Preparation and Crystal Structure of the Mercury(I) Dimolybdate(VI) $\text{Hg}_2\text{Mo}_2\text{O}_7$

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Dedicated to Prof. Dr. Gerhard Thiele on the occasion of his 60th birthday

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Crystal Structure, Magnetic Susceptibility, Mercury Molybdates(VI)

Yellow, flat, needle-shaped, diamagnetic crystals of $\text{Hg}_2\text{Mo}_2\text{O}_7$ were obtained by decomposition of Hg_2MoO_4 in evacuated, sealed silica tubes at 550 °C. Their crystal structure was determined from four-circle diffractometer data: $P\bar{1}$, $a = 709.7(2)$, $b = 714.4(2)$, $c = 803.8(2)$ pm, $\alpha = 64.89(1)^\circ$, $\beta = 66.09(1)^\circ$, $\gamma = 66.45(1)^\circ$, $Z = 2$, $R = 0.030$ for 3165 structure factors and 66 variables. The molybdenum atoms are coordinated by four oxygen atoms at 171 to 195 pm in a very distorted tetrahedral arrangement. These tetrahedra are linked via a common oxygen atom, thus forming Mo_2O_7 groups. The tetrahedral oxygen coordination of each molybdenum atom is augmented by two additional oxygen atoms at 218 to 231 pm, which leads to a distorted octahedral coordination for the molybdenum atoms. These MoO_6 octahedra are connected *via* common corners and edges and in this way they form two-dimensionally infinite sheets, which are separated by the Hg_2 pairs (Hg–Hg distance: 252.2 pm).

Introduction

Only few mercury molybdates are known. Hg_2MoO_4 was first described by Berzelius and later by Lelubre [1]. Gupta and Saxena investigated the influence of the pH value on the precipitation of HgMoO_4 [2, 3] and Hg_2MoO_4 [4, 5]. The synthesis of HgMoO_4 was also described by Sleight and Licis [6] and by Blasse [7], and its crystal structure was determined [8, 9]. The synthesis of three unstable mercury peroxomolybdate hydrates was reported by Bogdanov, Savina, and Petrova [10].

Here we describe the preparation of $\text{Hg}_2\text{Mo}_2\text{O}_7$, for which we find a new triclinic structure type. A light yellow, flocculent precipitate of this composition was first mentioned by Struve in 1853 and 1854 [11], however it was not further characterized. A preliminary account of the presently reported results has been given at a conference [12].

Sample Preparation and Properties

Starting materials were $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (Riedel-de Haën, 99.5%) and $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Merck, 98%). These compounds were reacted in aqueous solution to form a precipitate of Hg_2MoO_4 , which was dried in a vacuum desiccator

over calcium chloride for two days [2, 3]. *Ca.* 0.4 g of this compound were then sealed in evacuated silica tubes of about 4 to 6 cm³ and annealed at 550 °C for one week. The samples were cooled to 300 °C within five hours and then quenched in air. Visible reaction products are yellow, sometimes up to 7 mm long, needle-shaped crystals of $\text{Hg}_2\text{Mo}_2\text{O}_7$, the previously characterized compound HgMoO_4 [6–9] in microcrystalline as well as in good crystallized form, and metallic mercury. Apparently the decomposition proceeds by the equations $4\text{Hg}_2\text{MoO}_4 \rightarrow 2\text{Hg}_2\text{Mo}_2\text{O}_7 + 4\text{Hg} + \text{O}_2$ and $\text{Hg}_2\text{MoO}_4 \rightarrow \text{HgMoO}_4 + \text{Hg}$. The second reaction is favoured at higher temperatures. Occasionally we have obtained MoO_3 and another yet unidentified mercury molybdate.

In microcrystalline form $\text{Hg}_2\text{Mo}_2\text{O}_7$ is light yellow, the needles have a color like elemental sulfur, in contrast to HgMoO_4 , which is white in microcrystalline form and colorless in the form of the small crystals, which we obtained, while larger crystals are reported to be light yellow [6].

