

## Structure of Lead Bis(dihydrogenphosphate)

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**Abstract.**  $\text{Pb}(\text{H}_2\text{PO}_4)_2$ , triclinic,  $P\bar{1}$ ,  $a = 9.029$  (3),  $b = 5.863$  (1),  $c = 7.815$  (3) Å,  $\alpha = 96.92$  (2),  $\beta = 119.56$  (3),  $\gamma = 104.92$  (2)°,  $V = 332.3$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 4.03$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 25.6$  mm<sup>-1</sup>, final  $R = 0.099$ . The seven shortest Pb–O distances are in the range 2.44–2.88 Å. Hydrogen-bonded dimers form a three-dimensional network.

**Introduction.** The investigation of the crystal structure of  $\text{Pb}(\text{H}_2\text{PO}_4)_2$  was performed as part of a study of acidic phosphates. To obtain crystals of  $\text{Pb}(\text{H}_2\text{PO}_4)_2$ , first  $\text{Pb}(\text{HPO}_4)$  was prepared.  $\text{PbCO}_3$  was added to 50%  $\text{H}_3\text{PO}_4$  and heated at 353 K until a precipitate began to appear. The solution was then heated at 373 K to dissolve all  $\text{PbCO}_3$ . On cooling, tiny plates of  $\text{Pb}(\text{HPO}_4)$  crystallized. The precipitate was washed with water, dried and dissolved in 96%  $\text{H}_3\text{PO}_4$  at 453 K. By cooling slowly, prismatic needles of  $\text{Pb}(\text{H}_2\text{PO}_4)_2$  were obtained. The crystals are sensitive to moisture. The excess of  $\text{H}_3\text{PO}_4$  is difficult to wash out. Treatment with ether, as recommended by Mellor (1947), has no appreciable effect on the stability of the crystals.

For all crystallographic measurements, crystals sealed in Lindemann-glass capillaries were used. Preliminary Weissenberg photographs indicated triclinic symmetry. A crystal of dimensions 0.09 × 0.14 × 0.28 mm was mounted on a Syntex P1 diffractometer. Cell parameters were determined by least squares from  $2\theta$  values for 14 strong general reflexions. The intensity measurements were made by the  $\omega$ -scan technique, using graphite-monochromated Mo  $K\alpha$  radiation. Intensities of 1730 reflexions in the sphere  $\theta \leq 30^\circ$  which satisfied the criterion  $I \geq 3\sigma(I)$  were used in the subsequent analyses. In the absence of a suitable program no absorption correction was applied.

The structure was solved by the heavy-atom method. Isotropic refinement of the nonhydrogen atoms terminated at  $R = 0.136$ . Refinement with anisotropic thermal parameters for Pb led to a non-definite value for the vibrational tensor. The least-squares refinement in space group  $P\bar{1}$  was unsuccessful. At that stage of

Table 1. Fractional coordinates ( $\times 10^5$  for Pb,  $\times 10^4$  for P, O) and thermal parameters

	x	y	z	$B_{\text{iso}}$ (Å <sup>2</sup> )
Pb	7666 (9)	24556 (12)	11132 (10)	*
P(1)	3493 (6)	3590 (8)	1012 (7)	0.64 (6)
P(2)	1934 (6)	−1368 (8)	4176 (7)	0.65 (6)
O(1)	3904 (20)	1672 (26)	−94 (22)	1.21 (21)
O(2)	5334 (21)	4724 (29)	3253 (23)	1.53 (23)
O(3)	1899 (20)	2008 (27)	1094 (22)	1.32 (21)
O(4)	3221 (18)	5605 (25)	22 (20)	0.97 (19)
O(5)	659 (20)	−10 (27)	3960 (22)	1.21 (21)
O(6)	1855 (20)	−3024 (27)	5613 (22)	1.25 (21)
O(7)	3873 (21)	545 (28)	5239 (23)	1.45 (22)
O(8)	1376 (19)	−3064 (25)	2178 (20)	1.01 (19)

\* Anisotropic thermal parameters ( $\times 10^4$ ) for the Pb atom, with their e.s.d.'s in parentheses, are:  $\beta_{11} = 42$  (1),  $\beta_{22} = 73$  (2),  $\beta_{33} = 70$  (2),  $\beta_{12} = 18$  (1),  $\beta_{13} = 52$  (1),  $\beta_{23} = 36$  (1).

