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Cubane-Type Molybdenum Aqua Ions. Preparation and Structures of $[Mo_4(\mu_3\text{-}O)(\mu_3\text{-}S)_3(H_2O)_{12}]^{5+}$ and $[Mo_4(\mu_3\text{-}S)_4(H_2O)_{12}]^{5+}$

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Two cubane-type molybdenum aqua compounds, $[Mo_4OS_3(H_2O)_{12}](CH_3.C_6H_4.SO_3)_5.14H_2O$ and $[Mo_4S_4(H_2O)_{12}](CH_3.C_6H_4.SO_3)_5.14H_2O$ have been prepared, and characterized by X-ray crystallography, electronic spectroscopy, and cyclic voltammetry. Their reduced species, $[Mo_4OS_3(H_2O)_{12}]^{4+}$ and $[Mo_4S_4(H_2O)_{12}]^{4+}$, have also been characterized.

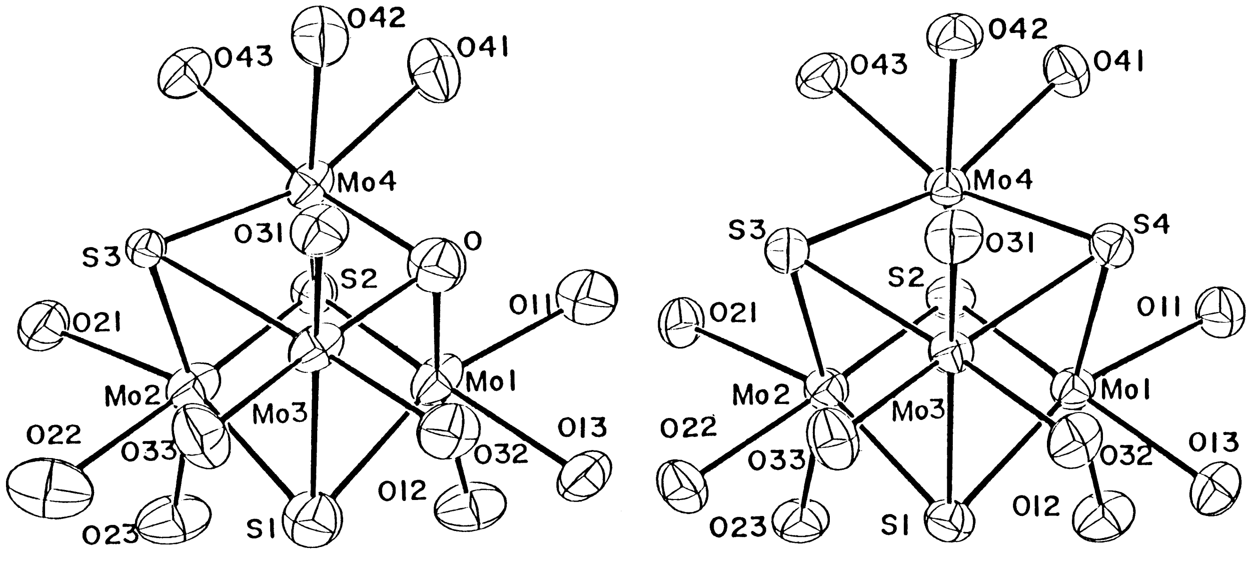
A series of incomplete cubane-type molybdenum aqua ions with $Mo_3O_{4-n}S_n$ core ($n = 0 - 4$) have been prepared and characterized,¹⁾ and many complexes with these cores have been described.²⁾ As for the cubane-type aqua ions, however, the sulfur-bridged aqua ion, $Mo_4S_4(aq)^{n+}$ (n = 4, 5, and 6), is the only aqua ion reported so far and no other cubane-type aqua ions with $Mo_4O_{4-n}S_n$ core ($n = 0 - 3$) have been reported.³⁾ Although several complexes with Mo_4S_4 core are known,⁴⁾ $[Mo_4OS_3(S_2P(OEt)_2)_6]$ is the only compound with the Mo_4OS_3 core.⁵⁾

We now report the preparation, X-ray structure, and properties of a novel oxo- and sulfido-bridged cubane-type aqua compound, $[Mo_4OS_3(H_2O)_{12}](CH_3.C_6H_4\text{-}SO_3)_5.14H_2O$ (**1**). Preparation and X-ray structure of the sulfido-bridged cubane-type aqua compound, $[Mo_4S_4(H_2O)_{12}](CH_3.C_6H_4.SO_3)_5.14H_2O$ (**2**), are also described.

