

chemistry of these and other complexes in which small molecules are bound and activated between two metals attached to binucleating tropocoronands.

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Supplementary Material Available: Tables of atomic positional and thermal parameters for compounds **2a** and **2b** (6 pages). Ordering information is given on any current masthead page.

The Mo₃S₄⁴⁺ Aquo Ion

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There is an extensive chemistry of the Mo₃O₄⁴⁺ aquo ion,¹⁻³ whose complete formula is almost certainly [Mo₃O₄(H₂O)₉]⁴⁺, although no compound containing the ion itself has yet been reported. It is well-known that molybdenum has an extraordinary proclivity to form binuclear and cluster compounds containing terminal μ₂ or μ₃ sulfur atoms, some of which are of biological importance. We have, therefore, been working on the chemistry of compounds containing equilateral triangular arrays of molybdenum atoms in which there are μ₂-S and/or μ₃-S groups. We⁴ and others⁵⁻⁷ have previously reported reactions giving complexes of the Mo₃S₄⁴⁺ ion by employing the compound (NH₄)₂[Mo₃S(S₂)₆] as a starting material.⁸ For a number of reasons, we have been seeking ways to obtain the Mo₃S₄⁴⁺(aq) ion cleanly in aqueous solution and then use it to produce complexes and other derivatives conveniently. We report here our success in doing this.

One method of obtaining the [Mo₃S₄(H₂O)_n]⁴⁺ ion (where n is probably 9) begins with the previously reported [Mo₃S₄(HNTA)₃]²⁻ complex⁴ (where HNTA²⁻ = [N(CH₂CO₂)₂(CH₂CO₂H)]²⁻). Hydrolysis of this anion in 2 M HCl for 8 h was essentially quantitative and gave a clear green solution, which was diluted with a 3-fold volume of water and passed through a Dowex 50W × 2 cationic exchange column. The green species was adsorbed on the column as a sharp green band at the top, which could be eluted only with relatively strong simple acids, such as 2 M HClO₄ or 4 M HCl. This is consistent with the presence of a highly charged ion such as Mo₃S₄⁴⁺(aq). The 4 M HCl eluate has a visible spectrum, Figure 1, very similar to that of the [Mo₃S₄(HNTA)₃]²⁻ ion and also quantitatively comparable to that of the Mo₃O₄⁴⁺(aq) ion. When this HCl solution was freeze-dried only an oily green deposit was obtained. However,

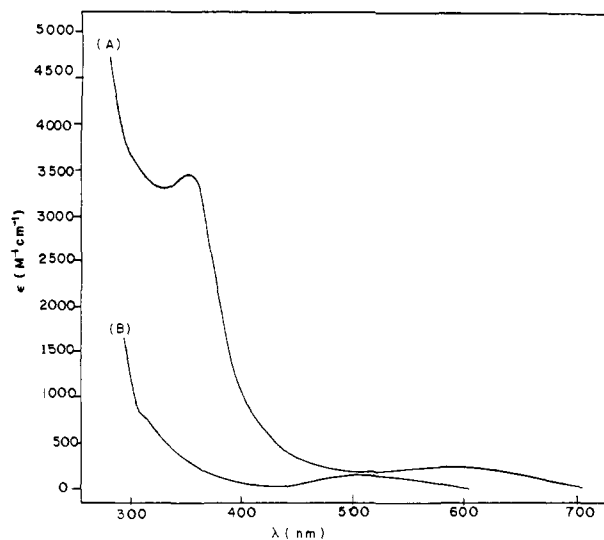


Figure 1. Electronic absorption spectra of (A) the Mo₃S₄⁴⁺(aq) ion and (B) the Mo₃O₄⁴⁺(aq) ion in 2 M HClO₄.

this easily redissolved in 0.01 M HCl to give a clear green solution that is stable in air for days, at least. To place the absorbance scale for the spectrum of the Mo₃S₄⁴⁺(aq) ion on an absolute scale, an accurately weighed amount of the [Mo₃S₄(HNTA)₃]²⁻ compound was completely hydrolyzed, the ion was collected on the cation exchange resin, and then quantitatively eluted to form a known volume of solution, whose spectrum was recorded.

