

The Crystal Structure of Magnesium Dimolybdate

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The structure of magnesium dimolybdate, MgMo_2O_7 , monoclinic with space group $P2_1/c$ and $a = 8.111$ (2), $b = 5.700$ (1), $c = 15.002$ (3) Å, $\beta = 115.26$ (2)°, $Z = 4$, was determined by the heavy-atom method and refined by full-matrix least squares to an R of 0.095 for 2558 counter reflexions. The $\text{Mo}_2\text{O}_7^{2-}$ pyro-anion consists of two corner-sharing MoO_4 tetrahedra, which are twisted from the ideal eclipsed configuration by an average of 12.3°. Mo_2O_7 groups form anionic sheets parallel to the (100) plane. Mg^{2+} ions are situated between the anionic sheets in a distorted-octahedral environment of O atoms. MgO_6 octahedra share one edge forming Mg_2O_{10} units.

Introduction

The phase equilibrium diagram for the system of MgMoO_4 – MoO_3 has been investigated (Zhukovskii, Tkachenko & Rakova, 1970) and only one compound, of the composition $\text{Mg}_2\text{Mo}_3\text{O}_{11}$, was found. Our preliminary studies showed that two compounds, of chemical formulae $\text{Mg}_2\text{Mo}_3\text{O}_{11}$ and MgMo_2O_7 , exist in this system.

Attempts to obtain single crystals of the MgMo_2O_7 compound proved successful and the crystal structure investigation was undertaken.

Experimental

Single crystals of MgMo_2O_7 were grown from a melt of 0.15 mol% MgO and 0.85 mol% MoO_3 ,* making use of the sublimation of MoO_3 at higher temperatures. Crystallization was performed in an open quartz tube by heating the mixture at 800°C for 48 h. After cooling, a large number of pale-pink crystals of poorly defined morphology were obtained. The Mg/Mo atomic ratio in the crystals, as determined by atomic absorption spectroscopy, was 1:2. Laue photographs showed well-formed reflexions and Weissenberg photographs indicated monoclinic symmetry with space group $P2_1/c$ (systematic absences: $0k0$ for k odd, $h0l$ for l odd). Cell parameters were obtained by least-squares refinement from the setting angles of the 15 strong reflexions used in the auto-indexing procedure. The density of the investigated crystals was determined by a pycnometric method in carbon tetrachloride.

* Both are commercial products.

Crystal data

MgMo_2O_7 , monoclinic, $M_r = 328.2$, space group $P2_1/c$, $a = 8.111$ (2), $b = 5.700$ (1), $c = 15.002$ (3) Å, $\beta = 115.26$ (2)°, $V = 627.3$ Å³, $Z = 4$, $D_x = 3.475$, $D_m = 3.22$ g cm⁻³, $F(000) = 608$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 42.58$ cm⁻¹.

For a crystal ground to the approximate shape of an ellipsoid with dimensions $0.27 \times 0.21 \times 0.21$ mm, intensity data were collected on a CAD-4 single-crystal diffractometer (Enraf–Nonius) using graphite-monochromated Mo $K\alpha$ radiation.* Measurements were taken in the range of theta from 1 to 35° with the θ – 2θ scan mode and a scan width of $0.65^\circ + 0.40^\circ \tan \theta$. The intensities were corrected for background, Lorentz and polarization effects and the absorption correction for an ellipsoid was applied with Buda's (1977) program. No correction was made for extinction. Scaling of intensities was achieved with a reference reflexion recorded after each group of 47 measurements. The fluctuation in the intensity of the standard reflexion was random and less than 5%. Out of 2628 independent reflexions measured, 21 were found to have intensities less than zero and 49 were not significantly above background [$I < 1.5\sigma(I)$]. Therefore, 2558 intensities were used in further calculations.

Structure solution and refinement

The coordinates of the two Mo atoms in the asymmetric unit were determined from a three-dimensional

* The intensity measurement was carried out in the X-ray Division of the Regional Laboratory of Physicochemical Analysis and Structure Research, Kraków.

