Gladyshevskii, 1983; Parthé & Chabot, 1984) as an intergrowth of CrB-type slabs and slabs composed of TiNiSi segments. The TiNiSi and the hypothetical *RTM* structure are composed of the same kind of $ThCr_2Si_2$- and W-type columns; however, there are no *T*—*T* contacts in the first.

We wish to acknowledge the help of Mme. Birgitta Künzler with the preparation of the drawings. This study was supported by the Swiss National Science Foundation under contract 2–5.537.

References

Bodak, O. I., Gladyshevskii, E. I. & Kripyakevich, P. I. (1970). *J. Struct. Chem. USSR*, **11**, 283–288.

Bodak, O. I., Kotur, B. Ya. & Gladyshevskii, E. I. (1976). *Dokl. Akad. Nauk Ukr. SSR Ser. A*, pp. 656–659.

Gelato, L. M. & Parthé, E. (1987). *J. Appl. Cryst.* **20**, 139–143.

Gladyshevskii, E. I. & Kotur, B. Ya. (1978). *Sov. Phys. Crystallogr.* **23**, 533–535.

Hall, S. R. & Stewart, J. M. (1988). Editors. *XTAL*2.4 *Users Manual*. Univs. of Western Australia, Australia, and Maryland, USA.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Kotur, B. Ya. & Gladyshevskii, E. I. (1983). *Sov. Phys. Crystallogr.* **28**, 271–273.

Mokraya, I. R. & Bodak, O. I. (1979). *Dopov. Akad. Nauk Ukr. RSR Ser. A*, pp. 312–315.

Parthé, E. & Chabot, B. A. (1984). In *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 6, edited by K. A. Gschneidner Jr & L. Eyring, Ch. 48, pp. 113–334. Amsterdam: North-Holland.

Shoemaker, C. B. & Shoemaker, D. P. (1965). *Acta Cryst.* **18**, 900–905.

Yarmolyuk, Ya. P., Grin', Yu. N. & Gladyshevskii, E. I. (1977). *Sov. Phys. Crystallogr.* **22**, 416–419.

Zhao, J. T. & Parthé, E. (1989). *J. Less-Common Met.* **154**, 31–37.

Acta Cryst. (1989). **C45**, 1856–1858

Crystal Chemistry of *cyclo*-Hexaphosphates. III. Structure of Dilithium Dimanganese *cyclo*-Hexaphosphate Decahydrate

By M. T. Averbuch-Pouchot

Laboratoire de Cristallographie, Laboratoire associé à l'Université J. Fourier, CNRS, 166*X*,
38042 *Grenoble CEDEX, France*

(*Received* 21 *January* 1989; *accepted* 4 *April* 1989)

Abstract. $Li_2Mn_2P_6O_{18}.10H_2O$, $M_r = 777{\cdot}732$, triclinic, $P\bar{1}$, $a = 7{\cdot}286\,(5)$, $b = 9{\cdot}761\,(7)$, $c = 10{\cdot}026\,(6)$ Å, $\alpha = 118{\cdot}31\,(5)$, $\beta = 110{\cdot}62\,(5)$, $\gamma = 86{\cdot}27\,(5)°$, $V = 583\,(2)$ Å^3, $Z = 1$, $D_x = 2{\cdot}215$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}7107$ Å, $\mu = 1{\cdot}673$ mm^{-1}, $F(000) = 390$, $T = 294$ K, final $R = 0{\cdot}027$ for 2386 reflections. The P_6O_{18} ring anion is centrosymmetric. The two associated cation polyhedra, a tetrahedron built up of three O atoms and one water molecule for the Li atom and an octahedron made up of three water molecules and three O atoms for the Mn atom, do not share any O atoms. Two of the ten water molecules [O(*W*2)] do not take part in the metal coordinations. The hydrogen-bond scheme is reported. Crystal data for the isotypic zinc salt are given.

Introduction. This work is part of a systematic investigation of *cyclo*-hexaphosphate crystal chemistry. We previously reported chemical preparations and crystal structures for various monovalent cation or mixed monovalent cation *cyclo*-hexaphosphates (Averbuch-Pouchot, 1989*a,b,c,d*) and for some divalent cation *cyclo*-hexaphosphates (Averbuch-Pouchot, 1989*e,f*).

