

pyramids are also connected by hydrogen bonds between the oxalato oxygen atoms and equatorial water, and between the crystalline and apical coordinated water molecules.

Available data about hepta-coordination are rather limited and it is not reasonable to draw any general conclusion upon this subject at this time. The seven-coordinated geometry was discussed by Muetterties & Wright (1967), based on the three idealized polyhedra: pentagonal bipyramid- $D_{5h}$ , capped trigonal prism- $C_{2v}$  and capped octahedron- $C_{3v}$ . (A fourth type of geometry, the tetragonal base-trigonal base- $C_s$  has also been mentioned.)

Other authors have tried to evaluate relative stabilities of the idealized seven-coordinated polyhedra (Duffey, 1950; Gillespie, 1960; Britton, 1963; Claxton & Benson, 1966) but these results are not applicable to seven-coordinated species with different ligands.

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## The Crystal Structure of $HgMoO_4$ and Related Compounds

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Mercuric molybdate crystallizes in the monoclinic system, space group  $C2/c$  with  $a = 11.282$  (2),  $b = 6.055$  (1),  $c = 5.154$  (1) Å,  $\beta = 112.27$  (1)°, and  $Z = 4$ . The structure was determined from single-crystal counter data by Patterson and Fourier methods. A full-matrix least-squares refinement with anisotropic thermal parameters resulted in a conventional  $R$  value of 0.023 for 849 reflections (unobserved included). The Hg atom is coordinated by two oxygen atoms forming a linear O-Hg-O arrangement with oxygen-mercury distances of 2.03 Å. Four more oxygens are further away at 2.67 ( $2 \times$ ) and 2.77 ( $2 \times$ ) Å, completing an approximately octahedral grouping. The oxygen environment of Mo is essentially octahedral with Mo-O distances between 1.72 and 2.23 Å indicating bond orders from two to one respectively. A qualitative description of bonding in the  $HgMoO_4$  structure is given. Mercuric tungstate,  $HgWO_4$  has the same structure with  $a = 11.375$  (2),  $b = 6.007$  (1),  $c = 5.145$  (1) Å,  $\beta = 113.20$  (1)°. The structure of  $HgMoO_4$  and  $HgWO_4$  is closely related to the structure of  $CdWO_4$  (Ni $WO_4$ -type). Results for solid solutions such as  $CdWO_4$ - $HgWO_4$  prepared at 65 kbar are reported.

### Introduction

$HgMoO_4$  and  $HgWO_4$  have been reported by Swindells (1951), Gupta & Saxena (1958), and Saxena & Gupta (1959), who prepared these substances by precipitation from aqueous solutions. Large (mm size) crystals can be

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grown by reaction of  $HgCl_2$  with  $Na_2MoO_4 \cdot 2H_2O$  or  $Na_2WO_4 \cdot 2H_2O$  respectively at 700°C in collapsible gold tubes under 3 kbar pressure. They have been characterized as monoclinic, space group  $C2/c$  or  $Cc$ , with the lattice constants given in Table 1 (Sleight & Licis, 1971). Preliminary results of a structure determination of  $HgMoO_4$  were also reported (Jeitschko & Sleight, 1972). This paper gives a full account of the crystal

\* Contribution No. 1976

Table 1. Unit-cell dimensions and densities of  $HgMoO_4$  and  $HgWO_4$ 

		$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\beta(^{\circ})$	$V(\text{\AA}^3)$	$\rho_c(\text{g cm}^{-3})$	$\rho_z(\text{g cm}^{-3})$
$HgMoO_4$	$C2/c$	11.282 (2)	6.055 (1)	5.154 (1)	112.27 (1)	325.8	7.345	7.349
	$I2/a$	5.154 (1)	6.055 (1)	10.477 (2)	85.20 (1)			
$HgWO_4$	$C2/c$	11.375 (2)	6.007 (1)	5.145 (1)	113.20 (1)	323.1	9.182	9.217
	$I2/a$	5.145 (1)	6.007 (1)	10.476 (2)	86.37 (1)			

structures of  $HgMoO_4$  and  $HgWO_4$ . The relation of this structure to the wolframite structure and results of solid solutions between compositions of the two structural types are also reported.

### Structure determination

#### Experimental

The single crystal of  $HgMoO_4$  used for the structure determination was of elongated prismatic shape with a length of 230  $\mu$  and irregular hexagonal cross section  $30 \times 22 \times 18 \mu$ . Buerger precession photographs con-

Table 2. Observed and calculated structure factors of  $HgMoO_4$ 

The columns contain the values  $hkl$ ,  $F_o$ ,  $F_c$ . Structure factors not included in the least squares refinement are marked with an asterisk.

