

Structures of CdSrP₂O₇ and CdBaP₂O₇

BY AHMED ALAOUI EL BELGHITI AND ALI BOUKHARI

Laboratoire de Chimie du Solide Appliquée, Département de Chimie, Faculté des Sciences, Université Mohammed V, Avenue Ibn Batouta, Rabat, Morocco

AND ELIZABETH M. HOLT*

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, USA

(Received 25 June 1990; accepted 17 July 1990)

Abstract. (I) CdSrP₂O₇, $M_r = 374.0$, monoclinic, $P2_1/n$, $a = 5.414$ (1), $b = 8.615$ (3), $c = 12.878$ (5) Å, $\beta = 90.01$ (3)°, $V = 600.6$ (4) Å³, $Z = 4$, $D_m = 4.10$ (5), $D_x = 4.135$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 126.6$ cm⁻¹, $F(000) = 688$, $T = 298$ K, $R = 6.0\%$ for 942 observed reflections. (II) CdBaP₂O₇, $M_r = 423.7$, triclinic, $P\bar{1}$, $a = 5.641$ (1), $b = 7.038$ (2), $c = 7.624$ (2) Å, $\alpha = 78.55$ (2), $\beta = 89.83$ (2), $\gamma = 86.79$ (2)°, $V = 296.2$ (2) Å³, $Z = 2$, $D_m = 4.68$ (5), $D_x = 4.750$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 107.1$ cm⁻¹, $F(000) = 380$, $T = 298$ K, $R = 6.0\%$ for 1217 observed reflections. The single-crystal structures of two mixed alkaline earth/transition metal diphosphates show them to exist in the solid state as dichromates with Cd in a distorted octahedral environment and the alkaline earth atoms, Sr and Ba, respectively eight and nine coordinate.

Introduction. Diphosphates, $A_2P_2O_7$, $A =$ divalent cation, have received wide attention in the structural literature. Each of the materials, $A =$ alkaline earth dication (Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+}) (Mg^{2+} : Calvo, 1965, 1967; Lukaszewicz, 1967*b*; Ca^{2+} : Calvo, 1968; Webb, 1966; Sr^{2+} : Grenier & Masse, 1967; Hagman, Jansson & Magnéli, 1968; Hoffman & Mooney, 1960; Ba^{2+} : Morris *et al.*, 1979*b*), is known to exist in at least two phases whose structures or isostructural relationships have been established by single-crystal or powder X-ray diffraction.

Structural information for $A =$ transition metal dication has also been reported (Co^{2+} : Krishnamachari & Calvo, 1972; Cu^{2+} : Robertson & Calvo, 1967, 1968; Ni^{2+} : Lukaszewicz, 1967*a*; Pietraszko & Lukaszewicz, 1968; Masse, Guitel & Durif, 1979; Zn^{2+} : Robertson & Calvo, 1970; Calvo, 1965; Mn^{2+} : Stefanidis & Nord, 1984; Cd^{2+} : Calvo & Au, 1969; Morris *et al.*, 1979*a*). $Pb_2P_2O_7$ is known (Mullica, Perkins, Grossie, Boatner & Sales, 1986). It has been observed that structures in which the radius

of A is greater than 0.97 Å (Brown & Calvo, 1970) are of the dichromate type ($A = Ba^{2+}$, Cd^{2+} , Ca^{2+} , Sr^{2+} and Pb^{2+}) in which pairs of $P_2O_7^{4-}$ groups in eclipsed conformation crystallize about a center of symmetry with bridging O atoms extending towards each other. When the radius of A is less than 0.97 Å ($A = Mg^{2+}$, Mn^{2+} , Co^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+}), the structures are of the type, thortveitite, in which $P_2O_7^{4-}$ exists in staggered conformation.

Mixed diphosphate structures of the type $A^{II}B^{II}P_2O_7$ are less well known. All are of the dichromate family. The single-crystal X-ray structures of $CaCoP_2O_7$ (Riou, Labbe & Goreaud, 1988*b*), $CaCuP_2O_7$, $SrCuP_2O_7$ (Moqine, 1986) and $BaCoP_2O_7$ (Riou, Labbe & Goreaud, 1988*a*) have been reported. The mixed diphosphates $Co_3Pb(P_2O_7)_2$ (Dindune, Krasnikov & Konstant, 1984) and $Ni_3Pb(P_2O_7)_2$ (Krasnikov, Konstant & Bel'skii, 1985), of structural type $A^{II}_3B^{II}(P_2O_7)_2$, are also known.

