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Structural order in complexes of the $A^{II}B^{II}P_2O_7$ series: $BaPbP_2O_7$, $PbCoP_2O_7$, $PbMnP_2O_7$ and $PbCuP_2O_7$

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Abstract

Four new diphosphate compounds of the type $A^{II}B^{II}P_2O_7$ have been synthesized and characterized by single-crystal X-ray diffraction. While all four have similar unit cell dimensions, $BaPbP_2O_7$ is isotypical with α-$Sr_2P_2O_7$ (space group *Pmnb*), whereas $PbCoP_2O_7$, $PbMnP_2O_7$ and $PbCuP_2O_7$ are similar to α-$Ca_2P_2O_7$ (space group $P2_1/n$).

$P_2O_7^{4-}$ groups show average O–P···P–O angles which range from 0.0° to 49.56° and are intermediate between the 0.0° expected of dichromate-type structures and the 60.0° expected of thorveities. The magnitude of the O–P···P–O angle is correlated with the ionic radius of the smaller cation in each compound. Furthermore, the change in space group for $BaPbP_2O_7$ may be seen to be a consequence of the ionic radii of the B atom.

Metal coordination numbers in the four complexes range from 5 to 9.

1. Introduction

Large numbers of diphosphates of the type $A^{II}B^{II}P_2O_7$ in which A and B are alkaline earth or divalent transition metals have been reported in the literature. Those complexes which crystallize in space group $P2_1/n$ and show unit cell dimensions close to $a = 12.7$ Å, $b = 8.4$ Å, $c = 5.3$ Å, $\beta = 90.2°$, are spoken of as isostructural to α-$Ca_2P_2O_7$. α-$Ca_2P_2O_7$ has two crystallographically distinct heavy atom sites; Ca(1) which lies in the "fold" of the P_2O_7 group and Ca(2) which is positioned at the ends of the P_2O_7 groups. Both the Ca(1) and the Ca(2) sites display eight-fold coordination to oxygen atoms. (Fig. 1(a)) [1]. α-$Ca_2P_2O_7$ is classed as a dichromate-type structure with $P_2O_7^{-4}$ groups related by a center of symmetry and found in pseudoeclipsed conformation. Thortveitite-type structures show a staggered conformation of these anionic groups. In α-$Ca_2P_2O_7$, the "torsion" angles, O–P···P–O, are 13.77°, 13.20° and 27.23° with the largest angle subtended by the oxygen atoms nearest to the bridging oxygen atom.

It has been observed that the larger or A atom of $A^{II}B^{II}P_2O_7$ structures crystallizing in space group $P2_1/n$ and thus spoken of as isostructural to α-$Ca_2P_2O_7$ occupies the Ca(1) site whereas the smaller or B atom occupies the Ca(2) site at the ends of the P_2O_7 groups. (Fig. 1(b)). Their coordination numbers may vary.

Structural data for the crystalline α-$Ca_2P_2O_7$ isotypes $CaCuP_2O_7$ [2], $SrCuP_2O_7$ [3], $SrCdP_2O_7$ [4], $SrCoP_2O_7$ [5], $PbZnP_2O_7$ [6], $PbMgP_2O_7$, $PbFeP_2O_7$ [7], $SrNiP_2O_7$ [8] and $BaMgP_2O_7$ [6] have been reported. Unit cell dimensions for $PbCoP_2O_7$ have been determined from powder data [9].

The term "isostructural" is often invoked when complexes of similar formulae (stoichiometry and identity of at least some of the atoms) crystallize in the same space group and display cell dimensions which do not differ by more than the "swelling" to be expected on substitution of larger atoms for smaller ones. The term is applied often without verification of identity or near identity of atomic positional parameters. A review of those compounds reported to be isostructural reveals a large variation in the O–P···P–O angle (average 18.07° for α-$Ca_2P_2O_7$ to 47.34° for $SrCuP_2O_7$).

We have prepared four new complexes of the type $A^{II}B^{II}P_2O_7$, A = Pb, and examined their single-crystal X-ray structures in order to examine the structural consequences of change in the identity of the B atom.

