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Preparation of the Incomplete Cubane-type Sulfur-capped $Mo_3O_2S_2^{4+}$ Aqua Ion and X-ray Structure of $(pyH)_5[Mo_3O_2S_2(NCS)_9]\cdot 2H_2O$

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Much attention has been paid to the trinuclear Mo(IV) aqua ions with and without sulfur bridge(s). The incomplete cubane-type structures of cores of $Mo_3O_4^{4+}$ [1], $Mo_3O_3S^{4+}$ [2], $Mo_3OS_3^{4+}$ [3], and $Mo_3S_4^{4+}$ [4] aqua ions have been confirmed by X-ray structure analyses of complexes derived from these aqua ions and appropriate ligands. We describe here the preparation and characterization of another trimeric complex in this series, the sulfur-capped $Mo_3O_2S_2^{4+}$ aqua ion, and the X-ray structure analysis of a derivative complex $(pyH)_5[Mo_3O_2S_2(NCS)_9]\cdot 2H_2O$.

Two methods have been employed for the preparation of the $Mo_3O_2S_2^{4+}$ aqua ion. Method A (in Okayama): The di-μ-sulfido cysteinato Mo(V) dimer, $[Mo_2O_2S_2(cys)_2]^{2-}$ (2 g in diluted HCl (0.03 M, 200 ml)) [5] was reduced with $NaBH_4$ (1 g); then concentrated HCl (30 ml) was added. The resultant brown solution turned to dark green as a result of air oxidation by heating on a water bath (7 h at 90 °C). The second band (greyish green)**, obtained from a Sephadex G-10 column separation (elution with 1 M HCl), was purified on a Dowex 50W-X2 cation exchange column (1 M HCl). A more concentrated solution was obtained by loading the 1 M HCl solution onto a cation exchanger and eluting with 2 M HCl. The product in 2 M HCl was analysed to give S/Mo ratio of 0.67 ± 0.03 (four determinations), which is consistent with a molecular formula of $Mo_3O_2S_2^{4+}$. The grey violet aqua ion in 2 M HPTS was obtained by absorption of the aqua ion in HCl on the cation exchanger followed by elution with 2 M HPTS. Method B (in Newcastle-upon-Tyne): A mixture of Mo(V) aqua dimer, $Mo_2O_2S_2^{2+}$ (4×10^{-3} M) [5], and $K_3[MoCl_6]$ in 2 M HPTS (1:2 mole ratio) was heated for 1 h at 80–90 °C under N_2 atmosphere. After being diluted to 0.5 M HPTS and kept overnight, the solution was purified by the use of the cation exchanger (2 M HPTS). More recently, an electrolytic method of preparation which yield the same product has been described [6]. The solution in 2 M HPTS is much more stable toward air oxidation than $Mo_3O_4^{4+}$. When stored under N_2 atmosphere, the spectrum is unchanged over more than four weeks.

Two different core structures of the aqua ion are possible: one has μ_3-S and the other μ_3-O. In order to confirm the incomplete cubane-type core structure and to ascertain which isomer is present, $(pyH)_5[Mo_3O_2S_2(NCS)_9]\cdot 2H_2O$ was prepared and the structure determined by X-ray structure analysis. The procedure involved addition of solid KSCN (10 g) to the aqua ion in 0.2 M HCl (50 ml, 7×10^{-3} M). The solution was heated at *ca.* 60 °C for 30 min and was allowed to stand overnight at room temperature. After pyridine (0.7 ml) was added dropwise, the solution was kept at room temperature for a couple of days, when greenish-brown needle shape crystals were obtained. *Anal.* Found (Calc.): N, 14.58(14.63); C, 29.95(30.47); H, 2.28(2.56)%.

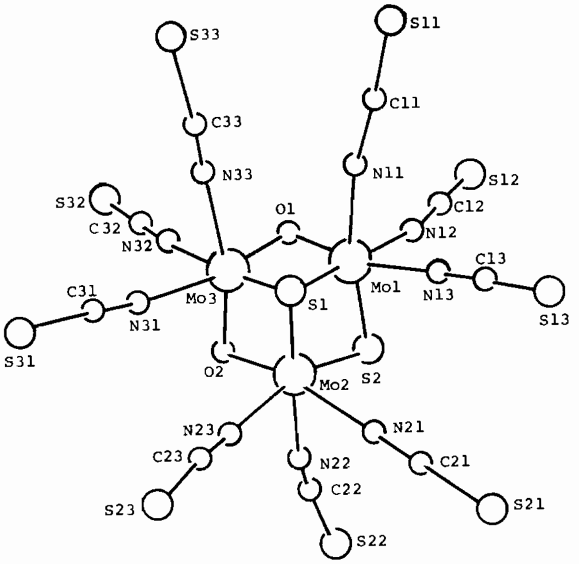

Fig. 1. Perspective view of $[Mo_3O_2S_2(NCS)_9]^{5-}$. Bond distances (Å): Mo1–Mo2, 2.715(4); Mo1–Mo3, 2.635(3); Mo2–Mo3, 2.635(4); Mo1–S1, 2.300(10); Mo2–S1, 2.320(10); Mo3–S1, 2.340(10); Mo1–S2, 2.258(7); Mo1–O1, 1.953(22); Mo2–S2, 2.255(8); Mo2–O2, 1.956(15); Mo3–O1, 1.956(22); Mo3–O2, 1.913(14).

