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Structure of Tetraammonium Octamolybdobis(diaquacuprate(II)) Hexahydrate

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A novel type of heteropolymolybdate containing Cu(II) was obtained and its crystal structure was determined by X-ray diffraction method. In the structure, two CuO_6 octahedra connect two adjacent Mo_8O_{28} units by corner-sharing to form an infinite chain. The CuO_6 prolates along the chain. The axial Cu-O distances and equatrial ones are ca. 2.5 and 2.0 Å respectively, which shows a Jahn-Teller distortion.

Concerning heteropolymolybdate of Cu(II), only $(NH_4)_4[H_6CuMo_6O_{24}].5H_2O$ was prepared from the NH_4^+-Cu^{2+}-MoO_4^{2-} system.[1,2] Recently we obtained a novel heteropolymolybdate with the ratio Cu/Mo=1/4 from this system. Here we report its crystal structure determined by X-ray diffraction method.

The typical preparative procedure is; a 2.65 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ was dissolved in 50 cm^3 of H_2O. An aqueous solution of $CuSO_4.5H_2O$ (0.62 g/10 cm^3) was added to the molybdate solution dropwise under stirring. The pH of the solution was adjusted to 3.5 with conc. H_2SO_4. Parallelepiped crystals formed from the solution kept at 10 °C for two weeks.[3] The blue color of this compound is deeper than that of hexamolybdocuprate(II). The crystal data for $(NH_4)_4[Cu_2Mo_8O_{28}(H_2O)_4].6H_2O$ are as follows: FW=1594.90, triclinic, $P\bar{1}$, a=10.384(6), b=11.014(8), c=8.791(6) Å, α=116.06(5), β=78.39(6), γ=107.34(6)°, V=859(1) $Å^3$, Z=1, Dm=3.06, Dx=3.08 g cm^{-3}, μ(Mo Kα)=40.92 cm^{-1}. Of total 4280 reflections measured by Mo Kα radiation ($4<2\theta<55°$), independent 3159 ones with $Fo>3\sigma(Fo)$ were used for calculation.[4] The positions of Mo atoms were determined from Patterson function. Remaining non H atoms were located by successive Fourier syntheses. Refinement with anisotropic thermal parameters for all atoms by the block-diagonal least-squares led to an R of 0.050.

The structure of $(NH_4)_4[Cu_2Mo_8O_{28}(H_2O)_4].6H_2O$ is shown in Fig. 1. There are two CuO_6 octahedra and eight MoO_6 octahedra in the unit cell. The eight octahedra form a centrosymmetric Mo_8O_{28} unit by sharing edges.[5] The CuO_6 octahedra connect the Mo_8O_{28} moieties by corner-sharing to form an infinite chain along the a axis. The CuO_6 octahedron shows a Jahn-Teller distortion. The axial Cu-O bonds are almost parallel to the chain and are about 0.5 Å longer than the equatrial ones. The Mo-O-Mo linkages are considerably asymmetric and each MoO_6 octahedron is very

irregular. Three of the four central Mo atoms are displaced toward outer edges of the octahedra. On the other hand, Mo(4) shifts toward an outer face of the MoO_6, where the bond valences[6] of three Mo-O bonds are greater than 1.4. It is not very common that a Mo atom in polymolybdates has three or more multiple Mo-O bonds.[7]

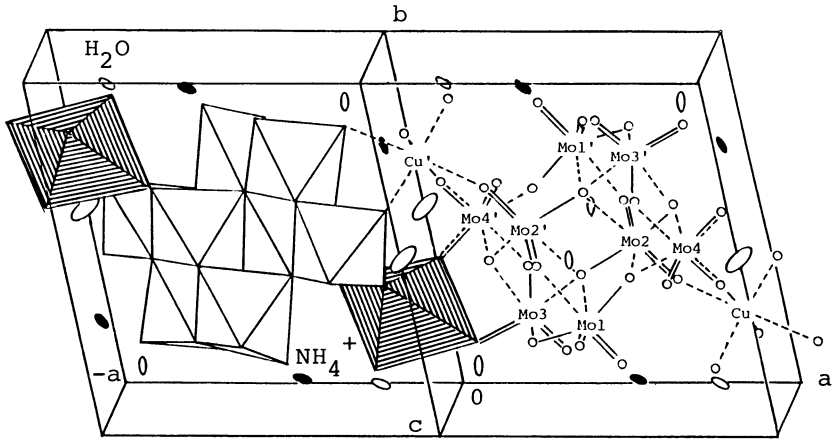

Fig. 1. Two adjacent cells along the a axis. Coordination polyhedra and bond valences are illustrated. Bond valences are classified into four groups. Their ranges are 0.0-0.5 (--), 0.5-1.0 (—), 1.0-1.5 (=) and 1.5-2.0 (=).

Table 1. Bond distances of Cu-O (Å)

$Cu-O_{ax}(1)$	2.478(9)
$Cu-O_{ax}(2)$	2.554(9)
$Cu-O_{eq}(1)$	1.927(6)
$Cu-O_{eq}(2)$	1.930(6)
$Cu-O_{eq}(3)(H_2O)$	1.986(6)
$Cu-O_{eq}(4)(H_2O)$	1.990(7)

References

1) Gmelins Handbuch der Anorganischen Chemie, 8. Aufl., 53, p.393 (1935).
2) The investigation of hexamolybdocuprate(II) is in progress.
3) Our experiments have indicated that the formation of different species (2:8 or 1:6) is governed only by temperature.
4) The calculation was carried out with UNICS-III program on a HITAC M-680H/682H computer at the Computer Centre of the University of Tokyo.
5) There are ten examples of analogous octameric structures. See for example: P.K. Bharadwaj, Y. Ohashi, Y. Sasada, Y. Sasaki, and T. Yamase, Acta Crystallogr., Sect. C, 42, 545 (1986).
6) I.D. Brown and K.K. Wu, Acta Crystallogr., Sect. B, 32, 1957 (1976).
7) W.N. Lipscomb, Inorg. Chem., 4, 132 (1965).

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