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INCOMPLETE CUBANE-TYPE SULFUR-CAPPED $Mo_3OS_3{}^{4+}$ AQUA ION AND X-RAY STRUCTURE ANALYSIS OF $Ba[Mo_3OS_3(HN(CH_2CO_2)_2)_3]\cdot 7H_2O$

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A molybdenum(IV) aqua ion with sulfur bridges, $Mo_3OS_3{}^{4+}$, has been prepared and characterized. An X-ray structure analysis of the iminodiacetato complex prepared from the aqua ion has revealed the core structure of $Mo_3(\mu\text{-}O)(\mu\text{-}S)_2(\mu_3\text{-}S)$.

Extensive studies on the molybdenum(IV) aqua ion, $Mo_3O_4{}^{4+}$, have been reported.1) Several molybdenum(IV) aqua ions2) with sulfur bridge(s), e.g., $Mo_3O_3S^{4+}$,3) $Mo_3O_2S_2{}^{4+}$,4) and $Mo_3S_4{}^{4+}$ 5) are also known. X-Ray structure analyses of the complexes derived from these aqua ions and appropriate ligands have revealed the presence of incomplete cubane-type core structures.1,3,4,5a,5b)

We describe here the preparation and characterization of the $Mo_3OS_3{}^{4+}$ aqua ion and the X-ray structure of $Ba[Mo_3OS_3(ida)_3]\cdot 7H_2O$ (H_2ida = iminodiacetic acid) having the Mo_3OS_3 core.

Di-μ-sulfido cysteinato Mo(V) dimer, $[Mo_2O_2S_2(cys)_2]^{2-}$ 6) was reduced with $NaBH_4$ in diluted HCl (0.03 M; 1 M = 1 mol dm^{-3}). Following the addition of concentrated HCl, air was passed through the resultant brown solution to give a dark green-colored one, which was separated into four greenish bands by Sephadex G-10 column chromatography. The species in the third band was purified by Dowex 50W-X2 cation exchanger.7) The species in 2 M HCl was analyzed to give S/Mo ratio of 1.00 ± 0.03 (four determinations). An HPTS (p-toluenesulfonic acid) solution of the species was obtained as described elsewhere.3) Observation of S/Mo ratio and estimation of 4+ charge,8) as well as comparison of absorption maxima of $Mo_3O_nS_{4-n}{}^{4+}$ (n = 0–4) aqua ions in a region of 500–600 nm or so (vide infra), suggested that the species is $Mo_3OS_3{}^{4+}$ aqua ion. The aqua ion is stable toward air oxidation.

Two different core structures of the aqua ion are possible; $Mo_3(\mu\text{-}O)(\mu\text{-}S)_2(\mu_3\text{-}S)^{4+}$ and $Mo_3(\mu\text{-}S)_3(\mu_3\text{-}O)^{4+}$. In order to determine the structure, $Ba[Mo_3OS_3(ida)_3]\cdot 7H_2O$ was prepared from the aqua ion and H_2ida,9) and its X-ray structure analysis was performed.10)

A perspective view of the $[Mo_3OS_3(ida)_3]^{2-}$ anion is shown in Fig. 1 together with the selected bond distances. The complex anion has an incomplete cubane-type core structure of $Mo_3(\mu\text{-}O)(\mu\text{-}S)_2(\mu_3\text{-}S)$. Two nitrogen atoms occupy the δ position11) and the other nitrogen atom resides in the γ position, while all the nitrogen atoms occupy the δ position in the related complexes, $[Mo_3S_4(Hnta)_2(nta)]^{3-}$ 5a) (H_3nta = nitrilotriacetic acid), $[Mo_3S_4(ida)_3]^{2-}$, 5b) $[Mo_3O_3S(Hnta)_3]^{2-}$, 3) $[Mo_3O_4(mida)_3]^{2-}$ 12) (H_2mida = methyliminodiacetic acid), and $[Mo_6O_8(edta)_3]^{4-}$. 11) The Mo–Mo bond bridged by μ-O (Mo1–Mo2) is distinctly shorter than those bridged by μ-S (Mo1–Mo3 and Mo2–Mo3) and longer than those (av. 2.589 Å) in $[Mo_3O_3S(Hnta)_3]^{2-}$. The Mo–Mo bond bridged by μ-S is shorter than those (av. 2.754 Å) in $[Mo_3S_4(ida)_3]^{2-}$.

