2848 measured reflections
1101 independent reflections

3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.093$
$S = 1.235$
1101 reflections
42 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0322P)^2 + 0.7559P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.051$
$\Delta\rho_{max} = 0.380$ e Å^{-3}
$\Delta\rho_{min} = -0.409$ e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

P—O1	1.545 (2)	Ca2—F^v	2.2851 (4)
P—O3	1.5436 (13)	Ca2—O4^v	2.309 (4)
P—O3^i	1.5436 (13)	Ca2—O3^{iii}	2.3521 (13)
P—O2	1.549 (2)	Ca2—O2^{vi}	2.404 (2)
Ca1—O1	2.4007 (13)	Ca2—O3^v	2.5067 (14)
Ca1—O2^{ii}	2.4565 (14)	Ca2—O1^{viii}	2.672 (2)
Ca1—O3^{iii}	2.808 (2)		
O1—P—O3	111.26 (7)	O1—P—O2	111.52 (10)
O3—P—O3^i	107.12 (11)	O3—P—O2	107.73 (8)

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

The general structure of apatite was used as a starting point (Sudarsanan & Young, 1969). In a first step, the distributions of the Ca and Nd atoms in the 6*h* and 4*f* Ca sites were optimized. Then the P and Si occupancies were refined. Chemical analysis had shown that the stoichiometry of the compound was not strictly Ca$_9$Nd(PO$_4$)$_5$(SiO$_4$)F$_2$; a lack of Si and F atoms was observed. In order to take this observation into account, an electro-neutrality constraint involving these atoms was used. As the resulting $\Delta\rho$ map revealed a residual peak near the F atom and out of the mirror plane, an extra O atom was introduced in a 4*e* site, as in calcium hydroxy-apatite (Sudarsanan & Young, 1969). The electro-neutrality constraint was modified accordingly, assuming the added ion to be O^{2-}. The final cycles of refinement revealed that a vacancy still existed in the 4*e* tunnel site.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *CADAK* (Savariault, 1991). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1515). Services for accessing these data are described at the back of the journal.

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A Mixed Zinc–Cobalt Diphosphate, ZnCoP$_2$O$_7$

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Abstract

The structure of the mixed zinc cobalt diphosphate ZnCoP$_2$O$_7$ presents a low-dimensional system not previously observed in the diphosphates of 3*d* transition elements. The paramagnetic Co^{2+} ions are grouped into dimers linked by P$_2$O$_7^{4-}$ groups, forming tunnels in which the diamagnetic Zn^{2+} ions are located. The metal environments can be described as a distorted octahedron and a distorted square-based pyramid for Co and Zn, respectively, the two coordination polyhedra sharing common edges through the O atoms O1–O2 and O6–O7.

Comment

Until now, the diphosphates of the 3*d* transition elements have rarely shown a restricted cationic order. The structure of the simple diphosphates M_2P$_2$O$_7$ (M = Cr, Co, Ni, Cu or Zn), with two principal allotropic varieties α (low temperature) and β (high temperature), shows a fivefold and/or sixfold metal atom coordination. The

metal sites are five-coordinate and octahedral in the α variety, and only octahedral in β. The latter, isotypic with thortveitite, $Sc_2Si_2O_7$ (Cruickshank *et al.*, 1962), crystallizes in the monoclinic system, space group $C2/m$. The α variety crystallizes in the same system, space group $P2_1/c$ for M = Co and Ni (Krishnamachari & Calvo, 1972; Lukaszewics, 1967), $C2/c$ for M = Cr and Cu (Glaum *et al.*, 1991; Robertson & Calvo, 1967), and $I2/c$ for M = Zn (Robertson & Calvo, 1970). Exceptionally, $Ni_2P_2O_7$ presents two other allotropic varieties, σ and δ (Masse *et al.*, 1979; Lukaszewics, 1967), while $Mn_2P_2O_7$ (Stefanidis & Nord, 1984) and $Fe_2P_2O_7$ (Hoggins *et al.*, 1983) present a unique phase isotypic with the β form. We stress the bidimensional character of all these varieties of diphosphate compounds.