Table 1. *Positional parameters* ($\times 10^4$) *with estimated standard deviations in parentheses*

	x	y	z
Mo(1)	7474.1 (5)	6259.9 (4)	3638.5 (3)
Mo(2)	12073.7 (5)	6340.2 (6)	3712.9 (3)
Mg	5155 (2)	1265 (2)	4103 (1)
O(1)	6955 (5)	3913 (6)	4220 (3)
O(2)	6090 (6)	6133 (6)	2392 (3)
O(3)	7005 (5)	8805 (5)	4102 (3)
O(4)	9931 (5)	6245 (4)	3906 (3)
O(5)	13208 (5)	3688 (5)	4021 (3)
O(6)	13619 (5)	8646 (5)	4335 (3)
O(7)	11452 (6)	6777 (9)	2486 (3)

Patterson map. After refinement of the Mo parameters ($R = 0.23$), a difference map revealed all the missing atoms. The structure was refined by the full-matrix least-squares method on the basis of 2558 observed reflexions. All calculations were performed with the *SHELX* program system (Sheldrick, 1975) in which the following weighting scheme was used: $w = k[\sigma^2(F_o) + |g|F_o^2]^{-1}$.

Values of k and g were refined to 1 and 0.0857 respectively. The atomic scattering factors of Mo and Mg were taken from *International Tables for X-ray Crystallography* (1974) and $\Delta f'$ and $\Delta f''$ corrections for anomalous dispersion were from Cromer (1965). The refinement with anisotropic temperature factors for all atoms was stopped when the shifts of the parameters were less than 0.1 of their estimated standard deviations for all atoms, except those for U_{22} of Mo(1) and Mo(2) which, however, did not exceed 0.5 of their e.s.d.'s.

Despite the application of a damping factor, better convergence was difficult to obtain because of correlations between the anisotropic temperature factors of both Mo atoms. The last difference Fourier synthesis revealed several, randomly distributed peaks not larger than $2 e \text{ \AA}^{-3}$. The final discrepancy indices for all reflexions were as follows: $R = 0.095$, $R_w = 0.102$ and $R_G = 0.156$ where $R = \sum |F_o| - |F_c| / \sum |F_o|$, $R_w = \sum w^{1/2} |F_o| - |F_c| / \sum w^{1/2} |F_o|$ and $R_G = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$. There are about 80 strong reflexions observed (i.e. 3%) with $|F_o|$ considerably lower than $|F_c|$. These differences, resulting in the relatively high R factor, can be attributed to the effect of extinction. The final positional parameters are presented in Table 1.*

Description of the structure

The bond lengths and angles found in the structure of the title compound are given in Table 2. Mo atoms are

surrounded by four O atoms, arranged in a slightly distorted tetrahedron. The MoO_4 tetrahedra share corners forming discrete $\text{Mo}_2\text{O}_7^{2-}$ ions (Fig. 1a) with a $\text{Mo}(1)\text{—O}(4)\text{—Mo}(2)$ angle of $160.7(3)^\circ$. The unshared O atoms are twisted somewhat from the ideal eclipsed configuration of mm symmetry (Fig. 1b). According to Panagiotopoulos & Brown (1973) the

Table 2. *Interatomic distances* (\AA) *and bond angles* ($^\circ$) *with estimated standard deviations in parentheses*