Addition of nitrilotriacetic acid, oxalic acid, or KCN to this solution allows the isolation of salts of the [Mo₃S₄(HNTA)₃]²⁻, [Mo₃S₄(C₂O₄)₃(H₂O)₃]²⁻, and [Mo₃S₄(CN)₃]⁵⁻ ions. It is also possible to elute the green band from the column directly with 0.1 M solutions of H₃NTA/(NH₄)₃NTA, H₂C₂O₄/Na₂C₂O₄, or NaCN and isolate these same complexes from the eluates.

Although the results just summarized showed that the Mo₃S₄⁴⁺(aq) ion can be prepared, that it is stable in aqueous solution in air, and that anionic complexes of it can then be simply obtained, a convenient method for preparing the solution of Mo₃S₄⁴⁺ was not yet available. Such a method has been found which employs an entirely new reaction.

Molybdenum carbonyl (1.0 g), dry sodium sulfide (0.6 g), and 100 mL of acetic anhydride were refluxed for about 10 h under nitrogen. After it was cooled to room temperature, the solution was placed in the refrigerator for several hours and then filtered. The filtrate was hydrolyzed with 500 mL of water overnight, filtered, and passed through a Dowex 50 W × 2 cation exchange column. The column was washed with 0.2 M HCl and then eluted with 1.0 M HClO₄ to give a green solution (species I). A second green ion (species II) which is left on the column was then eluted with 4 M HCl. The perchloric acid solution of the green ion I was diluted with water and passed again through the column depositing a green band, which was then eluted with 2 M HCl. The green ion in this solution, I, was identified as the Mo₃S₄⁴⁺ aquo ions by its spectrum and formation of anionic salts as above. The relative amounts of I and II vary somewhat with reaction conditions. Typical yields are 15% of the Mo₃S₄⁴⁺ ion in 20% of species II (assuming an E comparable to that of I).

The solution of the green ion II, as obtained by elution with 4 M HCl, has an electronic spectrum very similar to, but not identical with, that of the aquo ion, I. There is only a shoulder at 640 nm (band at 620 nm in I) and, diagnostically more important, no band between 300 and 400 nm. Species II can also be removed from the column by treating it with 0.5 M H₂C₂O₄ under argon for ca. 8 h to give a solution of an oxalate derivative.⁹ Again, the spectrum is not identical with that of the authentic [Mo₃S₄(C₂O₄)₃(H₂O)₃]²⁻. However, upon addition of CsCl, crystals of Cs₂[Mo₃S₄(C₂O₄)₃(H₂O)₃]·3H₂O are deposited after

(9) We have now been able to show that species II is the Mo₃S₄⁴⁺(aq) ion. See the following paper in this issue.

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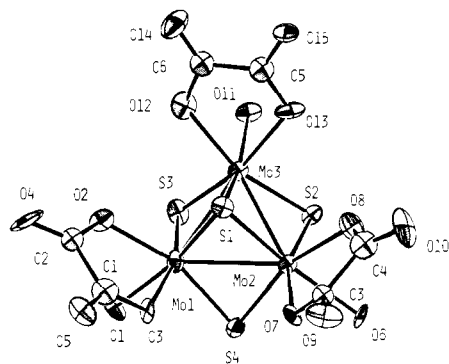


Figure 2. $[\text{Mo}_3\text{S}_4(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_3]^{2-}$ ion as found in the cesium salt described in the text.

several days. They have been fully characterized by crystallography¹⁰ and their solution spectrum is that of the oxalate trimer obtained from the reaction of $[\text{Mo}_3\text{S}_3]^{2-}$ and oxalic acid.⁴ The structure of the anion is shown in Figure 2.

An analogous reaction carried out with $\text{W}(\text{CO})_6$ gives a more complicated array of products (at least four, somewhat depending on the quantity of Na_2S used). One of these has been shown to be the $\text{W}_3\text{S}_4^{4+}(\text{aq})$ ion and the others are still under investigation.

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Registry No. $\text{Cs}_2[\text{Mo}_3\text{S}_4(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$, 98736-87-9; $\text{Mo}(\text{C}_2\text{O}_4)_3$, 13939-06-5.

Supplementary Material Available: A table of crystallographic parameters and a table of fractional coordinates (3 pages). Ordering information is given on any current masthead page.

