JOURNAL OF SOLID STATE CHEMISTRY 118, 202–205 (1995)

BRIEF COMMUNICATION

Crystal Structures of Isotypical Diphosphates $PbCo_3(P_2O_7)_2$ and $PbFe_3(P_2O_7)_2$[1]

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Received December 14, 1994; in revised form February 3, 1995; accepted February 6, 1995

Single crystals of the mixed metal diphosphates $PbCo_3(P_2O_7)_2$ (I) and $PbFe_3(P_2O_7)_2$ (II) have been prepared by direct fusion and characterized by single-crystal X-ray diffraction, for $PbCo_3(P_2O_7)_2$ (I), $a = 7.275(5)$, $b = 7.725(11)$, $c = 9.511(4)$ Å, $\beta = 111.89(4)°$, monoclinic space group $P2_1/c$, $V = 509.3(5)$ Å^3, $d_{calc} = 4.768$ g cm^{-3}, $Z = 2$, $R/R_w = 3.9/5.1\%$ for 1192 observed reflections. For $PbFe_3(P_2O_7)_2$ (II), $a = 7.487(1)$, $b = 7.739(1)$, $c = 9.516(2)$ Å, $\beta = 111.95(1)°$, monoclinic space group $P2_1/c$, $V = 511.4(2)$ Å^3, $d_{calc} = 4.693$ g cm^{-3}, $Z = 2$, $R/R_w = 4.13/4.87\%$ for 1153 observed reflections. (I) and (II) are isotypical with $PbNi_3(P_2O_7)_2$ and $SrNi_3(P_2O_7)_2$. The solid lattice is characterized by layers of $P_2O_7^{4-}$ groups, parallel to the crystallographic plane (001) and joined by Pb^{2+} and Co^{2+} ions in (I) and Pb^{2+} and Fe^{2+} ions in (II). Lead is seen surrounded by eight oxygen atoms whereas the transition elements are found in chains of linked trimers extending in the [010] direction [Co–Co 3.182(3) and 3.256(3) Å; Fe–Fe, 3.186(3) and 3.264 (3) Å] with distorted octahedral geometry at each metal atom. © 1995 Academic Press, Inc.

INTRODUCTION

$A^{II}M_3^{II}(P_2O_7)_2$ (A = divalent ion) complexes are uncommon in the literature. Dindune *et al.* (1) identified $PbCo_3(P_2O_7)_2$ and $PbNi_3(P_2O_7)_2$ by IR and powder diffraction. A single crystal X-ray examination of the latter has been reported by Krasnikov *et al.* (2). Preliminary examination of solid solutions of powder samples of the system $Sr_2P_2O_7$–$Ni_2P_2O_7$ permitted identification of $SrNi_3(P_2O_7)_2$ (3). Structural and magnetic properties of this compound have been reported by ElBali (4). The two examples for which structural information is available, show linked trimers of M polyhedra which share edges. Each M-oxygen polyhedron shares two edges, each of them with two different metal oxygen polyhedra.

We have determined the single crystal structures of $PbCo_3(P_2O_7)_2$ and $PbFe_3(P_2O_7)_2$ in order to effect a structural comparison with the solid state forms of $PbNi_3(P_2O_7)_2$ and $SrNi_3(P_2O_7)_2$.

EXPERIMENTAL

Synthesis

Single crystals corresponding to the formula $PbCo_3(P_2O_7)_2$ (**I**) (lavender) and $PbFe_3(P_2O_7)_2$ (**II**) (red-purple were found in products resulting from the following procedures. A mixture of $(NH_4)_2HPO_4$, PbO, and $CoCl_2 \cdot 6H_2O$ (99% pure) or FeO was ground together and heated to fusion at 1233 K (**I**) or 875 K (**II**) after prior heating to effect elimination of volatile products.

$$2(NH_4)_2HPO_4 + PbO + CoCl_2 \cdot 6H_2O \rightarrow PbCoP_2O_7 + 4NH_3\uparrow + 8H_2O\uparrow + 2HCl\uparrow$$

$$6(NH_4)_2HPO_4 + 3PbO + Fe_2O_3 \rightarrow \text{“}Pb_3Fe_2^{III}(P_2O_7)_3\text{”} + 12NH_3\uparrow + 9H_2O\uparrow.$$

For (**I**), the molten mass was maintained at this temperature for 12 h and then cooled slowly (4 K/h).