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Table 1
Crystallographic data for **I**, **II**, **III**, and **IV**

Compound	$BaPbP_2O_7$(**I**)	$PbCoP_2O_7$(**II**)	$PbMnP_2O_7$(**III**)	$PbCuP_2O_7$(**IV**)
Colour	colourless	purple	lavender	blue-green
Formula weight	518.5	440.1	436.1	444.7
Space group	*Pmnb*	$P2_1/n$	$P2_1/n$	$P2_1/n$
Temp. (°C)	28	28	28	28
Cell constants				
a(Å)	5.594(1)	5.322(1)	5.393(1)	5.381(1)
b(Å)	9.108(2)	8.292(2)	8.461(2)	8.194(2)
c(Å)	13.426(4)	12.777(2)	12.848(3)	12.569(1)
β, deg		90.18(1)	90.00(3)	90.39(1)
Cell volume ($Å^3$)	684.0(3)	563.8(2)	586.3(2)	554.3(2)
Formula units (unit cell)	4	4	4	4
D_{calc}($Mg\ m^{-3}$)	5.035	5.184	4.940	5.329
μ_{calc}(mm^{-1})	30.758	33.313	31.363	34.732
Diffractometer(scan)	θ-2θ	θ-2θ	θ-2θ	θ-2θ
Radiation, graphite monochromator	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71069$ Å)
Max. crystal dimensions (mm)	0.12 × 0.2 × 0.2	0.4 × 0.4 × 0.4	0.3 × 0.3 × 0.4	0.4 × 0.4 × 0.4
Scan width	1.2°	1.2°	1.2°	1.2°
Decay of standards	0.008%	0.006%	0.006%	0.005%
Reflections measured	2781	2389	2472	1506
2θ range (deg)	7.0–45.0	7.0–45.0	7.0–45.0	4.0–45.0
range of *h*, *k*, *l*	$-1 \leq h \leq 7$	$-1 \leq h \leq 7$	$-1 \leq h \leq 7$	$-1 \leq h \leq 6$
	$-1 \leq k \leq 12$	$-11 \leq k \leq 1$	$-1 \leq k \leq 11$	$-1 \leq k \leq 9$
	$-18 \leq l \leq 18$	$-17 \leq l \leq 17$	$-18 \leq l \leq 18$	$-14 \leq l \leq 14$
Reflections observed [$F_0 \geq V\sigma(F_0)$]	650 ($V = 8.0$)	1020($V = 9.0$)	1041($V = 9.0$)	812($V = 5.0$)
R_{int}	6.08%	7.00%	5.36%	6.84%
Computer programs	SHELXI	SHELXI	SHELXI	SHELXI
Structure solution	SHELXS	SHELXS	SHELXS	SHELXS
No. of parameters varied	62	101	101	101
Weights	$w^{-1} = \sigma^2(F) + 0.0008F^2$	$w^{-1} = \sigma^2(F) + 0.0008F^2$	$w^{-1} = \sigma^2(F) + 0.0008F^2$	$w^{-1} = \sigma^2(F) + 0.0008F^2$
Goodness of fit	1.21	1.04	1.35	1.36
$R = \Sigma \lvert F_0 \rvert - \lvert F_c \rvert / \Sigma \lvert F_0 \rvert$	4.39	6.42	4.85	4.43
R_w	5.87	8.11	6.01	5.46
Largest feature final diff. map $eÅ^{-3}$	3.21	8.31	3.77	2.69
Transmission factors	0.08–0.32	0.09–0.36	0.09–0.36	0.09–0.34

2. Experimental

The complexes $BaPbP_2O_7$**I**, $PbCoP_2O_7$ **II**, $PbMnP_2O_7$ **III** and $PbCuP_2O_7$ **IV** were prepared by direct fusion of PbO, $(NH_4)_2HPO_4$ and $BaCO_3$, $CoCl_2 \cdot 6H_2O$, $MnCO_3$, or CuO (1:1:1) at a temperature of 1233 K (973 K for $MnCO_3$) for 24 h after successive cycles of heating to progressively higher temperatures and regrinding. Cooling (4 K h^{-1}) to 875 K (823 K for $MnCO_3$ and CuO) followed by extinction of the oven heating element and cooling to room temperature produced crystalline forms of each material.