refinement,  $\sigma(I) = 99.0$  was ascribed to 76 reflexions. These reflexions, with low  $hkl$  indices, exhibited large differences between  $F_o$  and  $F_c$  and were considered to be the most affected by absorption. Refinement of the positional and thermal parameters (anisotropic for Pb and isotropic for P and O) by full-matrix least squares was normal and converged at  $R = 0.099$ ,  $R_w = 0.100$ . Scattering factors and anomalous-dispersion corrections for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). The main programs used on the CDC-36000 computer were *FORDAP*, Zalkin's (1965) Fourier program, *NUCLS*, a modification by J. A. Ibers and R. J. Doedens of the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962) and *GEOM*, L. W. Muir & P. Mallinson's program for molecular geometry calculations. The atomic coordinates are given in Table 1.\*

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35774 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Discussion.** The crystal structure of  $\text{Pb}(\text{H}_2\text{PO}_4)_2$  consists of  $\text{Pb}^{2+}$  ions and  $\text{H}_2\text{PO}_4^-$  tetrahedra (Fig. 1). The  $\text{Pb}^{2+}$  ion is surrounded by seven O atoms belonging to seven different  $\text{H}_2\text{PO}_4^-$  groups, five at short distances and two further away. The next O atom is 3.13 Å from the  $\text{Pb}^{2+}$  ion, and probably involves a van der Waals contact. The coordination polyhedron is irregular. By sharing the edges O(3)–O(3) and O(8)–O(8), the coordination polyhedra form infinite chains running in the  $y$  direction (Fig. 2). The distance between Pb atoms in the chain is 3.917 Å.

Comparison of the crystal structures of  $\text{Pb}(\text{H}_2\text{PO}_4)_2$  and  $\text{Sn}(\text{H}_2\text{PO}_4)_2$  (Herak, Prelesnik, Čurić & Vasić, 1978) shows that in both compounds the coordination polyhedra of the metal ions form infinite chains instead of the layers that are present in the structures of PbO and SnO. However, in  $\text{Sn}(\text{H}_2\text{PO}_4)_2$  the coordination of  $\text{Sn}^{2+}$  is very similar to that in tetragonal SnO, while in  $\text{Pb}(\text{H}_2\text{PO}_4)_2$  the coordination around  $\text{Pb}^{2+}$  is much more complicated than in both forms of PbO. Nevertheless, the geometry of PbO is retained in the structure of  $\text{Pb}(\text{H}_2\text{PO}_4)_2$ ; four of the five shorter Pb–O bonds generally show the same basic pattern of PbO.

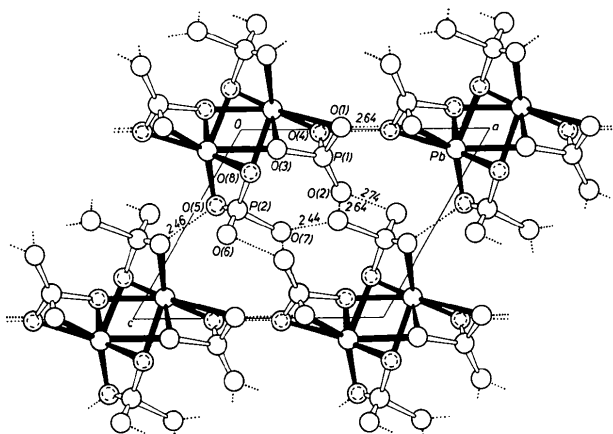


Fig. 1. View of the structure of  $\text{Pb}(\text{H}_2\text{PO}_4)_2$  down the  $b$  axis. Dotted lines represent hydrogen bonds (distances are in Å). The dashed circles represent atoms belonging to a phosphate group below.

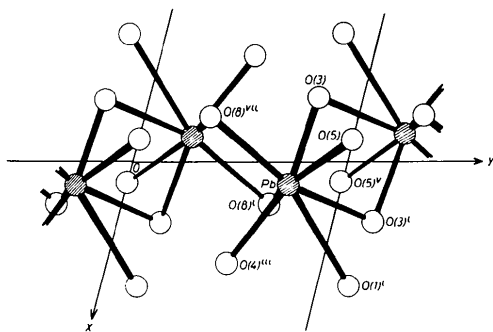


Fig. 2. The chains of Pb coordination polyhedra. The transformation notation is as in Table 2.