For (**II**), a quantity of metallic iron was added to effect the reduction of Fe^{III} to Fe^{II}.

$$Pb_3Fe_2^{III}(P_2O_7)_2 + Fe^0 \rightarrow 3PbFeP_2O_7.$$

The mixture was placed in a silica tube which was sealed under vacuum and heated to fusion (1223 K). The molten liquid was cooled at a rate of 4 K/h. Crystals of (**I**) and (**II**) were found in the product mixtures.

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[1] See NAPS document No. 05205 for 25 pages of supplementary material. Order from ASIS/NAPS Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy. $7.75 up to 20 pages plus $0.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material, $1.50 for postage of any microfiche orders.

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TABLE 1
Crystal Data for $PbCo_3(P_2O_7)_2$ (I) and $PbFe_3(P_2O_7)_2$ (II)

Formula	$PbCo_3(P_2O_7)_2$ (I)	$PbFe_3(P_2O_7)_2$ (II)
MWT	731.9	722.6
a	7.475(5) Å	7.487(1) Å
b	7.725(4)	7.739(1)
c	9.511(4)	9.516(2)
α	90.0°	90.0°
β	111.89(4)	111.95(0)
γ	90.0	90.0
V	509.6(5) $Å^3$	511.4(2) $Å^3$
$F(000)$	670	664
$\mu MoK\alpha$	221.04 cm^{-1}	213.02 cm^{-1}
$\lambda MoK\alpha$	0.71069 Å	0.71073 Å
D_{calc}	4.768 g cm^{-3}	4.693 g cm^{-3}
Z	2	2
Space group	$P2_1/c$	$P2_1/c$
Obs. refl.	1192	1153
Octants meas.	$\pm h, k, l$	$\pm h, k, l$
R/R_w	3.9/5.1%	4.13/4.87%
G.O.F.	1.25	1.05

X-RAY CRYSTALLOGRAPHY

Single crystals of $PbCo_3(P_2O_7)_2$ (**I**) and $PbFe_3(P_2O_7)_2$ (**II**) (0.1 × 0.1 × 0.1 mm) were mounted on a Syntex P3 (**I**) or Siemens P4 (**II**) automated diffractometer. Unit cell dimensions (Table 1) were determined by least-squares refinement of the best angular positions for 15 independent reflections ($2\theta \geq 20°$) during normal alignment procedures using molybdenum radiation (λ = 0.71069 Å (**I**), 0.71073 Å (**II**)). Data (1457 (**I**), 1494 (**II**) independent points after removal of redundant and space group forbidden data) were collected at room temperature using a variable scan rate, a θ–2θ scan mode and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 60.0°. 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. The intensities of these reflections showed less than 5% variation. Data were corrected for Lorentz, polarization, centering, absorption, and background effects (5, 6). Observed reflections [1192 points [$I > 3.0\sigma(I)$] (**I**); 1153 points [$F > 4.0\sigma(F)$] (**II**)] were used for solution of heavy atom positions by direct methods using MULTAN80 (7) (**I**) or SHELX (**II**) (8). K, P and O atoms were located by a difference Fourier synthesis. Refinement ((**I**) (9), (**II**) (10)) of scale factor, positional, and anisotropic thermal parameters for these atoms was carried out to convergence. Final refinement [function minimized, $\Sigma(|F_o| - |F_c|)^2$] led to a final agreement factor, R = 3.9 (**I**), 4.13% (**II**) [$R = (\Sigma(|F_o| - |F_c|| / \Sigma|F_o|) \times 100$]. In the final stages of refinement a weight of $1/\sigma(F)^2$ (**I**), or $w^{-1} = \sigma^2(F) + 0.0008F^2$ (**II**) was used, R_2 = 5.1 (**I**), 4.87% (**II**). Corrections for anomalous scattering were made for Pb, Co, Fe, and P atoms (11).

DESCRIPTION OF THE STRUCTURE

Diphosphates $PbCo_3(P_2O_7)_2$ (**I**) and $PbFe_3(P_2O_7)_2$ (**II**) are isotypical with $PbNi_3(P_2O_7)_2$ and $SrNi_3(P_2O_7)_2$. Figure 1 shows a projection view of $PbCo_3(P_2O_7)_2$ on the (010) plane based on the positional parameters of Table 2. The positional parameters for $PbFe_3(P_2O_7)_2$ are given in Table 3. The solid lattice is characterized by layers of $P_2O_7^{4-}$ groups parallel to the crystallographic plane (001). Adjacent layers are separated by layers of metal atoms.