Single crystals of **I**, **II**, **III** and **IV** were mounted on a

Table 2
Atomic coordinates and equivalent isotropic displacement coefficients for $PbCoP_2O_7$**II**

	x	*y*	*z*	*U*(eq)*
Pb1	0.2121(2)	0.6695(1)	0.2208(1)	0.021(1)
Co1	0.6804(6)	0.8521(3)	0.3928(3)	0.018(1)
P1	0.1818(11)	0.8009(6)	0.5189(5)	0.016(1)
P2	0.2508(10)	0.5382(6)	0.6640(4)	0.014(1)
O11	−0.0984(31)	0.8339(22)	0.5238(12)	0.021(4)
O12	0.2978(33)	0.8105(20)	0.4107(12)	0.021(4)
O13	0.3215(36)	0.9006(22)	0.6001(14)	0.025(5)
O14	0.2201(35)	0.6118(21)	0.5532(14)	0.023(5)
O21	0.1858(30)	0.3614(17)	0.6507(15)	0.021(4)
O22	0.0580(27)	0.6183(19)	0.7347(13)	0.016(4)
O23	0.5145(32)	0.5619(21)	0.7004(16)	0.026(5)

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Atomic coordinates and equivalent isotropic displacement coefficients for $PbMnP_2O_7$**III**

	x	*y*	*z*	*U*(eq)*
Pb1	0.2075(1)	0.6763(1)	0.2244(1)	0.019(1)
Mn2	0.6748(5)	0.8524(3)	0.3965(2)	0.017(1)
P1	0.1848(9)	0.7944(5)	0.5204(3)	0.015(1)
P2	0.2443(8)	0.5374(5)	0.6668(3)	0.014(4)
O11	−0.0898(23)	0.8287(16)	0.5277(9)	0.019(3)
O12	0.2878(28)	0.8034(15)	0.4104(10)	0.022(4)
O13	0.3340(26)	0.8945(16)	0.5954(9)	0.019(3)
O14	0.2286(28)	0.6137(16)	0.5541(10)	0.021(4)
O21	0.1854(25)	0.3652(14)	0.6540(9)	0.017(3)
O22	0.0471(26)	0.6152(16)	0.7339(10)	0.022(4)
O23	0.5032(26)	0.5676(16)	0.7089(11)	0.025(4)

*Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Atomic coordinates and equivalent isotropic displacement coefficients for $PbCuP_2O_7$ **IV**

	x	y	z	U(eq)*
Pb1	0.2126(1)	0.6667(1)	0.2206(1)	0.025(1)
Cu2	0.7052(3)	0.8564(2)	0.3875(2)	0.021(1)
P1	0.1798(7)	0.8043(5)	0.5130(3)	0.020(1)
P2	0.2569(7)	0.5365(5)	0.6605(3)	0.020(1)
O11	−0.1006(20)	0.8364(13)	0.5185(9)	0.022(3)
O12	0.2881(21)	0.8210(14)	0.4048(9)	0.026(3)
O13	0.3208(20)	0.9041(14)	0.5986(8)	0.023(3)
O14	0.2205(22)	0.6181(14)	0.5456(9)	0.025(3)
O21	0.1829(19)	0.3692(13)	0.6511(9)	0.021(3)
O22	0.0732(19)	0.6211(13)	0.7355(9)	0.022(3)
O23	0.5188(22)	0.5612(15)	0.6949(9)	0.029(4)

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5
Bond angles (Å) and distances (°) for $PbCoP_2O_7$ **II**