$h$	$k$	$l$	$F_o$	$F_c$
0	0	0	100.0	100.0
0	0	1	100.0	100.0
0	0	2	100.0	100.0
0	0	3	100.0	100.0
0	0	4	100.0	100.0
0	0	5	100.0	100.0
0	0	6	100.0	100.0
0	0	7	100.0	100.0
0	0	8	100.0	100.0
0	0	9	100.0	100.0
0	0	10	100.0	100.0
0	0	11	100.0	100.0
0	0	12	100.0	100.0
0	0	13	100.0	100.0
0	0	14	100.0	100.0
0	0	15	100.0	100.0
0	0	16	100.0	100.0
0	0	17	100.0	100.0
0	0	18	100.0	100.0
0	0	19	100.0	100.0
0	0	20	100.0	100.0
0	0	21	100.0	100.0
0	0	22	100.0	100.0
0	0	23	100.0	100.0
0	0	24	100.0	100.0
0	0	25	100.0	100.0
0	0	26	100.0	100.0
0	0	27	100.0	100.0
0	0	28	100.0	100.0
0	0	29	100.0	100.0
0	0	30	100.0	100.0
0	0	31	100.0	100.0
0	0	32	100.0	100.0
0	0	33	100.0	100.0
0	0	34	100.0	100.0
0	0	35	100.0	100.0
0	0	36	100.0	100.0
0	0	37	100.0	100.0
0	0	38	100.0	100.0
0	0	39	100.0	100.0
0	0	40	100.0	100.0
0	0	41	100.0	100.0
0	0	42	100.0	100.0
0	0	43	100.0	100.0
0	0	44	100.0	100.0
0	0	45	100.0	100.0
0	0	46	100.0	100.0
0	0	47	100.0	100.0
0	0	48	100.0	100.0
0	0	49	100.0	100.0
0	0	50	100.0	100.0
0	0	51	100.0	100.0
0	0	52	100.0	100.0
0	0	53	100.0	100.0
0	0	54	100.0	100.0
0	0	55	100.0	100.0
0	0	56	100.0	100.0
0	0	57	100.0	100.0
0	0	58	100.0	100.0
0	0	59	100.0	100.0
0	0	60	100.0	100.0
0	0	61	100.0	100.0
0	0	62	100.0	100.0
0	0	63	100.0	100.0
0	0	64	100.0	100.0
0	0	65	100.0	100.0
0	0	66	100.0	100.0
0	0	67	100.0	100.0
0	0	68	100.0	100.0
0	0	69	100.0	100.0
0	0	70	100.0	100.0
0	0	71	100.0	100.0
0	0	72	100.0	100.0
0	0	73	100.0	100.0
0	0	74	100.0	100.0
0	0	75	100.0	100.0
0	0	76	100.0	100.0
0	0	77	100.0	100.0
0	0	78	100.0	100.0
0	0	79	100.0	100.0
0	0	80	100.0	100.0
0	0	81	100.0	100.0
0	0	82	100.0	100.0
0	0	83	100.0	100.0
0	0	84	100.0	100.0
0	0	85	100.0	100.0
0	0	86	100.0	100.0
0	0	87	100.0	100.0
0	0	88	100.0	100.0
0	0	89	100.0	100.0
0	0	90	100.0	100.0
0	0	91	100.0	100.0
0	0	92	100.0	100.0
0	0	93	100.0	100.0
0	0	94	100.0	100.0
0	0	95	100.0	100.0
0	0	96	100.0	100.0
0	0	97	100.0	100.0
0	0	98	100.0	100.0
0	0	99	100.0	100.0
0	0	100	100.0	100.0

firmed the unit cell. The Laue symmetry was  $2/m$ . Systematic absences  $-hkl$  observed with  $h+k=2n$  and  $h0l$  with  $l=2n$  only - indicate space group  $C2/c$  or  $Cc$  of which  $C2/c$  was found to be correct during the structure determination. X-ray intensity data were measured with an automated Picker diffractometer. The long axis - the direction perpendicular to the (10 $\bar{1}$ ) face - of the diffractometer. Mo  $K\alpha$  radiation was used with an incident-beam graphite monochromator, scintillation counter, and pulse-height discriminator. The scans were along  $2\theta$  with a scan angle of  $1.6^\circ(2\theta)$  and a speed of  $1/4^\circ(2\theta)$  per min. Background counts were 80 sec at the beginning and end of the scans. The intensity of a standard reflection, measured every 10 h, varied  $\pm 0.6\%$  during the period of data collection. All reflections within the asymmetric unit up to  $(\sin \theta)/\lambda = 0.87$  were measured. Intensities were divided by the angular factor of the monochromator-modified Lorentz-polarization correction  $L_p = (\cos^2 2\alpha + \cos^2 2\theta) / \sin \theta$ , where  $2\alpha$  is the angle between incident and diffracted beam of the monochromator whose diffracting plane is normal to the diffracting plane of the sample crystal. Since the linear absorption coefficient of  $HgMoO_4$  is rather high ( $\mu = 516 \text{ cm}^{-1}$ ), care was taken to describe the shape of the crystal accurately using a microscope and an optical goniometer. The program *ACACA* written by Prewitt (1967), based on a procedure described by Wuensch & Prewitt (1965), was used for the absorption correction. Transmission values varied between 22 and 41%.