We have studied the mixed systems $A^{II}B^{II}P_2O_7$, in which $A = Ca$, Sr , Ba and $B = Cd$, (Alaoui El Belghiti, 1990), and have found CdSrP₂O₇ and CdBaP₂O₇ to form solid materials with A/B ratios of 1/1. Single-crystal X-ray diffraction studies of these materials are presented here. For $A = Ca$, the ratio A/B is equal to three and a mixed calcium/cadmium site is observed. These results will be published elsewhere (Alaoui El Belghiti, Boukhari & Holt, 1990).

Structures of the parent or non-mixed materials, $Sr_2P_2O_7$, and $Cd_2P_2O_7$ have been reported. SrP_2O_7 exists in a high-temperature or α form above 1033 K and also in a low temperature or β form. α - $Sr_2P_2O_7$ crystallizes with 9-coordinate Sr (Grenier & Masse, 1967; Hagman, Jansson & Magnéli, 1968) and is related to the structure of α - $Ca_2P_2O_7$. The β - $Sr_2P_2O_7$ modification, identified from powder diffraction studies (Hoffman & Mooney, 1960), has not been subjected to full single-crystal X-ray structure examination but appears isostructural with β - $Ca_2P_2O_7$ (Webb, 1966) in which Ca atoms show

* To whom correspondence should be addressed.

7, 8 and 9 coordination to O atoms. α -Ba₂P₂O₇ is reported to be isostructural with α -Sr₂P₂O₇. β -Sr₂P₂O₇ is unknown; however, the existence of γ -Ba₂P₂O₇ has been reported (Morris *et al.*, 1979b).

Cd₂P₂O₇ has been examined by single-crystal X-ray crystallography; cadmium is found to be 5 and 6 coordinate (Calvo & Au, 1969; Morris *et al.*, 1979a).

Experimental. Single crystals of CdSrP₂O₇ (I) were prepared by heating a stoichiometric mixture of CdCO₃, SrCO₃, and (NH₄)₂HPO₄ to liquid state (1350 K) in a platinum carrier, followed by a period of slow cooling (4 K h⁻¹) to 1170 K and further cooling (10 K h⁻¹) to 473 K. Single crystals of CdBaP₂O₇ (II) were prepared using the same procedure of controlled cooling following fusion at 1370 K.

Crystals of (I) and (II), dimensions 0.12 × 0.10 × 0.10 mm, (I); 0.11 × 0.11 × 0.11 mm, (II), were mounted on a Syntex P2₁ automated diffractometer. Unit-cell dimensions were determined by least-squares refinement of angular positions for fifteen independent reflections ($2\theta > 15^\circ$) during normal alignment procedures. Data [1717 (I), 1731 (II) independent points after removal of space-group forbidden, (I), and redundant data, (I) and (II)] were collected at room temperature using a variable scan rate, a θ - 2θ scan mode and a scan width of 1.2° below $K\alpha_1$ to 1.2° above $K\alpha_2$ to a maximum 2θ value of 60°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections. As the intensities of these reflections showed less than 5% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz and polarization effects. Observed reflections [942 (I), 1217 (II), points $I > 3.0\sigma(I)$; (I) $-7 < h < 7$, $0 < k < 12$, $0 < l < 15$, (II) $-7 < h < 7$, $-9 < k < 0$, $-10 < l < 10$] were used for solution and refinement. Direct methods (MULTAN80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) permitted location of the heavy-atom positions. A cycle of least-squares refinement followed by a difference Fourier synthesis allowed location of the P₂O₇⁴⁻ groups. Refinement (XRAY; Stewart, 1978) of scale factor, positional and isotropic thermal parameters was carried out to convergence, function minimized $\sum w(|F_o| - |F_c|)^2$, leading to a final agreement factor. For both structures, scattering factors were taken from Cromer & Mann (1968). Anomalous-dispersion corrections were made for Cd, Ba and Sr (*International Tables for X-ray Crystallography*, 1974, Vol. IV). In the final stages of refinement a weight of $1/\sigma(F)^2$ was used. $R/wR = 6.0/7.2\%$, (I); $6.0/6.9\%$, (II). $(\Delta/\sigma)_{\max} = 0.07, 0.03$;

$\Delta\rho_{\min} = -0.18, -0.08$; $\Delta\rho_{\max} = 0.18, 0.20 \text{ e } \text{\AA}^{-3}$ for (I) and (II) respectively.