Co2	O11[a]		2.048(16)
Co2	O22[b]		2.135(17)
Co2	O12		2.079(18)
Co2	O13[c]		2.053(19)
Co2	O21[d]		1.988(15)
Pb1	O12		2.730(16)
Pb1	O13[e]		2.649(19)
Pb1	O23[e]		2.477(18)
Pb1	O21[f]		2.696(17)
Pb1	O11[b]		2.715(16)
Pb1	O23[d]		2.608(18)
Pb1	O22[b]		2.552(15)
P1	O11		1.518(18)
P1	O12		1.518(17)
P1	O13		1.519(19)
P1	O14		1.640(18)
P2	O14		1.550(19)
P2	O21		1.516(15)
P2	O22		1.522(16)
P2	O23		1.490(18)
O14	P1	O11	106.4(10)
O14	P1	O13	106.1(10)
O11	P1	O13	110.7(10)
O14	P1	O12	104.0(9)
O12	P1	O11	115.5(10)
O12	P1	O13	113.2(10)
O14	P2	O22	107.5(10)
O14	P2	O21	104.8(10)
O22	P2	O21	109.6(9)
O14	P2	O23	109.2(11)
O23	P2	O22	113.1(10)
O23	P2	O21	112.2(10)
P1	O14	P2	129.3(12)

[a] = 1.0 + x, y, z.
[b] = 0.5 + x, 0.5 − y, 0.5 + z.
[c] = 1.0 − x, 2.0 − y, 1.0 − z.
[d] = 1.0 − x, 1.0 − y, 1.0 − z.
[e] = −0.5 + x, 1.5 − y, −0.5 + z.
[f] = −x, 1.0 − y, 1.0 − z.

Siemens P4 single-crystal diffractometer. Details of crystal alignment, data collection and structure solution and refinement are presented in Table 1. Extinction was refined for each structure but was insignificant. Data reduction was accomplished using the Siemens XSCANS package [10]. Solution and refinement calculations were carried out using SHELX [11].

3. Discussion

The diphosphates $PbCoP_2O_7$ **II**, $PbMnP_2O_7$ **III** and $PbCuP_2O_7$ **IV** (positional parameters in Tables 2, 3 and 4 respectively) are isotypical with α-$Ca_2P_2O_7$ and show the atom of larger radius to occupy the Ca1 site whereas the smaller cation occupies the Ca2 site. Thus lead occupies the Ca1 site in $PbCuP_2O_7$ whereas Cu occupies the Ca2 site (Fig. 1(c)). The atoms in the Ca1 and Ca2 sites of α-$Ca_2P_2O_7$ both have eight-fold coordination to oxygen whereas the numbers of coordination neighbors are seven and five in the compounds studied (coordination number of atom in parentheses; bond distances in Tables 5–7) $PbCoP_2O_7$,

Table 6
Bond angles (Å) and distances (°) for $PbMnP_2O_7$ **III**

Mn2	O11[a]		2.119(12)
Mn2	O22[b]		2.218(13)
Mn2	O12		2.135(15)
Mn2	O13[c]		2.145(13)
Mn2	O21[d]		2.093(12)
Pb1	O12		2.656(13)
Pb1	O13[e]		2.676(13)
Pb1	O23[e]		2.439(14)
Pb1	O21[f]		2.655(13)
Pb1	O11[b]		2.754(12)
Pb1	O23[d]		2.726(14)
Pb1	O22[b]		2.546(14)
P1	O11		1.512(13)
P1	O12		1.521(14)
P1	O13		1.515(13)
P1	O14		1.606(14)
P2	O14		1.588(13)
P2	O21		1.500(13)
P2	O22		1.519(14)
P2	O23		1.519(15)
O14	P1	O12	104.1(7)
O12	P1	O11	113.9(8)
O12	P1	O13	111.7(8)
P1	O14	P2	129.8(9)
O14	P2	O23	107.8(8)
O23	P2	O22	111.6(8)
O23	P2	O21	113.4(8)

[a] = 1.0 + x, y, z.
[b] = 0.5 + x, 0.5 − y, 0.5 + z.
[c] = 1.0 − x, 2.0 − y, 1.0 − z.
[d] = 1.0 − x, 1.0 − y, 1.0 − z.
[e] = −0.5 + x, 1.5 − y, −0.5 + z.
[f] = −x, 1.0 − y, 1.0 − z.