#### Solution and refinement of the structure

The positions of the metal atoms were found through interpretation of a three-dimensional Patterson function computed with a program written by Fritchie & Guggenberger (1967). The oxygen atoms were located on a difference-Fourier map. The structure was refined with a full-matrix least-squares program by Finger (1969). Atomic scattering factors for neutral atoms were taken from Cromer & Waber (1965), corrected for anomalous dispersion (Cromer, 1965). The function  $\sum w(KF_o - |F_c|)^2$  was minimized where  $w$  is the weight based on counting statistics and  $K$  a scale factor. To account for secondary extinction the relation  $I_{\text{cor}} = I_{\text{uncor}} / (1 - cI_{\text{uncor}})$  was used (Zachariasen, 1963), where  $c$  was  $0.45 \times 10^{-6}$ . Reflections for which this correction amounted to more than 20% were given zero weight. They are marked with an asterisk in the list of observed

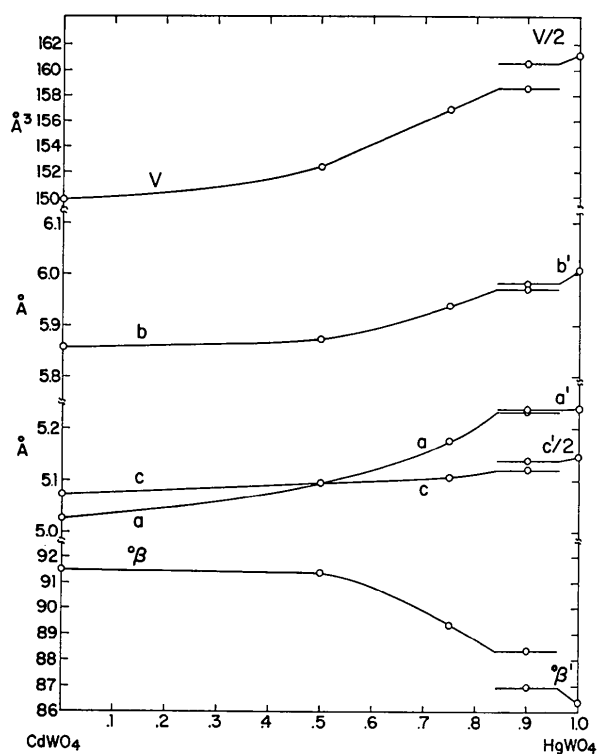


Fig. 1. Unit-cell dimensions of the solid solutions  $\text{HgWO}_4$  in  $\text{CdWO}_4$  ( $\text{NiWO}_4$ -wolframite structure) and  $\text{CdWO}_4$  in  $\text{HgWO}_4$  ( $\text{HgMoO}_4$  structure). The lattice constants of  $\text{CdWO}_4$  correspond to the conventional setting of the wolframite structure, as shown in Fig. 3. The lattice constants  $a', b', c', \beta$  correspond to the body-centered cell of  $\text{HgWO}_4$  given in Table 1 and drawn with broken lines in Fig. 3.

and calculated structure factors (Table 2). Reflections where  $F_o$  was less than three standard deviations were given zero weight.

For a refinement of the metal positions with isotropic thermal parameters, excluding oxygen atoms, the  $R$  value was 0.11 ( $R = \sum |F_c| - F_o / \sum F_o$ ). The refinement of the whole structure with isotropic thermal parameters resulted in an  $R$  value of 0.072. Allowing for anisotropic thermal motion for all atoms lowered  $R$  to 0.021 for the 813 reflections included in the refinement. For the total of 849 structure factors including the un-

Table 3. Positional and thermal parameters of  $\text{HgMoO}_4$

Numbers in parentheses are e.s.d.'s in the last significant digits. Vibrational parameters ( $\times 10^5$ ) are defined through  $T = \exp(-\sum \sum h_i h_j \beta_{ij})$ .

	Hg	Mo	O(1)	O(2)
$C2/c$	$4(c); \bar{1}$	$4(e); 2$	$8(f); 1$	$8(f); 1$
$x$	$\frac{1}{4}$	0	0.0982 (2)	0.1141 (3)
$y$	$\frac{1}{2}$	0.18801 (6)	0.0906 (4)	0.3641 (5)
$z$	0	$\frac{1}{4}$	0.0320 (4)	0.4688 (5)
$\beta_{11}$	145 (2)	135 (2)	234 (15)	330 (18)
$\beta_{22}$	637 (6)	385 (9)	619 (50)	708 (47)
$\beta_{33}$	1019 (8)	594 (10)	1387 (71)	1286 (72)
$\beta_{12}$	-104 (1)	0	-135 (23)	-101 (27)
$\beta_{13}$	208 (3)	147 (4)	374 (28)	183 (30)
$\beta_{23}$	-18 (2)	0	-182 (46)	-117 (52)

observed ones (Table 2) the  $R$  value is 0.023. Final positional thermal parameters are given in Table 3.

### Isostructural $\text{HgWO}_4$ and solid solutions

The great similarity in unit-cell dimensions of  $\text{HgMoO}_4$  and  $\text{HgWO}_4$  (Table 1) suggested that  $\text{HgWO}_4$  has the  $\text{HgMoO}_4$  structure. This was confirmed through an intensity calculation (Yvon, Jeitschko & Parthé, 1969) for the powder pattern (Table 4) using positional parameters as found for  $\text{HgMoO}_4$ .

