Preparation and Crystal Structure of the Mercury(I) Molybdate(VI) $Hg_2Mo_5O_{16}$

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Colorless crystals of the new compound $Hg_2Mo_5O_{16}$ were obtained by reaction of $HgMoO_4$ and MoO_2 in evacuated, sealed silica tubes. Their crystal structure was determined from single-crystal X-ray data: $P2/c$, $a = 913.9(1)$ pm, $b = 551.3(1)$ pm, $c = 1428.9(2)$ pm, $\beta = 110.65(1)°$, $Z = 2$, $R = 0.043$ for 2262 structure factors and 66 variable parameters. The molybdenum atoms are tetrahedrally coordinated by oxygen atoms at distances covering the range from 168.4(4) to 197.4(4) pm. Five of these tetrahedra are linked via common corners forming chains with the composition Mo_5O_{16}. The tetrahedral oxygen coordination of each molybdenum atom is augmented by two additional oxygen atoms at distances between 217.7(5) and 252.5(5) pm. The resulting distorted MoO_6 octahedra are linked by common corners and edges, thus forming two-dimensionally infinite sheets, as are known for the related structure of $Cs_2Mo_5O_{16}$. The mercury pairs are situated between these sheets with a Hg–Hg distance of 247.4(1) pm. The structures of $Hg_2Mo_5O_{16}$ and $Cs_2Mo_5O_{15}$ differ in the arrangement of the metal atoms and also in the stacking of the $^2_\infty(Mo_5O_{16}^{2-})_n$ sheets. Distorted tetrahedral MoO_4 groups, augmented by two additional, weakly bonded oxygen atoms, are found in many other molybdates. In several of these, the tetrahedra form chains via corner sharing like the five-membered Mo_5O_{16} chain in $Hg_2Mo_5O_{16}$. Examples are $Cs_2Mo_7O_{22}$, $Cs_2Mo_5O_{16}$, the two modifications of $Li_2Mo_4O_{13}$, and $Tl_2Mo_4O_{13}$, where the chains are seven-, five-, and four-membered, respectively; pairs of MoO_4 tetrahedra occur in $Hg_2Mo_2O_7$. © 1997 Academic Press

INTRODUCTION

Only two mercury molybdates have been structurally characterized up to now. In the structure of the mercury(II) molybdate(VI) $HgMoO_4$ the molybdenum atoms are octahedrally coordinated by oxygen atoms, and the MoO_6 octahedra are linked via common edges, thus forming zigzag chains, which are arranged parallel to each other (1). The other compound is the mercury(I) dimolybdate(VI)

$Hg_2Mo_2O_7$ (2), where the molybdenum atoms are also octahedrally coordinated by oxygen atoms. In this structure the MoO_6 octahedra share edges and corners resulting in two-dimensionally infinite sheets. Similar sheets of linked MoO_6 octahedra are also found in the mercury molybdate of the present publication. However, it is possible to visualize the architecture of this molybdate and several others (including that of $Hg_2Mo_2O_7$) in a different way. The Mo–O distances within the MoO_6 octahedra of these compounds show a large spread. If only the four shortest Mo–O distances of each MoO_6 octahedron are considered, the structures can also be described by the way these distorted MoO_4 tetrahedra are linked via common corners.

SAMPLE PREPARATION AND LATTICE CONSTANTS

$Hg_2Mo_5O_{16}$ was prepared by reaction of $HgMoO_4$ and MoO_2 powders. Starting materials were $Na_2MoO_4 \cdot 2H_2O$ (Riedel-de Haën, 99.5%), $Hg(NO_3)_2 \cdot H_2O$ (Fluka, 99%), MoO_3 (Merck, 99.5%), and molybdenum powder (Ventron, 99.9%). $HgMoO_4$ was obtained by precipitation, reacting aqueous solutions of Na_2MoO_4 and $Hg(NO_3)_2$. MoO_2 was prepared by chemical transport of Mo and MoO_3 with iodine from 1000 to 800°C (3). Well-developed crystals of $Hg_2Mo_5O_{16}$ were obtained by annealing a mixture of $HgMoO_4$ and MoO_2 (2:1) in an evacuated, sealed silica tube for 1 week at 460°C, cooling at a rate of 100°C/h to 300°C, followed by quenching in air. The main reaction possibly proceeded by the equation $4HgMoO_4 + 3MoO_2 \rightarrow Hg_2Mo_5O_{16} + 2MoO_3 + 2Hg$. $Hg_2Mo_2O_7$ (2) was observed as an additional reaction product.

