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CUBANE-TYPE CLUSTER $[Mo_4S_4(NH_3)_{12}]Cl_4 \cdot 7H_2O$

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Ammonia-coordinated cubane-type cluster complex $[Mo_4S_4(NH_3)_{12}]Cl_4 \cdot 7H_2O$ has been prepared from $[Mo_4S_4(H_2O)_{12}]^{5+}$ and ammonia and the remarkably long $Mo-NH_3$ distance of 2.34 Å (av.) disclosed by X-ray structure analysis.

The chemistry of dinitrogen complexes of molybdenum, including X-ray structure determination, has been studied extensively to understand the chemistry of nitrogen-fixing system, and it is known that ammonia can be liberated from some of the complexes by the action of acids.1) No report, however, has appeared on the X-ray structure determination of molybdenum complexes with ammonia as a ligand,2) some of the preparation and properties being described.3)

We describe here the preparation, properties and X-ray structure determination of the first example of ammonia-coordinated cubane-type Mo_4S_4 cluster, $[Mo_4S_4(NH_3)_{12}]Cl_4 \cdot 7H_2O$ (**1**).

Concentrated ammonia water (20 cm^3) was added with stirring to the aqua ion $[Mo_4S_4(H_2O)_{12}]^{5+}$ (**2**)(0.05 mol dm^{-3}, 20 cm^3)4) in 2 M HCl which had been cooled with ice water under dinitrogen atmosphere. The solution was filtered and the filtrate was allowed to stand for a few days at room temperature. Orange crystals were obtained by filtration. Found(calcd for **1**): N, 17.39(17.07); H, 4.75(5.11)%. Yield 38% on Mo. The color of the crystals turns green on the exposure to the air. Dissolution of the crystals in acids gives **2**.

The compound crystallizes in triclinic system, space group $P\bar{1}$ with cell dimensions a = 10.503(3) Å, b = 17.431(4) Å, c = 9.934(3) Å, α = 96.55(3)°, β = 116.25(2)°, γ = 83.01(3)°, V = 1605.6(9) $Å^3$, Z = 2. The current R value is 0.0706 for 5793 reflections ($Fo \geq 3\sigma(Fo)$).5) A perspective view of **1** is shown in Fig. 1 together with selected bond distances. The presence of cubane-type Mo_4S_4 core has been confirmed. The Mo_4 tetrahedron has an approximate symmetry of S_4, the Mo—Mo bond distances being distributed in a relatively narrow range (2.783—2.802 Å), and every molybdenum has an average oxidation state of 3.00. Neither $[Mo_4S_4(edta)_2]^{n-}$ nor $[Mo_4S_4(H_2O)_{12}]^{m+}$ shows absorption peaks in the visible region, when their mean oxidation state of molybdenum is 3.00 (n = 4, m = 4).6) The electronic spectrum of **1** in concentrated ammonia-water has no absorption peak in visible region which supports the assignment of oxidation state of 3.00. The volume (2.576(10) $Å^3$) of Mo_4 in **1** lies between those of $[Mo_4S_4(edta)_2]^{4-}$ (2.540(5)

Å^3) and $[Mo_4S_4(edta)_2]^{3-}$ (2.601(6) Å^3). The average Mo—N distance in **1** is longer than the other metal—nitrogen (NH_3) distances (e.g., $[Ru_2(NH_3)_{10}N_2]^{4+}$ (2.12 Å)).$^{7)}$

Bond distances/Å:

Mo1—Mo2, 2.802(3);
Mo1—Mo3, 2.799(3);
Mo1—Mo4, 2.800(3);
Mo2—Mo3, 2.798(3);
Mo2—Mo4, 2.783(3);
Mo3—Mo4, 2.798(3);
Mo—S, 2.361 - 2.379 (av. 2.37);
Mo—N, 2.313 - 2.360 (av. 2.34).

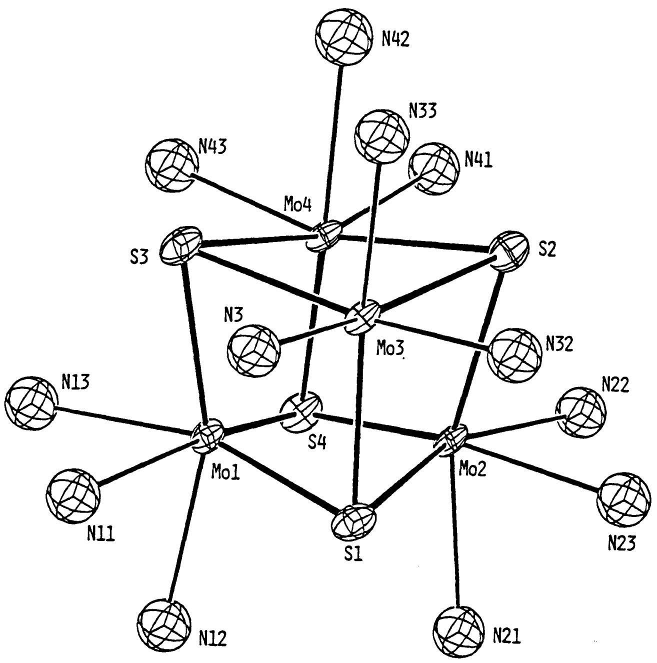

Fig. 1. Perspective view of $[Mo_4S_4(NH_3)_{12}]^{4+}$.

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