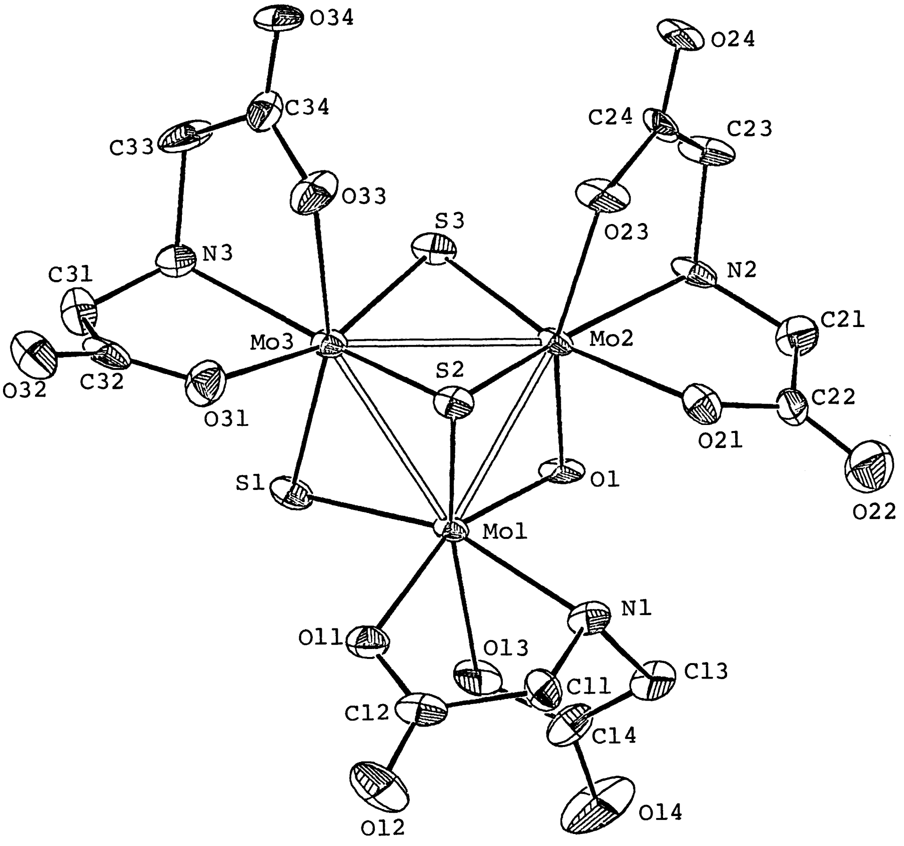

Fig. 1. Perspective view of $[Mo_3OS_3(ida)_3]^{2-}$. Bond distances/Å: Mo1–Mo2, 2.612(2); Mo1–Mo3; 2.716(2); Mo2–Mo3, 2.733(2); Mo1–S2, 2.361(4); Mo2–S2, 2.358(4); Mo3–S2, 2.336(4); Mo1–S1, 2.298(5); Mo3–S1, 2.317(5); Mo2–S3, 2.294(5); Mo3–S3, 2.325(5); Mo1–O1, 1.938(11); Mo2–O1, 1.949(11); Mo1–N1, 2.256(13); Mo2–N2, 2.233(13); Mo3–N3, 2.259(14); Mo1–O11, 2.106(11); Mo1–O13, 2.163(12); Mo2–O21, 2.141(11); Mo2–O23, 2.120(11); Mo3–O31, 2.096(12); Mo3–O33, 2.154(11).

The electronic spectrum of the aqua ion is shown in Fig. 2 together with that of the iminodiacetato complex. The peak positions of the aqua ion shift on the whole toward longer wavelength on the coordination of iminodiacetate anion.