The title compound is the first example of a hydrated divalent–monovalent-cation *cyclo*-hexaphosphate.

The corresponding zinc salt $Li_2Zn_2P_6O_{18}.10H_2O$ is isotypic, with the following unit-cell dimensions: $a = 7{\cdot}160\,(5)$, $b = 9{\cdot}741\,(7)$, $c = 9{\cdot}928\,(6)$ Å, $\alpha = 118{\cdot}49\,(5)$, $\beta = 110{\cdot}57\,(5)$, $\gamma = 86{\cdot}96\,(5)°$. Its chemical preparation is similar to that described for the title compound.

Experimental. $Li_2Mn_2P_6O_{18}.10H_2O$ crystals have been obtained by mixing an aqueous solution of manganese chloride and an aqueous solution of lithium *cyclo*-hexaphosphate hexahydrate so as to obtain a ratio Li/Mn = 2 in the final solution. After some days of evaporation at room temperature pale-pink calcite-like triclinic prisms appear in the solution.

Crystal size: $0{\cdot}16 \times 0{\cdot}16 \times 0{\cdot}16$ mm. Density not measured. Nicolet diffractometer, graphite monochromator. 14 reflections ($9 < \theta < 11°$) for refining unit-cell dimensions. ω scan, scan width: 1·40°, scan-speed variable between 1·20 and 3·60° min^{-1}, total background measuring time: 20% of the scan. 3382 reflections collected, $2 < \theta < 30°$, $\pm h$, $\pm k$, l, $h_{\max}$

Table 1. *Final atomic coordinates and* B_{eq} *for non-*H *atoms*

Starred atoms have been refined isotropically. Estimated standard deviations are given in parentheses.

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j\beta_{ij}.$$

	x	*y*	*z*	B_{eq}(Å^2)
Mn	−0·56256 (5)	0·28899 (4)	0·19191 (4)	1·236 (7)
Li	0·1120 (7)	0·3101 (5)	0·6684 (5)	1·54 (9)
P(1)	0·00549 (9)	−0·15256 (7)	0·15455 (6)	0·95 (1)
P(2)	−0·16798 (8)	0·32446 (7)	0·10561 (6)	0·95 (1)
P(3)	−0·09358 (9)	−0·19103 (7)	−0·30093 (6)	0·93 (1)
O(*L*13)	0·1289 (3)	0·0118 (2)	0·2211 (2)	1·34 (3)
O(*L*12)	−0·1376 (3)	0·2675 (2)	−0·0623 (2)	1·47 (3)
O(*E*11)	−0·0275 (3)	0·1777 (2)	−0·2937 (2)	1·56 (4)
O(*E*21)	0·1954 (3)	0·1636 (2)	−0·0388 (2)	1·79 (4)
O(*E*12)	0·0467 (3)	0·5224 (2)	0·7719 (2)	1·62 (4)
O(*E*22)	−0·3857 (3)	0·3108 (2)	0·0656 (2)	1·64 (4)
O(*E*13)	−0·7249 (3)	0·2834 (2)	0·3352 (2)	1·40 (4)
O(*E*23)	0·0238 (3)	0·2345 (2)	−0·5634 (2)	1·64 (4)
O(*L*23)	−0·0854 (3)	0·1897 (2)	0·1504 (2)	1·32 (3)
O(*W*1)	0·6076 (3)	0·7076 (2)	0·2379 (2)	2·52 (5)
O(*W*2)	0·3707 (4)	0·9771 (3)	0·5613 (3)	3·43 (6)
O(*W*3)	0·6919 (3)	0·4029 (3)	0·4212 (3)	2·43 (5)
O(*W*4)	0·6578 (3)	0·4817 (3)	0·7596 (3)	4·11 (6)
O(*W*5)	−0·5398 (3)	−0·0695 (2)	−0·1746 (2)	2·20 (4)
H(1*W*1)	0·554 (7)	0·690 (5)	0·147 (5)	3 (1)*
H(2*W*1)	0·617 (7)	0·798 (5)	0·304 (5)	3 (1)*
H(1*W*2)	0·65 (1)	0·932 (8)	0·375 (8)	9 (2)*
H(2*W*2)	0·252 (8)	0·921 (6)	0·473 (6)	4 (1)*
H(1*W*3)	0·698 (7)	0·495 (5)	0·496 (5)	3 (1)*
H(2*W*3)	0·217 (7)	0·632 (5)	0·559 (5)	3 (1)*
H(1*W*4)	0·747 (6)	0·471 (5)	0·768 (5)	2 (1)*
H(2*W*4)	0·394 (7)	0·573 (5)	0·246 (5)	3 (1)*
H(1*W*5)	0·392 (7)	−0·022 (5)	0·868 (5)	2 (1)*
H(2*W*5)	0·438 (8)	0·937 (6)	0·746 (6)	4 (1)*