(a) $\text{Mo}_2\text{O}_7^{2-}$			
Mo(1)—O(1)	1.744 (3)	Mo(2)—O(4)	1.881 (4)
Mo(1)—O(2)	1.723 (4)	Mo(2)—O(5)	1.727 (3)
Mo(1)—O(3)	1.720 (3)	Mo(2)—O(6)	1.781 (3)
Mo(1)—O(4)	1.857 (4)	Mo(2)—O(7)	1.707 (4)
O(2)—Mo(1)—O(1)	109.0 (2)	O(5)—Mo(2)—O(4)	110.8 (2)
O(3)—Mo(1)—O(1)	107.6 (2)	O(6)—Mo(2)—O(4)	115.5 (2)
O(4)—Mo(1)—O(1)	110.8 (2)	O(7)—Mo(2)—O(4)	107.6 (2)
O(3)—Mo(1)—O(2)	108.6 (2)	O(6)—Mo(2)—O(5)	109.3 (2)
O(4)—Mo(1)—O(2)	112.1 (2)	O(7)—Mo(2)—O(5)	107.2 (2)
O(4)—Mo(1)—O(3)	108.6 (2)	O(7)—Mo(2)—O(6)	106.0 (2)
Mo(2)—O(4)—Mo(1)	160.7 (3)		
(b) Mg environment			
Mg—O(1)	2.055 (4)	O(3 ^{iv})—Mg—O(2 ⁱⁱⁱ)	89.6 (2)
Mg—O(2 ⁱⁱⁱ)	2.031 (4)	O(5 ^{vi})—Mg—O(2 ⁱⁱⁱ)	87.2 (2)
Mg—O(3)	2.054 (4)	O(6 ^v)—Mg—O(2 ⁱⁱⁱ)	96.2 (2)
Mg—O(5 ^{vi})	2.061 (4)	O(6 ⁱ)—Mg—O(2 ⁱⁱⁱ)	178.2 (2)
Mg—O(6 ^v)	2.067 (3)	O(5 ^{vi})—Mg—O(3 ^{iv})	176.7 (2)
Mg—O(6 ⁱ)	2.119 (4)	O(6 ^v)—Mg—O(3 ^{iv})	90.0 (2)
O(2)—Mg—O(1)	97.0 (2)	O(6 ⁱ)—Mg—O(3 ^{iv})	91.1 (2)
O(3)—Mg—O(1)	90.5 (2)	O(6 ^v)—Mg—O(5 ^{vi})	89.6 (2)
O(5 ^{vi})—Mg—O(1)	90.6 (1)	O(6 ⁱ)—Mg—O(5 ^{vi})	92.1 (2)
O(6 ^v)—Mg—O(1)	84.7 (2)	O(6 ⁱ)—Mg—O(6 ^v)	82.1 (2)
O(6 ^v)—Mg—O(1)	166.8 (2)		
(c) Some non-bonding distances with e.s.d.'s in the range 0.005–0.007 \AA			
$\text{Mo}_2\text{O}_7^{2-}$		Mg environment	
O(2)—O(1)	2.823	O(2 ⁱⁱⁱ)—O(1)	3.060
O(3)—O(1)	2.795	O(3 ^{iv})—O(1)	2.919
O(4)—O(1)	2.965	O(5 ^{vi})—O(1)	2.926
O(3)—O(2)	2.797	O(6 ⁱ)—O(1)	2.811
O(4)—O(2)	2.971	O(3 ^{iv})—O(2 ⁱⁱⁱ)	2.878
O(4)—O(3)	2.906	O(5 ^{vi})—O(2 ⁱⁱⁱ)	2.823
O(5)—O(4)	2.971	O(6 ^v)—O(2 ⁱⁱⁱ)	3.050
O(6)—O(4)	3.097	O(6 ^v)—O(3 ^{iv})	2.914
O(7)—O(4)	2.897	O(6 ⁱ)—O(3 ^{iv})	2.980
O(6)—O(5)	2.861	O(6 ^v)—O(5 ^{vi})	2.908
O(7)—O(5)	2.763	O(6 ⁱ)—O(5 ^{vi})	3.009
O(7)—O(6)	2.786	O(6 ⁱ)—O(6 ^v)	2.750
Others			
O(2 ⁱⁱⁱ)—O(7)	3.140	Mo(1)—Mo(2)	3.685
O(4 ⁱⁱⁱ)—O(7)	3.179	Mo(1)—Mg	3.640
O(7 ⁱⁱⁱ)—O(7)	3.709	Mo(2 ^{iv})—Mg	3.636
O(2 ⁱⁱⁱ)—O(2)	3.441	Mo(1)—Mg ⁱⁱⁱ	3.739
Mg—Mg ⁱ	3.156	Mo(2 ^{iv})—Mg ⁱ	3.371

Symmetry code

- | | | | |
|-------|--|------|-------------------|
| (i) | $-x, -y, -z$ | (iv) | $x, y - 1, z$ |
| (ii) | $x, \frac{1}{2} - y, \frac{1}{2} + z$ | (v) | $x - 1, y - 1, z$ |
| (iii) | $-x, \frac{1}{2} + y, \frac{1}{2} - z$ | (vi) | $x - 1, y, z$ |

