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# Unprecedented Influence of the Acid Medium in the Synthesis of $Mo_3M'S_4$ Cubane-like Clusters: Preparation of $[Mo_3PbS_4(H_2O)_{9+x}]^{4+}$

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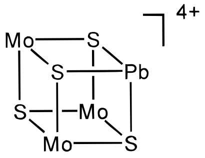
Mainly through the work of Shibahara and co-workers, a number of different metal atoms have been incorporated into the incomplete cubane-like clusters $Mo_3S_4$ (Cr,[1] Mo,[2] Fe,[3] Co,[4] Ni,[5,6] Pd,[7] Cu,[8] Hg,[4] In,[9] Sn,[10] Sb[11]) and $W_3S_4$ (Ni,[12] Cu,[13] Ge,[14] Sn[14]) to produce bimetallic, complete cubane-like $M_3M'S_4$ units (M = Mo, W). These bimetallic clusters are generally synthesized by reaction of an acidic aqueous solution of $[M^{IV}{}_3S_4]^{4+}$ either with the free metal M′ or with solid $NaBH_4$ in the simultaneous presence of $(M')^{m+}$. In a few cases (Hg, Sn, Sb) corner-shared double-cubanes $(Mo_3S_4)M'(Mo_3S_4)$ may be obtained, but normally the products are single-cubanes $M_3M'S_4$. For some metals (Co, Cu, Pd) edge-linked dimers of $Mo_3M'S_4$ are isolated in the solid state. The monomeric cubanes may formally be looked upon as 1:1 complexes between the ligand $[M^{IV}{}_3S_4]^{4+}$ and the central ion or atom $(M')^{m+}$ where $m$ is often 0. However, in reality the oxidation state of the heterometal is more like +1, +2, or +3 (e.g. ref 15) with a corresponding increase in electron density on the molybdenum or tungsten atoms.

A common feature of all the heterometals that have been incorporated[1−14] into the $M_3S_4$ units so far is that they have a large, or at least relatively large, affinity for sulfide. Thus, a cluster containing Pb would be expected to be easily synthesized and to have a high stability. However, an attempt to produce a $Mo_3PbS_4$ cluster by the conventional method, i.e. by reaction of $[Mo^{IV}{}_3S_4]^{4+}$ with metallic lead in dilute hydrochloric acid, gave, somewhat surprising, $[Mo^{III}{}_4S_4]^{4+}$ in 80% yield.[16]

Addition of excess solid $NaBH_4$ to a solution in 1 mol·dm$^{-3}$ HCl containing $[Mo_3S_4]^{4+}$ and a 10 times excess of $Pb^{2+}$ produced a dark green species, which even under rigorous anaerobic conditions decomposed within less than 5 min. In order to avoid the presence of chloride, the reduction was instead carried out in a 2 mol·dm$^{-3}$ $CF_3SO_3H$ solution. Since $[Mo_3S_4(H_2O)_9]^{4+}$ can only be eluted in a very low concentration from a Dowex 50W-X2 cation-exchange column (even by 6 mol·dm$^{-3}$ $CF_3SO_3H$), a high concentration of $[Mo_3S_4(H_2O)_9]^{4+}$ (0.005 mol·dm$^{-3}$) was produced by dissolution of the new crystalline formato compound $K_4[Mo_3S_4(HCO_2)_8]\cdot 3H_2O$[17] in 2 mol·dm$^{-3}$ $CF_3SO_3H$. In line with previous observations concerning formato complexes of molybdenum,[18] hydrolysis of $[Mo_3S_4(HCO_2)_8]^{4-}$ quickly took place in the strongly acidic medium and the corresponding aqua complex was generated. All the following operations were carried out under a protective atmosphere of $N_2$. Reduction by means of $NaBH_4$ of the $[Mo_3S_4(H_2O)_9]^{4+}$ solution to which a 10 times excess of lead(II) acetate had been added gave a dark turquoise, very air-sensitive solution from which some dark brown precipitate was removed by millipore filtration. Alternatively, reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ in aqueous $CF_3SO_3H$ with a 10 times excess of lead powder (<100 μm) for 2 h at room temperature produced the same dark turquoise species, but without generating any solid, dark brown byproduct. The solutions thus obtained were purified by Dowex cation-exchange chromatography, and the turquoise species was eluted with 2 mol·dm$^{-3}$ *p*-toluenesulfonic acid (Hpts). In neither case could any unreacted $[Mo_3S_4]^{4+}$ be detected.