The colorless, equidimensional, almost globular crystals of $Hg_2Mo_5O_{16}$ are stable in air. Their lattice constants (Table 1) were obtained by least-squares fits of the Guinier powder data. $CuK\alpha_1$ radiation was used with α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard. The identification of the diffraction lines was facilitated by intensity calculations (4) using the positional parameters of the refined structure.

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TABLE 1
Crystal Data of $Hg_2Mo_5O_{16}$

Space group	$P2/c$ (No. 13)
Lattice constants (Guinier powder)	
a (pm)	913.9(1)
b (pm)	551.3(1)
c (pm)	1428.9(2)
β (°)	110.65(1)
V (nm^3)	0.6737
Formula mass	1136.87
Formula units/cell	$Z = 2$
Calculated density (g/cm^3)	5.604
Absorption coefficient $\mu_{MoK\alpha}$ (cm^{-1})	272
Crystal dimensions (μm^3)	$70 \times 30 \times 30$
Highest/lowest transmission	1.74
$\theta/2\theta$ scans up to	$2\theta = 64°$
Range in h, k, l	$\pm 13, \pm 8, \pm 20$
Total number of reflections	10766
Unique reflections	3203
Inner residual	$R_i = 0.030$
Reflections with $I_0 > 1\sigma(I_0)$	2262
Number of variables	66
Conventional residual	$R = 0.043$
Weighted residual	$R_w = 0.037$

TABLE 2
Atomic Parameters of $Hg_2Mo_5O_{16}$[a]

Atom	$P2/c$	x	y	z	B_{eq} or B
Hg	$4g$	0.40880(4)	0.69867(9)	0.29663(2)	2.675(8)
Mo1	$4g$	0.13171(6)	0.17762(12)	0.08853(4)	0.522(9)
Mo2	$4g$	0.23432(7)	0.27420(11)	0.42890(4)	0.578(9)
Mo3	$2e$	0	0.63153(15)	1/4	0.53(1)
O1	$4g$	0.0135(5)	0.3263(9)	0.1567(3)	0.72(7)
O2	$4g$	0.0607(6)	0.1750(10)	0.6770(3)	0.88(7)
O3	$4g$	0.1218(6)	0.0985(9)	0.5011(3)	0.81(8)
O4	$4g$	0.1577(6)	0.4045(10)	0.0151(4)	1.18(8)
O5	$4g$	0.2150(6)	0.5437(9)	0.3357(3)	0.71(7)
O6	$4g$	0.2759(7)	0.0427(11)	0.3639(4)	1.42(9)
O7	$4g$	0.3109(6)	0.1470(10)	0.1764(4)	1.27(8)
O8	$4g$	0.4095(6)	0.3253(11)	0.5209(4)	1.37(9)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg	128(1)	707(3)	220(1)	19(2)	110(1)	162(2)
Mo1	66(2)	59(2)	74(2)	5(2)	26(1)	$-14(2)$
Mo2	60(2)	82(2)	79(2)	$-3(2)$	26(1)	15(1)
Mo3	75(3)	61(3)	59(3)	0	17(2)	0

[a] The isotropic thermal parameters B_{eq} and B are listed in units of 10^4 pm^2. The anisotropic thermal parameters U (pm^2) are defined by $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2klb^*c^*U_{23})]$. The positional parameters were standardized using the program STRUCTURE TIDY (7). Standard deviations are listed in parentheses throughout the paper.

STRUCTURE DETERMINATION

The intensity data for the structure determination of $Hg_2Mo_5O_{16}$ were collected on an automated four-circle diffractometer with graphite-monochromated MoKα radiation, a scintillation counter, and a pulse-height discriminator. The background was determined at both ends of each $\theta/2\theta$ scan. Empirical absorption corrections were applied from psi-scan data. The lattice constants obtained from the four-circle diffractometer were practically the same as those refined from the powder data. Further details of the data collection are summarized in Table 2.