(10) Green prismatic crystals with a pronounced tendency for twin growth; $\text{Cs}_2\text{Mo}_3\text{S}_4\text{O}_{18}\text{C}_6\text{H}_6$; $P\bar{1}$, $a = 9.677$ (3) Å, $b = 20.753$ (6) Å, $c = 6.654$ (2) Å, $\alpha = 97.03$ (3)°, $\beta = 106.17$ (2)°, $\gamma = 79.79$ (3)°, $Z = 2$, $V = 1259$ (1) Å³, $R = 0.054$, $R_w = 0.065$.

The Cuboidal $\text{Mo}_4\text{S}_4^{6+}$ Aquo Ion and Its Derivatives

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Interest in tri- and tetranuclear molybdenum-sulfur cluster species has been growing rapidly in recent years. In addition to the perthio species²⁻¹⁵ $\text{Mo}_3\text{S}_4^{n+}$ and $\text{Mo}_4\text{S}_4^{n+}$, there have been

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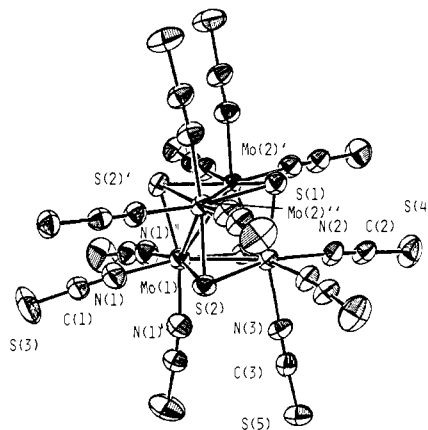


Figure 1. Structure of the $[\text{Mo}_4\text{S}_4(\text{NCS})_{12}]^{6-}$ ion. The Mo-Mo distances have the following values: Mo(1)-Mo(2), 2.791 (1) Å; Mo(2)-Mo(2)', 2.869 (1) Å.

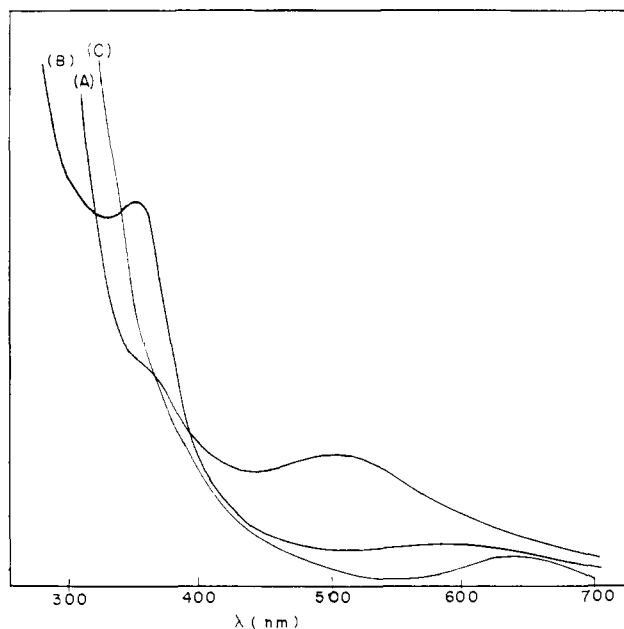


Figure 2. Electronic absorption spectra of the $\text{Mo}_3\text{S}_4^{4+}(\text{aq})$ ion (B), $\text{Mo}_4\text{S}_4^{6+}(\text{aq})$ ion (C), and $[\text{Mo}_4\text{S}_4(\text{NCS})_{12}]^{6-}$ ion (A).

recent reports of the mixed oxo-thio species¹⁴⁻¹⁷ $\text{Mo}_3\text{O}_3\text{S}^{4+}$, $\text{Mo}_3\text{O}_2\text{S}_2^{4+}$ and $\text{Mo}_3\text{OS}_3^{4+}$ (each of which occurs in two isomeric forms). The trinuclear species so far described are all of the electron-precise type, that is, they contain the exact number of cluster electrons (six) necessary to form a full set (three) of Mo-Mo bonds. The tetranuclear species with a central Mo_4S_4 core vary in their electron count.¹⁸ The $[\text{Mo}_4\text{S}_4(\text{CN})_{12}]^{8-}$ species⁸

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