A Molybdenum Polynuclear Complex as Small Metallic Particles

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Synopsis. The crystal structure of $(H_3O)_2[(Mo_6Cl_8)Cl_6]\cdot 6H_2O$ was determined by the X-ray method and its near-infrared absorption spectra were measured. These results can be interpreted by a view that the molybdenum nuclei of this complex are regarded as a small metallic particle.

The energy levels of conduction electrons in metal are generally regarded as continuous. However, in small metallic particles, the intervals of the energy levels are no longer small in comparison with other energies such as the thermal energy, kT and the electronic Zeeman energy, μH. It has been theoretically predicted[1] that anomalies occur in the macroscopic properties of small metallic particles, such as the electron heat capacity and the spin paramagnetic susceptibility, due to the restriction of the excitations of conduction electrons.

Some experiments have been recently performed[2] in order to detect these kinds of anomalies. The samples used in these experiments were small metallic particles prepared by the gas evaporation method and other techniques, the average diameters of which were 40—200 Å. With regard to such samples, size and shape of each particle were inhomogeneous, and only the average properties of all particles were measurable. Then the authors paied their attention to a polynuclear complex $(H_3O)_2[(Mo_6Cl_8)Cl_6]\cdot 6H_2O$ as the sample of this kind. They thought that the molybdenum nuclei of this complex could be regarded as a small metallic particle homogeneous in both size and shape, and some anomalies as small metallic particles would be detectable. In the present paper, the X-ray structure analysis and the near-infrared absorption spectra measurement for $(H_3O)_2[(Mo_6Cl_8)Cl_6]\cdot 6H_2O$ crystal are reported.

Experimental and Structure Determination

The sample was prepared by the method of Sheldon modified by Jolly.[3] Single crystals were obtained from the 6 mol dm^{-3} HCl solution by evaporating the solvent slowly. For the X-ray experiment a single crystal enclosed in a glass capillary with its mother liquor was used to prevent its efflorescence. Intensity data were collected on the Weissenberg camera with Ni-filtered Cu $K\alpha$ radiation. Crystal data are: Monoclinic, $a=17.27(11)$, $b=9.17(6)$, $c=18.55(12)$ Å, $\beta=98.0(7)°$, $Z=4$, and space group C2/c. The structure factors for 865 independent reflections were obtained. The structure was solved by the heavy atom method, refined by the full-matrix least-squares method, and the final R factor was 0.117. The positions of H atoms could not be determined. The near-infrared absorption spectra were measured on a Varian Cary 17-I spectrophotometer at 77 K and room temperature. In the measurement a quartz Dewer vessel was used. The measured data were corrected for the blank data measured in the absence of the sample.

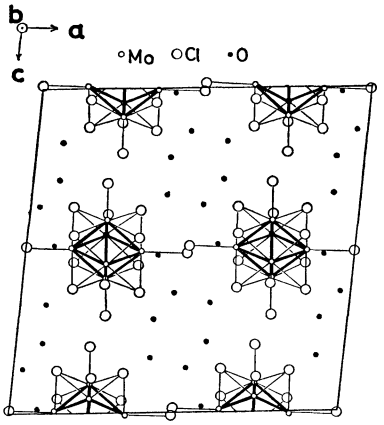

Fig. 1. The crystal structure of $(H_3O)_2[(Mo_6Cl_8)Cl_6]\cdot 6H_2O$ viewed along the b axis.

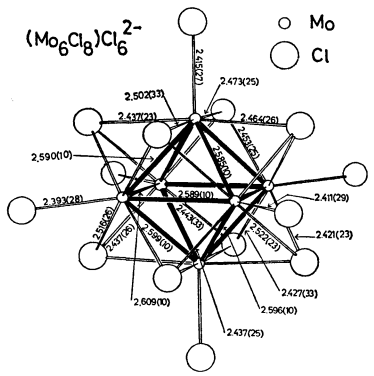

Fig. 2. $(Mo_6Cl_8)Cl_6^{2-}$ unit with the bond lengths(Å). There is an inversion center at the center of this unit. The estimated standard deviations are in parentheses.