When a mixture of the turquoise cluster and $[Mo_3S_4(H_2O)_9]^{4+}$ was eluted by means of 2 mol·dm$^{-3}$ Hpts, $[Mo_3S_4(H_2O)_9]^{4+}$ showed the larger affinity for the Dowex column. This clearly rules out a very high ionic charge for the turquoise cluster, e.g. 8+, which would have been the case had it been of the corner-shared or edge-linked type. In agreement with ICP analysis of a pure eluate, which gave a Mo:Pb ratio of 2.9, the cluster must be of the single-cubane type, i.e. $[Mo_3PbS_4(H_2O)_{9+x}]^{n+}$. If it is assumed that the turquoise cluster does not form unusually strong complexes or ion pairs with $pts^-$, the elution behavior indicates $n = 4$, i.e. the formula $[Mo_3PbS_4(H_2O)_{9+x}]^{4+}$ (**1**). This ionic charge is corroborated by magnetic measurements (see below).



**1**

The electronic spectrum of $[Mo_3PbS_4(H_2O)_{9+x}]^{4+}$ in 2 mol·dm$^{-3}$ $CF_3SO_3H$ is shown in Figure 1.

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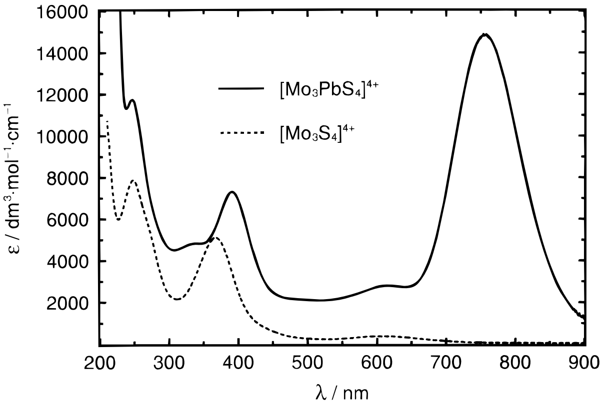

**Figure 1.** Electronic spectra in 2 mol·dm$^{-3}$ $CF_3SO_3H$ of $[Mo_3PbS_4(H_2O)_{9+x}]^{4+}$ (solid line) and $[Mo_3S_4(H_2O)_9]^{4+}$ (dashed line). Spectral characteristics, ($\lambda$/nm; $\epsilon$/dm$^3$·mol$^{-1}$·cm$^{-1}$), per cube of $[Mo_3PbS_4(H_2O)_{9+x}]^{4+}$: $(246; 11.7 \times 10^3)_{max}$, $(335; 4.8 \times 10^3)_{sh}$, $(391; 7.3 \times 10^3)_{max}$, $(615, 2.8 \times 10^3)_{max}$ and $(755; 14.8 \times 10^3)_{max}$. The concentration of $[Mo_3PbS_4(H_2O)_{9+x}]^{4+}$ was determined by complete atmospheric oxidation to $[Mo_3S_4(H_2O)_9]^{4+}$.[20] Oxidation was characterized by a substantial loss of color intensity. The $[Mo_3PbS_4(H_2O)_{9+x}]^{4+}$ spectral band at 755 nm is surprisingly intense; its $\epsilon$ value is some 20 times larger than the near-IR band $\epsilon$ of any $Mo_3M'S_4$ cluster synthesized so far. In 2 mol·dm$^{-3}$ HCl, where the cluster is unstable, this band is shifted to 790 nm, which indicates coordination of chloride to Pb. A similar shift upon coordination of chloride to the heterometal is seen for e.g. $[Mo_3NiS_4]^{4+}$.[6]

An anaerobically eluted solution of $[Mo_3PbS_4(H_2O)_{9+x}]^{4+}$ in 4 mol·dm$^{-3}$ HCl decomposed essentially completely within 2 h according to the reaction 1. It is not clear what was reduced; bubbles of hydrogen were not observed.

$$[Mo_3PbS_4]^{4+} + 2Cl^- \rightarrow [Mo_3S_4]^{4+} + PbCl_2(s) + 2e^- \quad (1)$$

Numerous attempts were made to produce crystals for an X-ray crystal structure characterization of the $[Mo_3PbS_4]^{4+}$ cluster. Attempts to crystallize a *p*-toluenesulfonate salt (e.g. refs 4−6, 8−10, and 12) from very concentrated solutions of $[Mo_3PbS_4(H_2O)_{9+x}]^{4+}$ in 5 mol·dm$^{-3}$ Hpts at −18 or +5 °C were unfruitful. In this connection, decomposition of the cluster, producing a white precipitate of $Pb(pts)_2$ (identified by X-ray powder diffraction) by a reaction analogous to (1), was observed at 40 °C. Similarly, attempts to isolate acetate or thiocyanate containing complexes failed due to extraction of Pb from the cluster as shown by the loss of solution color intensity (cf. Figure 1).