Discussion. Projection views of the cell contents of (I) and (II) are shown in Figs. 1 and 2, based on the positional parameters of Table 1,* respectively. Bond angles and distances for (I) and (II) are listed in Table 2.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53443 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

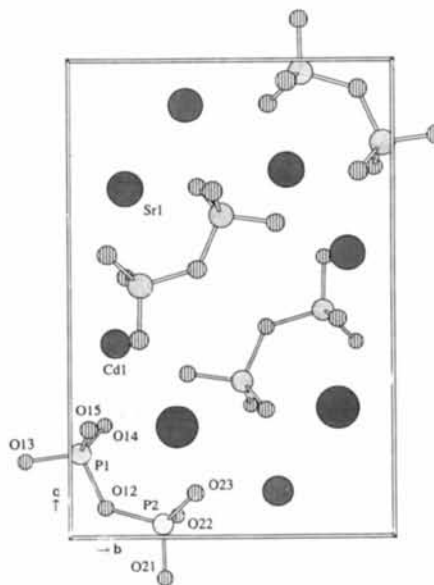


Fig. 1. Projection view of CdSrP₂O₇ (I) on the plane (100).

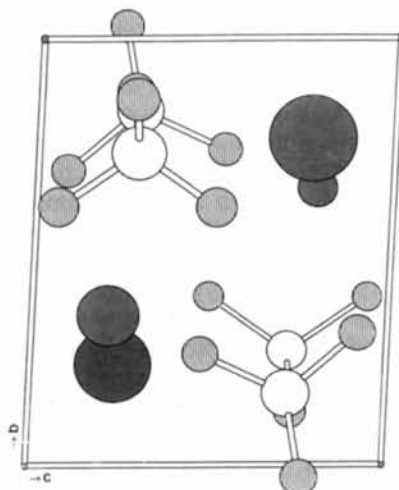


Fig. 2. Projection view of CdBaP₂O₇ (II) on the plane (100).

Table 1. Positional parameters for (I) and (II)

	$U_{eq} = (U_{11} + U_{22} + U_{33})/3$.			
	x	y	z	$U_{eq}(\text{Å}^2) \times 10^3$ *
(I)				
Cd1	0.1957 (3)	0.1397 (2)	0.4054 (1)	11.9 (6)
Sr1	0.2212 (3)	0.1723 (2)	0.7302 (1)	7.1 (7)
P1	0.2401 (9)	0.0309 (6)	0.1744 (4)	6.3 (2)
P2	0.2076 (9)	0.2829 (6)	0.0253 (4)	6.0 (2)
O12	0.2534 (27)	0.1061 (16)	0.0617 (11)	12.0 (6)
O13	0.1815 (26)	-0.1376 (17)	0.1596 (11)	11.7 (6)
O14	0.0262 (29)	0.1054 (17)	0.2340 (11)	14.3 (6)
O15	0.4833 (26)	0.0573 (18)	0.2254 (12)	14.7 (6)
O21	0.2823 (27)	0.2872 (18)	-0.0849 (11)	13.7 (6)
O22	-0.0609 (27)	0.3289 (19)	0.0455 (12)	15.0 (6)
O23	0.3762 (29)	0.3831 (19)	0.0908 (12)	17.7 (7)
(II)				
Ba1	0.2340 (2)	0.2349 (1)	0.4343 (1)	10.7 (3)
Cd1	0.2151 (2)	0.3507 (2)	-0.1002 (1)	14.4 (5)
P1	0.7223 (7)	0.2683 (6)	0.7011 (5)	8.0 (8)
P2	0.7238 (7)	0.1668 (6)	1.0956 (5)	8.3 (8)
O11	0.9347 (20)	0.3911 (17)	0.6864 (15)	12.0 (4)
O12	0.7373 (19)	0.1257 (17)	0.8943 (14)	13.3 (4)
O13	0.7277 (22)	0.1407 (18)	0.5623 (15)	15.0 (4)
O14	0.4941 (21)	0.3962 (17)	0.6900 (15)	12.7 (4)
O21	0.9144 (21)	0.3084 (17)	1.1097 (15)	13.3 (4)
O22	0.7679 (21)	-0.0298 (18)	1.2116 (14)	14.0 (4)
O23	0.4797 (20)	0.2632 (18)	1.1167 (14)	13.0 (4)

$$* \sigma(U_{eq}) = \frac{1}{3}[\sigma(U_{11})^2 + \sigma(U_{22})^2 + \sigma(U_{33})^2]^{1/2}.$$