Pb(7), Pb–O average 2.63(2) Å, Co(5), Co–O average 2.06(2) Å; $PbMnP_2O_7$, Pb(7), Pb–O average 2.64(1) Å, Mn(5), Mn–O average 2.14(1) Å; $PbCuP_2O_7$, Pb(7), Pb–O average 2.63(1) Å, Cu(5), Cu–O average 2.03(1) Å.

$PbCoP_2O_7$, $PbMnP_2O_7$ and $PbCuP_2O_7$ have torsional angles of 38.94°, 41.81°, 60.27° (average 47.01°), 35.22°, 35.32°, 54.53° (average 41.69°) and 40.93°, 42.93°, 64.82° (average 49.56°) respectively. Undistorted dichromate-type structures should exhibit

Table 7
Bond angles (Å) and distances (°) for $PbCuP_2O_7$**IV**

Cu2	O11[a]	1.951(11)	
Cu2	O22[b]	2.043(11)	
Cu2	O12	2.275(12)	
Cu2	O13[c]	1.975(11)	
Cu2	O21[d]	1.930(11)	
Pb1	O12	2.667(11)	
Pb1	O13[e]	2.663(11)	
Pb1	O23[e]	2.481(12)	
Pb1	O21[f]	2.687(11)	
Pb1	O11[b]	2.738(11)	
Pb1	O23[d]	2.586(12)	
Pb1	O22[b]	2.611(11)	
P1	O11	1.533(11)	
P1	O12	1.490(12)	
P1	O13	1.545(11)	
P1	O14	1.594(12)	
P2	O14	1.602(12)	
P2	O21	1.511(11)	
P2	O22	1.536(11)	
P2	O23	1.485(12)	
O13	P1	O12	113.2(6)
O14	P1	O12	105.6(6)
O11	P1	O12	114.6(6)
O14	P1	O13	105.2(6)
O11	P1	O13	110.9(6)
O14	P1	O11	106.6(6)
P2	O14	P1	130.3(8)
O22	P2	O23	111.9(6)
O14	P2	O23	108.4(7)
O14	P2	O22	106.8(6)
O21	P2	O23	113.8(7)
O21	P2	O22	108.2(6)
O14	P2	O21	107.5(6)

[a] = 1.0 + x, y, z.
[b] = 0.5 + x, 0.5 − y, 0.5 + z.
[c] = 1.0 − x, 2.0 − y, 1.0 − z.
[d] = 1.0 − x, 1.0 − y, 1.0 − z.
[e] = −0.5 + x, 1.5 − y, −0.5 + z.
[f] = −x, 1.0 − y, 1.0 − z.

Table 8
Atomic coordinates and equivalent isotropic displacement coefficients for $BaPbP_2O_7$**I**

	x	y	z	U(eq)*
Ba1	0.2500	0.6655(1)	0.2373(1)	0.016(1)
Pb1	0.7500	0.8629(1)	0.4117(1)	0.026(1)
P1	0.2500	0.7779(7)	0.5346(5)	0.018(2)
P2	0.2500	0.5395(7)	0.6804(4)	0.018(2)
O13	0.4748(26)	0.8499(16)	0.5742(10)	0.034(4)
O12	0.2500	0.7738(23)	0.4259(12)	0.033(6)
O14	0.2500	0.6072(20)	0.5693(12)	0.026(6)
O21	0.2500	0.3763(17)	0.6657(14)	0.026(5)
O22	0.0274(25)	0.5911(13)	0.7354(9)	0.023(3)

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 9
Bond angles (Å) and distances (°) for $BaPbP_2O_7$ **I**