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32845 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

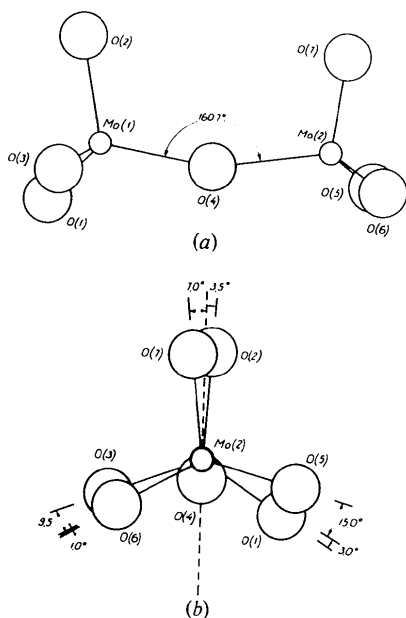


Fig. 1. (a) View of the dimolybdate ion $\text{Mo}_2\text{O}_7^{2-}$ projected on the Mo(1), O(4), Mo(2) plane; (b) projection down the Mo(1)–Mo(2) direction.

relative orientation of MoO_4 groups in pyro-anions can be described by two torsion angles, α_1 and α_2 . They are defined as the rotation angles of the terminal O atoms about the Mo(1)–Mo(2) axis out of the plane of the bridging O and both Mo atoms. The α_1 , α_2 angles are positive when the terminal O is rotated clockwise from this plane as viewed from the bridging O atom. The mean value of α_1 is $+5.3^\circ$, that of α_2 is $+7.0^\circ$ and the average twist angle of $\alpha_1 + \alpha_2$ equals 12.3° in the structure of MgMo_2O_7 .

The bridging Mo(1)–O(4) and Mo(2)–O(4) distances are 1.857 (4) and 1.881 (4) Å respectively. The Mo(2)–O(7) distance of 1.707 (4) Å is the shortest Mo–O bond length in MgMo_2O_7 . O(7) forms contacts

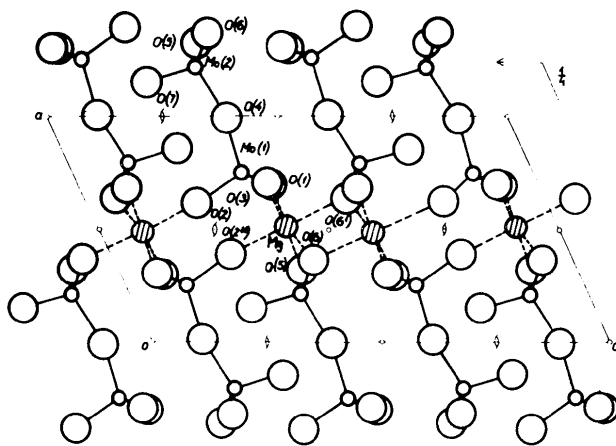


Fig. 2. MgMo_2O_7 structure projected down *b*.

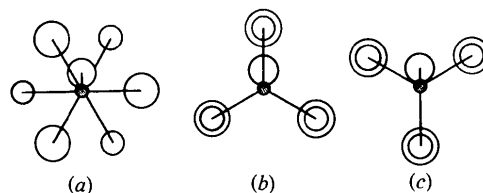


Fig. 3. Conformation types of the $X_2\text{O}_7$ group from Panagiotopoulos & Brown (1973): (a) staggered, (b) and (c) eclipsed.

only with O(4ⁱⁱⁱ), O(2ⁱⁱⁱ) and O(7ⁱⁱⁱ) oxygen atoms. The Mo–O bond lengths involving O(1), O(2) and O(5), which are coordinated to one Mg atom, vary from 1.720 (3) to 1.744 (3) Å, while in the case of O(6), coordinated to two Mg atoms, the Mo(2)–O(6) distance is 1.781 (3) Å. The mean Mo–O bond length of 1.77 (2) Å agrees very well with that of 1.77 Å quoted by Schröder (1975) as the characteristic average Mo–O distance in MoO_4 tetrahedra. The mean interbond O–Mo–O angle in Mo_2O_7 of $109.4 (7)^\circ$ is in agreement with the ideal value of the tetrahedral angle. The thermal vibration of the bridging O atom is not larger than those of the terminal atoms. The direction defined by the Mo(1) and Mo(2) atoms of the same pyro-anion is almost parallel to **a**. The packing of the dimolybdate groups in the unit cell is shown in Fig. 2.