The preparation of solid solutions of the type  $\text{Hg}_{1-x}\text{A}_x\text{MoO}_4$  and  $\text{Hg}_{1-x}\text{A}_x\text{WO}_4$  was attempted where A is Pb, Cd, Zn, Cu, or Mg. We observed only

Table 4. Calculated and observed lattice spacings  $d$  (Å) and intensities for Guinier-Hägg patterns of  $\text{HgMoO}_4$  and  $\text{HgWO}_4$

$\text{HgMoO}_4$					$\text{HgWO}_4$				
hk l	$d_c$	$d_o$	$I_c$	$I_o$	hk l	$d_c$	$d_o$	$I_c$	$I_o$
11 0	5.2379	5.2263	8	s	20 0	5.2276	--	<1	m
20 0	5.2202	5.2085	11	s	11 0	5.2085	5.2060	14	m
11-1	3.9167	3.9174	16	s	11-1	3.9031	--	<1	-
11 1	3.2337	3.2349	100	vvvs	11 1	3.2023	3.2021	100	vvvs
31-1	3.0410	3.0391	85	vvvs	31-1	3.0577	3.0580	88	vvvs
02 0	3.0275	3.0391	33	vvvs	31 0	3.0145	--	3	-
31 0	3.0173	--	2	-	02 0	3.0035	3.0034	32	vs
22 0	2.6189	2.6184	12	w	40 0	2.6138	2.6132	22	s
40 0	2.6101	2.6099	19	m	22 0	2.6043	--	2	-
20-2	2.5679	2.5683	26	s	20-2	2.5673	2.5672	28	s
02 1	2.5560	2.5559	3	vw	02 1	2.5354	2.5348	7	vw
22-1	2.5054	--	<1	-	22-1	2.4977	2.4983	2	vvvw
00 2	2.3848	2.3845	7	vw	00 2	2.3645	2.3627	1	vvvw
11-2	2.3151	--	<1	-	11-2	2.3322	2.3326	1	vvvw
31-2	2.2683	--	<1	-	31-2	2.2745	2.2737	1	vvw
31 1	2.2391	2.2375	6	vw	40-2	2.2487	--	<1	-
40-2	2.2313	--	1	-	31 1	2.2218	--	<1	-
22 1	2.1310	2.1308	6	vw	51-1	2.1250	--	<1	-
51-1	2.1106	2.1108	6	vw	22 1	2.1127	2.1125	8	vw
42-1	2.0457	--	1	-	42-1	2.0489	2.0487	2	vvw
11 2	2.0297	--	1	-	11 2	2.0097	2.0102	1	vvw
13 0	1.9816	--	2	-	51 0	1.9748	--	<1	-
42 0	1.9769	1.9769	24	s	42 0	1.9717	1.9714	23	s
51 0	1.9740	--	<1	-	13 0	1.9665	1.9665	5	vw
22-2	1.9583	1.9589	24	s	22-2	1.9515	1.9514	23	s
20 2	1.9124	1.9118	12	w	51-2	1.9037	--	1	-
51-2	1.8890	--	1	-	20 2	1.8925	1.8926	12	w
13-1	1.8785	1.8772	7	w	13-1	1.8655	1.8649	3	vvvw
02 2	1.8734	1.8772	4	w	02 2	1.8579	--	<1	-
42-2	1.7962	1.7960	4	vvw	42-2	1.8001	--	<1	-
13 1	1.7851	1.7856	12	w	60-2	1.7762	1.7761	13	m
60-2	1.7583	1.7586	12	w	13 1	1.7699	1.7698	10	w
33-1	1.7505	1.7514	15	m	33-1	1.7443	1.7440	12	w
33 0	1.7460	--	2	-	60 0	1.7425	--	<1	-
60 0	1.7401	1.7413	2	vvvw	33 0	1.7362	1.7373	5	vw
42 1	1.6650	1.6641	2	vvvw	42 1	1.6537	1.6540	3	vvw
31-3	1.6474	1.6474	2	vvvw	31-3	1.6460	--	<1	-
51 1	1.6293	1.6284	16	m	51 1	1.6205	1.6206	17	m
31 2	1.6287	--	<1	-	31 2	1.6126	--	<1	-
22 2	1.6169	1.6164	13	m	62-1	1.6027	--	3	-
11-3	1.6087	1.6090	13	m	22 2	1.6012	1.5999	12	s
62-1	1.5972	1.5968	2	vvvw	11-3	1.5982	1.5982	14	s
13-2	1.5810	1.5813	2	vvvw	13-2	1.5703	--	3	-
33-2	1.5569	--	1	-	71-1	1.5634	1.5635	14	m
71-1	1.5538	1.5536	13	m	33-2	1.5523	--	2	-
33 1	1.5473	1.5468	5	vw	51-3	1.5433	1.5438	17	m
51-3	1.5358	1.5363	16	m	33 1	1.5352	--	2	-
62-2	1.5205	1.5207	10	w	62-2	1.5288	1.5287	11	w
04 0	1.5138	--	2	-	71-2	1.5219	--	1	-
62 0	1.5086	1.5079	2	vvvw	62 0	1.5072	--	<1	-
71-2	1.5083	1.5079	1	vvvw	53-1	1.5022	1.5030	1	vvvw
53-1	1.5030	1.5033	3	vvvw	04 0	1.5018	--	1	-
40 2	1.5001	--	<1	-	40 2	1.4862	--	<1	-
22-3	1.4905	1.4901	2	vvvw	22-3	1.4837	1.4843	3	vvvw
13 2	1.4729	1.4717	2	vvvw	42-3	1.4611	1.4603	2	vvvw