The transition metal ions Co^{2+} and Fe^{2+} are seen in two independent sites. $M(1)$ in general position and $M(2)$ on a site of inversion symmetry. Each is seen in octahedral

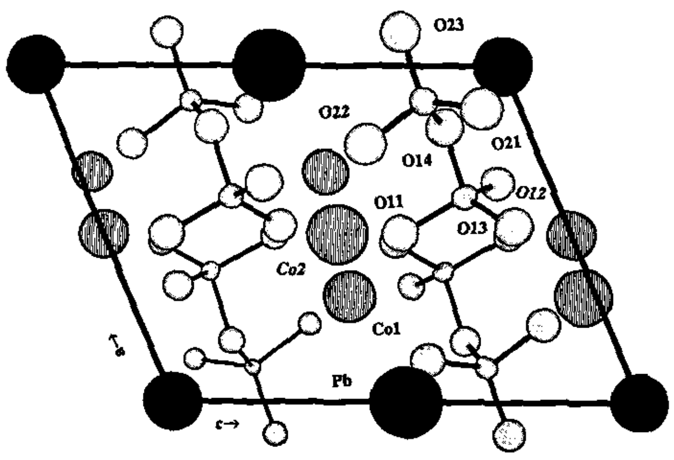

FIG. 1. Projection view of $PbCo_3(P_2O_7)_2$ on the (010) plane.

TABLE 2
Atomic Coordinates and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $PbCo_3(P_2O_7)_2$ (I)

Atom	x	y	z	U^*_{eq}
Pb1	0.0000	0.0000	0.5000	12.4(2)
Co1	0.3142(2)	0.3753(1)	0.4716(1)	4.7(5)
Co2	0.5000	0.0000	0.5000	4.0(7)
P1	0.6121(3)	0.2039(3)	0.8055(2)	1.4(8)
P2	0.8959(3)	−0.0573(3)	0.7993(2)	1.6(8)
O11	0.5040(9)	0.2112(8)	0.6355(6)	0.6(2)
O12	0.6541(8)	0.3759(8)	0.8870(7)	0.8(2)
O13	0.5255(8)	0.0784(8)	0.8847(7)	0.6(2)
O14	0.8176(8)	0.1296(8)	0.8215(7)	0.6(2)
O21	0.8736(7)	−0.1755(7)	0.9175(6)	0.1(2)
O22	0.7678(8)	−0.1181(8)	0.6384(6)	0.4(2)
O23	1.0975(9)	−0.0188(8)	0.8087(8)	0.8(3)

Note * = 1/3(U11 + U22 + U33) × 10^3; × 10^4 for Co, Pb, and P.

TABLE 3
Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $PbFe_3(P_2O_7)_2$ (II)

Atom	x	y	z	U^*_{eq}
Pb1	0.0000	0.0000	0.5000	17(1)
Fe1	0.3142(2)	0.1250(2)	−0.0282(1)	9(1)
Fe2	0.5000	0.0000	0.5000	8(1)
P1	0.1049(3)	0.0573(3)	0.2010(3)	11(1)
P2	0.3884(3)	−0.2037(3)	0.1945(2)	10(1)
O11	−0.0987(9)	0.0192(10)	0.1918(7)	14(2)
O12	0.1261(10)	0.1761(9)	0.0825(7)	15(2)
O13	0.2283(10)	0.1163(8)	0.3612(7)	13(2)
O14	0.1833(10)	−0.1295(9)	0.1790(7)	13(2)
O21	0.3471(9)	−0.3755(8)	0.1146(7)	11(2)
O22	0.4720(10)	−0.0774(9)	0.1133(7)	13(2)
O23	0.4985(9)	−0.2119(9)	0.3656(6)	14(2)

geometry with little or no axial distortion: Co(1)–O av. 2.116(7) Å, Co(2)–O av. 2.099(6) Å (**I**) (Table 4) and Fe(1)–O av. 2.117(7) Å., Fe(2)–O av 2.143(7) Å (**II**) (Table 5). While the geometry at Co is similar to that observed for octahedral cobalt in α-$Co_2P_2O_7$ (av. Co–O, 2.116(7) Å), (12) the two observations of $Fe_2P_2O_7$ both show one extremely long Fe–O distance and thus slightly larger averages (C1 bar, Fe–O av. 2.180(4); P1, Fe–O av. 2.158(9) and 2.206(9) Å) (13, 14).