The structure of CdSrP_2O_7 resembles the high temperature or $\alpha\text{-Sr}_2\text{P}_2\text{O}_7$ form. $\alpha\text{-Sr}_2\text{P}_2\text{O}_7$ is orthorhombic, space group, $Pnma$, in which layers of Sr and $\text{P}_2\text{O}_7^{4-}$ exist on mirror planes. CdSrP_2O_7 is isotypic with $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$, space group $P2_1/n$, in which the crystallographic mirror plane is absent and $\text{P}_2\text{O}_7^{4-}$ groups show significant deviation from symmetry about pseudo-mirror planes at $x = \frac{1}{4}$ and $\frac{3}{4}$, yet Ca atoms remain at coordinates approximately on these planes. In CdSrP_2O_7 (also $P2_1/n$), both heavy atoms and $\text{P}_2\text{O}_7^{4-}$ groups show deviation from the pseudo-mirror planes at $x = 0.25$ and 0.75 (Fig. 3). Thus the major structural change on introduction of Cd into $\alpha\text{-Sr}_2\text{P}_2\text{O}_7$ is the loss of mirror symmetry at 0.25 and 0.75 of the short axis of the cell and a resultant increase in cell dimension in this direction [CdSrP_2O_7 , $5.414(1) \text{ \AA}$ as compared to $\alpha\text{-Sr}_2\text{P}_2\text{O}_7$, $5.4035(4) \text{ \AA}$; $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$, $5.315(5) \text{ \AA}$].

Cadmium has a distorted octahedral environment in CdSrP_2O_7 with five O atoms at distances $2.20(1)$ – $2.41(1) \text{ \AA}$ and a sixth at $2.88(2) \text{ \AA}$. The Sr^{2+} atoms are found in the folds of the $\text{P}_2\text{O}_7^{4-}$ with eight Sr—O distances [average $2.635(1) \text{ \AA}$].

CdBaP_2O_7 is isostructural with BaCoP_2O_7 and BaCuP_2O_7 . CdBaP_2O_7 crystallizes with layers of $(\text{CdP}_2\text{O}_7)^{2-}$ modules perpendicular to the a axis of the cell (Fig. 4) and separated by Ba atoms. It may be seen that these layers are composed of $(\text{CdP}_2\text{O}_7)^{2-}$ units related by centers of symmetry with bridging O atoms extending towards each other. Another point of view reveals the layers to be com-

Table 2. Bond distances (Å) and angles (°)