A powder containing $[Mo_3PbS_4]^{4+}$ in the form of a formato complex was produced analogously[17] to $K_4[Mo_3S_4(HCO_2)_8]\cdot 3H_2O$: A solution of $[Mo_3PbS_4]^{4+}$ in dilute $CF_3SO_3H$ was absorbed on a short Dowex cation-exchange column. After the column had been washed with water and allowed to run dry, the cluster was eluted in a very concentrated form by means of a solution 5 mol·dm$^{-3}$ in cesium formate and 10 mol·dm$^{-3}$ in formic acid. Two volumes of ethanol were added to the eluate, and after some days at 5 °C a dark green powder formed. Elemental analyses (C, 6.87; H, 0.99; S, 9.40; Mo, 19.1; Pb, 12.5; Cs, 23.5) corresponded roughly to the composition $Cs_3H[Mo_3PbS_4(HCO_2)_8]\cdot 3H_2O$. Dissolution of the powder in 2 mol·dm$^{-3}$ $CF_3SO_3H$ produced the spectrum of $[Mo_3PbS_4(H_2O)_{9+x}]^{4+}$ shown in Figure 1.

Magnetic measurements on the $Cs-Mo_3PbS_4-HCO_2$ powder were made by using a Sherwood Scientific magnetic susceptibility balance. The powder was weakly paramagnetic ($\chi_{mass} = 0.29 \times 10^{-6}$ cgsu at 23 °C) with no increase in $\chi$ when the sample was measured immediately after cooling in liquid nitrogen. Large temperature-independent paramagnetic contributions to $\chi$ were also observed for $[Mo_3S_4]^{4+}$ formato complexes.[17] Since no unpaired electrons were observed for $[Mo_3PbS_4]^{n+}$, the cluster charge must be +4 rather than +5, which the eluation behavior could not rule out completely (see above).

On the basis of published[1−14] structures of $M_3M'S_4$ clusters, each molybdenum in $[Mo_3PbS_4]^{4+}$ is expected to coordinate three water ligands. The number, $x$, of water ligands on Pb is unknown, but in other $M_3M'S_4$ clusters M′ has been found to coordinate one (e.g. Fe[3] and Ni[5,6]) or three (Cr[1] and Mo[2]) water ligands. Even though $Pb^{II}$ is known[19] to sometimes adopt pyramidal coordination, the possibility of $x = 0$ is unlikely in the present case, as the electronic spectrum of $[Mo_3PbS_4]^{4+}$ varied substantially with the anion of the acid medium (cf. caption to Figure 1).

The present results show that the choice of acid medium may be very critical in the synthesis of bimetallic $M_3S_4$ derivatives. They suggest that the reason that $[Mo_4S_4]^{4+}$ and not $[Mo_3PbS_4]^{4+}$ is produced when metallic lead is reacted with $[Mo_3S_4]^{4+}$ in dilute hydrochloric acid is that $[Mo_3PbS_4]^{4+}$ is unstable in that medium. One may envisage that $[Mo_3PbS_4]^{4+}$ is formed initially and that lead is extracted as $Pb^{2+}$ because of its affinity for chloride. Subsequently, the remaining reduced state $[Mo_3S_4]^{2+}$ units react to form $[Mo_4S_4]^{4+}$.

Further studies aimed at producing new bimetallic clusters in innocent acid media are being carried out by employment of both the $NaBH_4$ and free-metal reduction techniques.

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(20) Dissolution of $K_4[Mo_3S_4(HCO_2)_8]\cdot 3H_2O$ in 2 mol·dm$^{-3}$ $CF_3SO_3H$ gave $(\lambda, \epsilon) = (367, 5.1 \times 10^3)_{max}$ for $[Mo_3S_4(H_2O)_9]^{4+}$.