The magnetic susceptibility of $\text{Hg}_2\text{Mo}_2\text{O}_7$ was determined with a SQUID magnetometer. The sample is diamagnetic with a susceptibility of $\chi = (-1.4 \pm 0.3) \cdot 10^{-9} \text{ m}^3/\text{mol}$.

The lattice constants (Table I) were obtained by a least-squares fit of Guinier powder data. $\text{CuK}\alpha_1$ radiation was used with α -quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard.

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Table I. Crystal data for $\text{Hg}_2\text{Mo}_2\text{O}_7$. Standard deviations in the positions of the least significant digits are given in parentheses throughout the paper.

Space group	P $\bar{1}$ (No. 2)	
Lattice constants from Guinier powder [and single crystal] data		
<i>a</i> [pm]	709.7(2)	[709.1(1)]
<i>b</i> [pm]	714.4(2)	[713.3(1)]
<i>c</i> [pm]	803.8(2)	[802.9(1)]
α [°]	64.89(1)	[64.85(1)]
β [°]	66.09(1)	[66.10(1)]
γ [°]	66.45(1)	[66.50(2)]
<i>V</i> [nm ³]	0.3244	[0.3233]
Formula units/cell	<i>Z</i> = 2	
Formula weight	705.06	
Calculated density [g/cm ³]	7.22	
Crystal size [μ m ³]	40×50×70	
$\theta/2\theta$ scans up to	2 θ = 84°	
Range in <i>hkl</i>	± 13, ± 13, ± 15	
Highest/lowest transmission	1.41	
Total number of reflections	9030	
Absorption correction from	psi scans	
Unique reflections	4515	
Inner residual	<i>R</i> _i = 0.035	
Reflections with <i>I</i> _o > 3 σ (<i>I</i> _o)	3165	
Number of variables	66	
Conventional residual	<i>R</i> = 0.030	
Weighted residual	<i>R</i> _w = 0.037	

Structure Determination

Single-crystals of $\text{Hg}_2\text{Mo}_2\text{O}_7$ were examined in a Weissenberg camera to establish their suitability for the intensity data collection. The lattice constants obtained from the four-circle diffractometer (Table I) were slightly smaller than those from the Guinier film data, because of systematic errors due to absorption. Therefore the latter are considered more reliable. The intensity data were mea-

sured on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation, a scintillation counter with pulse-height discriminator, and background counts on both ends of each $\theta/2\theta$ scan. An absorption correction was made from psi scan data. Further details are summarized in Table I.

$\text{Hg}_2\text{Mo}_2\text{O}_7$ has triclinic symmetry and the structure was refined in the centrosymmetric group $P\bar{1}$. The positions of some metal atoms were obtained from a Patterson synthesis and the other atoms were located by difference Fourier syntheses. The structure was refined by a full-matrix least-squares program using atomic scattering factors [13], corrected for anomalous dispersion [14]. The weighting scheme provided for the counting statistics and a parameter correcting for isotropic secondary extinction was optimized as a least-squares variable. In the final least-squares cycles the metal atoms were refined with anisotropic and the oxygen with isotropic displacement parameters. A final difference Fourier synthesis did not give any indications for the occupancy of additional atomic sites. The structure factor tables are available from the authors [15]. The atomic parameters and interatomic distances are listed in the Tables II and III.

Discussion

The new mercury molybdate crystallizes with a novel structure type. The compound may be formulated as $[\text{Hg}_2^{2+}][\text{Mo}_2\text{O}_7^{2-}]$, indicating the oxidation numbers +1 and +6 for the mercury and the molybdenum atoms, respectively. The two dif-

Table II. Atomic parameters of $\text{Hg}_2\text{Mo}_2\text{O}_7$. The fifth column contains the isotropic displacement parameters of the oxygen atoms and the equivalent isotropic B values of the metal atoms in units of 10^{-2} nm^2 . The anisotropic displacement parameters have the form $\exp[-0.25 \cdot (h^2 a^{*2} B_{11} + \dots + k l h^* c^* B_{23})]$.