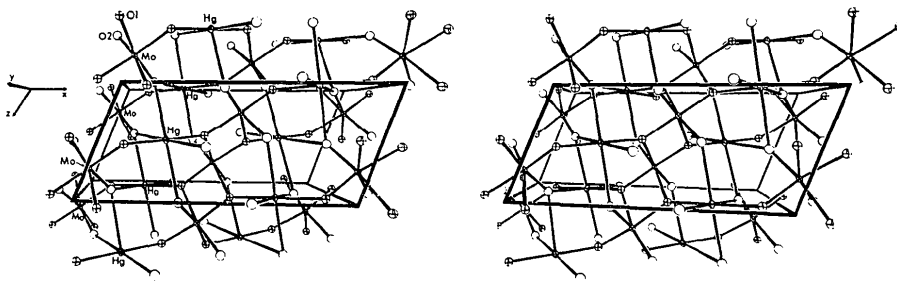


Fig. 2. Stereodrawing of the  $\text{HgMoO}_4$  structure. Johnson's (1965) *ORTEP* program was used for this drawing. The sizes of the atoms correspond to the 50% probability limit. Metal atoms are drawn with their anisotropic thermal ellipsoids while the corresponding isotropic thermal parameters were used for the oxygen atoms.

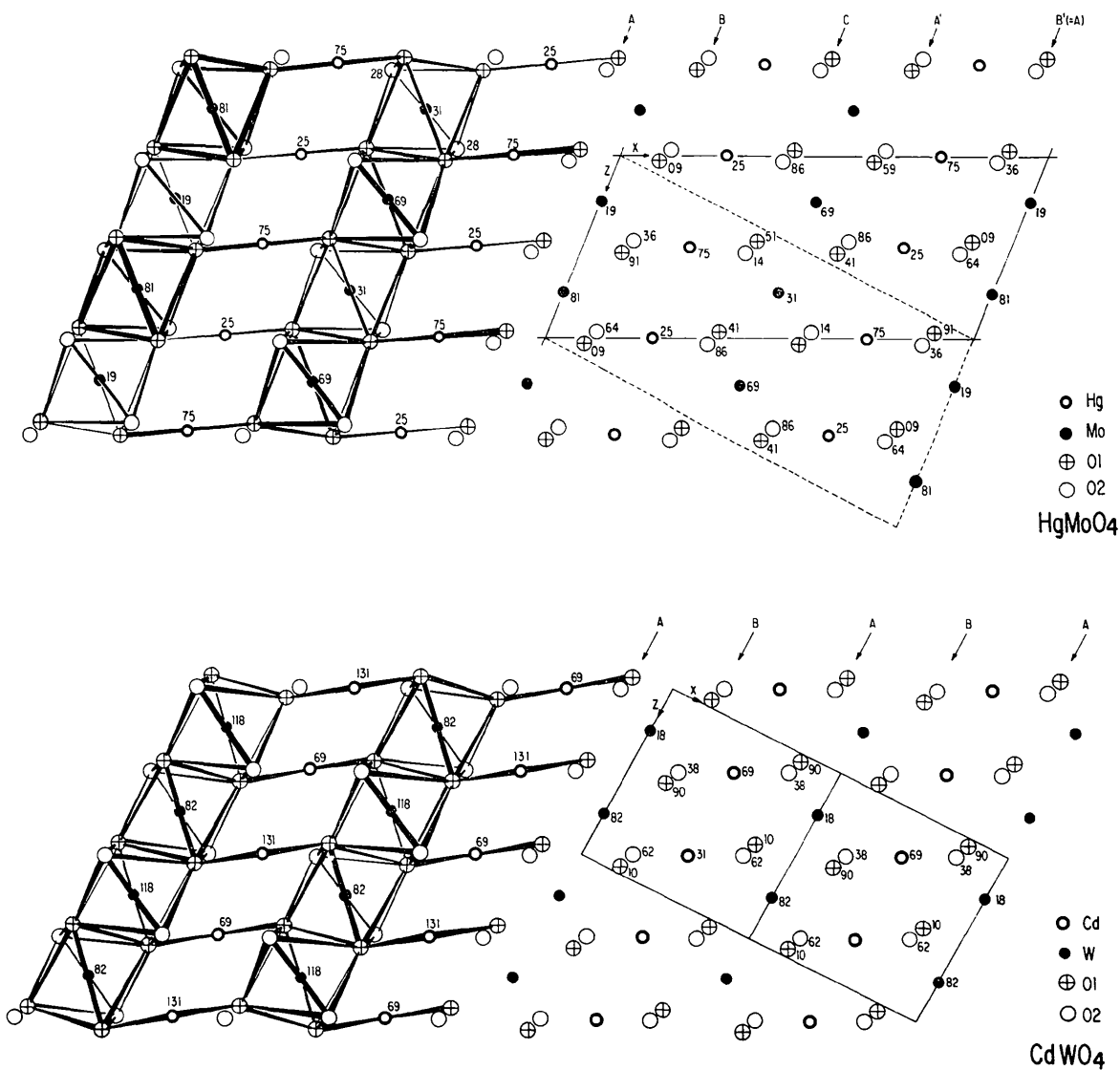


Fig. 3. Structure of  $\text{HgMoO}_4$  as compared to the  $\text{CdWO}_4$  structure with wolframite ( $\text{NiWO}_4$ ) type. Unit cells corresponding to the conventional settings are drawn with solid lines. Broken lines in the structure of  $\text{HgMoO}_4$  indicate the unit cell for  $12/a$  setting corresponding to the  $\text{CdWO}_4$  structure. The  $y$  coordinates of the atoms are given in hundredths.