$\text{Mo}_2\text{O}_7^{2-}$ ions form anionic sheets parallel to the (100) plane. The Mg atoms are situated between anionic sheets so that each Mg atom is coordinated by six O atoms arranged in a distorted octahedron. The mean Mg–O distance is 2.06 (1) Å and the average O–Mg–O interbond angle $90 (1)^\circ$. MgO_6 octahedra share one edge forming Mg_2O_{10} units in which the distance Mg–Mgⁱ is 3.156 Å.

Discussion

So far, dimolybdate crystal structures of Na^+ (Seleborg, 1967), K^+ (Maganill & Klevtsova, 1971), NH_4^+ (Knöpnadel, Hartl, Hunnius & Fuchs, 1974) and Ag^+ (Gatehouse, 1974; Gatehouse & Leverett, 1976) have been determined. None contain discrete $\text{Mo}_2\text{O}_7^{2-}$ ions, their structures being composed of octahedral (Ag^+ salt), or octahedral–tetrahedral (Na^+ , K^+ , NH_4^+ salts) infinite chains. Nor have isolated $\text{W}_2\text{O}_7^{2-}$ anions been found in the structures of Na^+ (Okada, Morikawa, Marumo & Iwai, 1975*a*) and Li^+ (Okada *et al.*, 1975*b*) ditungstates. MgMo_2O_7 is, thus, the first dimolybdate which has been found to belong to a large class of compounds containing isolated $X_2\text{O}_7$ groups composed of XO_4 tetrahedra sharing corners. This class of compounds can be divided into three groups differing with respect to the relative conformation of the $X_2\text{O}_7$ group. These idealized conformations are illustrated in Fig. 3 (Panagiotopoulos & Brown, 1973). In part (a) of

this figure, the unshared O atoms are in the staggered conformation, whereas (b) and (c) represent two possible eclipsed forms. Further classification of the discussed group of compounds is based on the value of the $X-O-X$ interbond angle which, in theory, can vary from 102 to 180° (Clark, 1972). Usually it falls within the range 110–155°. The $Mo_2O_7^{2-}$ ion described in the present paper is close to the configuration in Fig. 3(c) with a twist angle of 12° and Mo–O–Mo angle of 161°.

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Solid-State Phase Transition in Carbon Tetrabromide.

II. The Crystal Structure of Phase I

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Phase I of CBr_4 (above 47°C) is cubic, space group $Fm\bar{3}m$, with $a = 8.82$ Å, $Z = 4$. The molecules are orientationally disordered and the structure is described by the use of symmetry-adapted functions. The orientational probability is discussed in terms of these functions.

Introduction

The high-temperature phase of CBr_4 (above 47°C) is 'plastic' with the molecules orientationally disordered.

As a first approximation, the disorder can be interpreted by assuming that the molecule occupies at random any one of N distinguishable orientations, the mean symmetry being cubic (Frankel model). If one neglects correlations, thermal entropy, *etc.*, the transition entropy is approximately $\Delta S_t = R \ln N$.

In CBr_4 , $\Delta S_t = 4.98$ cal K^{-1} mol $^{-1}$ (Marshall, Staveley & Hart, 1956; Hildebrand & Scott, 1950).

Guthrie & McCullough (1961) suppose that the orientational disorder corresponds to the 10 distinguishable orientations of the combined T_d and C_{3v} symmetry ($R \ln 10 = 4.58$ cal K^{-1} mol $^{-1}$).

In a previous paper (More, Baert & Lefebvre, 1977), we reported that one can expect six different molecular orientations corresponding to D_{2d} local symmetry.

However, a classical refinement of the high-temperature-phase diffraction data, based on a Frankel model with six equilibrium positions, has failed.

In this paper, we report the structure refined by the use of symmetry-adapted functions. This method takes