Atom	x	y	z	B	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Hg1	0.19023(3)	0.32561(3)	0.36437(3)	1.074(3)	1.298(4)	1.368(5)	0.792(4)	-0.467(3)	-0.730(3)	-0.045(3)
Hg2	0.37441(3)	0.18055(3)	0.62200(3)	1.165(4)	1.350(4)	1.548(5)	0.773(5)	-0.476(3)	-0.733(3)	-0.040(4)
Mo1	0.30011(5)	0.88204(6)	0.11810(6)	0.477(6)	0.469(7)	0.556(8)	0.510(9)	-0.221(5)	-0.144(6)	-0.180(6)
Mo2	0.80974(5)	0.37535(6)	0.13540(6)	0.473(6)	0.500(7)	0.550(7)	0.495(9)	-0.242(5)	-0.165(6)	-0.161(6)
O1	0.0343(5)	0.4503(5)	0.1542(5)	0.73(5)						
O2	0.1056(5)	0.1101(6)	0.0401(6)	0.83(5)						
O3	0.1674(6)	0.7651(7)	0.3488(6)	1.30(6)						
O4	0.4585(5)	0.0098(5)	0.1646(5)	0.75(5)						
O5	0.5933(6)	0.5970(6)	0.1773(6)	0.94(5)						
O6	0.6983(6)	0.2970(6)	0.0035(6)	0.94(5)						
O7	0.7735(6)	0.1792(7)	0.3516(6)	1.32(6)						

Table III. Interatomic distances in the structure of $\text{Hg}_2\text{Mo}_2\text{O}_7$. All distances shorter than 330 pm (Hg–Hg, Hg–Mo, Mo–Mo, Hg–O, Mo–O) and 260 pm (O–O) are listed. The standard deviation of the Hg–Hg bondlength is 0.1 pm; for the other distances the standard deviations vary between 0.4 and 0.7 pm.

Hg1:	Hg2	252.2	O1:	Mo2	194.8
	O1	207.9		Hg1	207.9
	O3	273.5		Mo2	217.9
	O4	290.9		(O1	246.9)
	O3	303.0	O2:	Mo1	172.9
	O6	311.2		Mo2	231.0
Hg2:	Hg1	252.2		Hg2	305.3
	O4	213.9	O3:	Mo1	171.0
	O7	278.4		Hg1	273.5
	O5	281.9		Hg1	303.0
	O7	304.4	O4:	Mo1	192.0
	O2	305.3		Hg2	213.9
Mo1:	O3	171.0		Mo1	226.0
	O2	172.9		Hg1	290.9
	O6	190.6		(O4	252.1)
	O4	192.0	O5:	Mo2	175.2
	O4	226.0		Mo1	230.1
	O5	230.1		Hg2	281.9
Mo2:	O7	170.5	O6:	Mo2	189.7
	O5	175.2		Mo1	190.6
	O6	189.7		Hg1	311.2
	O1	194.8	O7:	Mo2	170.5
	O1	217.9		Hg2	278.4
	O2	231.0		Hg2	304.4

