A Novel Electrochemical Method for the Preparation of Triangular and Cubic Molybdenum Clusters as Aqua Ions

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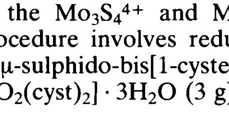
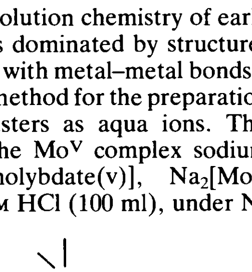
Aqua ions of $Mo_3S_4^{4+}$ and $Mo_4S_4^{5+}$ have been obtained in high yield in a single electrochemical experiment, which is applicable also to the preparation of $Mo_3O_4^{4+}$ and $Mo_4O_4^{5+}$ and other analogous clusters.

The synthesis of cubic Fe_4S_4 cluster complexes[1] as analogues of the biologically important ferredoxins,[2] of complexes containing two Fe_3MoS_4 cubes linked by bridging ligands,[3] and more recently of the single $MoFe_3S_4$ cube,[4] believed to be relevant in the nitrogenase context,[5] has attracted much attention. No aqua ions of Fe_4S_4 have been prepared, and the few water-soluble Fe_4S_4 complexes which have been reported[6] are not noted for their stability except over a very limited range of pH.

It is now clear that the aqueous solution chemistry of early transition metal ions such as Mo is dominated by structures having more than one metal,[7] many with metal–metal bonds.[8] Here we report an electrochemical method for the preparation of the $Mo_3S_4^{4+}$ and $Mo_4S_4^{5+}$ clusters as aqua ions. The procedure involves reduction of the Mo^V complex sodium di-μ-sulphido-bis[1-cysteinato-oxomolybdate(V)], $Na_2[Mo_2S_2O_2(cyst)_2]\cdot 3H_2O$ (3 g),[9–11] in 2 M HCl (100 ml), under N_2 (or Ar) using a Hg pool electrode at a constant potential (0.85 V *vs.* normal hydrogen electrode, n.h.e.) for 12 h.† The dark brown solution obtained was diluted to $[H^+] = 0.3$ M, and 2 l of 0.5 M toluene-*p*-sulphonic acid (HPTS) added. After being left in air for 24 h the solution was loaded onto a Dowex 50W-X2 column, and washed with 0.5 M (250 ml) and then 1.0 M (200 ml) HPTS. A dark-green band (~60% of Mo used) was eluted with 2 M HPTS, and a leaf-green band (~30% of Mo) with 3 M HPTS. Both bands were further purified by recolumning.



$[Mo_3S_4(H_2O)_9]^{4+}$



$[Mo_4S_4(H_2O)_{12}]^{5+}$

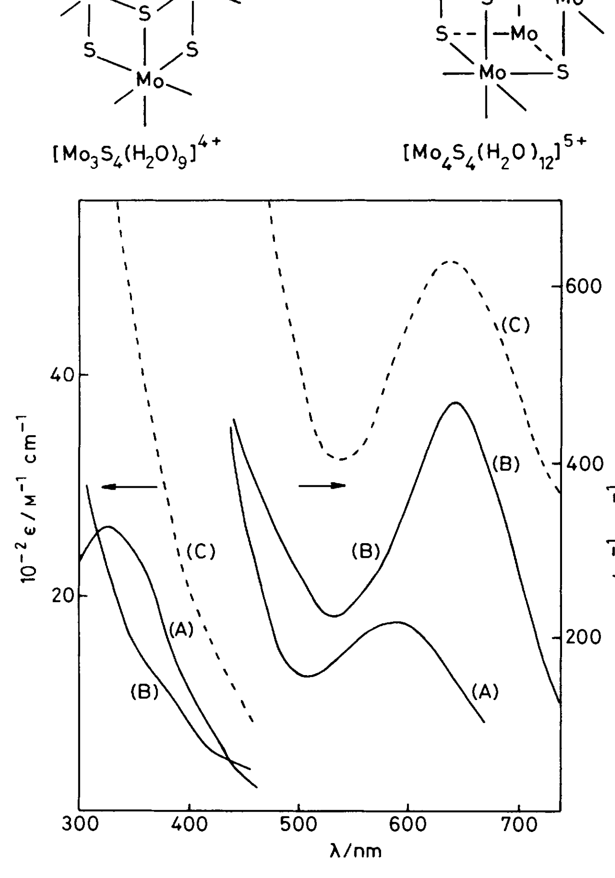


Figure 1. U.v.–visible spectra of $[Mo_3S_4(H_2O)_9]^{4+}$ (A) and $[Mo_4S_4(H_2O)_{12}]^{5+}$ (B) in aqueous acidic solutions, [HPTS] = 2.0 M. On reaction of the 5+ complex with edta the complex $[Mo_4S_4(edta)_2]^{3-}$ (C) is obtained.