Preparation of **1** is as follows: An iron wire (1 g) was introduced to a conical flask containing the incomplete cubane-type Mo$_3$(IV, IV, IV) aqua ion $Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(aq)^{4+}$ (**3'**; 0.3 M per Mo, 15 mL; 1 M = 1 mol dm^{-3}) in 2 M HCl, which was allowed to stand for a couple of days under a dinitrogen atmosphere. The resultant dark brown solution was filtered in air and Dowex 50W-X2 column chromatography (3.0 cm x 30 cm) was applied. Ferrous ion and **3'** were eluted with 0.5 and 1 M HCl, respectively, and the green aqua ion **1'** was obtained by use of 2 M HCl (λ_{max} = 670 nm). Yield 35%. This was analyzed to give Mo/S = 1.33. The solution was absorbed on the cation exchanger again and eluted with 4 M HPTS (p-toluenesulfonic acid). The resultant solution was kept in a refrigerator, and dark green crystals of **1** were obtained in a week. Anal. Found (Calcd): C, 22.87 (23.09); H, 4.63 (4.81)%. **1'** in 2 M HPTS is slightly air-sensitive and the spectrum changes ca. 15% a day in air.

The reduced species of **1'**, $[Mo_4OS_3(H_2O)_{12}]^{4+}$ (**1R'**), was obtained by two methods: (A) To **1'** (0.016 M, 15 mL) in 1 M HCl was added solid $NaBH_4$ (0.1 g) under a dinitrogen atmosphere. Dowex column chromatography was applied (2 M HPTS) and red-brown solution was obtained. Yield 55%. (B) In the preparation of **1**, if all the procedures were carried out under a dinitrogen atmosphere, and Sephadex column chromatography (1 M HCl) in stead of Dowex 50W-X2 column chromatography was applied, **1R'** was obtained. Yield 20%. **1R'** is readily air-oxidized to give **1'**.

The sulfur-bridged cubane-type aqua ion **2'** is prepared as one of the by-products of $Mo_3S_4(aq)^{4+}$.[6] The crystals of **2** were obtained as **1**. Anal. Found (Calcd for **2**): C, 23.08 (22.89); H, 4.60 (4.77)%.



a b

Fig. 1. Perspective views of $[Mo_4OS_3(H_2O)_{12}]^{5+}$ in **1** (**a**) and $[Mo_4S_4(H_2O)_{12}]^{5+}$ in **2** (**b**) with selected bond distances (Å) and angles (deg). The values are in order of **1** and **2**. Mo1-Mo2, 2.758(1), 2.827(1); Mo1-Mo3, 2.719(1), 2.785(1); Mo1-Mo4, 2.739(1), 2.820(1); Mo2-Mo3, 2.742(1), 2.800(1); Mo2-Mo4, 2.735(1), 2.785(1); Mo3-Mo4, 2.728(1), 2.794(1); Mo-(μ_3-S) (av.), 2.361[18], 2.349[4]; Mo-(μ_3-O) (av.), 1.96[7]; Mo-H_2O (av.), 2.18[1], 2.19[1].