Table 2. Selected interatomic distances (Å) and angles ( $^\circ$ )

(a) Pb coordination polyhedron

Pb–O(1) <sup>i</sup>	2.880 (14)	Pb–O(5)	2.758 (16)
Pb–O(3)	2.494 (15)	Pb–O(8) <sup>i</sup>	2.444 (14)
Pb–O(3) <sup>i</sup>	2.581 (14)	Pb–O(8) <sup>ii</sup>	2.570 (14)
Pb–O(4) <sup>iii</sup>	2.567 (14)		

(b) The geometry of the phosphate groups

P(1)–O(1)	1.564 (15)	P(2)–O(5)	1.517 (16)
P(1)–O(2)	1.597 (15)	P(2)–O(6)	1.586 (18)
P(1)–O(3)	1.534 (16)	P(2)–O(7)	1.531 (16)
P(1)–O(4)	1.548 (16)	P(2)–O(8)	1.507 (13)

O(1)–P(1)–O(2)	102.3 (6)	O(5)–P(2)–O(6)	105.7 (6)
O(1)–P(1)–O(3)	104.2 (7)	O(5)–P(2)–O(7)	108.3 (7)
O(1)–P(1)–O(4)	112.1 (8)	O(5)–P(2)–O(8)	114.3 (6)
O(2)–P(1)–O(3)	110.9 (7)	O(6)–P(2)–O(7)	109.7 (6)
O(2)–P(1)–O(4)	109.1 (8)	O(6)–P(2)–O(8)	107.6 (7)
O(3)–P(1)–O(4)	117.2 (8)	O(7)–P(2)–O(8)	111.2 (6)

(c) O...O distances including hydrogen bonds

O(1)···O(4) <sup>iv</sup>	2.64 (2)	O(5)···O(5) <sup>v</sup>	2.44 (2)
O(2) <sup>ii</sup> ···O(7)	2.64 (2)	O(7)···O(7) <sup>vi</sup>	2.46 (2)
O(6) <sup>iii</sup> ···O(2) <sup>ii</sup>	2.74 (2)		

Symmetry code

(i)	$-x, -y, -z$	(v)	$-x, -y, 1-z$
(ii)	$1-x, 1-y, 1-z$	(vi)	$1-x, -y, 1-z$
(iii)	$-x, 1-y, -z$	(vii)	$x, y+1, z$
(iv)	$1-x, 1-y, -z$		

The geometries of the two unique  $\text{PO}_4^-$  groups are given in Table 2. The P(1) $\text{O}_4$  group is coordinated to three different  $\text{Pb}^{2+}$  ions through the O(1)···O(3) edge, O(3) and O(4). The P(2) $\text{O}_4$  group is also coordinated to three  $\text{Pb}^{2+}$  ions, through the apices O(5) and O(8), the latter being coordinated to two  $\text{Pb}^{2+}$  ions related by an inversion centre.

The O···O distances between neighbouring phosphate groups indicate clearly the positions of the H atoms and hence the hydrogen-bond network (Table 2).

Two short, symmetrical hydrogen bonds exist between symmetry-related atoms [O(5)···O(5)<sup>v</sup> and O(7)···O(7)<sup>vi</sup>] forming chains of  $\text{H}_2\text{P}(2)\text{O}_4^-$  tetrahedra parallel to the  $x$  axis. The O(1)···O(4)<sup>iv</sup> hydrogen bonds link  $\text{H}_2\text{P}(1)\text{O}_4^-$  tetrahedra into dimers across the inversion centre at 0.5, 0.5, 0. These two arrangements of phosphate tetrahedra are linked together by O(2)···O(7) and O(6)···O(2) hydrogen bonds in a three-dimensional network.

The same hydrogen bonding is found in the structures of  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  (Dickens, Prince, Schroeder & Brown, 1973) and its arsenate isomorph  $\text{Ca}(\text{H}_2\text{AsO}_4)_2$  (Ferraris, Jones & Yerkess, 1972). The barium analogue  $\text{Ba}(\text{H}_2\text{PO}_4)_2$  (Herak & Krstanović, 1975; Gilbert & Lenhart, 1978) has a two-dimensional network of strong hydrogen bonds, some of them connecting symmetry-related O atoms. The simultaneous presence of symmetrical and nonsymmetrical

hydrogen bonds has also been observed in the crystal structures of  $\text{CsH}_2\text{PO}_4$  (Uesu & Kobayashi, 1976) and  $\text{TiH}_2\text{PO}_4$  (Oddon, Tranquard & Pèpe, 1979). The extended linkage of  $\text{PO}_4$  groups through symmetrical hydrogen bonds suggests a possible ferroelectric behaviour. Because of its remarkable sensitivity to moisture, measurements of dielectric properties and pyroelectric temperature analysis (Topić, 1979) were performed on polycrystalline samples of  $\text{Pb}(\text{H}_2\text{PO}_4)_2$ . No determinate results could be gathered from these measurements.