very limited solid solubility for any A cation at 3 kb and 700°C. Preparations carried out in a tetrahedral anvil press (Lloyd, Hutton & Johnson, 1959; Bither, Gillson & Young, 1966) at 65 kbar and 900°C gave significant solid solution only when A was Cd.  $\text{HgWO}_4$  is very soluble in  $\text{CdWO}_4$ , and  $\text{CdWO}_4$  is somewhat soluble in  $\text{HgWO}_4$ . The extent of the solid solution is shown in Fig. 1 with the cell dimensions.  $\text{HgMoO}_4$  is also very soluble in  $\text{CdMoO}_4$ . The limit is about  $\text{Cd}_{0.4}\text{Hg}_{0.6}\text{MoO}_4$  where the scheelite cell dimensions are  $a=5.20$  and  $c=11.30$  Å as compared to  $a=5.15$  and  $c=11.19$  Å for  $\text{CdMoO}_4$ .  $\text{CdMoO}_4$  is only very slightly soluble in  $\text{HgMoO}_4$  under these conditions.

Preparations under normal pressure were not attempted since, because of the low stability of  $\text{HgO}$ , temperatures would be limited to 600°C. Furthermore, extrapolation of the results obtained at 65 and 3 kbar did not suggest significant solid solutions at lower pressures.

#### Description of the structure and its relation to $\text{CdWO}_4$

The structure of  $\text{HgMoO}_4$  (Fig. 2) is similar to the wolframite ( $\text{NiWO}_4$ ) structure. The unit cell may be redefined as  $I2/a$  (Table 1), so that the axes of  $\text{HgMoO}_4$

and  $\text{HgWO}_4$  correspond to those of wolframite. Fig. 3 gives a comparison of the two structures.\* Both have zigzag chains of edge-shared  $\text{WO}_6$  or  $\text{MoO}_6$  octahedra extending parallel to the  $c$  axis. The differences between the two structures may be seen in the packing of the oxygen atoms. In both structures they form close-packed layers parallel to the  $yz$  plane. The stacking of these layers is almost perfectly hexagonal close-packed in the  $\text{CdWO}_4$  structure, while it comes close to cubic close packing in  $\text{HgMoO}_4$ . Adjacent oxygen layers  $ABC$  in  $\text{HgMoO}_4$  are, however, slightly displaced relative to each other such that the fifth layer  $B'$  corresponds to the  $A$  layer (see Fig. 3). Thus the octahedral voids accommodating the Hg and Mo atoms are far from ideal: Hg forms its characteristic two short collinear Hg-O bonds, and the oxygen environment of Mo is transitional from octahedral to tetrahedral (Fig. 4(a), Table 5).

\* The wolframite ( $\text{NiWO}_4$ ) structure has been refined for  $\text{CdWO}_4$  by Chichagov, Ilyukhin & Belov (1966). The data for our drawing of  $\text{CdWO}_4$  were taken from that publication except for the  $z$  coordinates of Cd and W which are obviously misrepresented. We have recalculated interatomic distances for  $\text{CdWO}_4$ . Agreement between our calculated distances and their distances is obtained for  $z_{\text{Cd}} = \frac{1}{4}$  and  $z_{\text{W}} = \frac{1}{4}$ .

