)} + \mathrm{Mo_3CuS_4}^{4+} \tag{20}$$

Discussion

An absorption peak in the near-infrared region at 975 nm is observed for $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ in 2 M Hpts (ϵ = 473 M^{-1} cm^{-1}). This peak disappears when the Hpts is replaced by HCl or relatively small amounts of Cl^- are added. A perfectly plausible explanation that a dimeric structure exists in Hpts solutions, and a monomeric structure in HCl solutions was proposed.[9] However in the course of this work we have found that the peak also disappears on replacing Hpts with noncomplexing 2.0 M $HClO_4$. From the dependence of the absorbance at 975 nm on the concentration of cube in 2.0 M Hpts the double cube is present in such solutions. EPR studies on $MoCuS_4^{4+}$ at 77 K in 2 M HCl and 2 M Hpts are however similar and compatible with a single cube (containing one unpaired electron) as the dominant species. Absorbance changes observed on addition of $HClO_4$ to $Mo_3CuS_4^{4+}$ in 2.0 M Hpts are assigned as the release of pts^- in the reverse of (21), where K = 2.07 M^{-1} at 25 °C and I = 2.00 M ($HClO_4$). The $Mo_3CuS_4^{4+}$ cube elutes more readily than $Mo_3CoS_4^{4+}$ from cation-exchange columns using HCl and Hpts, consistent with the predominance of single and double cubes respectively in these solutions.[18] No evidence has been obtained for a dimer form of the 5+ cube.

$$\mathrm{Mo_3CuS_4}^{4+} + \mathrm{pts}^- \overset{K}{\rightleftharpoons} \mathrm{Mo_3CuS_4}^{4+}, \mathrm{pts}^- \tag{21}$$

From XPS measurements on the solid, a Cu(I) assignment has been proposed for the Cu in $[Mo_3CuS_4(H_2O)_{10}]^{4+}$.[9] At first this seemed an acceptable assignment with the Cu in $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ in the Cu(II) state. The similarity of the UV–vis spectra, Figure 2, also suggests that the Mo's have identical oxidation states, e.g. $Mo^{III}Mo^{IV}_2$, in the 4+ and 5+ clusters. However the EPR experiments described in the experimental section suggest that the odd electron on $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ is delocalized over the cube rather than being localized on the copper as Cu(II). We also note that the EPR spectrum of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$, Figure 5, has unusual features, the interpretation of which is at present uncertain.

The formation constant determined for 1:1 Cl^- complexing to $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ (K = 3500 M^{-1}), compares with a value

($K = 500\ M^{-1}$) for complexing of Cl^- with Cu^+ at $[H^+] = 0.10$ M and $I = 5.0$ M ($NaClO_4$).[29] The reaction of Cl^- with $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ ($t_{1/2} < 3$ ms) is assigned as rapid substitution at the tetrahedrally coordinated Cu. The observation that UV–vis spectrophotometric changes are largest when $[Cl^-]$ is less than or comparable to $[Mo_3CuS_4(H_2O)_{10}{}^{4+}]$, with little subsequent change, suggests that the dominant reaction involves a single Cl^-. The 1:1 complexing of Cl^- to the tetrahedrally coordinated Ni and Fe atoms of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ ($K = 106\ M^{-1}$) and $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ ($K = 560\ M^{-1}$) are also fast and are in the stopped-flow range (Ni) or faster (Fe).[14,19] However in the case of $[Mo_4S_4(H_2O)_{12}]^{5+}$ 1:1 complexing of Cl^- is much less favorable ($K = 1.98\ M^{-1}$), with a substantially smaller rate constant $9.7 \times 10^{-3}\ M^{-1}\ s^{-1}$.[29] Substitution of H_2O at the Mo's is believed to play a secondary role therefore in the case of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ and other related heterometallic cubes.

The oxidation of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ with excess hexaaquairon(III) results in a two-electron change with formation of Cu^{2+} and $[Mo_3S_4(H_2O)_9]^{4+}$, (22). The same 2:1 stoichiometry is

$$[Mo_3CuS_4(H_2O)_{10}]^{4+} + 2Fe(III) \rightarrow [Mo_3S_4(H_2O)_9]^{4+} + Cu^{2+} + 2Fe^{2+} \quad (22)$$

observed in the case of $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ and $[Mo_3NiS_4(H_2O)_{10}]^{4+}$.[14,19] The reaction of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ is different in that biphasic kinetics are observed. The intermediate spectrum obtained on reacting 1:1 amounts of Fe(III) and $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ corresponds to that of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ prepared by direct addition of Cu^+ to $[Mo_3S_4(H_2O)_9]^{4+}$. Further evidence for $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ as an intermediate comes from the rate constants for the second stage of the reaction, which are identical to those from the separate study of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ with Fe(III). Studies on the $[Co(dipic)_2]^-$ oxidation of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ similarly yield two rate constants.