Recently, this bidimensional character has been broken down; the substitution of all the fivefold-coordinated Ni^{2+} ions by Li^+ gives rise to zigzag chains formed by trimers of NiO_6 octahedra. We thereby obtained a monodimensional system in $LiNi_{1.5}P_2O_7$ (Rissouli *et al.*, 1996). The mixed diphosphates $MM'P_2O_7$, with M, M' = Mn, Fe, Co, Ni or Cu, also exhibit a bidimensional character without cationic order (Benkhouja *et al.*, 1991, 1992, 1995; Handizi *et al.*, 1994). Exceptionally, $CoCuP_2O_7$ shows a regular repetition, Co–Cu–Co–Cu. However, the planar distribution of the metal cations in hexagons remains (Handizi *et al.*, 1994). In spite of the presence of the diamagnetic Zn^{2+} ion, the bidimensional character is conserved, with a mixed octahedral Zn–Cu site for $ZnCuP_2O_7$ (El Maadi *et al.*, 1994).

As a logical progression of our various attempts to reduce the dimensionality of the diphosphate systems, we investigated the structures of the $ZnCoP_2O_7$ and $ZnNiP_2O_7$ compounds, which appear to be isotypic. However, only the structure of $ZnCoP_2O_7$ can be described with accuracy because of the poor quality of the $ZnNiP_2O_7$ crystals.

The structure of $ZnCoP_2O_7$ is illustrated in Fig. 1. The $P_2O_7^{4-}$ groups have a staggered conformation (Fig. 3) and therefore belong to the thortveitite structure type.
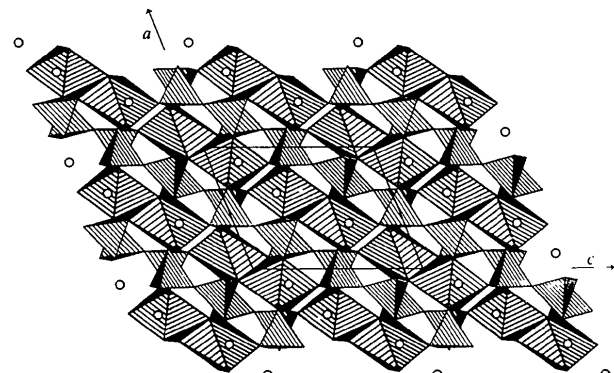
The distances between phosphorus and the terminal oxygens vary between 1.485 (4) and 1.526 (4) Å, and the average distance between phosphorus and the bridging oxygen is 1.583 (5) Å. The P—O—P angle is 144.2 (3)° and is close to that in α-$Co_2P_2O_7$. The Co^{2+} cations occupy octahedral sites which share a common edge with the nearest $P_2O_7^{4-}$ group, and thus form tunnels parallel to the [100] direction. Pairs of Zn^{2+} ions are located in these tunnels (Fig. 2). The structure can also be described as a succession of dimers of Co^{2+} cations separated by dimers of Zn^{2+} cations, forming sheets