(I)			
Sr1...O15 ⁱⁱ	2.66 (1)	Cd1...O21 ⁱⁱ	2.33 (2)
Sr1...O22 ⁱ	2.65 (1)	Cd1...O13 ⁱⁱⁱ	2.20 (1)
Sr1...O23 ⁱⁱⁱ	2.63 (2)	Cd1...O23 ^{iv}	2.24 (2)
Sr1...O21 ^v	2.60 (1)	P1—O12	1.59 (2)
Sr1...O13 ^{vi}	2.62 (1)	P1—O13	1.50 (2)
Sr1...O14 ^{vii}	2.78 (1)	P1—O14	1.53 (2)
Sr1...O14 ^{viii}	2.53 (1)	P1—O15	1.49 (2)
Sr1...O15 ^{ix}	2.61 (1)	P2—O12	1.61 (1)
Cd1...O14	2.41 (1)	P2—O21	1.48 (1)
Cd1...O15	2.88 (2)	P2—O22	1.53 (2)
Cd1...O22 ⁱ	2.25 (1)	P2—O23	1.51 (2)
O14—Cd1—O15	55.8 (5)	O13 ⁱⁱⁱ —Cd1—O23 ^{iv}	157.0 (5)
O14—Cd1—O22 ⁱ	166.5 (6)	O12—P1—O13	106.7 (8)
O14—Cd1—O21 ⁱⁱ	73.5 (5)	O12—P1—O14	108.7 (8)
O14—Cd1—O13 ⁱⁱⁱ	82.7 (5)	O12—P1—O15	107.5 (8)
O14—Cd1—O23 ^{iv}	80.4 (5)	O13—P1—O14	108.1 (8)
O15—Cd1—O22 ⁱ	110.9 (5)	O13—P1—O15	113.0 (8)
O15—Cd1—O21 ⁱⁱ	129.0 (4)	O14—P1—O15	112.6 (8)
O15—Cd1—O13 ⁱⁱⁱ	75.2 (5)	P1—O12—P2	130.0 (9)
O15—Cd1—O23 ^{iv}	82.4 (5)	O12—P2—O21	105.1 (8)
O22 ⁱ —Cd1—O21 ⁱⁱ	119.1 (5)	O12—P2—O22	109.9 (8)
O22 ⁱ —Cd1—O13 ⁱⁱⁱ	91.3 (5)	O12—P2—O23	106.5 (8)
O22 ⁱ —Cd1—O23 ^{iv}	101.7 (6)	O21—P2—O22	114.7 (9)
O21 ⁱⁱ —Cd1—O13 ⁱⁱⁱ	94.3 (5)	O21—P2—O23	110.9 (9)
O21 ⁱⁱ —Cd1—O23 ^{iv}	95.7 (6)	O22—P2—O23	109.3 (9)
(II)			
Ba1...O13	2.95 (1)	Cd1...O11 ⁱⁱ	2.24 (1)
Ba1...O14	2.89 (1)	Cd1...O22 ⁱⁱⁱ	2.58 (1)
Ba1...O23 ⁱ	2.76 (1)	Cd1...O21 ^{iv}	2.46 (1)
Ba1...O21 ⁱⁱ	3.01 (1)	P1—O11	1.51 (1)
Ba1...O11 ^{iv}	2.73 (1)	P1—O12	1.61 (1)
Ba1...O14 ^v	3.07 (1)	P1—O13	1.52 (1)
Ba1...O11 ^v	2.89 (1)	P1—O14	1.52 (1)
Ba1...O13 ^{vi}	2.64 (1)	P2—O12	1.62 (1)
Ba1...O22 ^{vii}	2.80 (1)	P2—O21	1.52 (1)
Cd1...O14 ^{viii}	2.25 (1)	P2—O22	1.49 (1)
Cd1...O23 ⁱ	2.20 (1)	P2—O23	1.52 (1)
Cd1...O21 ⁱⁱ	2.32 (1)		
O14 ^{viii} —Cd1—O23 ⁱ	92.0 (2)	O22 ⁱⁱⁱ —Cd1—O21 ^{iv}	154.2 (2)
O14 ^{viii} —Cd1—O21 ⁱⁱ	178.3 (3)	O11—P1—O12	107.2 (6)
O14 ^{viii} —Cd1—O11 ⁱⁱ	90.4 (3)	O11—P1—O13	111.7 (7)
O14 ^{viii} —Cd1—O22 ⁱⁱⁱ	77.0 (3)	O11—P1—O14	110.2 (7)
O14 ^{viii} —Cd1—O21 ^{iv}	98.8 (2)	O12—P1—O13	107.0 (6)
O23 ⁱ —Cd1—O21 ⁱⁱ	80.6 (2)	O12—P1—O14	108.7 (6)
O23 ⁱ —Cd1—O11 ⁱⁱ	171.2 (2)	O13—P1—O14	111.9 (7)
O23 ⁱ —Cd1—O22 ⁱⁱⁱ	97.7 (2)	P1—O12—P2	132.2 (8)
O23 ⁱ —Cd1—O21 ^{iv}	108.0 (2)	O12—P2—O21	106.5 (6)
O21 ⁱⁱ —Cd1—O11 ⁱⁱ	88.0 (2)	O12—P2—O22	103.9 (6)
O21 ⁱⁱ —Cd1—O22 ⁱⁱⁱ	103.1 (3)	O12—P2—O23	107.3 (6)
O21 ⁱⁱ —Cd1—O21 ^{iv}	80.3 (2)	O21—P2—O22	114.3 (6)
O11 ⁱⁱ —Cd1—O22 ⁱⁱⁱ	74.6 (2)	O21—P2—O23	109.5 (7)
O11 ⁱⁱ —Cd1—O21 ^{iv}	80.0 (2)	O22—P2—O23	114.7 (6)

Symmetry codes for (I): (i) = $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) = $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) = $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) = $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (v) = $x, y, -1 + z$; (vi) = $-x, -y, 1 - z$; (vii) = $1 - x, -y, 1 - z$ and for (II): (i) = $-1 + x, y, z$; (ii) = $-1 + x, y, -1 + z$; (iii) = $1 - x, -y, 1 - z$; (iv) = $1 - y, -1 - y, 1 - z$; (v) = $x, y, -1 + z$; (vi) = $2 - x, -y, 1 - z$.

prised of chains of $(\text{CdP}_2\text{O}_7)_\infty^{2-}$ units extending in the c direction with each Cd atom linked in square planar geometry to four O atoms bound to the four different P atoms of two different $\text{P}_2\text{O}_7^{4-}$ groups [average Cd—O distance $2.25(1) \text{ \AA}$]. Cadmium achieves six coordination by further linkage to an O atom of each of the two neighboring chains;

Cd1—O22^{iv} 2.58 (1) Å, Cd1—O21^{iv} 2.46 (1) Å. The resulting octahedron shows severe distortion from octahedral geometry; O22^{iv}—Cd1—O21^{iv} 154.2 (2)°.