$= 10$, $k_{\rm max} = 13$, $l_{\rm max} = 14$. Three orientation and intensity control reflections ($1\bar{4}\bar{1}$, $\bar{1}4\bar{1}$, 224) without any significant variation. Lorentz and polarization corrections, no absorption correction.

Structure solved by direct methods (*MULTAN*77, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1977). H atoms located by difference-Fourier synthesis. Anisotropic full-matrix least-squares refinements (on *F*), isotropic for H atoms. Unit weights. Final refinement cycles with 2386 reflections ($I > 4\sigma_I$). Final $R = 0{\cdot}027$ ($wR = 0{\cdot}030$), $S = 0{\cdot}784$. Max. $\Delta/\sigma = 0{\cdot}05$. Max. peak height in the final difference-Fourier synthesis 0·609 e Å^{-3}. No extinction correction. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). The *R* value is 0·044 for the total set of 3382 reflections. Enraf–Nonius (1977) *SDP* used for all calculations. Computer used: MicroVAX II. Table 1 reports the final atomic coordinates.*

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in the atomic arrangement of* $Li_2Mn_2P_6O_{18}.10H_2O$

Estimated standard deviations are given in parentheses.

The P(1)O_4 tetrahedron

P(1)	O(*L*13)	O(*L*12)	O(*E*11)	O(*E*21)
O(*L*13)	1·605 (2)	2·429 (2)	2·515 (3)	2·523 (2)
O(*L*12)	98·8 (1)	1·595 (2)	2·467 (3)	2·544 (3)
O(*E*11)	109·1 (1)	106·6 (1)	1·481 (2)	2·563 (3)
O(*E*21)	109·4 (1)	111·4 (1)	119·5 (1)	1·485 (2)

The P(2)O_4 tetrahedron

P(2)	O(*L*12)	O(*E*12)	O(*E*22)	O(*L*23)
O(*L*12)	1·597 (2)	2·506 (2)	2·472 (3)	2·490 (3)
O(*E*12)	108·9 (1)	1·480 (2)	2·565 (2)	2·542 (3)
O(*E*22)	106·3 (1)	119·4 (1)	1·492 (2)	2·493 (3)
O(*L*23)	102·3 (1)	111·1 (1)	107·4 (1)	1·601 (2)

The P(3)O_4 tetrahedron

P(3)	O(*L*13)	O(*E*13)	O(*E*23)	O(*L*23)
O(*L*13)	1·589 (2)	2·471 (2)	2·544 (2)	2·447 (3)
O(*E*13)	106·6 (1)	1·490 (2)	2·549 (2)	2·539 (2)
O(*E*23)	111·7 (1)	118·0 (1)	1·484 (2)	2·511 (3)
O(*L*23)	100·0 (1)	110·2 (1)	108·7 (1)	1·605 (2)

P(1)—O(*L*12)—P(2)	136·5 (1)	P(1)—P(2)	2·964 (1)
P(1)—O(*L*13)—P(3)	135·8 (1)	P(1)—P(3)	2·960 (1)
P(2)—O(*L*23)—P(3)	132·8 (1)	P(2)—P(3)	2·938 (1)

P(2)—P(1)—P(3)	111·48 (3)
P(1)—P(2)—P(3)	90·61 (2)
P(1)—P(3)—P(2)	114·06 (2)