#### References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
- DICKENS, B., PRINCE, E., SCHROEDER, L. W. & BROWN, W. E. (1973). *Acta Cryst.* **B29**, 2057–2070.
- FERRARIS, G., JONES, D. W. & YERKES, J. (1972). *Acta Cryst.* **B28**, 2430–2437.
- GILBERT, J. D. & LENHART, P. G. (1978). *Acta Cryst.* **B34**, 3309–3312.
- HERAK, R. & KRSTANOVIĆ, I. (1975). *Proceedings of the Yugoslav Centre of Crystallography*, Vol. 10, p. 68.
- HERAK, R., PRELESNIK, B., ČURIĆ, M. & VASIĆ, P. (1978). *J. Chem. Soc. Dalton Trans.* pp. 566–569.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- MELLOR, J. W. (1947). *A Comprehensive Treatise of Inorganic and Theoretical Chemistry*, Vol. VII, p. 879. London: Longmans.
- ODDON, Y., TRANQUARD, A. & PÈPE, G. (1979). *Acta Cryst.* **B35**, 542–546.
- TOPIĆ, M. (1979). *J. Appl. Cryst.* **12**, 75–77.
- UESU, Y. & KOBAYASHI, J. (1976). *Phys. Status Solidi*, **34**, 475–481.
- ZALKIN, A. (1965). *FORDAP*. A Fortran program for Fourier calculation, Univ. of California, Berkeley.

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## Structure of Trirubidium Heptachlorodicuprate(II)

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**Abstract.**  $\text{Rb}_3[\text{Cu}_2\text{Cl}_7]$ , orthorhombic, *Ccca*,  $T = 295$  K,  $a = 24.843$  (4),  $b = 7.216$  (1),  $c = 7.216$  (1) Å,  $V = 1293.59$  Å<sup>3</sup>,  $Z = 4$ . Intensity measurements were made on a four-circle diffractometer. The final  $R_w$  value is 0.022 for 5448 reflections. The structure of this new phase in the system  $\text{RbCl}-\text{CuCl}_2$  can be derived from the  $\text{Rb}_3[\text{Mn}_2\text{Cl}_7]$  structure [Amit, Horowitz & Makovsky (1972). *Isr. J. Chem.* **10**, 715–719]; in addition, the title compound shows a static cooperative Jahn–Teller effect. The  $\text{CuCl}_6$  octahedra are elongated and order antiferrodistortively in the double layer and between similar double layers.

**Introduction.** In the phase diagram of  $\text{RbCl}$  and  $\text{CuCl}_2$  a new compound was found in an attempt to prepare  $\text{Rb}[\text{CuCl}_3]$ . Because of the interest of our department in the cooperative Jahn–Teller effect, the structure of this compound could be valuable for understanding the cooperative effects in similar structure types. The related structure of  $\text{K}[\text{CuF}_3]$  (Tsukuda & Okazaki, 1972) is not uniquely defined with respect to the stacking of the  $\text{CuCl}$  layers. In another related structure,  $\text{K}_2[\text{CuF}_4]$  (Haegle & Babel, 1974) there seems to be a unique interaction over quite a longer distance,

but different from that found in  $(\text{NH}_4)_2[\text{CuCl}_4]$  (Willett, 1964). In these compounds the  $\text{Cu}^{2+}$  ions are found in square layers together with  $\text{F}^-$  or  $\text{Cl}^-$  ions. Nearest and next-nearest interlayer interactions between the Jahn–Teller centres seem to be important. Perhaps the structure of  $\text{Rb}_3[\text{Cu}_2\text{Cl}_7]$  can help to clarify the cooperative Jahn–Teller interactions between layers in this kind of structure.

By means of DTA an endothermic transition was found at 495 K. This is also the case in  $\text{Rb}_2[\text{CuCl}_4]$  (495 K) (Witteveen, Jongejan & Brandwijk, 1974). This could be related to a transition to a Jahn–Teller disordered phase as described by Höck, Schröder & Thomas (1978). The compound melts/decomposes at 644 K.

Single crystals of  $\text{Rb}_3[\text{Cu}_2\text{Cl}_7]$  were grown in a methyl alcohol solution. A saturated solution of  $\text{RbCl}$  in methyl alcohol was poured into a  $\text{CuCl}_2$ -methyl alcohol solution. The latter contains a molar excess (10%) of  $\text{CuCl}_2$  and the concentration was such that no immediate crystallization occurred. Both solutions contained some ethyl orthoformate to avoid the formation of hydrates. After several hours dark-brown crystals appeared; these had a bipyramidal shape with