Barium shows ninefold coordination with Ba—O distances ranging from 2.64 (1)–3.07 (1) Å.

In both (I) and (II), P₂O₄²⁻ anions crystallize in groups of two linked by inversion centers of the unit cell. P₂O₄²⁻ groups are quasi-eclipsed. These solid materials are thus of the dichromate class. The packing of dichromate pairs in CdBaP₂O₇ differs from that observed for CdSrP₂O₇ (Figs. 4 and 1). In CdSrP₂O₇, lines connecting bridging O atoms of each pair alternate in direction within the cell whereas in CdBaP₂O₇ these vectors are parallel.

In CdSrP₂O₇, spatial needs of Sr appear to have dominated the crystallization process. The resulting solid state material resembles that of α-Sr₂P₂O₇ with only small disruption of symmetry upon introduction

of cadmium. The CdBaP₂O₇ structure appears to be determined by the coordination needs of cadmium and thus resembles that of BaCoP₂O₇ and BaCuP₂O₇ in which the metal atom (Co, Cu, Cd) is located in a square pyramidal polyhedron of O atoms and coordination needs of the metal appear to dominate.

The authors express their thanks to the National Science Foundation for assistance in the form of a grant to permit collaborative investigation.

References

- ALAOUI EL BELGHITI, A. (1990). Thèse de 3ème Cycle, Rabat, Morocco.
- ALAOUI EL BELGHITI, A., BOUKHARI, A. & HOLT, E. M. (1990). In the press.
- BROWN, I. D. & CALVO, C. (1970). *J. Solid State Chem.* **1**, 173–179.
- CALVO, C. (1965). *Can. J. Chem.* **43**, 1139–1145.
- CALVO, C. (1967). *Acta Cryst.* **23**, 289–295.
- CALVO, C. (1968). *Inorg. Chem.* **7**, 1345–1351.
- CALVO, C. & AU, P. K. L. (1969). *Can. J. Chem.* **47**, 3409–3417.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- DINDUNE, A., KRASNIKOV, V. & KONSTANT, Z. A. (1984). *Izv. Akad. Nauk SSSR, Neogr. Mater.* **20**, 1553–1556.
- ERRAGH, F., BOUKHARI, A., ABRAHAM, F. & ELOUADI, B. (1990). *J. Cryst. Spectrosc. Res.* In the press.
- GRENIER, J.-C. & MASSE, R. (1967). *Bull. Soc. Fr. Minéral. Crystallogr.* **110**, 285–292.
- HAGMAN, L.-O., JANSSON, I. & MAGNÉLI, C. (1968). *Acta Chem. Scand.* **22**, 1419–1429.
- HOFFMAN, C. W. W. & MOONEY, R. W. (1960). *J. Electrochem. Soc.* **107**, 854–855.
- KRASNIKOV, V. V., KONSTANT, Z. A. & BEL'SKII, V. V. K. (1985). *Izv. Akad. Nauk SSSR, Neogr. Mater.* **21**(9), 1560–1563.
- KRISHNAMACHARI, N. & CALVO, C. (1972). *Acta Cryst.* **B28**, 2883–2885.
- LUKASZEWICZ, K. (1967a). *Bull. Acad. Pol. Sci. Sér. Sci. Chim.* **105**, 47–51.
- LUKASZEWICZ, K. (1967b). *Bull. Acad. Pol. Sci. Sér. Sci. Chim.* **105**, 53–57.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
- MASSE, R., GUITEL, J. C. & DURIF, A. (1979). *Mater. Res. Bull.* **14**, 337–341.
- MOQINE, A. (1986). Thèse de 3ème Cycle, Rabat, Morocco.
- MORRIS, M. C., MCMURDIE, H. F., EVANS, E. H., PARETZKIN, B., DEGROOT, J. H., HUBBARD, C. R. & CARMEL, S. J. (1979a). *Editors. Natl Bur. Stand. US Monogr.* **25**, **16**, 26.
- MORRIS, M. C., MCMURDIE, H. F., EVANS, E. H., PARETZKIN, B., DEGROOT, J. H., HUBBARD, C. R. & CARMEL, S. J. (1979b). *Editors. Natl Bur. Stand. US Monogr.* **25**, **16**, 19.
- MULLICA, D. F., PERKINS, H. O., GROSSIE, D. A., BOATNER, L. A. & SALES, B. C. (1986). *J. Solid State Chem.* **62**, 371–376.
- PIETRASZKO, K. & LUKASZEWICZ, K. (1968). *Bull. Acad. Pol. Sci. Sér. Sci. Chim.* **105**, 183–187.
- RIOU, D., LABBE, P. & GOREAUD, M. (1988a). *C. R. Acad. Sci. Sér. C*, **307**, 903–907.
- RIOU, D., LABBE, P. & GOREAUD, M. (1988b). *C. R. Acad. Sci. Sér. C*, **307**, 1751–1756.
- ROBERTSON, B. E. & CALVO, C. (1967). *Acta Cryst.* **22**, 665–672.
- ROBERTSON, B. E. & CALVO, C. (1968). *Can. J. Chem.* **46**, 605–612.