The structure was solved by interpretation of the Patterson map, which led to the positions of the mercury atoms. The other atoms were located by difference Fourier syntheses. The structure was refined by a full-matrix least-squares program using atomic scattering factors (5), corrected for anomalous dispersion (6). The weighting scheme accounted for the counting statistics. A parameter correcting for the secondary extinction was optimized during the least-squares refinements. In the final least-squares cycles the metal atoms were refined with anisotropic and the oxygen atoms with isotropic thermal parameters. A stereoplot of the structure is shown in Fig. 1. The atom parameters and interatomic distances are listed in Tables 2 and 3. The structure factor table is available from the authors (8).
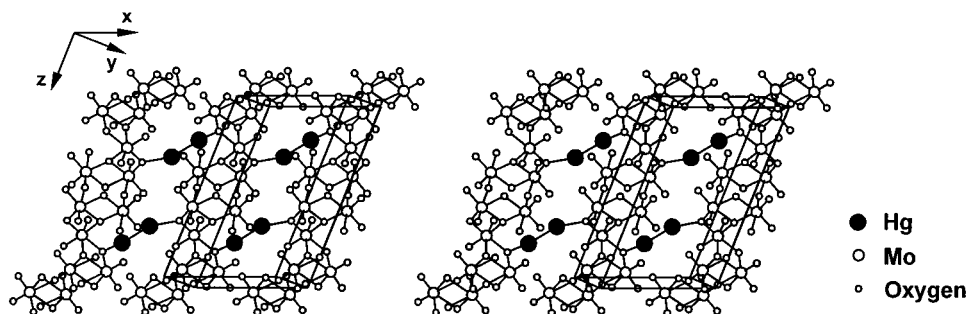
FIG. 1. A stereoplot of the crystal structure of $Hg_2Mo_5O_{16}$.

TABLE 3
Interatomic Distances in $Hg_2Mo_5O_{16}$[a]

Hg:			Mo2:			O3:		
	Hg	247.4(1)		O6	169.8(5)		Mo1	195.1(5)
	O5	220.8(4)		O8	169.9(5)		Mo2	195.2(4)
	O8	255.3(5)		O3	195.2(4)		Mo1	225.9(4)
	O6	261.2(5)		O5	196.1(5)	O4:	Mo1	170.2(5)
	O7	296.2(6)		O1	218.0(4)		Mo2	239.9(5)
	O2	311.3(4)		O4	239.9(5)	O5:	Mo1	196.1(5)
Mo1:	O7	168.4(4)	Mo3:	2O2	171.6(5)		Mo3	197.4(4)
	O4	170.2(5)		2O5	197.4(4)		Hg	220.8(4)
	O1	187.9(4)		2O1	217.7(5)	O6:	Mo2	169.8(5)
	O3	195.1(5)	O1:	Mo1	187.9(4)		Hg	261.2(5)
	O3	225.9(4)		Mo3	217.7(5)	O7:	Mo1	168.4(4)
	O2	252.5(5)		Mo2	218.0(4)		Hg	296.2(6)
			O2:	Mo3	171.6(5)	O8:	Mo2	169.9(5)
				Mo1	252.5(5)		Hg	255.3(5)
				Hg	311.3(4)			

[a] All distances shorter than 330 pm (Hg–Hg, Hg–Mo, Mo–Mo, Hg–O, Mo–O) and 240 pm (O–O) are listed.

DISCUSSION

The mercury atoms in $Hg_2Mo_5O_{16}$ form pairs (Fig. 2), as is known for most mercury(I) compounds. The Hg–Hg distance of 247.4(1) pm is within the range from 244.6(6) to 255.7(3) pm found for about 50 Hg–Hg bonds in some 30 mercury(I) oxocompounds, but slightly shorter than their average Hg–Hg distance of 251.3 pm (8). The short Hg–O distance of 220.8(4) pm also compares well with the average short Hg(I)–O distance of 216.6 pm observed in these 30 compounds. The corresponding Hg–Hg–O bond angle of 152.7(1)°, however, deviates considerably from the ideal value of 180°.

The molybdenum atoms have highly distorted octahedral oxygen coordination. As frequently observed for molybdates(VI) (9), the two shortest Mo–O distances of the three different molybdenum sites are in *cis* coordination (in $Hg_2Mo_5O_{16}$ these distances vary between 168.4 and 171.6 pm), the two medium distances (which vary between 187.9 and 197.4 pm) are *trans* to each other, and the long distances (between 217.7 and 252.5 pm) have again *cis* arrangement. The averages Mo–O distances for the Mo1, Mo2, and Mo3 atoms are 200.0, 198.1, and 195.6 pm, respectively, and as could be expected (10), the largest average Mo–O distance occurs for the molybdenum atom (the Mo1 atom) that has the widest spread of Mo–O distances with the extreme values of 168.4 and 252.5 pm. The oxygen atoms occupy eight general positions. They have either two or three different metal neighbors, as can be seen from Table 3 and the lower part of Fig. 2.

