The Crystal Structure of Li$_2$W$_2$O$_7$

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The crystal structure of Li$_2$W$_2$O$_7$ has been determined from three-dimensional X-ray diffractometer data and refined to a conventional R value of 0·069. Li$_2$W$_2$O$_7$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 8\cdot283$ (3), $b = 7\cdot050$ (1), $c = 5\cdot037$ (1) Å, $\alpha = 85\cdot40$ (2), $\beta = 102\cdot13$ (3), $\gamma = 110\cdot29$ (1)°, $V = 269\cdot7$ (1)Å^3, $Z = 2$ and $D_x = 6\cdot08$ g cm^{-3}. The structure is built up of distorted WO$_6$ octahedra and LiO$_4$ tetrahedra. By sharing edges the WO$_6$ octahedra form (W$_2$O$_7$)$^{2-}$ anion chains running parallel to the c axis. The W–O bond lengths vary from 1·74 (2) to 2·30 (1) Å and W$\cdots$W distances between the edge-sharing WO$_6$ octahedra vary from 3·214 (2) to 3·284 (3) Å. The lithium ions occupy distorted tetrahedral interchain sites joining the (W$_2$O$_7$)$^{2-}$ chains laterally. The Li–O bond lengths vary from 1·90 (5) to 2·11 (4) Å.

Introduction

According to Hoermann (1928), Spitsyn & Kuleshov (1950) and Gelsing, Stein & Stevels (1965), four phases, A$_2$W$_2$O$_7$, A$_2$W$_3$O$_{10}$, A$_2$W$_4$O$_{13}$ and A$_2$W$_6$O$_{19}$ (A = Li, Na, K or Rb), have been recognized in alkali isopolytungstates crystallized from the melt. Though the crystal structures of alkali tungstates (A$_2$WO$_4$) have been well established by the X-ray single-crystal diffraction technique, only those of Na$_2$W$_2$O$_7$ (Lindqvist, 1950; Okada, Morikawa, Marumo & Iwai, 1975) and K$_2$W$_4$O$_{13}$ (Seleborg, 1967*a*) are known to date among the alkali isopolytungstates. On the other hand, the structures of alkali isopolymolybdates, which are supposed to be closely related to the corresponding tungstates, have been well investigated, and the structures of the following substances are known: Na$_2$Mo$_2$O$_7$ (Lindqvist, 1950, 1960; Seleborg, 1967*b*), K$_2$Mo$_2$O$_7$ (Magarill & Klevtsova, 1971), K$_2$Mo$_3$O$_{10}$ (Seleborg, 1966; Gatehouse & Leverett, 1968), Li$_2$Mo$_4$O$_{13}$ (Gatehouse & Miskin, 1974), K$_2$Mo$_4$O$_{13}$ and Rb$_2$Mo$_4$O$_{13}$ (Gatehouse & Leverett, 1971). All of these structures are made up of (Mo$_n$O$_{3n+1}$)$^{2-}$ anion chains, and the construction of the chains depends on the value of n. Na$_2$W$_2$O$_7$ is isomorphous with Na$_2$Mo$_2$O$_7$ and K$_2$Mo$_2$O$_7$. The structure consists of (W$_2$O$_7$)$^{2-}$ chains containing WO$_6$ octahedra and WO$_4$ tetrahedra. According to Klevtsov, Kozeeva & Klevtsova (1971), Li$_2$W$_2$O$_7$ belongs to the triclinic system, in contrast to the orthorhombic symmetry of Na$_2$W$_2$O$_7$. It was desirable to determine the structure of Li$_2$W$_2$O$_7$ to clarify its relation to that of Na$_2$W$_2$O$_7$ and to those of other alkali isopolymolybdates and isopolytungstates.

Experimental

The crystals of Li$_2$W$_2$O$_7$ were synthesized by heating an intimate mixture of Li$_2$CO$_3$ and WO$_3$ in a platinum crucible at 800°C for 5 h and by cooling at the rate of 30–50°C h^{-1}. They are long prismatic, colourless and

transparent. A preliminary X-ray study with Weissenberg photographs confirmed the symmetry and the cell dimensions reported by Klevtsov *et al.* (1971).

