A New Molybdenum Cluster Compound. An X-Ray Investigation

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It was in 1957, when McCarroll, Katz and Ward[1] discovered the presence of an equilateral triangle of molybdenum atoms in the crystal structure of $Zn_2Mo_3O_8$, which was only one representative of a series of isostructural compounds of the general formula $A_2^{II}Mo_3^{IV}O_8$ where A might be Mg, Mn, Fe, Co, Ni, Zn, or Cd. More recently, Ansel and Katz[2] have carried out a refinement on the $Zn_2Mo_3O_8$ structure and the essential structural features of the original proposal of McCarroll, Katz and Ward were found to be correct. After the refinement, the Mo—Mo distance in the triangle was 2.524 ± 0.002 Å.

Compounds of the type $LiM^{III}Mo_3O_8$ (M = Sc, Y, Ga) were also prepared and their structures investigated using X-ray powder diffraction data[3,4]. The positions of the molybdenum atoms were successfully determined, and conformed to the tight triangular groupings previously observed in the $A_2Mo_3O_8$ compounds.

A theoretical calculation for these compounds was carried by Cotton[5] using an LCAO-MO method. The pattern of the molecular orbital energies which was obtained accounted satisfactorily for the strong metal-to-metal bonding and the absence of unpaired electrons.

A general name for such compounds, after Cotton,[6] is »metal atom cluster compounds and they can be formally defined as those containing a finite group of metal atoms which are held together entirely, mainly, or at least to a significant extent, by bonds directly between the metal atoms even though some non-metal atoms may be associated intimately with the cluster«.

A new compound containing the triangular cluster of molybdenum atoms is reported here.

The dark brown crystals of oxo molybdenum acetylacetone with ethanol were prepared by Grdenić and Korpar[7]. On the grounds of its chemical analysis the authors propose the formula $MoO_2(C_5H_8O_2)(C_2H_6O)$. Unfortunately, no suitable solvent is found for molecular weight determination[7]. The present X-ray crystal structure determination has shown that the compound is trimeric, exhibiting a triangular cluster of molybdenum atoms.

Crystallographic Data

The crystals are orthorhombic and only the faces of the {011} prism and of the {100} pinacoid are developed. Almost all crystals are aggregates of two or more intergrown individua with common (or nearly parallel) b or c axes.

The unit cell dimensions determined from oscillation photographs, using CuK_α radiation, are: $a = 19.26$ Å, $b = 7.95$ Å, $c = 18.24$ Å, $V = 2793$ Å^3. The

unit cell contains 12 formula units $MoO_2(C_5H_8O_2)$ (C_2H_6O). The density is determined by a flotation method and amounts to 1.87 g. cm.$^{-3}$ while the calculated value is 1.95 g. cm^{-3}.

The observed reflections are consistent with two space groups $Pnam$-D_{2h}^{16} and $Pna2_1$-C_{2v}^9. The crystal morphology, the absence of a piezoelectric effect and the Patterson projection along [001] confirm the centrosymetric space group.

The positions of the molybdenum atoms were derived from the (001) and (010) Patterson projections. A three dimensional Fourier synthesis was calculated with the signs obtained on the basis of the molybdenum atom contribution. From this synthesis it was possible to confirm the position of the molybdenum atoms and to locate almost all oxygen and carbon atoms[8].

In the structure, eight molybdenum atoms, Mo_1, occupy a general position, 8d ,and the remaining four atoms, Mo_2, a special position, 4c; the coordinates are:

Mo_1	$x = .0.999$	$y = 0.192$	$z = 0.183$	(8d)
Mo_2	$x = 0.086$	$y = 0.024$	$z = 0.250$	(4c)

It follows from these coordinates that there are four triangular groups of tightly bonded molybdenum atoms in the unit cell. Each group is composed of two Mo_1 and one Mo_2 atoms. The triangles are equilateral with their plane normal to the mirror plane. Molybdenum atoms in the triangle are separated by 2.47 Å. This distance is shorter than the molybdenum to molybdenum distance in molybdenum metal itself (2.725 Å) and together with the observed diamagnetism of the compound in question[7], accounts for a metal to metal bond. This characteristic is consistent with Cotton's definition, so we have named it a »metal atom cluster compound«.

The refinement of the structure is now in progress and will be published shorthy.

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IZVOD

Novi molibdenov spoj s nakupinom metalnih atoma — rendgensko strukturno ispitivanje

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Difrakcijom rendgenskih zraka dokazana je prisutnost trokutaste nakupine metalnih atoma u okso molibdenovom acetilacetonatu s etanolom. Udaljenost Mo—Mo unutar trokuta iznosi 2,47 Å, što je kraće od Mo—Mo udaljenosti u metalnom molibdenu (2,725 Å) i dokazuje čvrstu metal—metal vezu.

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