X-Ray structure analyses[7] of **1** and **2** revealed the existence of cubane-type $Mo_4(\mu_3\text{-}O)(\mu_3\text{-}S)_3$ and $Mo_4(\mu_3\text{-}S)_4$ cores, respectively, as shown in Fig. 1 together with selected bond distances. During the structure determination of **1**, a peak assignable to a μ_3-S was disclosed by Fourier synthesis near the μ_3-O, which can be explained by the statistical disorder between one μ_3-O and three μ_3-S's.[8] Only μ_3-O is included in the ORTEP drawing of **a** for clarity. In order to make sure that we picked up the correct crystal of **1**, one crystal was cut into two, and one half was used for the X-ray-data collection and the other was used for the measurement of the electronic spectrum, which was identical to the spectrum of **1'**. The mean Mo-Mo distance of **1** (2.737[13] Å) is shorter than that of **2** (2.802[18] Å), and no especially short Mo-Mo distances exist among six Mo-Mo distances in **1**. Shortening of Mo-Mo distances have been observed through the substitution of μ_3-O for μ_3-S in the incomplete cubane-type compounds with $Mo_3O_{4-n}S_n$ core,[1] and the leveling of the Mo-Mo distances in **1** seems due to the statistical disorder.

Figure 2 shows the electronic spectra of **1'** and **2'** together with respective reduced species (**1R'** and **2R'**) in 2 M HPTS. The average oxidation states of Mo in **1'**, **2'**, **1R'**, **2R'** are 3.25, 3.25, 3.00, and 3.00, respectively. Peak positions, $\lambda_{\mathrm{max,nm}}$ (ε/M^{-1} cm^{-1} per Mo), are 1020 (21), 667 (78), 580sh (66) for **1'**. A splitting of the peak (667 nm and 580sh nm) in the visible region of the spectrum of **1'** is conspicuous, while that of **2'** has only one peak at 645 nm in the region. This splitting may be caused by the lowering of symmetry in **1'** through the substitution of one μ_3-O for μ_3-S. Both the reduced species have no peaks in visible and near-infrared region. This is similar to the case of $[Mo_4S_4(edta)_2]^{4-}$ and is approximately explained by the full occupation of the six bonding orbitals of the Mo_4 tetrahedron in **1R'** and **2R'**.[3c)]

Both the cyclic voltammograms of **1'** and **2'** show two quasi-reversible, one-electron waves (Fig. 3).[3c)] Existence of $[Mo_4OS_3(H_2O)_{12}]^{6+/5+/4+}$ and $[Mo_4S_4(H_2O)_{12}]^{6+/5+/4+}$ is evident. Addition of iron alum to **1R'** (Fe^{3+}/Mo_4 = 1) gives **1'**, which also supports the argument discussed above. The peak positions shift slightly towards negative side by the substitution of one μ_3-O for μ_3-S.

While the reaction of incomplete cubane-type aqua ion, $Mo_3S_4(aq)^{4+}$ (**4'**), with iron metal gives the cubane-type mixed-metal aqua ion, $Mo_3FeS_4(aq)^{4+}$,[9)] the reaction of **3'** with iron metal does not give such a mixed-metal complex as $Mo_3FeOS_3(aq)^{4+}$ as a main product, but

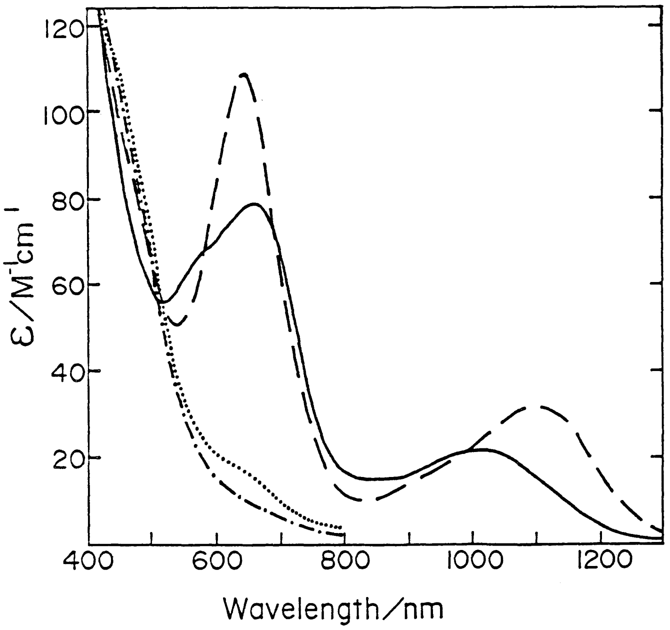


Fig. 2. Electronic spectra in 2 M HPTS.