Figure 2 shows a projection view of Co^{2+} cations and associated oxygen atoms of the unit cell of $PbCo_3(P_2O_7)_2$ on the (100) plane. Transition metals are observed in chains of trimers parallel to the [010] direction. M(2) occupies the central position in each trimeric series, M1–M2–M1. The angle at M2 is constrained by symmetry to 180°. The angles at M1 (M2–M1–M1) are 101.9° and 102.0°, respectively. Within each trimer Co–Co separations are 3.182 Å. Co–Co distances between trimers are 3.256 Å [comparable Fe–Fe distances are 3.186 and 3.264 Å, respectively]. Successive metal atoms are bridged by two oxygen atoms and may thus be viewed as adjacent MO_6 octahedra sharing an edge. The structures of Pb $Co_3(P_2O_7)_2$ (**I**) and $PbFe_3(P_2O_7)_2$ (**II**) are consistent with those of others of the family, $A^{II}M^{II}_3(P_2O_7)_2$, showing each M atom to share edges with two adjacent M atoms.

TABLE 4
Bond Angles(°) and Distances (Å) for $PbCo_3(P_2O_7)_2$ (I)

Co1-O11	2.097(6)	O11-P1-O12	116.2(3)
Co1-O22^{i}	2.222(6)	O11-P1-O13	113.4(3)
Co1-O13^{ii}	2.068(8)	O11-P1-O14	103.1(4)
Co1-O23^{iii}	2.093(6)	O12-P1-O13	110.7(4)
Co1-O21^{iv}	2.083(7)	O12-P1-O14	105.0(3)
Co1-O13^{iv}	2.132(6)	O13-P1-O14	107.3(3)
Co2-O22	2.146(5)	P1-O14-P2	134.4(4)
Co2-O11	2.072(6)	O21-P2-O22	110.8(3)
Co2-O22^{i}	2.146(5)	O21-P2-O23	117.6(3)
Co2-O11^{i}	2.072(6)	O21-P2-O14	107.5(4)
Co2-O12^{ii}	2.079(7)	O22-P2-O23	110.9(4)
Co2-O12^{v}	2.079(7)	O22-P2-O14	106.4(3)
Pb1-O22^{i}	2.699(7)	O23-P2-O14	102.8(4)
Pb1-O21^{iv}	2.691(6)		
Pb1-O12^{v}	2.586(6)		
Pb1-O23^{i}	2.753(6)		
Pb1-O21^{vi}	2.691(6)		
Pb1-O12^{vii}	2.586(6)		
Pb1-O23^{viii}	2.753(6)		
Pb1-O22^{viii}	2.699(7)		
P1-O11	1.516(6)		
P1-O12	1.510(6)		
P1-O13	1.514(7)		
P1-O14	1.593(7)		
P2-O14	1.601(7)		
P2-O21	1.506(6)		
P2-O22	1.545(6)		
P2-O23	1.505(8)		

Note. i = $1 - x, -y, 1 - z$; ii = $x, 1/2 - y, -1/2 + z$; iii = $-1 + x, 1/2 - y, -1/2 + z$; iv = $1 - x, 1/2 + y, 3/2 - z$; v = $1 - x, -1/2 + y, 3/2 - z$; vi = $-1 + x, -1/2 - y, -1/2 + z$; vii = $-1 + x, 1/2 - y, 1/2 + z$; viii = $-1 + x, y, z$.

TABLE 5
Bond Angles(°) and Distances (Å) for $PbFe_3(P_2O_7)_2$ (II)

Pb1-O11	2.748(7)	O11-P1-O12	117.2(4)
Pb1-O11^{i}	2.748(7)	O11-P1-O13	109.5(4)
Pb1-O12^{ii}	2.690(7)	O11-P1-O14	103.0(4)
Pb1-O21^{ii}	2.599(6)	O12-P1-O13	111.7(4)
Pb1-O13	2.677(8)	O12-P1-O14	107.9(4)
Pb1-O13^{i}	2.677(8)	O13-P1-O14	106.6(3)
Pb1-O12^{iii}	2.690(7)	O14-P2-O21	105.2(4)
Pb1-O21^{iv}	2.599(6)	O14-P2-O22	106.7(4)
Fe1-O12	2.088(8)	O14-P2-O23	103.3(4)
Fe1-O11^{v}	2.097(6)	O21-P2-O22	111.0(4)
Fe1-O22^{vi}	2.079(8)	O21-P2-O23	115.4(4)
Fe1-O22	2.115(6)	O22-P2-P23	114.1(4)
Fe1-O13^{vii}	2.242(6)	P1-O14-P2	134.4(5)
Fe1-O23^{viii}	2.081(6)		
P1-O11	1.522(7)		
P1-O12	1.509(8)		
P1-O13	1.528(6)		
P1-O14	1.603(7)		
P2-O14	1.594(8)		
P2-O21	1.505(6)		
P2-O22	1.518(8)		
P2-O23	1.527(6)		
Fe2-O21^{iii}	2.088(8)		
Fe2-O23^{ix}	2.077(7)		
Fe2-O21^{iv}	2.088(8)		
Fe2-O23	2.077(7)		
Fe2-O13^{ix}	2.164(6)		
Fe2-O13	2.164(6)		