Fig. 2. Structure of $ZnCoP_2O_7$ drawn on the (100) plane. The Zn^{2+} cations are represented by open circles and the Co^{2+} coordination is represented by the octahedra.
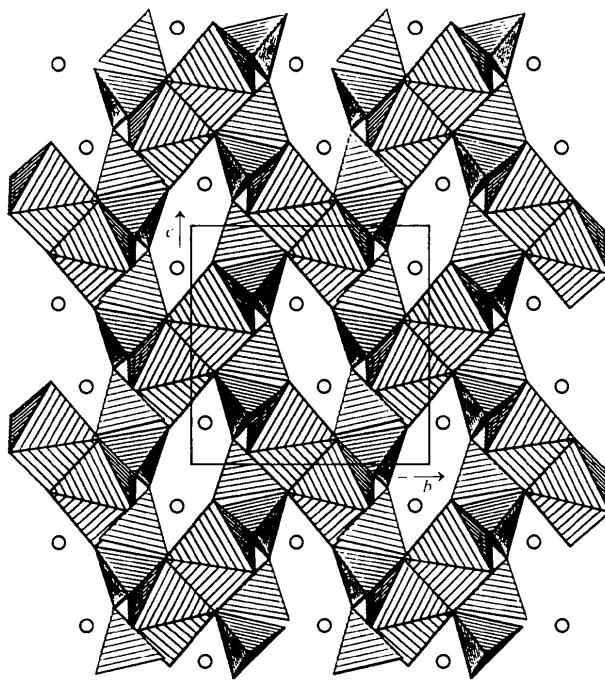
Fig. 1. Structure of $ZnCoP_2O_7$ drawn on the (010) plane. The Zn^{2+} cations are represented by open circles and the Co^{2+} coordination is represented by the octahedra.
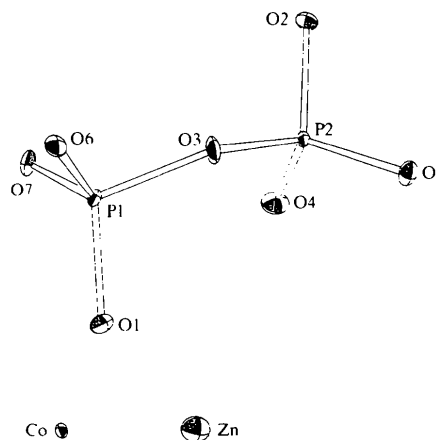
Fig. 3. *ORTEP*II (Johnson, 1976) view of the title compound. Displacement ellipsoids are shown at the 50% probability level.

of metallic ions. These sheets are linked by layers of $P_2O_7^{4-}$ groups.

Finally, dimers of Zn^{2+} and Co^{2+} cations are arranged in two systems of overlapping rings, which can be seen in Fig. 2; there are rings of Co^{2+} around the origin of the cell, including the dimers at $\pm(0,\frac{1}{2},0)$ and $\pm(0,0,\frac{1}{2})$ of the projection, and rings of Zn^{2+} formed by the dimers located at the origin and at $(0,1,0)$, $(0,\frac{1}{2},\frac{1}{2})$ and $(0,\frac{1}{2},-\frac{1}{2})$.

The Zn^{2+} ions are fivefold coordinated. The average Zn—O bond length is $2.047(4)$ Å [*cf.* $2.04(1)$ Å for the Ni compound]. These values are comparable to those obtained in α-$Zn_2P_2O_7$ for the Zn^{2+} ions in the fivefold-coordinated sites. The Co^{2+} ions occupy octahedral sites that are slightly irregular. The Co—O bonds range from $2.038(4)$ to $2.161(4)$ Å, with an average of $2.110(4)$ Å. These values are similar to those observed in α-$Co_2P_2O_7$ for Co^{2+} in octahedral sites. The intradimer Co···Co distance is $3.268(1)$ Å, while the shortest interdimer distance is $5.014(1)$ Å. These results reveal that the dimers are quasi-isolated, and justify the classification of these diphosphates as low-dimensional systems (0D). Such M_2O_{10} dimers are observed in the phosphates $BaCoP_2O_7$ and $BaNiP_2O_7$; the irregular octahedra share corners with the $P_2O_7^{4-}$ groups and create layers linked by Ba^{2+} cations (Riou *et al.*, 1988).

The O1, O2, O6 and O7 atoms coordinate Zn and Co, O5 bridges two Co, and O4 coordinates only one Zn atom. This is presumably the reason why the Zn—O4 bond is shorter. Indeed, the M—O bond is longer when the O atom is linked to more than one metal atom; the short Zn—O4 distance [$1.967(5)$ Å] is comparable to that given for α-$Zn_2P_2O_7$, where Zn^{2+} is fivefold coordinated and where the short Zn—O distance is equal to 1.956 Å. As is generally found in condensed phosphates, the bridging bonds are longer than the terminal bonds; the P1—O3 and P2—O3 distances are $1.576(5)$ and $1.591(5)$ Å, respectively, whereas the terminal P—O bonds vary between $1.485(4)$ and $1.526(4)$ Å.