———— $[Mo_4OS_3(H_2O)_{12}]^{5+}$ (**1'**)
— - — - — $[Mo_4OS_3(H_2O)_{12}]^{4+}$ (**1R'**)
— — — — $[Mo_4S_4(H_2O)_{12}]^{5+}$ (**2'**)
·········· $[Mo_4S_4(H_2O)_{12}]^{4+}$ (**2R'**)

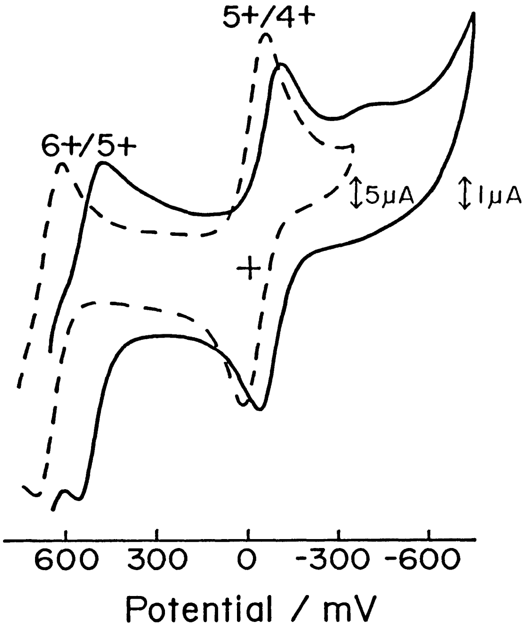


Fig. 3. Cyclic Voltammograms in 2 M HPTS at a glassy carbon electrode; scan rate, 100 mV/s; reference electrode, SCE.

———— $[Mo_4OS_3(H_2O)_{12}]^{5+}$ (3.0 mM)
— — — — $[Mo_4S_4(H_2O)_{12}]^{5+}$ (68 mM)

gives **1'**, though small amounts of unidentified mixed metal complexes may be present. Besides, though the aqua ion **4'** reacts with Hg to give $Mo_3HgS_4(aq)^{4+}$,[10] the aqua ion **3'** does not.

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7) The two structures are isomorphous. Crystal data: **1**; triclinic system, space group $P\bar{1}$, a = 16.309(4) Å, b = 16.691(5) Å, c = 13.187(4) Å, α = 91.34(2)°, β = 99.28(2)°, γ = 89.20(2)°, V = 3541.6(16) $Å^3$, Z = 2, D_c = 1.709 g cm^{-3}, D_m = 1.70 g cm^{-3}, $2\theta_{max}$ = 48°, R = 0.0494 for 6975 reflections ($F_o \geq 6\sigma(F_o)$). **2**; triclinic system, space group $P\bar{1}$, a = 16.351(5) Å, b = 16.713(4) Å, c = 13.108(4) Å, α = 91.05(3)°, β = 98.73(3)°, γ = 89.37(3)°, V = 3540.0(16) $Å^3$, Z = 2, D_c = 1.723 g cm^{-3}, D_m = 1.71 g cm^{-3}, $2\theta_{max}$ = 45°, R = 0.0406 for 6898 reflections ($F_o \geq 6\sigma(F_o)$). Intensity data were collected and structures were solved for both crystals as described in Ref. 1. Lists of atomic coordinates, thermal parameters, bond distances and bond angles for **1** and **2** can be obtained from the author (T. S.) on request.
8) Assignment of the occupancy factors of 0.5, 0.833 (= 1- 0.5/3), 0.833, 0.833, and 0.5 to the μ_3-O, S1, S2, S3, and the disclosed μ_3-S, respectively, followed by least-squares calculations gave reasonable isotropic temperature factors for these bridging atoms. Any μ_3-O's could not be found near S1, S2, and S3 atoms.
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