Note. i = $-x, -y, 1 - z$; ii = $-x, 1/2 + y, 1/2 - z$; iii = $x, 1/2 - y, 1/2 + z$; iv = $x, -1/2 - y, 1/2 + z$; v = $-x, -y, -z$; vi = $1 - x, -y, -z$; vii = $x, 1/2 - y, -1/2 + z$; viii = $1 - x, 1/2 + y, 1/2 - z$; ix = $1 - x, -y, 1 - z$.

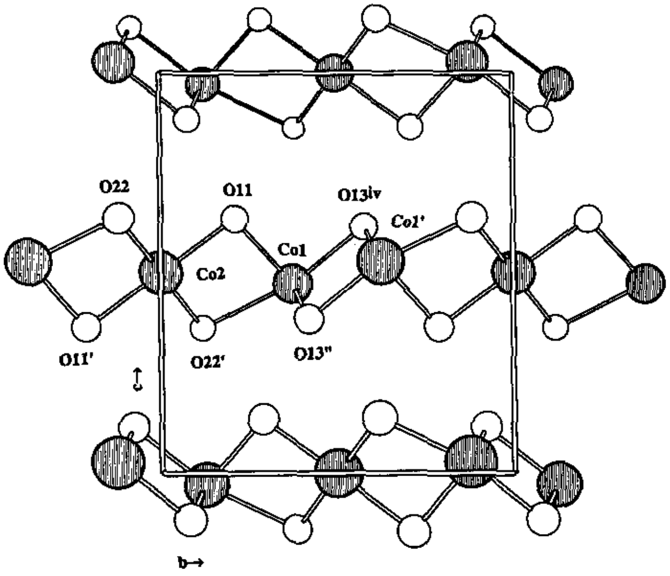

FIG. 2. View of linked trimers of $PbCo_3(P_2O_7)_2$.

Such trimers have been observed elsewhere in the literature other than in compounds of type $A^{II}M_3^{II}(P_2O_7)_2$ (A = divalent ion). $K_6Sr_2Ni_5(P_2O_7)_5$ crystallizes with a similar disposition of linked trimers composed of successive edge-sharing polyhedra (M–M, 3.018 Å within the trimer and 3.008 Å between trimers. The M–M–M angle within the trimer is 180° and that between ends of trimers is 105.73°. There is also an isolated Ni^{2+} in the unit cell (15).

$Co_3(PO_4)_2$ (16) and high-temperature $Mg_3(PO_4)_2$ (17) show a similar disposition of edge-sharing metal octahedra, Co–Co 3.151 Å within the trimeric unit and 3.033 Å between trimers (Co–Co–Co angle 123.33°, Mg–Mg 3.076 Å within the trimer and 2.920 Å between trimers) (Mg–Mg–Mg, ends of trimers, av. 127.5°). While Mg is not a transition element, its structural behavior is similar to that of elements of the 3*d* series.

Isolated trimers of metal atoms have been seen in $Ni_3(PO_4)_2$ (Ni–Ni 3.184 Å) (18) and $Fe_3(P_2O_7)_2$ $[Fe^{III}Fe^{II}_{0.5}P_2O_7]$ (19), in which isolated trimers ($Fe^{III} - Fe^{II} - Fe^{III}$) composed of octahedrally coordinated Fe^{3+} atoms which share a face with the trigonal prismatic central Fe^{2+} position (Fe–Fe distances 2.924(1) Å).

Pb^{2+} ions in (**I**) and (**II**) are found on sites of inversion symmetry and are eight coordinate with dicapped square bipyramidal geometry. Pb–O distances average 2.682(6) Å (**I**) and 2.678(7) Å (**II**). These values are similar to the value of 2.662(6) Å observed in $PbNi_3(P_2O_7)_2$ (20).

P–O–P angles in $P_2O_7^{4-}$ groups are 134.4(4)° (**I**) and 134.4(5)° in (**II**). P–O distances range from 1.505(8)–1.601(7) Å in (**I**) and 1.505(8)–1.603(7) Å in (**II**). These values are compatible with those seen in other diphosphates. $P_2O_7^{4-}$ groups are seen in nearly eclipsed conformation.

ACKNOWLEDGMENTS

The authors express their thanks to the National Science Foundation for a grant to permit collaborative work and to the Moroccan-American *Commission for Fulbright grants to E.M.H.*

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