The dark-green 2 M eluate gave a solid crystalline sample of the tetramethylammonium salt of the thiocyanato complex, $(Me_4N)_5[Mo_3S_4(NCS)_9]$; satisfactory elemental analyses were obtained [no H_2O of crystallization (over P_2O_5)]. The u.v.–visible spectrum of the aqua ion, $[Mo_3S_4(H_2O)_9]^{4+}$, gave a peak with $\lambda_{max.}$ at 585 nm (ε 221 M^{-1} cm^{-1}† per Mo) and 326 (2620) in excellent agreement with values already obtained for the same product from the reaction of $[Mo_2S_2O_2(cyst)_2]^{2-}$ with $NaBH_4$.[12] In 2 M $HClO_4$ the $Mo_3S_4^{4+}$ ion decomposes to give μ_2-oxo analogue complexes $Mo_3O_2S_2^{4+}$ and $Mo_3OS_3^{4+}$ which have not previously been reported.

The leaf-green product obtained in the same electrochemical experiment has been characterised as the mixed-valence $Mo^{III}{}_3Mo^{IV}$ cluster $[Mo_4S_4(H_2O)_{12}]^{5+}$, $\lambda_{max.}$ at 645 nm (ε 470 M^{-1} cm^{-1}). A thiocyanato complex has been isolated, $(Me_4N)_7[Mo_4S_4(NCS)_{12}]$, which gave satisfactory elemental analyses; no H_2O. On addition of disodium ethylenediamminetetra-acetate (edta) to the aqua ion a solid sample of $Na_3[Mo_4S_4(edta)_2]$, $\lambda_{max.}$ at 636 nm (ε 632 M^{-1} cm^{-1}) was obtained, Figure 1. The crystal structure of $Ca_3[Mo_4S_4(edta)_2]\cdot 26H_2O$, has been determined.[13] Addition of 3 M HPTS to the edta complex gives complex spectrophotometric changes and the edta cannot be removed by this means to generate the aqua ion. Crystal structures of $K_8[Mo_4S_4(CN)_{12}]\cdot 4H_2O$ and $K_8[Mo_4S_4(NO)_4(CN)_8]\cdot 4H_2O$ have been reported.[14,15]

Analogous electrochemical experiments using the di-μ-oxo Mo^V complex $Na_2[Mo_2O_4(cyst)_2]\cdot 5H_2O$ have furthermore yielded red products of $Mo_3O_4^{4+}$ (~20% of the Mo), $\lambda_{max.}$ 505 nm (ε 195 M^{-1} cm^{-1}), and $Mo_4O_4^{5+}$ (~3%), $\lambda_{max.}$ 400 nm (2740 M^{-1} cm^{-1}) and 545 (200). Whereas the $[Mo_3O_4(H_2O)_9]^{4+}$ ion is now well characterised,[16] the $Mo_4O_4^{5+}$ cluster has not previously been identified. Determinations of the Mo by atomic absorption and redox equivalents by titration with Ce^{IV} have indicated that the latter has mixed oxidation states corresponding to $Mo^{III}{}_3Mo^{IV}$.

Factors controlling the relative amounts of the triangular and cubic complexes and whether the Mo_4 cluster is the precursor of Mo_3 or *vice versa* are of interest. The two cubic aqua ions prepared for the first time are remarkably stable, with little decomposition (~10%) of $Mo_4S_4^{5+}$ and $Mo_4O_4^{5+}$ in $[H^+]$ = 0.10—3.0 M over 1 week at 20 °C. They are also unreactive in 1 M $HClO_4$ solutions over the same time, and stable up to 60 °C on heating at a rate of 20 °C per hour. Kinetic studies on the substitution of H_2O by NCS^- (0.5 mM) required the stopped flow method ($t_{\frac{1}{2}}$ *ca.* 1 s). Other ligating

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† M = mol dm^{-3}; all ε values are per mole complex.

groups can readily be attached to the aqua ion clusters in aqueous media.

Cyclic voltammetry on the $Mo_3S_4^{4+}$ ion in 2 M HPTS has indicated a 2 electron and a further 1 electron reduction processes. Experiments on the aqua ion $Mo_4S_4^{5+}$ in 2 M HPTS have indicated 1 electron oxidation and reduction processes with E° values of −0.08 V corresponding to the 5+/4+ change, and +0.54 V for the 6+/5+ change (vs. n.h.e.). For the $Mo_4O_4^{5+}$ ion an E° of 0.67 V has been observed for the 6+/5+ change.

The preparative method used is likely to have wider applications for other triangular and cubic molybdenum clusters, and for other early second and third row transition metals. We are currently investigating the chemistry of tungsten and niobium by this method.

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