A short prismatic crystal with dimensions $0\cdot2 \times 0\cdot15 \times 0\cdot1$ mm was used for intensity collection. Intensities were measured on a Philips automated four-circle diffractometer with Mo $K\alpha$ radiation, monochromated with graphite, up to $2\theta = 80°$ (partly up to $2\theta = 100°$) by the ω–2θ scan technique. The scan speed was 2° min^{-1} in ω and the scan was repeated twice when the total counts were less than 10000. A constant scan width of 1·5° was adopted for all reflexions. The intensities were corrected for Lorentz and polarization factors. Corrections for isotropic secondary extinction and absorption factors were carried out in the course of the structure refinement assuming a sphere of 0·14 mm diameter for the crystal shape. In all, 2995 independent intensity data were collected and used for the structure determination.

Structure determination

The structure was solved by the heavy-atom method. Two trial models for the arrangements of W atoms

Table 1. *Final atomic parameters for* Li$_2$W$_2$O$_7$

The positional and isotropic thermal parameters.

	x	y	z	B_o
W(1)	0·17852 (7)	0·24834 (9)	0·30834 (12)	0·86 (2)*
W(2)	0·66509 (7)	0·45137 (8)	0·18348 (12)	0·81 (2)*
Li(1)	0·2793 (57)	0·0085 (65)	0·8540 (87)	2·7 (6)
Li(2)	0·9032 (57)	0·2645 (65)	0·7089 (88)	1·9 (6)
O(1)	0·8689 (16)	0·6019 (18)	0·0450 (25)	1·0 (1)
O(2)	0·7005 (15)	0·7497 (18)	0·3511 (25)	1·0 (1)
O(3)	0·8181 (17)	0·9763 (20)	0·8232 (27)	1·2 (2)
O(4)	0·5757 (16)	0·5820 (18)	0·8222 (25)	1·0 (1)
O(5)	0·6268 (19)	0·2109 (22)	0·0685 (29)	1·5 (2)
O(6)	0·9628 (18)	0·1894 (20)	0·3517 (27)	1·2 (2)
O(7)	0·7635 (17)	0·4348 (19)	0·5313 (26)	1·1 (1)

* Calculated from anisotropic thermal parameters according to the expression: $B = 4(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{12}ab \cos \gamma + B_{13}ac \cos \beta + B_{23}bc \cos \alpha)/3$.

Table 1 (cont.)

The anisotropic thermal parameters ($\times 10^5$) for W atoms expressed in the form:

$$\exp\left[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)\right]$$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	394 (7)	441 (10)	793 (19)	154 (6)	158 (9)	−38 (10)
W(2)	353 (7)	415 (9)	814 (18)	175 (6)	130 (9)	−16 (10)

were derived from the three-dimensional Patterson function on the basis of the space groups $P1$ and $P\bar{1}$, respectively. Both models were refined by a full-matrix least-squares program *RSFLS*-4 (Sakurai, 1967). The centrosymmetric model gave a lower R value (0·103) than that (0·123) for the non-centrosymmetric one. Therefore, the structure determination proceeded in space group $P\bar{1}$. The positions of the oxygen atoms were found on the Fourier maps phased with the W atoms, and the R value dropped to 0·072. The positions of lithium atoms were then found with a difference synthesis based on the W and O atoms. The structure was refined by the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970) with anisotropic temperature factors assigned to the W atoms and isotropic ones to the remaining atoms. In the last cycle of the refinement, all the parameter shifts were less than $0·1\sigma$ and the conventional R value was reduced to 0·069 for the observed reflexions. The atomic scattering factors and the dispersion correction factors were taken from *International Tables for X-ray Crystallography* (1968). Unit weights were given for all the terms. The final positional and thermal parameters are listed in Table 1.*

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30875 (21 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion

The interatomic distances and bond angles are in Table 2 with their estimated standard deviations in parentheses.

Table 2. Interatomic distances (Å) and bond angles (°) for $Li_2W_2O_7$

Symmetry code

None	$x,$	$y,$	z	(v)	$x,$	$y,$	$-1+z$
(i)		$x,$	$-1+y,$	z	(vi)	$1-x,$	$-y,$	$2-z$
(ii)		$1-x,$	$1-y,$	$1-z$	(vii)	$1-x,$	$-y,$	$1-z$
(iii)		$1-x,$	$1-y,$	$-z$	(viii)	$2-x,$	$1-y,$	$1-z$
(iv)		$-1+x,$	$y,$	z				