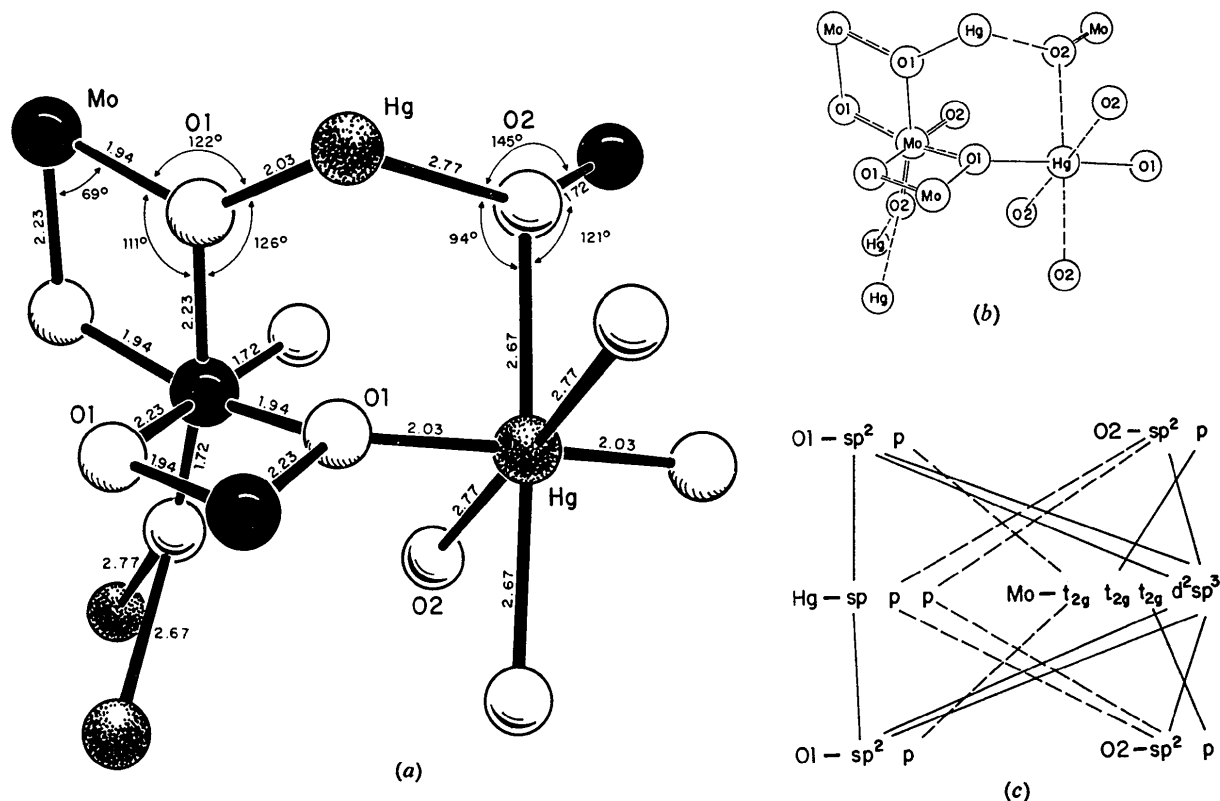


Fig. 4. Nearest-neighbor environments and bonding in the  $\text{HgMoO}_4$  structure. The relative arrangement of the four unique atoms (Hg, Mo, O1, O2) is shown in (a). Chemical bonding is shown schematically in (b) and (c). Continuous lines represent normal two-electron bonds. Half bonds are indicated by broken lines. The bonding atomic orbitals are indicated for one formula unit. In that representation (c) multiple lines connecting one metal atom with one oxygen atom do not necessarily represent multiple bonds [for instance the two lines from Mo  $d^2sp^3$  to O(1)  $sp^2$  represent two single bonds between one Mo and two O(1) atoms in the structure as shown in (b)].

There are two kinds of oxygen in both the wolframite and the HgMoO<sub>4</sub> structures. They are in threefold, essentially planar, coordination with the metal atoms.

For AMoO<sub>4</sub> and AWO<sub>4</sub> compounds with the wolframite structure it has been observed (Sleight, 1972) that *c* is always greater than *a*. The *c/a* ratio, however, decreases with the increasing size of the A cation, but there is a change to the scheelite structure just before the *c/a* ratio goes through unity. In the solid solution between CdWO<sub>4</sub> and HgWO<sub>4</sub> this change to the scheelite structure is suppressed because Hg is not a suitable A cation for the scheelite structure. Thus, this solid solution (Fig. 1) shows for the first time *c* and *a* actually crossing over and *a* becoming greater than *c*.

### Description of bonding

Fig. 4(b) and (c) schematically represent bonding in HgMoO<sub>4</sub>. Molybdenum is in approximately octahedral coordination to oxygen and *d*<sup>2</sup>*sp*<sup>3</sup> hybridization may be assumed for  $\sigma$  bonding to oxygen. The remaining three *t*<sub>2g</sub> orbitals of molybdenum are available for  $\pi$  bonding to oxygen. Cotton & Wing (1965) have compared structural and infrared data for various MoO<sub>n</sub> groups. They related force constants and bond distances to estimate bond orders and arrived at bond distances of 1.7<sub>5</sub>, 1.9, and 2.1 Å for bond orders of 2, 1½ and 1 respectively. These values are close to the three different Mo–O bond distances found in HgMoO<sub>4</sub> (Table 5).

Two of the three *t*<sub>2g</sub> orbitals of Mo form  $\pi$  bonds with *p* orbitals of the two O(2) atoms at 1.72 Å while the third *t*<sub>2g</sub> orbital overlaps with the *p* orbitals of two O(1) atoms at 1.94 Å. Thus the Mo–O(2) bonds may be considered as double bonds ( $\sigma + \pi$ ) and the Mo–O(1) bonds with 1.94 Å as bonds of order 1½ ( $\sigma + \frac{1}{2}\pi$ ). The remaining two Mo–O(1) bonds with 2.23 Å are single ( $\sigma$ ). The point symmetry 2 of the Mo atom is compatible with these assignments.

Mercury forms two short linear bonds to oxygen at distances of 2.03 Å. This distance is close to the short linear Hg–O distances in orthorhombic HgO (2.07 ± 0.03 Å) and in NaHg<sub>2</sub>O<sub>2</sub>I (2.01 ± 0.02 Å) (Aurivillius, 1964). It may be considered as a single bond. In view of the linear arrangement O–Hg–O *sp* hybridization may be assumed for Hg. This leaves two *p* orbitals to form four bonds to the four O(2) atoms at about 2.7 Å. Since each *p* orbital must participate in two bonds, these bonds may be considered to have a bond order of ½.

The *d* levels of mercury are very close in energy to the *s* level; thus, some of the mercury–oxygen bonds may possess considerable *d* character. However, since the *d* levels are filled, this is of subordinate importance in a qualitative bonding description (Orgel, 1958; Nyholm, 1961; Deacon, 1963).

Both oxygen atoms are in threefold, essentially planar, coordination to the metal atoms; thus *sp*<sup>2</sup> hybridization can be assumed. The planes defined by the

Table 5. *Interatomic distances and angles in HgMoO<sub>4</sub>*

Standard deviations are all less than 0.004 and 0.005 Å for metal–oxygen and oxygen–oxygen distances respectively. Standard deviations in interatomic angles are all less than 0.4°. Root mean square thermal displacements for principal bonds are listed after the semicolon. The oxygen environment of Mo is transitional between octahedral and tetrahedral. For comparison, ideal octahedral (octa) and tetrahedral (tetra) O–Mo–O angles are listed together with the real ones.