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**The first, third, and fourth bands contain $Mo_4S_4^{5+}$, $Mo_3OS_3^{4+}$, and $Mo_3S_4^{4+}$ aqua ions, respectively.

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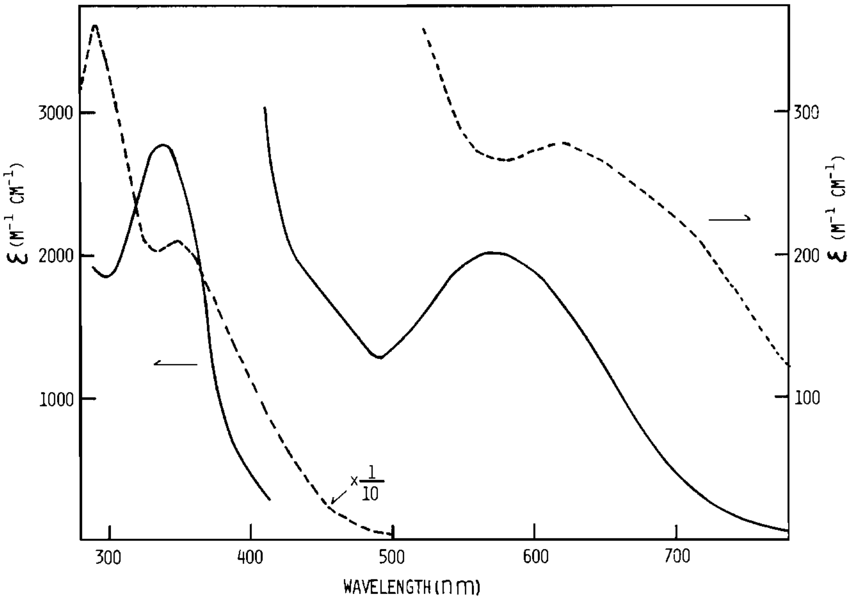

Fig. 2. Electronic spectra of trinuclear Mo(IV) ions. ε values are per trimer; (a) $Mo_3O_2S_2^{4+}$ in 2 M HPTS ———; (b) $[Mo_3O_2S_2(NCS)_9]^{5-}$ in 1 M KSCN – – –.

The compound crystallizes in monoclinic system, space group $P2_1$ with cell dimensions $a = 22.320(7)$, $b = 13.110(2)$, $c = 9.103(3)$ Å, $\beta = 95.57(3)^\circ$, $V = 2651(1)$ Å^3, $Z = 2$. Intensity data were collected on an automated four-circle diffractometer, RIGAKU AFC-6A, by the use of graphite-monochromated Mo Kα radiation in the $2\theta \leq 50^\circ$ range. The coordinates of three molybdenums were determined by means of MULTAN, and the remaining nonhydrogen atoms were located from Fourier maps. The current R value is 0.078 for 3887 reflections ($F_o \geq 3\sigma(F_o)$). A list of atomic coordinates and thermal parameters are available (see 'Supplementary Material').

A perspective view of $[Mo_3O_2S_2(NCS)_9]^{5-}$ is shown in Fig. 1, together with selected bond distances. The incomplete cubane-type $Mo_3O_2S_2$ core structure has been confirmed and the existence of the isomer with a μ_3-S ligand demonstrated. The NCS^- ions are all N-bonded, as has been demonstrated for $[Mo_3O_4(NCS)_8(H_2O)]^{4-}$ [1e]. The core structure is distorted: the Mo–Mo distance with μ_2-O (Mo1–Mo3 and Mo2–Mo3) is shorter than that with μ_2-S (Mo1–Mo2). The mean value (2.320 Å) of the Mo–μ_3-S distance is slightly shorter than those of $[Mo_3O_3S(Hnta)_3]^{2-}$ (2.360 Å) [2], $[Mo_3OS_3(ida)_3]^{2-}$ (2.352 Å) [3], $[Mo_3S_4(Hnta)_2(nta)]^{3-}$ (2.339 Å) [4a], $[Mo_3S_4(Hnta)_2(nta)]^{3-}$ (2.344 Å) [7]*, $[Mo_3S_4(ida)_3]^{2-}$ (2.349 Å) [4b], $[Mo_3S_4(SCH_2CH_2S)_3]^{2-}$ (2.35 Å) [8], and $[Mo_3S_4(CN)_9]^{5-}$ (2.363 Å) [9], and is similar to that of $[Mo_3S_4(h_5\text{-}C_5H_5)_3]^+$ (2.314 Å) [10].

The electronic spectrum of the aqua ion is shown in Fig. 2, together with that of the thiocyanato complex. The peak position of the aqua ion (572 nm; $\epsilon = 202$ M^{-1} cm^{-1} per trimer) in the visible region is situated between those of $Mo_3O_3S^{4+}$ (512 nm; $\epsilon = 153$) and $Mo_3OS_3^{4+}$ (588 nm; $\epsilon = 263$) aqua ions.

Electrochemical experiments have indicated that it is possible to reduce the $Mo(IV)_3$ ion to the $Mo(III)_3$ state. Intermediate formation of Mo(III,III,IV) is indicated, as with the analogous $Mo_3O_4^{4+}$ ion [11]. Reduction potentials of −172 mV (2e) and −232 mV (1e) *vs.* NHE are indicated for the two processes.

The results of kinetic studies will be reported elsewhere.

Supplementary Material

Atomic coordinates and thermal parameters; available from author T.S. on request.

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*Counter ion is NH_4^+ in this case, while that of ref. 4a is Ca^{2+}.

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