W(1)–W(2^{ii})	3·224 (3)		W(2)–W(2^{iii})	3·214 (2)
W(1)–W(2^{iii})	3·284 (3)			
W(1)–Li(1)	3·24 (4)		W(2)–Li(1^{ii})	3·67 (5)
W(1)–Li(2^{ii})	3·72 (5)		W(2)–Li(2)	3·42 (4)
W(1)–O(1^{iii})	2·01 (1)		W(2)–O(1)	1·89 (1)
W(1)–O(2^{ii})	1·82 (1)		W(2)–O(2)	2·23 (1)
W(1)–O(3^{ii})	1·76 (1)		W(2)–O(4^{ii})	1·92 (1)
W(1)–O(4^{ii})	2·17 (1)		W(2)–O(4^v)	2·09 (1)
W(1)–O(6^{iv})	1·75 (1)		W(2)–O(5)	1·74 (2)
W(1)–O(7^{ii})	2·30 (1)		W(2)–O(7)	1·78 (1)
Li(1)–Li(1^{vi})	3·68 (7)		Li(1)–Li(2^{vi})	3·09 (6)
Li(1)–O(2^{ii})	1·90 (5)		Li(2)–O(1^{viii})	1·99 (5)
Li(1)–O(3^{vi})	1·98 (5)		Li(2)–O(3^i)	1·99 (4)
Li(1)–O(5^{vii})	1·94 (5)		Li(2)–O(6)	2·11 (5)
Li(1)–O(6^{vii})	2·11 (4)		Li(2)–O(7)	1·98 (5)

O(2^{ii})–Li(1)–O(3^{vi})	109 (2)		O(1^{viii})–Li(2)–O(3^i)	107 (2)
O(2^{ii})–Li(1)–O(5^{vii})	143 (3)		O(1^{viii})–Li(2)–O(6)	107 (2)
O(2^{ii})–Li(1)–O(6^{vii})	102 (2)		O(1^{viii})–Li(2)–O(7)	118 (2)
O(3^{vi})–Li(1)–O(5^{vii})	106 (2)		O(3^i)––Li(2)–O(6)	92 (2)
O(3^{vi})–Li(1)–O(6^{vii})	93 (2)		O(3^i)––Li(2)–O(7)	129 (2)
O(5^{vii})–Li(1)–O(6^{vii})	91 (2)		O(6)–––Li(2)–O(7)	97 (2)

Table 2 (cont.)

The values in the upper-right column indicate the O–O bond lengths in the WO_6 octahedron. Those in the lower-left column indicate the O–W–O bond angles in the WO_6 octahedron. The values underlined indicate the shared edge of the WO_6 octahedron.

$W(1)O_6$	O(1^{iii})	O(2^{ii})	O(3^{ii})	O(4^{ii})	O(6^{iv})	O(7^{ii})
O(1^{iii})		3·69 (2)	2·92 (2)	2·41 (2)	2·72 (2)	2·77 (2)
O(2^{ii})	149·3 (4)		2·78 (2)	2·80 (2)	2·78 (2)	2·51 (2)
O(3^{ii})	100·7 (6)	101·7 (6)		2·81 (2)	2·78 (2)	4·04 (2)
O(4^{ii})	70·3 (5)	88·8 (5)	90·5 (6)		3·85 (2)	2·82 (2)
O(6^{iv})	92·0 (6)	102·3 (6)	104·4 (6)	158·9 (6)		2·83 (2)
O(7^{ii})	79·5 (5)	74·2 (5)	167·9 (5)	78·2 (5)	87·6 (6)	