Pb1	O21[a]		2.414(16)	
Pb1	O22[b]		2.708(13)	
Pb1	O22[c]		2.708(13)	
Pb1	O13		2.673(14)	
Pb1	O13[d]		2.673(14)	
Pb1	O13[e]		2.909(14)	
Pb1	O12[f]		2.919(14)	
Pb1	O13[g]		2.909(14)	
Pb1	O12		2.919(14)	
P2	O22		1.522(14)	
P2	O22[h]		1.522(14)	
P1	O12		1.459(18)	
P1	O13[h]		1.515(15)	
P2	O21		1.499(17)	
P2	O14		1.614(17)	
P1	O13		1.515(15)	
P1	O14		1.623(19)	
Ba1	O13[b]		2.681(14)	
Ba1	O13[c]		2.681(14)	
Ba1	O22[c]		2.705(13)	
Ba1	O22[i]		2.705(13)	
Ba1	O12		2.717(17)	
Ba1	O22[f]		2.830(13)	
Ba1	O22[j]		2.830(13)	
Ba1	O21[f]		3.109(8)	
Ba1	O21[a]		3.109(8)	
O21	P2	O22		111.7(6)
O22	P2	O14		109.3(6)
O21	P2	O22[h]		111.7(6)
O14	P2	O22[h]		109.3(6)
O13	P1	O14		108.3(7)
O13	P1	O13[h]		112.3(11)
O14	P1	O13[h]		108.3(7)
O21	P2	O14		104.9(10)
O22	P2	O22[h]		109.8(10)
O13	P1	O12		111.2(7)
O12	P1	O14		105.2(10)
O12	P1	O13[h]		111.2(7)
P2	O14	P1		129.2(11)

[a] = 1 − x, 1 − y, 1 − z.
[b] = 1.5 − x, 1.5 + y, −0.5 − z.
[c] = 0.5 + x, 1.5 − y, −0.5 + z.
[d] = 1.5 − x, y, z.
[e] = 0.5 + x, 2.0 − y, 1.0 − z.
[f] = −x, 1 − y, 1 − z.
[g] = 1.0 − x, 2.0 − y, 1.0 − z.
[h] = 0.5 − x, y, z.
[i] = −x, 1.5 − y, −0.5 + z.
[j] = 0.5 + x, 1.0 − y, 1.0 − z.