We conclude that the diphosphate $ZnCoP_2O_7$ presents an original crystal structure associated with a cationic order that has not been observed in other mixed diphosphates of $3d$ transition elements. The presence of quasi-isolated dimers of paramagnetic ions therefore confers a low dimensionality on the system.

Experimental

The diphosphates $ZnCoP_2O_7$ and $ZnNiP_2O_7$ were prepared by a solid-state reaction from ZnO, $CoCO_3$ or NiO, and $(NH_4)_2HPO_4$, with an excess of P_2O_5 as flux. Each mixture was finely ground, placed in a quartz tube and then heated progressively, to 923 K for the Co compound and 773 K for the Ni one. Once the release of H_2O, NH_3 and CO_2 was complete, the mixture was melted in air at 1273 K for 2 h. It was then cooled to 773 K at a rate of $2\,K\,h^{-1}$ and then to 473 K at $10\,K\,h^{-1}$. The furnace was turned off below this temperature. Afterwards, the final products were placed in dilute HCl to dissolve the amorphous constituents.

Crystal data

$ZnCoP_2O_7$	Mo $K\alpha$ radiation
$M_r = 298.25$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 6.981(2)$ Å	$\theta = 10\text{--}15°$
$b = 8.334(1)$ Å	$\mu = 9.209$ mm^{-1}
$c = 8.924(1)$ Å	$T = 294$ K
$\beta = 112.32(2)°$	Prism
$V = 480.3(3)$ Å^3	$0.16 \times 0.08 \times 0.08$ mm
$Z = 4$	Violet
$D_x = 4.12$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	1274 reflections with $I > 3\sigma(I)$
$\theta/2\theta$ scans	$R_{int} = 0.033$
Absorption correction:	$\theta_{max} = 34°$
refined empirical (Walker & Stuart, 1983)	$h = -10 \rightarrow 10$
$T_{min} = 0.370$, $T_{max} = 0.479$	$k = 0 \rightarrow 13$
2165 measured reflections	$l = 0 \rightarrow 14$
1413 independent reflections	3 standard reflections frequency: 60 min intensity decay: 1.21%

Refinement

Refinement on F	$\Delta\rho_{max} = 1.299$ e Å^{-3}
$R = 0.041$	$\Delta\rho_{min} = -1.241$ e Å^{-3}
$wR = 0.064$	Extinction correction:
$S = 2.011$	isotropic (Zachariasen,
1268 reflections	1963)
101 parameters	Extinction coefficient:
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$	$2.5(2) \times 10^{-7}$
$(\Delta/\sigma)_{max} = 0.036$	Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Co—O2	2.084 (4)	Zn—O2	2.054 (4)
Co—O1	2.092 (4)	Zn—O4	1.967 (5)
Co—O5	2.132 (5)	Zn—O1	2.064 (4)
Co—O5^i	2.038 (4)	Zn—O6^{ii}	2.034 (4)
Co—O6	2.154 (5)	Zn—O7^{ii}	2.117 (5)
Co—O7	2.161 (4)		
O2—Co—O1	79.6 (1)	O5^i—Co—O7	91.9 (2)
O2—Co—O5	89.7 (2)	O6—Co—O7	77.5 (2)
O2—Co—O5^i	96.6 (2)	O2—Zn—O4	93.5 (2)
O2—Co—O6	80.2 (2)	O2—Zn—O1	81.0 (2)
O2—Co—O7	157.7 (2)	O2—Zn—O6^{ii}	169.4 (2)
O1—Co—O5	88.0 (2)	O2—Zn—O7^{ii}	92.5 (2)
O1—Co—O5^i	164.4 (2)	O4—Zn—O1	150.2 (2)
O1—Co—O6	85.3 (2)	O4—Zn—O6^{ii}	96.9 (2)
O1—Co—O7	97.2 (2)	O4—Zn—O7^{ii}	115.8 (2)
O5—Co—O5^i	76.8 (2)	O1—Zn—O6^{ii}	90.9 (2)
O5—Co—O6	168.8 (2)	O1—Zn—O7^{ii}	93.7 (2)
O5—Co—O7	112.3 (2)	O6^{ii}—Zn—O7^{ii}	81.2 (2)
O5^i—Co—O6	109.1 (2)		