Observation of an $[H^+]^{-1}$ dependence of the kind $a + b[H^+]^{-1}$ for both stages of the Fe(III) oxidation of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ supports in the case of b an inner-sphere involvement of $[Fe(H_2O)_5OH]^{2+}$. Bridging of the OH^- of $[Fe(H_2O)_5OH]^{2+}$ to the Cu is expected to be rapid and to precede electron transfer. The a term on the other hand corresponds to the reaction of $[Fe(H_2O)_6]^{3+}$, and since an H_2O-bridged activated complex is unlikely, this term very likely corresponds to an outer-sphere electron-transfer process. The rate law terms a ($1.33 \times 10^3\ M^{-1}\ s^{-1}$) and b ($5.1 \times 10^3\ s^{-1}$) for the oxidation of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ to $[Mo_3CuS_4(H_2O)_{10}]^{5+}$, compare with values a ($0.72 \times 10^3\ M^{-1}\ s^{-1}$) and b ($2.38 \times 10^3\ s^{-1}$) for oxidation of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$. In the course of the latter reaction (or as a sequel to) loss of Cu^{2+} occurs with the formation of $[Mo_3S_4(H_2O)_9]^{4+}$. Using the acid dissociation constant for $[Fe(H_2O)_6]^{3+}$, $K_a = 1.0 \times 10^{-3}$ M at 25 °C and $I = 2.0$ M ($NaClO_4$),[31] second-order rate constants b' ($=b/K$) for the reaction of $[Fe(H_2O)_5OH]^{2+}$ with $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ ($5.0 \times 10^6\ M^{-1}\ s^{-1}$) and $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ ($2.4 \times 10^6\ M^{-1}\ s^{-1}$) are obtained. The similarity of these values is noted. The b'/a ratios of an order of magnitude of $\sim 10^3$ support the inner- and outer-sphere assignments.[32]

The reaction of Cu^+ with $[Mo_3S_4(H_2O)_9]^{4+}$ occurs in two stages. The slightly slower $[Cu^+]$-dependent stage can be assigned to the initial attachment of the Cu^+ to one of the three μ_2-S groups on the aqua ion $[Mo_3S_4(H_2O)_9]^{4+}$. Initial formation of a linear Cu(I) product is suggested. Reorientation of the Cu to establish contact with one of the two remaining μ_2-S groups gives the $[Cu^+]$-independent second stage. With Cu^+ in excess no reduction of the $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ cube to the $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ state is observed, which suggests that the reduction potential $[Mo_3CuS_4]^{5+}/[Mo_3CuS_4]^{4+}$ is less than 0.15 V for the Cu^{2+}/Cu^+ couple.[33] The aqua ion $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ is however reduced by $[Ru(NH_3)_5H_2O]^{2+}$ ($E^{\circ\prime}$) = 0.080 V.[24] Thus the reduction potential of $[Mo_3CuS_4]^{4+/5+}$ very likely lies between this value and 0.15 V. We were unable to determine a reduction potential for the $[Mo_3CuS_4H_2O)_{10}]^{5+/4+}$ by cyclic voltammetry because of the air sensitivity of the clusters, and difficulty in avoiding some contamination by Cu^{2+}. In the presence of Cu^{2+} reversible behavior of the cube is not observed.

The rate laws observed in the redox studies are of the simplest possible kind with no evidence for any rate-controlling equilibria of double $\rightleftharpoons$ single cubes. Also uniphasic processes were observed, and any double cube present in solutions is therefore converted to the more reactive single cube (or vice versa) in a rapid process. More significantly equation 14, applying in the case of the Cl^- complexation study and yielding a monomeric Cl^- to Cu coordinated product, applies only for a single cube reactant.

Finally we refer to the interesting observations of Shibahara and colleagues that on addition of $[Cu(H_2O)_6]^{2+}$ to $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ and $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ the Cu^{2+} displaces the heterometal atom.[19] It was suggested that a multistage substitution process involving cleavage and formation of heterometal bonds to the three core S^{2-} ligands is occurring. As a result of the present work, and in particular the demonstration that Cu^+ reacts with $[Mo_3S_4(H_2O)_9]^{4+}$ to give a second oxidation state of the Mo_3CuS_4 core, we suggest an alternative mechanism involving electron transfer. The latter can be summarized by a thermodynamically unfavorable equilibrium step (23), followed

$$Mo_3MS_4{}^{4+} + 2Cu^{2+} \rightleftharpoons Mo_3S_4{}^{4+} + M^{2+} + 2Cu^+ \quad (23)$$

by the rapid reaction of Cu^+ with $[Mo_3S_4(H_2O)_9]^{4+}$, (24). We

$$Mo_3S_4{}^{4+} + Cu^+ \rightarrow Mo_3CuS_4{}^{5+} \quad (24)$$

have column purified the product from both the M = Fe and Ni reactions and demonstrated from UV–vis spectrophotometry that the 5+ and not the 4+ cube is obtained. It is known that $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ reacts much more rapidly with O_2 than $[Mo_3NiS_4(H_2O)_{10}]^{4+}$,[14,34] consistent with Cu^{2+} reacting $>10^4$ times faster with the Fe cube. Similar reactions of Cu^{2+} with other Mo_3MS_4 clusters have been observed.[13] That there is no reaction between Ni^{2+} and $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ (with displacement of Fe^{2+}), or between Fe^{2+} and $[Mo_3NiS_4(H_2O)_{10}]^{4+}$,[19] is not surprising since it would be difficult in these cases to invoke an electron-transfer mechanism as in (23)–(24).

Acknowledgment. We wish to acknowledge post-doctoral support under an SERC research grant (M.N. and Y.-J.L.), and the Royal Society for the award of a Royal Fellowship under the Anglo–Chinese exchange program (Y.-J.L.). We thank David Saysell for some check experiments.

---

(29) Li, Y.-J.; Nasreldin, M.; Humanes, M.; Sykes, A. G. *Inorg. Chem.* **1992**, *31*, 3011.

(30) Ahrland, S.; Rawsthorne, J. *Acta. Chem. Scand.* **1970**, *24*, 157.

(31) Baes, C. F.; Mesmer, R. E. *Hydrolysis of Cations*; Wiley: New York, 1976; p 230.

(32) Sutin, N. *Acc. Chem. Res.* **1968**, *1*, 225.

(33) Latimer, W. M. In *Oxidation States of the Elements and their Potentials in Aqueous Solution*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1952.

(34) Dimmock, P. W.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1990**, 3101.