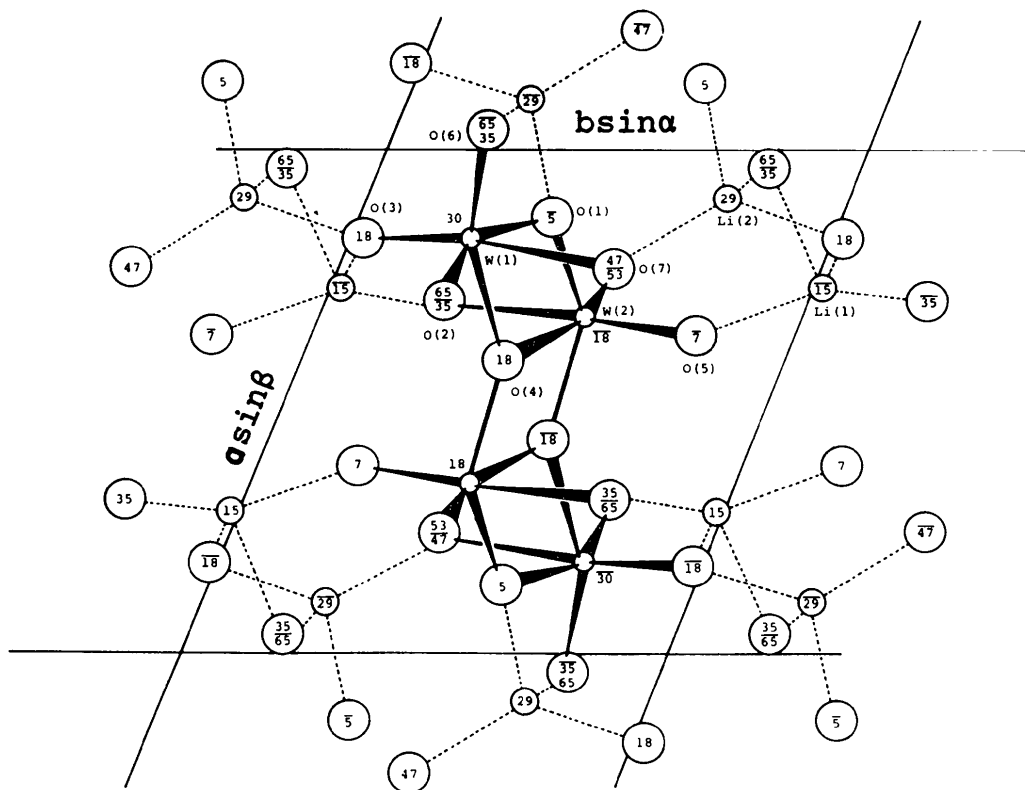| $W(2)O_6$	O(1)	O(2)	O(4^{ii})	O(4^v)	O(5)	O(7)
O(1)		2·75 (2)	3·64 (2)	2·41 (2)	2·80 (2)	2·81 (2)
O(2)	83·2 (5)		2·69 (1)	2·84 (2)	3·96 (2)	2·51 (2)
O(4^{ii})	145·3 (5)	80·5 (5)		2·39 (2)	2·73 (2)	2·96 (2)
O(4^v)	74·4 (5)	82·1 (5)	73·2 (5)		2·93 (2)	3·80 (2)
O(5)	100·8 (6)	175·9 (6)	96·5 (6)	99·8 (6)		2·73 (2)
O(7)	99·4 (5)	76·6 (5)	106·3 (6)	158·5 (5)	101·6 (6)	

Fig. 1. The crystal structure of $Li_2W_2O_7$ viewed along the c axis. Heights of atoms from the ab plane are indicated as percentages of the c length.
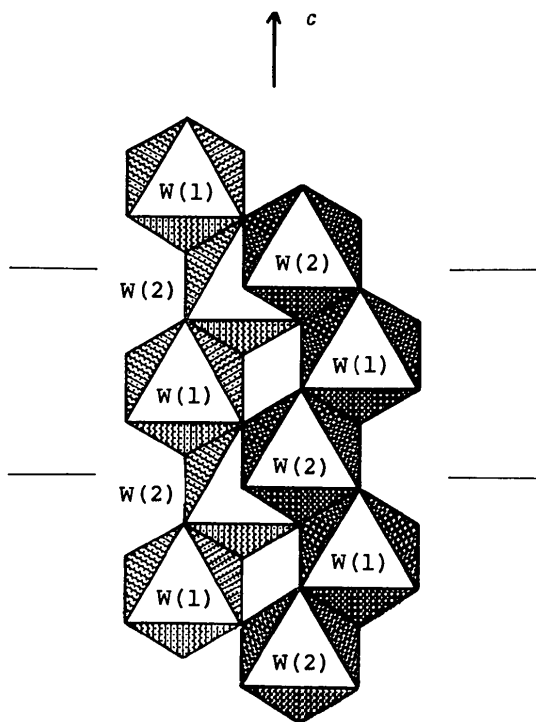

Fig. 2. Part of the double chain extending infinitely along the c axis shown in an idealized form.

