Crystal Structure of Dimethyltin Molybdenum Tetraoxide, $(CH_3)_2SnMoO_4$

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Synopsis. Single-crystal X-ray analysis has shown that the title compound is tetragonal, $P4_2/mbc$, with a= 13.705(2), c=7.271(1) Å. The structure is made of octahedra of *trans*-$Sn(CH_3)_2O_4$ and tetrahedra of MoO_4. These polyhedra share apices to form a three-dimensional structure.

In 1953, Rochow *et al.* reported the synthesis of dimethyltin molybdenum tetraoxide. They treated dimethyltin dichloride with sodium molybdate in aqueous solution, and obtained the compound as a flocculent precipitate.[1] Later, ^{119}Sn Mössbauer spectroscopy of the compound showed that the asymmetry parameter of the tin atom was nearly zero, which indicated the trans-octahedral coordination.[2] Recently we have succeeded in preparing large single crystals of the compound by using isopolymolybdate as the molybdate source, and determined the structure by the single-crystal X-ray analysis.

Experimental

Dimethyltin dichloride (1 g) was added to the aqueous solution of ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (6 g in 60 cm^3 water). Immediately after the addition, pH of the solution decreased to *ca.* 2. After several hours, colorless rectangular crystals of dimethyltin molybdenum tetraoxide $(CH_3)_2SnMoO_4$ were obtained (Found: C, 7.86; H, 2.01%). The largest crystals were *ca.* 10 mm long.

Weissenberg photographs showed that the space group of the crystal was $P4_2/mbc$ (centrosymmetric) or $P4_2bc$ (noncentrosymmetric). The cell parameters were determined by least-squares refinements from 21 reflections ($45°<2\theta<60°$). X-Ray reflection data were collected with a Rigaku automated four-circle diffractometer (crystal, cubic in shape and *ca.* 0.2 mm long; radiation, Mo $K\alpha$ monochromatized by a graphite plate; scan method, ω-2θ, $2\theta\leq 60°$).[3] Intensities of three standard reflections were monitored for every 50 reflections and found to be constant. The structure was solved by the heavy atom method with the space group $P4_2/mbc$, and refined both in $P4_2/mbc$ and $P4_2bc$ by the block-diagonal least-squares method, where 879 independent reflections were used. The function minimized was $\sum w(|F_o|-|F_c|)^2$ where w=0.2 for $|F_o|<10$ and w=1 otherwise. Atomic scattering factors were taken from "International Tables for X-Ray Crystallography" (1974). The refinement in the space group $P4_2bc$ included the anomalous dispersions for heavy atoms. Computations were performed with a local version of *UNICS* at the Computer Center of the University of Tokyo.

The comparision of the results of the refinements in the space group $P4_2/mbc$ and $P4_2bc$ were summarized as follows:

(a) The final R-values were almost equal (0.031 for $P4_2/mbc$ and 0.030 for $P4_2bc$), though the number of parameters in $P4_2/mbc$ is much smaller than in $P4_2bc$ (46 for $P4_2/mbc$ and 73 for $P4_2bc$).

(b) Both refinements yielded substantially the same x and y values. Their standard deviations in $P4_2bc$ were 1—2 times larger than the corresponding values in $P4_2/mbc$.

(c) The standard deviations of the z values were very large in $P4_2bc$ (0.0006 for heavy atoms and 0.0011—0.0082 for light atoms), while in $P4_2/mbc$ they were small or zero due to the crystallographic symmetry. The z values of heavy atoms were significantly different in the two refinements, because the differences were 10 times of their standard deviations. However, for light atoms the differences of the z values were not very significant (1—3 times of their standard deviations). From these results we concluded that the space group $P4_2bc$ was very improbable.

Results and Discussion

The cell, positional, and thermal parameters are listed in Table 1, and bond lengths and angles are shown in Fig. 1.

The tin atom has the *trans*-octahedral coordination, *trans*-$Sn(CH_3)_2O_4$. This is consistent with the result of previous Mössbauer studies.[2] The molybdenum atom is tetrahedrally coordinated by four oxygen atoms. All oxygen atoms are bridging tin and molybdenum atoms (Fig. 1).

The structure extends three-dimensionally. It has zig-zag chains of $(-Sn-O-Mo-O-)_\infty$ along the a axis exactly on the plane at z=0, and identical chains along the b axis at z=1/2. These chains are not connected with other chains on the same plane, but with those on the neighboring planes through O(3) atoms (Fig. 2). The location of the tin atoms can be approximately described as a body-centered cubic arrangement as shown in Fig. 3. A unit cell contains four body-centered cells of the tin atoms. The body-centered cells are elongated 6% along the c axis, and the tin atoms are shifted on the xy plane 0.21 Å from the ideal positions. The molybdenum atoms are in the tetrahedral holes of this body-centered packing of the tin atoms, and oxygen atoms are placed between the metal atoms.