ferent molybdenum sites are both coordinated by six oxygen atoms at bond distances covering the range from 170.5 to 231.0 pm. Four of these six Mo–O bonds are distinctly shorter than the other two. These short Mo–O bonds have average distances of 181.6 and 182.5 pm for the Mo1 and Mo2 atoms, respectively. These grossly distorted MoO_4 tetrahedra are linked *via* one corner (the O6 atom), thus forming Mo_2O_7 groups as they are well known for the analogs in diphosphates and disilicates. Such Mo_2O_7 groups “in pure form” are found in the structure of $\text{Ce}_6(\text{MoO}_4)_8(\text{Mo}_2\text{O}_7)$ [16]. Therefore the average Mo–O distance in that compound is shorter (177.4 pm) than in our case, where the two additional oxygen atoms (at average distances of 228.1 and 224.5 pm for Mo1 and Mo2) augment the tetrahedral molybdenum coordination to a considerably distorted octahedral one (Fig. 1). Such molybdenum atoms with four short and two long Mo–O bonds were observed before in $\text{Ag}_2\text{Mo}_2\text{O}_7$ [17] and $\text{Ce}_2(\text{MoO}_4)_2(\text{Mo}_2\text{O}_7)$ [18]. In $\text{Hg}_2\text{Mo}_2\text{O}_7$ these distorted MoO_6 octahedra are linked *via* common corners and edges, thus forming two-dimensionally infinite sheets, which extend along the *xy* plane (Fig. 2). The O1 and O4 atoms participate in the edge sharing, while the O2, O5, and

Fig. 1. Near-neighbor environments in the structure of $\text{Hg}_2\text{Mo}_2\text{O}_7$. The molybdenum atoms have four oxygen neighbors (filled bonds) at distances between 171 and 195 pm in very distorted tetrahedral arrangements. With two more oxygen atoms (open bonds) the coordinations become distorted octahedral. One-digit numbers correspond to the designation of the oxygen atoms. The location of some centers of symmetry are indicated by asterisks.

Fig. 2. The packing of the corner- and edge-sharing MoO_6 octahedra in the two-dimensionally infinite Mo_2O_7 layers of $\text{Hg}_2\text{Mo}_2\text{O}_7$.

O6 atoms belong to corner sharing octahedra. The remaining oxygen atoms (O3 and O7) belong to only one molybdenum atom. They have two mercury neighbors, while the others have one with the exception of the O4 atom, which has two molybdenum and two mercury neighbors.

The two-dimensionally infinite sheets of linked MoO_6 octahedra of $\text{Hg}_2\text{Mo}_2\text{O}_7$ are connected in the third dimension *via* Hg_2 pairs (Fig. 3). Both mercury atoms are strongly bonded to one mercury and one oxygen atom in nearly linear arrangement (Hg2-Hg1-O1 : $178.8(1)^\circ$, Hg1-Hg2-O4 : $167.3(1)^\circ$) as is frequently observed for Hg(I) atoms. The short Hg-O bonds of 207.9 and

213.9 pm compare well with the analogous bond distances of: 209(2), 211(2), 213(2), 215(2), and 222(2) pm in $[(\text{Hg}_2)_5(\text{OH})_4(\text{NO}_3)_2](\text{NO}_3)_4$ [19], 212(2), 219(2), 224(4), and 231(2) pm in $[(\text{Hg}_2)_2\text{O}(\text{NO}_3)]\text{NO}_3 \cdot \text{HNO}_3$ [19], 213(2) pm in $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ [20], 213.5(7) and 214.3(7) pm in Hg_2ReO_5 [21], 213.6(9) pm in $\text{Hg}_4\text{O}_2(\text{NO}_3)_2$ [22], and 214(3) pm in $\text{Hg}_2(\text{CF}_3\text{CO}_2)_2$ [23]. In these compounds the Hg-Hg distances cover the range from 249.5(1) pm in $[(\text{Hg}_2)_5(\text{OH})_4(\text{NO}_3)_2](\text{NO}_3)_4$ to 252.1(1) pm in Hg_2ReO_5 with an average of 250.7 pm. These values are only marginally smaller than the Hg-Hg distance of 252.2(1) pm in the present investigation for $\text{Hg}_2\text{Mo}_2\text{O}_7$. All of these Hg-Hg distances correspond to a bond valence of approximately one [24].

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Fig. 3. Stereoplot of the $\text{Hg}_2\text{Mo}_2\text{O}_7$ structure.

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