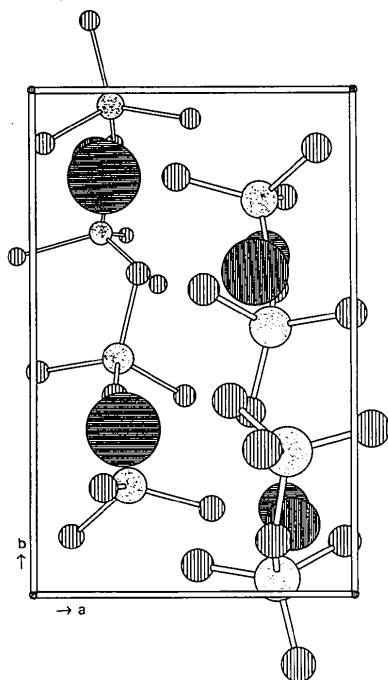


Fig. 3. View of CdSrP₂O₇ (I), projected on the (001) plane.

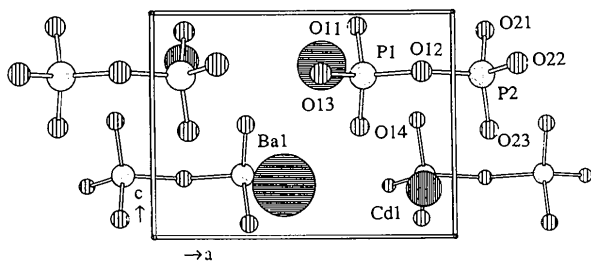


Fig. 4. View of CdBaP₂O₇ (II), along the [010] axis.

ROBERTSON, B. E. & CALVO, C. (1970). *J. Solid State Chem.* **1**, 120–133.

STEFANIDIS, T. & NORD, A. G. (1984). *Acta Cryst.* **C40**, 1995–1999.

STEWART, J. M. (1978). The *XRAY76* system. Version of 1978. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

WEBB, N. C. (1966). *Acta Cryst.* **21**, 942–948.

Acta Cryst. (1991). **C47**, 477–479

Structure de $\text{LaH}(\text{PO}_3\text{H})_2 \cdot 3\text{H}_2\text{O}$

PAR M. LOUKILI

Ecole Supérieure de Technologie, Département Génie Chimique, BP 2427 Fès, Maroc

J. DURAND, A. LARBOT ET L. COT

Laboratoire de Physicochimie des Matériaux (URA 1312), ENSCM, 8, Rue de l'Ecole Normale, 34075 Montpellier CEDEX 02, France

ET M. RAFIQ

Laboratoire de Chimie Minérale Appliquée, Faculté des Sciences, Fès, Maroc

(Reçu le 28 septembre 1989, accepté le 13 juli 1990)

Abstract. Lanthanum hydrogen bis(hydrogenphosphite) trihydrate, $\text{LaH}(\text{PO}_3\text{H})_2 \cdot 3\text{H}_2\text{O}$, $M_r = 353.8$, monoclinic, $P2_1/c$, $a = 9.687$ (3), $b = 7.138$ (2), $c = 13.518$ (5) Å, $\beta = 104.48$ (3)°, $V = 905.0$ (5) Å³, $Z = 4$, $D_m = 2.56$ (2), $D_x = 2.598$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu(\text{Mo } K\alpha) = 5.103$ mm⁻¹, $F(000) = 672$, $T = 300$ K, $R = 0.032$ for 1018 independent observed reflections. The structure contains two phosphite anions connected by a hydrogen bond. The La^{3+} cation is eight coordinated by seven O atoms from phosphite anions and one O atom of a water molecule.