The structure of $(CH_3)_2SnMoO_4$ consists of octahedra and tetrahedra in the ratio of 1:1, and

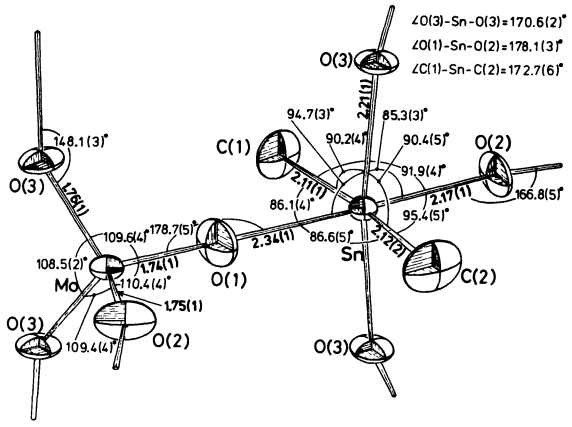

Fig. 1. ORTEP drawing of $(CH_3)_2SnMoO_4$ with bond lengths (in Å) and angles. The estimated standard deviations are in parentheses. The atoms, Sn, Mo, O(1), and O(2), are on a crystallographic mirror plane.

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Table 1. Cell,[a] positional, and thermal[b] parameters of $(CH_3)_2SnMoO_4$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	−0.01480(5)	0.24614(6)	0	17.1(3)	16.7(3)	10.7(2)	1.2(3)	0	0
Mo	0.24549(7)	0.10137(6)	0	15.4(3)	20.4(4)	11.8(3)	−4.0(3)	0	0
O(1)	0.1352 (7)	0.1646 (8)	0	23 (4)	53(6)	47(5)	13(4)	0	0
O(2)	0.3438 (7)	0.1831 (7)	0	30 (4)	56(6)	36(5)	−30(5)	0	0
O(3)	0.2522 (5)	0.0266 (4)	0.1965(6)	43 (3)	35(3)	9(2)	−4(3)	−2(3)	2(2)
C(1)	−0.0789(11)	0.1066 (9)	0	50 (8)	17(5)	51(8)	−13(5)	0	0
C(2)	0.0671(14)	0.3775(11)	0	75(11)	31(7)	56(9)	−28(8)	0	0

a) Space group: tetragonal $P4_2/mbc$. $a=13.705(2)$, $c=7.271(1)$ Å. b) In 10^{-3} Å^2.

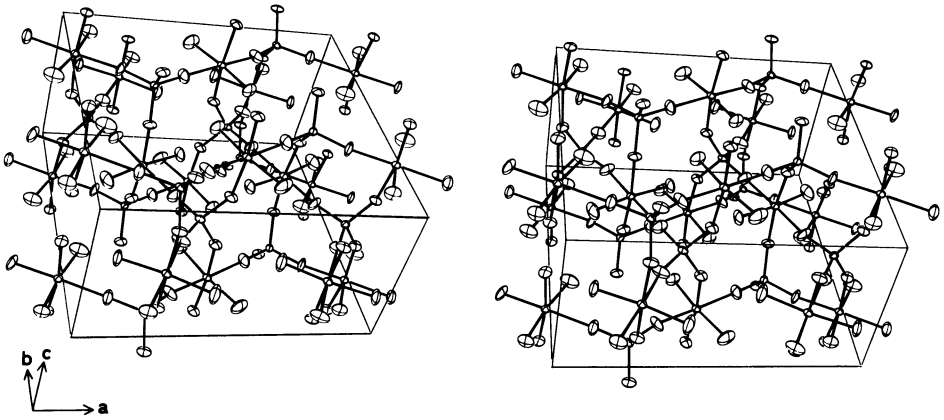

Fig. 2. Stereoscopic view of a unit cell of $(CH_3)_2SnMoO_4$ drawn by ORTEP.

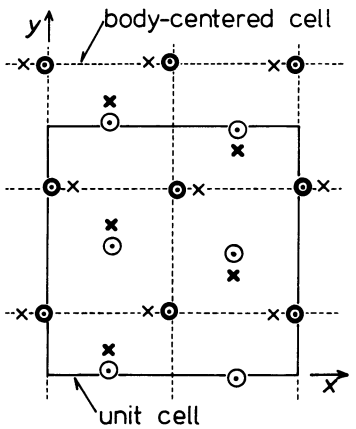

Fig. 3. Projection of metal atoms of $(CH_3)_2SnMoO_4$ along the c axis. Tin atoms are shown by open circles, and molybdenum atoms by crosses. The atoms drawn by thick lines are at $z=0$, and others at $z=1/2$.

these polyhedra share only apices. Compounds with these structural features are rare, and we have found only two examples. Neither of them is isostructural with $(CH_3)_2SnMoO_4$. The first example is a series of compounds $A(H_2O)_2BO_4$ (A=Al, In, Tl, or Fe; B= P or As).[4] These compounds have a cis coordination of aqua ligands around the A atoms in contrast with a trans coordination of methyl groups in $(CH_3)_2SnMoO_4$. The second example is the clathrate compound $Cd(NH_3)_2Hg(CN)_4\cdot 2C_6H_6$ which has octahedra of *trans*-$Cd(NH_3)_2(NC)_4$ and tetrahedra of $Hg(CN)_4$.[5] The metal atoms of this clathrate compound are arranged in the same way as the platinum and sulfur atoms in the PtS structure. This compound and $(CH_3)_2SnMoO_4$ are structurally very similar because both have approximately body-centered arrangement of the metal atoms with the *trans*-octahedral coordination. Furthermore, in the three-dimensional networks of both structures, the smallest rings are 8-membered when the CN ligand is regarded as one unit. However, the two structures are definitely different. In $(CH_3)_2SnMoO_4$ three atoms, Sn, O(2), and Mo, are shared by neighboring 8-memberd rings, while in the clathrate compound only one atom, Cd or Hg, is shared.

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References

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