Symmetry codes: (i) $2 - x$, $1 - y$, $-z$; (ii) $\frac{3}{2} - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$.

Despite the appreciable absorption of the crystal and the empirical correction applied, which led to significant residual electron density, the Zn and Co sites for the title compound could be distinguished without ambiguity through several refinement steps; changing Co to Zn decreased all the crystallographic quality criteria. The coordination of the two metals, octahedral for Co and fivefold for Zn, is also compatible with that found in the literature. The cell parameters of the $ZnNiP_2O_7$ compound are as follows: $a = 6.937\,(4)$, $b = 8.256\,(1)$, $c = 8.904\,(5)$ Å and $\beta = 112.18\,(6)°$, space group $P2_1/n$. We obtained the crystal structure, which is isotypic with $ZnCoP_2O_7$, but it was of poor quality.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *BEGIN* in *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: Patterson and Fourier methods in *SDP-Plus*. Program(s) used to refine structure: *LSFM* in *SDP-Plus*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *MolEN* (Fair, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1256). Services for accessing these data are described at the back of the journal.

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Pb₅O₄MoO₄

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Abstract

The structure of pentalead molybdenum octaoxide, Pb_5MoO_8, has been determined by single-crystal X-ray methods. The crystal structure is a 4:3:2 superstructure of tetragonal α-PbO (litharge), with embodied MoO_4^{2-} tetrahedra. Infinite double chains of OPb_4 tetrahedra are formed. Along these chains, the OPb_4 tetrahedra share vertices. Two of the O atoms form three nearly coplanar bonds with Pb atoms.

Comment

This work was carried out as part of a systematic study of the $PbO–MoO_3$ system (Nihtianova *et al.*, 1997), which was undertaken because of interest in the acousto-optical properties of single-crystal lead molybdates.

The lattice parameters and space group of Pb_5MoO_8 were determined by Mentzen *et al.* (1983). Considering the lattice parameters, a 4:3:2 superstructure of tetragonal α-PbO (litharge) can be expected. The low-temperature form of PbO (litharge) crystallizes in space group $P4/nmm$, with cell parameters $a = 3.9744\,(5)$ and $c = 5.0220\,(5)$ Å (Boher *et al.*, 1985). α-PbO is built up of layers of edge-sharing OPb_4 tetrahedra. The structure of the title compound can be represented as a litharge-like one, in which some of the Pb atoms are replaced by MoO_4^{2-} tetrahedra. The original litharge cell is multiplied four, three and two times in the **a**, **b** and **c** directions, respectively. Infinite double chains of OPb_4 tetrahedra are formed along the *a* axis by atoms O1–O4, Pb1–Pb4 and Pb7–Pb10. Two additional OPb_4 tetrahedra, with central atoms O5 and O6, are located on either side of the double chains. Pb—O bond lengths for the OPb_4 tetrahedra range from 2.201 (11) to 2.435 (10) Å, with a mean value of 2.315 Å, in good agreement with the Pb—O distance of 2.313 (1) Å found in α-PbO (Boher *et al.*, 1985). Pb—O—Pb angles are in the range 96.6 (4)–122.0 (5)°, with a mean value of 109.1°. All ten Pb atoms are part of OPb_4 tetrahedra, but only Pb7 and Pb9 are at the vertices of proper square pyramids, whose bases are formed by O1ⁱⁱⁱ, O3ⁱⁱ, O4ⁱⁱ