Introduction. Une étude récente nous a permis de mettre en évidence plusieurs types de sels acides de phosphites de terres rares. Ces composés sont différents par leur degré d'hydratation ou le nombre d'hydrogène acide.

Quelques phosphites alcalins: $\text{Na}_2\text{PO}_3\text{H} \cdot 5\text{H}_2\text{O}$ (Colton & Henn, 1971), $(\text{NH}_4)_2\text{PO}_3\text{H} \cdot \text{H}_2\text{O}$ (Rafiq, Durand & Cot, 1982), alcalinoterreux: $\text{MgPO}_3\text{H} \cdot 6\text{H}_2\text{O}$ (Corbridge, 1956), $\text{Ca}(\text{HPO}_3\text{H})_2 \cdot \text{H}_2\text{O}$ (Larbot, Durand & Cot, 1984), de métaux de transition divalents: $\text{CuPO}_3\text{H} \cdot 2\text{H}_2\text{O}$ (Handlovič, 1969) et $\text{Cd}(\text{HPO}_3\text{H}) \cdot \text{H}_2\text{O}$ (Loub, Podlahova & Jecny, 1978) et de métaux trivalents de lanthanides: $\text{NdH}(\text{PO}_3\text{H})_2 \cdot 2\text{H}_2\text{O}$ (Loukili, Durand, Cot & Rafiq, 1988) et $\text{La}(\text{HPO}_3\text{H})_3 \cdot \text{H}_2\text{O}$ (Tijani, Durand & Cot, 1988), ont fait l'objet de déterminations structurales.

Les phases déjà isolées sont du type: $\text{MH}(\text{PO}_3\text{H})_2 \cdot 1.5\text{H}_2\text{O}$ avec $M = \text{La}, \text{Ce}$; $\text{La}(\text{HPO}_3\text{H})_3 \cdot \text{H}_2\text{O}$, $\text{Ce}_2(\text{PO}_3\text{H})_3 \cdot 4\text{H}_2\text{O}$ (Larbot, Battou,

Durand & Cot, 1982) ou $\text{MH}(\text{PO}_3\text{H})_2 \cdot 2\text{H}_2\text{O}$ avec $M = \text{Y}, \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$ ou Lu (Durand, Loukili, Tijani, Rafiq & Cot, 1988).

La structure de $\text{LaH}(\text{PO}_3\text{H})_2 \cdot 3\text{H}_2\text{O}$ est un nouvel exemple d'arrangement dans cette famille de composés de terres rares.

Partie expérimentale. L'oxyde de lanthane La_2O_3 est dissous dans un excès d'acide phosphoreux. La solution obtenue est diluée puis conservée dans un dessiccateur. Des cristaux en forme de fines aiguilles se forment à température ambiante à partir de la solution. Paramètres de maille déterminés par enregistrement en chambre de Weissenberg (symétrie monoclinique $P2_1/c$) affinés par la méthode des moindres carrés à partir du spectre de poudre; densité mesurée par pycnométrie dans le benzène à 393 K; axe d'allongement c ; dimensions du cristal $0,02 \times 0,02 \times 0,2$ mm; diffractomètre Nicolet $R3m/V$. Mesures d'intensité effectuées avec balayage $\theta - 2\theta$; $\theta < 50^\circ$; largeur de balayage $1,20^\circ$; $0 \leq h \leq 11$, $0 \leq k \leq 8$, $-16 \leq l \leq 15$; trois réflexions contrôles mesurées toutes les 500 réflexions; pas de variation d'intensité supérieure à 0,3%, 1853 réflexions mesurées, 1603 réflexions indépendantes et 1018 observées [$F > 6\sigma(F)$]; correction d'absorption; structure résolue par méthodes directes; affinement des paramètres atomiques (sauf pour les atomes d'hydrogène) par la méthode des moindres carrés basée sur F ; atomes d'hydrogène de PO_3H^{2-} positionnés par synthèse différence de Fourier, mais non affinés, autres