The structure viewed along the c axis is shown in Fig. 1. W(1) and W(2) are both octahedrally coordinated to six oxygen atoms. The WO_6 coordination octahedra are largely distorted, the W(1)–O and W(2)–O bond lengths varying from 1·75 (1) to 2·30 (1) Å and from 1·74 (2) to 2·23 (1) Å, respectively. Both Li atoms are tetrahedrally coordinated to four oxygen atoms. The LiO_4 tetrahedra are also largely distorted giving average distances of 1·98 for $Li(1)O_4$ and 2·02 Å for $Li(2)O_4$ tetrahedra. The $W(1)O_6$ octahedron shares edges with two neighbouring $W(2)O_6$ octahedra and corners with one $Li(1)O_4$ and one $Li(2)O_4$ tetrahedra. The $W(2)O_6$ octahedron shares edges with two neighbouring $W(1)O_6$ and one $W(2)O_6$ octahedra, and corners with the two $Li(1)O_4$ and one $Li(2)O_4$ tetrahedra. Thus, the WO_6 octahedra form infinite double chains of $(W_2O_7)^{2-}$ extending along the c axis. Part of the chain is shown in Fig. 2 in an idealized form. The LiO_4 tetrahedra connect the chains laterally by sharing corners with WO_6 octahedra. This linkage of the octahedra gives much shorter lengths for the shared edges, ranging from 2·39 (2) to 2·51 (2) Å, compared with those of the unshared ones ranging from 2·69 (2) to 2·96 (2) Å. The W···W distances between the neighbouring octahedra in a chain range from 3·214 (2) to 3·284 (3) Å. The acicular crystal habit of this substance is well explained by the chain character of the structure.

Among alkali isopolymolybdates, most of the known structures are based on infinite chains of $(Mo_nO_{3n+1})^{2-}$ anions, and the chains are of the same type for a definite value of n irrespective of the kind of alkali metal. The chains in the structures of $Na_2Mo_2O_7$ (Lindqvist, 1950, 1960; Seleborg, 1967b) and $K_2Mo_2O_7$ (Magarill & Klevtsova, 1971) consist of MoO_4 tetrahedra and MoO_6 octahedra, while those in $K_2Mo_3O_{10}$ (Seleborg, 1966; Gatehouse & Leverett, 1968) consist of square-pyramidal MoO_5 polyhedra and MoO_6 octahedra. Furthermore, those in $K_2Mo_4O_{13}$ and $Rb_2Mo_4O_{13}$ (Gatehouse & Leverett, 1971) are composed purely of MoO_6 octahedra. An exception is the structure of $Li_2Mo_4O_{13}$ (Gatehouse & Miskin, 1974), which is based on a three-dimensional framework. On the other hand, some alkali isopolytungstates seem to have quite different structures from those of the corresponding isopolymolybdates. For example, the structure of $K_2W_4O_{13}$ (Seleborg, 1967a) is based on a stack of six-membered rings of WO_6 octahedra, and has no similarity with that of $K_2Mo_4O_{13}$ (Gatehouse & Leverett, 1971). Though the structure of $Li_2W_2O_7$ cannot be compared with that of $Li_2Mo_2O_7$, since the phase $Li_2Mo_2O_7$ does not exist (under atmospheric pressure), it is interesting that it is quite different from that of $Na_2W_2O_7$ (Lindqvist, 1950; Okada, Morikawa, Marumo & Iwai, 1974) which is isostruc tural with $Na_2Mo_2O_7$.

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Structure Cristalline de la Rifampicine C₄₃N₄O₁₂H₅₈.5H₂O

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The three-dimensional structure of the antibiotic rifampicin, used in human medicine, has been solved by X-ray crystallographic analysis. Crystal data are: space group $P2_12_12_1$, $Z=4$; $a=17\cdot508$, $b=19\cdot943$, $c=13\cdot896$ Å. The structure was determined by direct methods with the program *MULTAN*. The final R value is 0·0594. The five molecules of water of crystallization give a net of hydrogen bonds which are responsible for crystalline cohesion.

Introduction

Les rifamycines constituent un groupe important d'antibiotiques issus du métabolisme de *Streptomyces mediterrenei*.

La rifampicine qui appartient à ce groupe est le seul utilisé en thérapeutique pour son activité tuberculostatique (Fig. 1).

La structure cristalline des rifamycines B $(C_{45}H_{53}N_2O_{13}I)$ et Y $(C_{45}H_{51}N_2O_{14}I)$ ont déjà été décrites