If only the four shortest Mo–O distances are considered, the molybdenum coordinations may also be described as distorted tetrahedral. The corresponding MoO_4 tetrahedra in $Hg_2Mo_5O_{16}$ share corners, thus forming five-membered chains of the composition Mo_5O_{16} (Fig. 2). Therefore, all oxygen atoms of $Hg_2Mo_5O_{16}$ are already accounted for
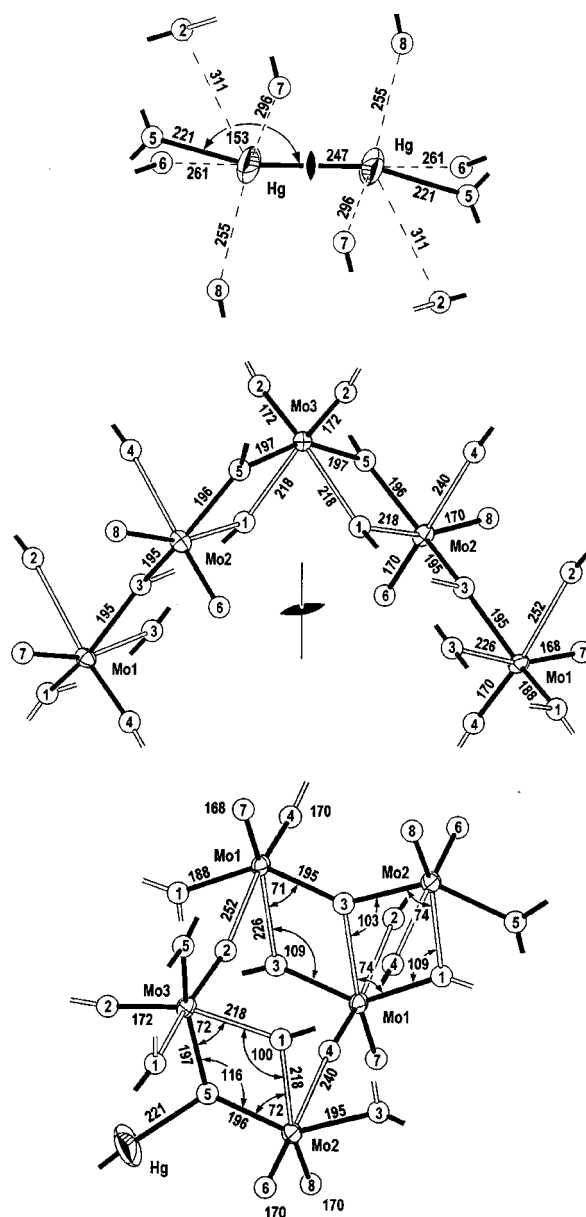

FIG. 2. Near-neighbor environments in the structure of $Hg_2Mo_5O_{16}$. Single-digit numbers correspond to the designations of the oxygen atoms. Interatomic distances are given in pm units. The thermal ellipsoids of the metal atoms correspond to the 90% probability limit; the oxygen atoms are drawn with a standardized size. In the top part of the figure the environment of the mercury pair is shown. There is a twofold axis in the viewing direction located between the mercury atoms. Strong Mo–O bonds (up to 198 pm) are indicated by solid lines. Each molybdenum atom has four strongly bonded oxygen neighbors. The corresponding MoO_4 tetrahedra are linked via common corners, and thus form a five-membered chain Mo_5O_{16} with the Mo3 atom in the center on a twofold axis. Additional oxygen neighbors at greater distances augment the molybdenum coordinations to distorted octahedral. In the lower part of the figure the environments of the oxygen atoms are shown. The five molybdenum atoms of this drawing belong to three different Mo_5O_{16} chains. It can be seen that the MoO_6 octahedra of adjacent chains are linked not only by common corners, but also via common edges. The bond angles around the three different kinds of common edges (interchain O1–O3 and O3–O3, intrachain O1–O5) are indicated in degrees of arc.

by considering these MoO_4 tetrahedra. Similar chains of corner-shared MoO_4 tetrahedra can be visualized in other molybdates; e.g., seven-, five-, and four-membered chains of the compositions Mo_7O_{22}, Mo_5O_{16}, and Mo_4O_{13} occur in $Cs_2Mo_7O_{22}$ (11), $Cs_2Mo_5O_{16}$ (11), the two modifications of $Li_2Mo_4O_{13}$ (9, 12), and in $Tl_2Mo_4O_{13}$ (13), respectively. Corner-shared pairs Mo_2O_7 have been emphasized already for $Hg_2Mo_2O_7$ (2). As can be seen from Fig. 2 the chains in $Hg_2Mo_5O_{16}$ are formed by the atoms Mo1–O3–Mo2–O5–Mo3–O5–Mo2–O3–Mo1. For the other just mentioned molybdates, the chains are not that readily discernible. In $Cs_2Mo_7O_{22}$ (11) they consist of the atoms Mo4–O11–Mo2–O4–Mo3–O2–Mo1–O2–Mo3–O4–Mo2–O11–Mo4, and in $Cs_2Mo_5O_{16}$ (11) the chain-forming atoms have the sequence Mo3–O5–Mo2–O1–Mo1–O1–Mo2–O5–Mo3. In the three compounds $Hg_2Mo_5O_{16}$, $Cs_2Mo_7O_{22}$, and $Cs_2Mo_5O_{16}$ the central molybdenum atoms of the chains are situated on a twofold axis, and therefore the whole chain reflects this symmetry, as can be seen for $Hg_2Mo_5O_{16}$ in Fig. 2. In the two modifications of $Li_2Mo_4O_{13}$ (9, 12) and in $Tl_2Mo_4O_{13}$ (13) the chains do not contain atoms on a twofold axis. In $Tl_2Mo_4O_{13}$ the entire chain, Mo3–O7–Mo2–