The MnO_6 octahedron

Mn—O(*E*21)	2·164 (2)	Mn—O(*W*3)	2·191 (2)
Mn—O(*E*22)	2·179 (2)	Mn—O(*W*4)	2·175 (2)
Mn—O(*E*13)	2·179 (2)	Mn—O(*W*5)	2·169 (2)

The LiO_4 tetrahedron

Li—O(*E*11)	1·938 (6)	Li—O(*E*23)	1·934 (5)
Li—O(*E*12)	1·943 (5)	Li—O(*W*1)	1·961 (5)

The hydrogen bonds

O(*W*)—H···O	O(*W*)—H	H···O	O(*W*)—H···O	O(*W*)—O
O(*W*1)—H(1*W*1)···O(*E*22)	0·79 (5)	2·05 (5)	167 (5)	2·821 (3)
O(*W*1)—H(2*W*1)···O(*W*2)	0·80 (4)	1·95 (4)	172 (6)	2·740 (3)
O(*W*2)—H(1*W*2)···O(*W*1)	0·86 (6)	1·92 (6)	157 (8)	2·740 (3)
O(*W*2)—H(2*W*2)···O(*E*11)	0·94 (4)	1·83 (4)	175 (6)	2·767 (2)
O(*W*3)—H(1*W*3)···O(*E*13)	0·85 (4)	1·98 (4)	176 (6)	2·827 (2)
O(*W*3)—H(2*W*3)···O(*E*23)	0·74 (5)	2·12 (5)	166 (4)	2·835 (3)
O(*W*4)—H(1*W*4)···O(*E*12)	0·64 (4)	2·25 (5)	154 (6)	2·838 (3)
O(*W*4)—H(2*W*4)···O(*W*1)	0·65 (6)	2·14 (6)	166 (6)	2·775 (4)
O(*W*5)—H(1*W*5)···O(*E*21)	0·76 (5)	2·28 (4)	163 (6)	3·016 (3)
O(*W*5)—H(2*W*5)···O(*W*2)	0·79 (6)	1·96 (6)	173 (5)	2·744 (4)

The H—O(*W*)—H angles

H(1*W*1)—O(*W*1)—H(2*W*1)	114 (5)
H(1*W*2)—O(*W*2)—H(2*W*2)	109 (5)
H(1*W*3)—O(*W*3)—H(2*W*3)	112 (4)
H(1*W*4)—O(*W*4)—H(2*W*4)	115 (6)
H(1*W*5)—O(*W*5)—H(2*W*5)	108 (5)

Discussion. *The* P_6O_{18} *ring anion.* In the present atomic arrangement the phosphoric ring anion is centrosymmetric, built up by three independent PO_4 tetrahedra. As can be seen from the P—P—P angles which range from 90·6 to 114·1° this ring is far from regular. These large distortions are common for centrosymmetrical P_6O_{18} groups; P—P—P angles ranging from 96·3 to 139·9° have been observed in $Cu_3P_6O_{18}.14H_2O$ (Averbuch-Pouchot, 1989*f*). The main geometrical features of this ring are reported in Table 2.

The associated cation polyhedra. The Li atom coordination gives an almost regular tetrahedron built up of three external O atoms of the phosphoric

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52125 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

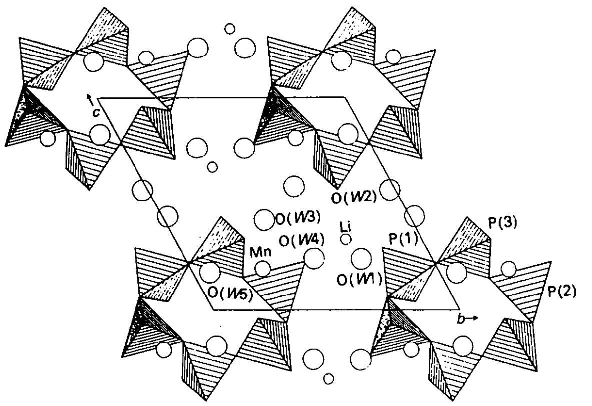

Fig. 1. Projection along the *a* axis of the atomic arrangement of $Li_2Mn_2P_6O_{18}.10H_2O$. The H atoms have been omitted.

ring and one water molecule. The Li—O distances vary from 1·934 to 1·961 Å, while the O—Li—O angles range from 105·0 to 113·2°.