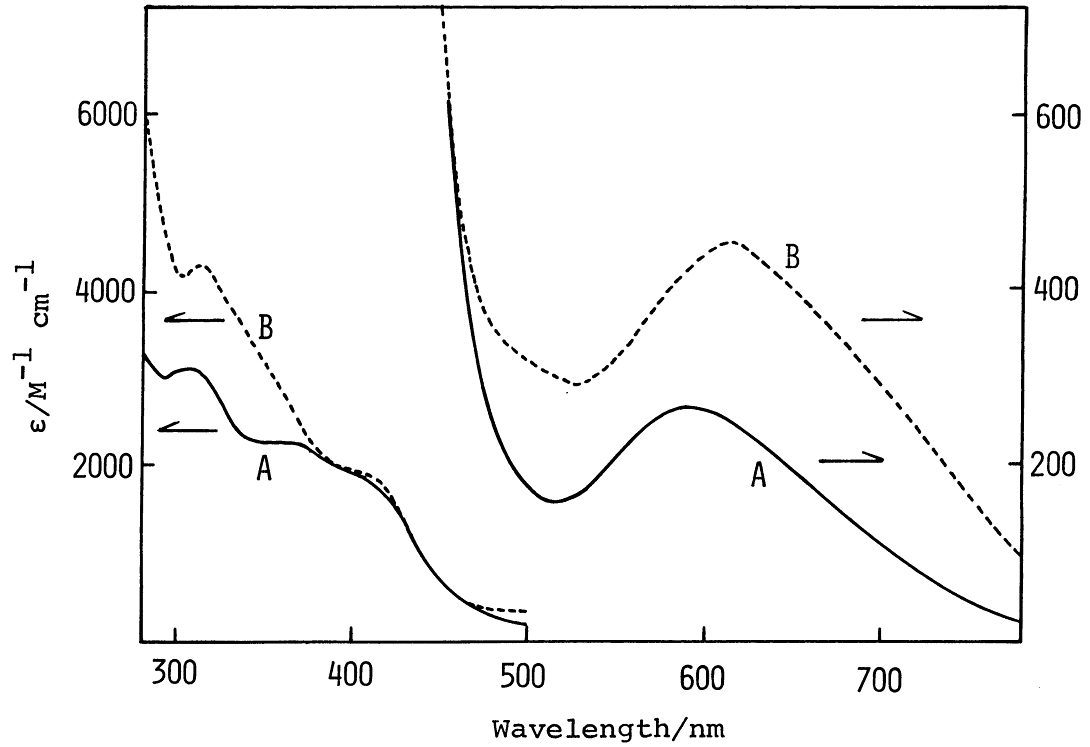

Fig. 2. Electronic spectra.

A) $Mo_3OS_3^{4+}$ in 2 M HPTS,

B) $[Mo_3OS_3(ida)_3]^{2-}$ in water,

Furthermore, it can be noted that the peak position shows also red-shift as substitution of sulfur(s) for oxygen(s) takes place in a series of $Mo_3O_4^{4+}$ aqua ion (505 nm, ε = 189 M^{-1} cm^{-1} per trimer),[13] $Mo_3O_3S^{4+}$ (512 nm, ε = 153),[3] $Mo_3O_2S_2^{4+}$ (572 nm, ε = 202),[4] $Mo_3OS_3^{4+}$ (588 nm, ε = 263; this work), and $Mo_3S_4^{4+}$ (602 nm, ε = 351).[5a,b]

Electrochemical and other studies of the present and related compounds are in progress.

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2) Strictly speaking, the term "aqua ion" may not be adequate for species containing sulfur atom(s). The term aqua ion, however, is used here for species in which bridging sulfur and oxygen atom(s) exist and other ligands are only water.

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7) The first, second, and fourth bands contain $Mo_4S_4^{5+}$, $Mo_3O_2S_2^{4+}$, and $Mo_3S_4^{4+}$ aqua ions, respectively.

8) The charge of the ion was estimated to be 4+ on the basis of its behavior similar to those of $Mo_3O_4^{4+}$ and $Mo_3S_4^{4+}$ aqua ions.

9) Iminodiacetic acid (mole ratio, H_2ida/Mo $\approx$ 10) in KOH was added to the $Mo_3OS_3^{4+}$ in 2 M HCl. After the pH adjustment to ca. 6 by KOH, the solution was absorbed on Dowex 1-X2 anion exchanger, from which dark green crystals were obtained by use of 0.25 M and 0.5 M $BaCl_2$ solution as eluent. Anal. Found (calcd): N, 3.98(3.98); C, 13.65(13.64); H, 2.71(2.76)%.

10) Crystal data: formula weight = 1056.59, triclinic system, space group $P\bar{1}$, a = 11.986(1) Å, b = 12.097(2) Å, c = 11.066(2) Å, α = 107.19(1)°, β = 105.60(1)°, γ = 87.39(1)°, V = 1475.0(4) Å^3, Z = 2, Dc = 2.379 g cm^{-3}. Intensity data were collected on a Rigaku AFC-6A four-circle diffractometer by use of graphite-monochromated Mo Kα radiation on the $2\theta \leq 50°$ range. The coordinates of Mo's and S's were determined by means of MULTAN and the remaining nonhydrogen atoms were located from difference Fourier maps. The current R value is 0.0626 for 5209 reflections ($Fo \geq 3\sigma(Fo)$). A list of atomic coordinates and thermal parameters can be obtained from the author (T. S.) on request.

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