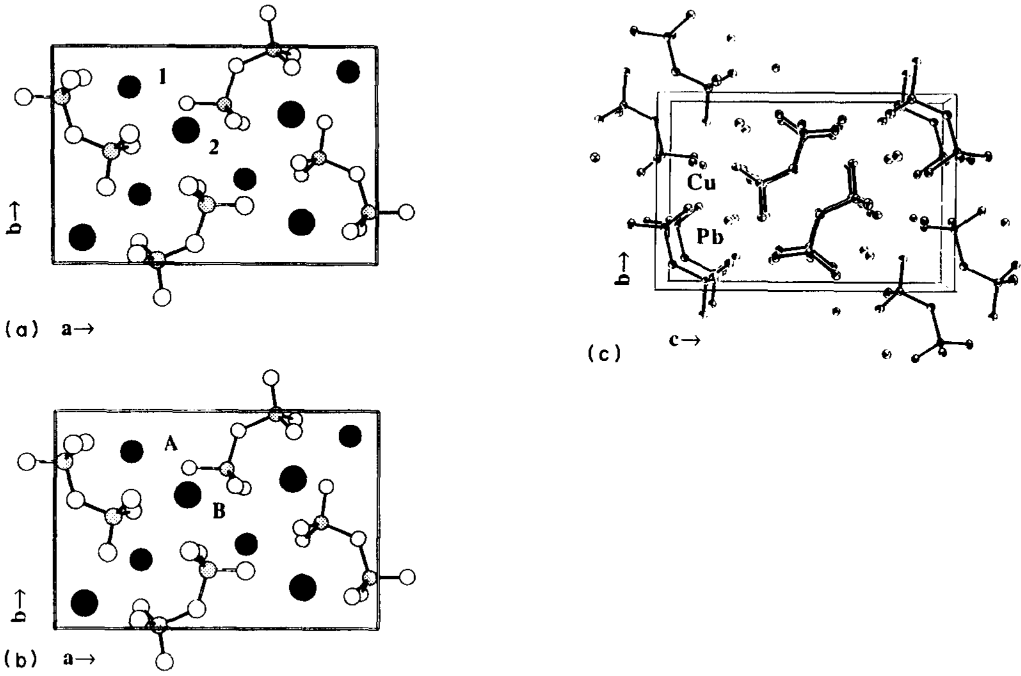

Fig. 1. (a) Projection view of α-$Ca_2P_2O_7$ with sites 1 and 2 indicated. (b) Projection view of $A^{II}B^{II}$–IP_2O_7 structure isotypical with α-$Ca_2P_2O_7$. Locations of A and B atoms indicated. (c) Projection view of $PbCuP_2O_7$.

O–P···P–O angles of 0.0° whereas thortveitites would be expected to have angles equal to 60°. Thus $PbCoP_2O_7$, $PbMnP_2O_7$ and $PbCuP_2O_7$ display conformations of $P_2O_7^{4-}$ groups which are closer to thortveitite conformation than to those of dichromate structures despite their isotypical relationship to the dichromate-type structure α-$Ca_2P_2O_7$.

Examination of projection views down the *c*-axis of α-$Ca_2P_2O_7$ (dihedral angle 18°) and $PbCuP_2O_7$ (torsion angle 52°) (Figs. 1(a) and 1(c)) shows that the

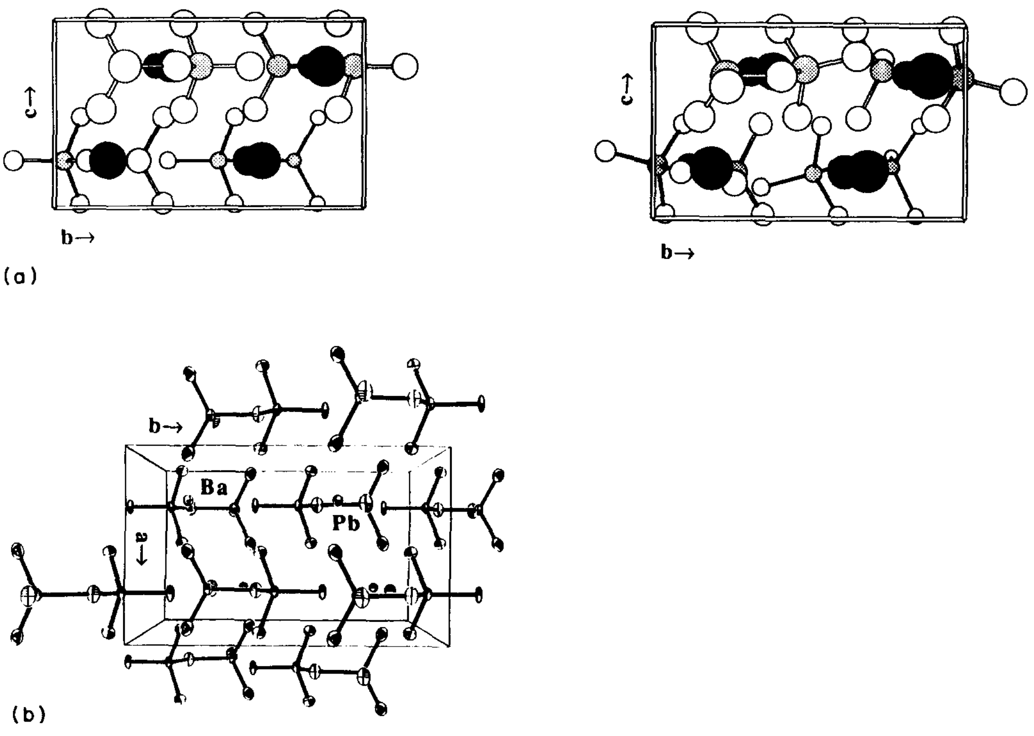

Fig. 2. (a) Projection view of α-$Sr_2P_2O_7$ and α-$Ca_2P_2O_7$. (b) Projection view of $BaPbP_2O_7$.