The Mn atom has six neighbours, three external O atoms of the ring anion and three water molecules. The octahedron formed by these six neighbours is slightly distorted with Mn—O distances varying from 2·164 to 2·191 Å and O—Mn—O angles in the range 86·0 to 89·0°.

It is worth noticing that these two coordination polyhedra do not share any O atoms. Li—O and Mn—O distances are reported in Table 2.

The water molecules. Four of the five independent water molecules belong to the associated cation coordinations. One of them [O(*W*2)] can be considered as zeolitic in nature since it is bound to the atomic framework by hydrogen bonds only. In spite of this character the thermal factor of this molecule is not significantly different ($B_{eq} = 3·43$ Å^2) from those observed for the four other molecules (Table 1).

The hydrogen-bond scheme. Geometrical details of the three-dimensional network of hydrogen bonds are given in Table 2. It is worth noticing that the non-bonded water molecule, O(*W*2), acts twice as an acceptor.

Fig. 1 depicts the atomic arrangement of $Li_2Mn_2P_6O_{18}.10H_2O$ as a projection along the *a* axis. The drawing was obtained using the *STRUPLO* program (Fischer, 1985).

References

Averbuch-Pouchot, M. T. (1989*a*). *Z. Kristallogr.* Accepted.

Averbuch-Pouchot, M. T. (1989*b*). *Z. Anorg. Allg. Chem.* Accepted.

Averbuch-Pouchot, M. T. (1989*c*). *Acta Cryst.* **C45**, 539–540.

Averbuch-Pouchot, M. T. (1989*d*). *Acta Cryst.* **C45**, 1273–1275.

Averbuch-Pouchot, M. T. (1989*e*). *Z. Anorg. Allg. Chem.* **570**, 138–144.

Averbuch-Pouchot, M. T. (1989*f*). *Acta Cryst.* **C45**, 1275–1277.

Enraf–Nonius (1977). *Structure Determination Package*. Version RSX11M. Enraf–Nonius, Delft, The Netherlands.

Fischer, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.

International Tables for X-ray Crystallography (1974). Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Acta Cryst. (1989). C**45**, 1858–1861

Structure du Sulfure d'Ytterbium et d'Indium $Yb_{18}In_{7,33}S_{36}$

Par P. Lemoine, A. Tomas, D. Carré, M. Guittard et A. Likforman

Laboratoire de Chimie Structurale associé au CNRS n° 200 (*Laboratoire de Physique*), *Faculté de Sciences Pharmaceutiques et Biologiques Paris-Luxembourg,* 4 *Avenue de l'observatoire,* 75270 *Paris CEDEX* 06, *France*

(*Reçu le* 28 *juillet* 1988, *accepté le* 7 *mars* 1989)

Abstract. $M_r = 5110·65$, hexagonal, $P6_3/m$, $a = 20·688$ (3), $c = 3·861$ (2) Å, $V = 1431$ (1) Å^3, $Z = 1$, D_m (293 K) = 5·8 (1), $D_x = 5·93$ (2) g cm^{-3}, Mo $K\overline{\alpha}$, $\lambda = 0·71069$ Å, $\mu = 347$ cm^{-1}, $F(000) = 2195$, $T = 293$ K, $R = 0·053$ for 895 independent observed reflections. The Yb^{III} atoms have two types of environment: sevenfold prismatic coordination (Yb—S: 2·80 to 3·11 Å) and sixfold octahedral coordination (Yb—S: 2·57 to 2·81 Å). However, the second sites are also occupied by In^{III}. Large channels around the threefold and sixfold axes are occupied by In^{I} and are empty, respectively.

Introduction. Une précédente étude du système $EuS–Bi_2S_3$, nous a conduit à déterminer la structure du sulfure ternaire $Eu_{1,1}Bi_2S_4$ (Lemoine, Carré & Guittard, 1986) dont la particularité est de posséder de larges canaux autour de l'axe 6, partiellement

0108-2701/89/121858-04$03.00