Hg: O(1)	2.026 (2 ×);	0.070 (1) Å	Mo: O(2)	1.722 (2 ×);	0.087 (1) Å
O(2)	2.672 (2 ×);	0.111 (1)	O(1)	1.944 (2 ×);	0.075 (1)
O(2')	2.766 (2 ×);	0.117 (1)	O(1')	2.228 (2 ×)	0.086 (1)
O(1')	3.142 (2 ×)				
O(1): Hg	2.026;	0.081 (4) Å	O(2): Hg	2.672;	0.125 (5) Å
Hg	3.142		Hg	2.766;	0.111 (5)
Mo	1.944;	0.094 (4)	Mo	1.722;	0.108 (5)
Mo	2.228;	0.102 (5)	O(2)	2.705	
O(1)	2.380		O(1)	2.745	
O(2)	2.745		O(1)	2.786	
O(2)	2.786		O(1)	2.911	
O(1)	2.801 (2 ×)		O(2)	3.058 (2 ×)	
O(2)	2.911		O(2)	3.174	
O(1)	2.911		O(2)	3.265	
O(1)–Hg–O(1)	180.0°		O(1)–Mo–O(1)	144.7	Octa
O(2)–Hg–O(2)	180.0		O(1')–Mo–O(1')	81.6	180°
O(2')–Hg–O(2')	180.0		O(1)–Mo–O(1')	84.0 (2 ×)	90
O(1)–Hg–O(2')	91.8 (2 ×)		O(1)–Mo–O(1')	69.2 (2 ×)	90
O(1)–Hg–O(2')	88.2 (2 ×)		O(1)–Mo–O(2)	105.0 (2 ×)	90
O(1)–Hg–O(2)	93.4 (2 ×)		O(1)–Mo–O(2)	96.8 (2 ×)	109
O(1)–Hg–O(2)	86.6 (2 ×)		O(1')–Mo–O(2)	163.6 (2 ×)	180
O(2)–Hg–O(2')	111.6 (2 ×)		O(1')–Mo–O(2)	88.7 (2 ×)	90
O(2)–Hg–O(2')	68.4 (2 ×)		O(2)–Mo–O(2)	103.5	90
Hg–O(1)–Mo	125.9		Hg–O(2)–Hg	93.9°	Tetra
Hg–O(1)–Mo	122.3		Hg–O(2)–Mo	120.5	109°
Mo–O(1)–Mo	110.8		Hg–O(2)–Mo	145.2	---

$sp^2$  hybrids are oriented in such a way as to give maximum overlap of the remaining oxygen  $p$  orbitals with the  $t_{2g}$  orbitals of Mo forming  $\pi$  bonds.

The oxygen(1) atom forms three full  $\sigma$  bonds: one to Hg, two to two Mo atoms. Its  $p$  orbital forms  $\frac{1}{2}\pi$  bond to one molybdenum atom. Oxygen(2) is doubly bonded to one Mo ( $\sigma + \pi$ ). Its remaining two  $sp^2$  orbitals participate each only in  $\frac{1}{2}$  bonds to two mercury atoms.

This bonding description involves 13 metal orbitals (Hg  $sp^3:4$ ; Mo  $d^5sp^3:9$ ) and thus accounts for 26 of the 32 valence electrons of the normal unit. The remaining 6 electrons are nonbonding and not shown in Fig. 4(c). They fill those oxygen orbitals forming the fractional bonds to the metal atoms: each O(1) can accommodate one more electron in the nonhybridized  $p$  orbital and each O(2) can hold 2 more electrons in two of the  $sp^2$  hybrids. Therefore these orbitals have much lone-pair character.

This account of bonding in  $HgMoO_4$  rationalizes the geometry of the structure and the peculiarities in bond lengths. It is also consistent with the site symmetries. It is a description for maximum covalency. Assuming that the bonding electrons belong equally to the atoms, negative formal charges of  $-2$  for Hg and  $-3$  for Mo result. On the other hand in the ionic formulation  $Hg^{2+}Mo^{6+}O_4^{2-}$  all 32 valence electrons are on the oxygen atoms. It is clear that the true electron distribution must be somewhere in between the extreme covalent and the extreme ionic formulation. The two formulations may actually be considered as two resonating states for a VB description of bonding in  $HgMoO_4$ .

#### Thermal vibrations

It has been mentioned above that the introduction of anisotropic thermal parameters during the least-squares refinement of the structure resulted in a substantial improvement in  $R$  value from 7.2 to 2.3%. Calculation of root-mean-square (r.m.s.) amplitudes of thermal ellipsoids showed that all atoms had significant thermal anisotropy with ratios of longest to shortest axis  $1.69 \pm 0.02$ ,  $1.20 \pm 0.02$ ,  $1.75 \pm 0.12$ ,  $1.37 \pm 0.09$  for Hg, Mo, O(1), O(2), respectively. The r.m.s. displacements along principal bonds are listed in Table 5 next to corresponding bonding distances. It can be seen that displacements for Hg–O bonds are larger for both Hg

and O atoms along the bonds with bond order  $\frac{1}{2}$  than for the full bond. The situation is more complex for Mo–O bonds since the short and long Mo–O bonds are on opposite sides of the Mo atom.

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