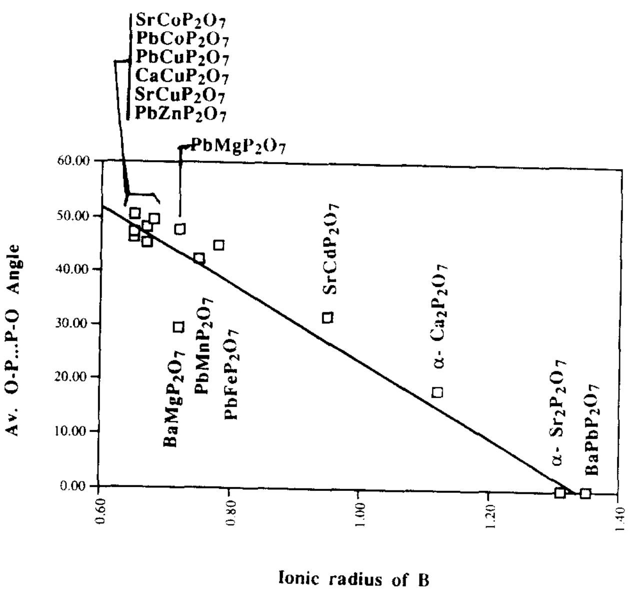

Fig. 3. Correlation of O–P···P–O angle with ionic radius of the smaller or B atom of $A^{II}B^{II}P_2O_7$ complexes (ionic radius for coordination multiplicity observed).

conformational change has been achieved by rotation of PO_4 groups to accommodate binding geometry preference together with slight displacement of the smaller or B atom.

The use of "isostructural" for $A^{II}B^{II}P_2O_7$ complexes crystallizing in space group $P2_1/n$ thus obscures the existence of a wide range of O–P···P–O angles in these complexes. Values of torsion angles observed fall in the full range between dichromate and thortveitite conformation.

$BaPbP_2O_7$, seen in octahedral unit cell, *Pmnb*, is isotypical with α-$Sr_2P_2O_7$ (Fig. 2). Ba is seven coordinate (Ba–O average 2.735(13) Å) but with two additional oxygen atoms at 3.109(13) Å whereas Pb has five oxygen neighbors at 2.71 Å or less and four more at a distance of 2.91–2.92 Å (Tables 8 and 9).

The solid state structures of α-$Sr_2P_2O_7$ [12] and α-$Ba_2P_2O_7$ [13], observed in space group *Pbnm*, differ from that of α-$Ca_2P_2O_7$ in the presence of a mirror plane perpendicular to the *a* axis (and thus the orthogonality of the unit cell). The O–P–O–P–O backbone of the P_2O_7 unit lies on the mirror and idealized eclipsed conformation is observed (Fig. 2(a)).

A plot of the O–P···P–O dihedral angle vs. the ionic radius for the smaller or B atom (using the ionic radius for the coordination multiplicity observed [14]) reveals a roughly linear correlation (Fig. 3). A similar plot of the ionic radius of the larger atom A and the observed dihedral angle reveals no correlation.

Thus in these "isotypical structures" it appears to be the size and preferences of coordination geometry of the smaller or B atom which dominate the packing of the solid. Increasing the ionic radius of the B atom leads to smaller torsion angles or eclipsing of the P_2O_7 groups. At some point, the radius of the B atom is sufficiently large to dictate torsion angles of zero and thus a change in space group from $P2_1/n$, in which these angles are not constrained, to *Pmnb* in which the torsion angles display idealized eclipsed values.

There are insufficient data to allow definition of the definitive ionic radius which leads to change of space group. The graph shows it to lie between 1.12 and 1.31 Å, suggesting that the space groups of unknown compounds $SrPbP_2O_7$, $BaCaP_2O_8$ and $BaSrP_2O_7$ should be *Pmnb* while $BaZnP_2O_7$, $SrZnP_2O_7$ and $CaZnP_2O_7$ might crystallize in $P2_1/n$.

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