Results and Discussion

The atomic parameters are deposited as Document No. 8212 at the Office of the Editor of the Bulletin of the Chemical Society of Japan, and Fig. 1 shows the crystal structure viewed along the b axis. The structure consists of the discrete units of $(Mo_6Cl_8)Cl_6^{2-}$ (shown in Fig. 2). In this unit, six Mo atoms form an approximate regular octahedron, and their configuration is very similar to that in bulk Mo metal, *i.e.*, b.c.c.structure. However, the distance between the neighboring Mo atoms (2.59 Å on the average) is shorter than in bulk Mo metal (2.72 Å), in other words, the Mo atoms are packed closer so that the overlap of the Mo atomic orbitals is large in this unit.

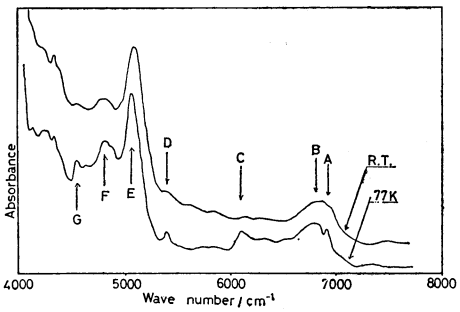

Fig. 3. The near-infrared absorption spectra of $(H_3O)_2[(Mo_6Cl_8)Cl_6]\cdot 6H_2O$ crystal at 77 K and room temperature.

Also eight Cl atoms form an approximate cube outside the Mo octahedron. The distance between Mo atoms and these 8 Cl atoms (2.46 Å on the average) agrees with the sum of the ion radii of sexivalent Mo^{6+} (0.62 Å) and Cl^- (1.81 Å), in contrast with that the Mo atoms are formally divalent in this material. Hence, the valence electrons of Mo atoms may be delocalized. These facts suggest that the feature of metallic bonding is still present even in such a small quasi-metallic system. In addition, these units are apart from one another in the crystal. It is quite possible to regard the crystalline state of this material as an aggregation of small metallic particles which are homogeneous in both size and shape.

Then the authors tried to estimate the order of the energy level interval of conduction electrons at the Fermi energy(δ), by regarding the 24 d-electrons of Mo atoms as conduction electrons and by applying the free electron model to this system. The formula $\delta=2\varepsilon_F/3N$ (ε_F: Fermi energy, N: number of electrons), which is applicable to a cube of bulk metal, was used in this estimation. The obtained order of energy level interval (about 1.0×10^{-19} $J=5.0\times10^3$ cm^{-1}) corresponded to the photon energy of the near-infrared region. Figure 3 shows the near-infrared absorption spectra measured for this crystal. The seven peaks observed are divided into two groups on the basis of their behaviors against temperature, *i.e.*, the A, C, D, F, and G peaks become broader at room temperature, while the B and E peaks do not show such temperature dependence. The latter peaks were ascertained to be attributable to the vibrational overtones of the water of crystallization. On the other hand, it is not adequate to attribute the former peaks to the molecular or lattice vibration of $(Mo_6Cl_8)Cl_6^{2-}$ unit, considering the heavy masses of the atoms which constitute this unit. In fact, the absorptions which arise from such vibrations were found in the far-infrared region.[4] Therefore, the peaks, except for B and E, should be related to various electronic transitions, where electronic levels split by low symmetry of the crystal may be involved. Also their peak positions fall satisfactorily within the range estimated above, though it remains a question that the valence electrons of molybdenum atoms in this case are assumed as free electrons. Then it is concluded that these absorption peaks may be attributed to the electronic transitions between the energy levels of conduction electrons which manifest the smallness of the system. From the standpoint of small metallic particles, the observation of such transitions is one of the evidences of energy quantization with respect to conduction electrons.

The basic concept of the authors is to regard the nuclei in a polynuclear complex as a small metallic particle. However, since the nuclei of single complex ion in the present material consist of only six molybdenum atoms, the energy level intervals of electrons are too large and the electronic states may not be well described by the Bloch functions. It is highly desired for the study of small metallic particles to synthesize complex ions which involve more metal atoms.

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