O6–Mo4–O11–Mo1, belongs to one asymmetric unit. This is also the case for the chains Mo2–O10–Mo1–O16–Mo4–O4–Mo3 and Mo2–O10–Mo1–O17–Mo4–O3–Mo3 of L-$Li_2Mo_4O_{13}$ (9) and H-$Li_2Mo_4O_{13}$ (12), respectively. Both compounds have additionally centrosymmetric chains with the sequence Mo6–O13–Mo5–O1–Mo5–O13–Mo6 for L-$Li_2Mo_4O_{13}$ and Mo6–O14–Mo5–O1–Mo5–O14–Mo6 for H-$Li_2Mo_4O_{13}$. In both of these centrosymmetric chains the symmetry center is located at the O1 atoms, and in all chains the Mo–O distances are of medium length, as discussed above for the MoO_6 octahedra, where the two oxygen neighbors of a molybdenum atom are in *trans* configuration.

The structure of $Hg_2Mo_5O_{16}$ is very closely related to that of $Cs_2Mo_5O_{16}$ (11). This is demonstrated in Fig. 3. It can be seen that the arrangement of the condensed MoO_6 octahedra is practically the same for both compounds. The octahedra form two-dimensionally infinite sheets, which extend parallel to the yz plane. Corresponding octahedra of two adjacent sheets are at the same height of the projection direction (y) in $Hg_2Mo_5O_{16}$, while they are shifted by $b/2$ relative to each other in $Cs_2Mo_5O_{16}$ because of the C centering, which doubles the a translation period of that compound. The chemical reason for this dissimilarity lies in the trivial difference between the mercury and the cesium atoms. The cesium atoms stay away from each other and have nine oxygen neighbors with Cs–O distances varying between 296 and 341 pm, while the mercury atoms form pairs and need only one close oxygen atom to satisfy their bonding requirements.

FIG. 3. The crystal structure of $Hg_2Mo_5O_{16}$ as compared to the structure of $Cs_2Mo_5O_{16}$. The heights of the mercury and cesium atoms in the projection direction are given in hundredths.

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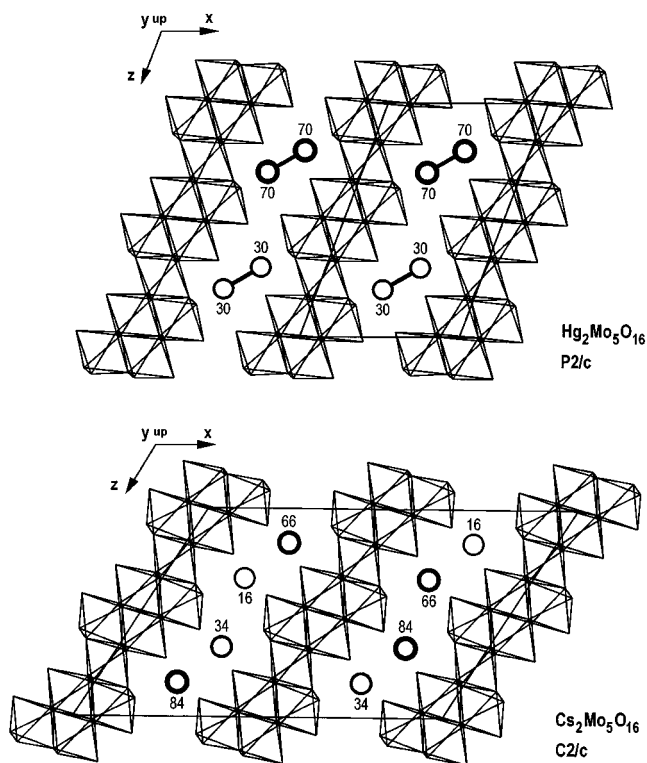13. P. Tolédano and M. Touboul, *Acta Crystallogr. B* **34,** 3547 (1978).