

- Wells, A. F. (1984). In *Structural Inorganic Chemistry*, 5th ed. Oxford: Clarendon Press.
- White, P. S., Gabe, E. J. & Le Page, Y. (1991). *Am. Crystallogr. Assoc. Annu. Meet.* Abstract H06.
- Wiles, D. B. & Young, R. A. (1981). *J. Appl. Cryst.* **14**, 149–151.
- Young, R. A., Sakthivel, A. & DeBoer, B. G. (1986). *Am. Crystallogr. Assoc. Annu. Meet.* Abstract No. PA10.

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β -Dicobalt Pyrophosphate

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Abstract

A new high-temperature or β form of dicobalt diphosphate, Co₂P₂O₇, has been isolated in space group *A2/m* (non-standard setting of *C2/m*). As in other high-temperature forms of transition-metal pyrophosphates, metal atoms lie on planes in a two-dimensional hexagonal array [Co—Co distances 3.461 (4) and 3.284 (3) Å] with adjacent metal atoms linked by two O-atom bridges. Co atoms are octahedrally coordinated with axial distortions [average Co—O_{eq} 2.14 (1), Co—O_{ax} 2.32 (1) Å]. The pyrophosphate groups lie along planes between metallic layers.

Comment

β -Co₂P₂O₇ is typical of β or high-temperature transition-metal structures [Cu, Ni, Zn; observed in space group *C2/m* (Robertson & Calvo, 1968; Pietraszko & Łukasiewicz, 1968; Calvo, 1968)] showing layers of metal atoms interspersed with layers of P₂O₇ groups; the metal atoms show a hexagonal disposition on the planes. Adjacent metal atoms of the hexagonal array are linked by two single-O-atom bridges and show two different intermetallic separations. Axial distortions of the octahedrally coordinated metal atoms are evident in *M*—O bond lengths. Co atoms bridged by equatorial O atoms are separated by a distance of 3.284 (3) Å, whereas those bridges involving axial O atoms result in a Co··Co separation of 3.461 (4) Å (Fig. 1). Structural rearrangement on transi-

tion from the α or low-temperature form to the β form involves a minor increase in density and is most evident from observation of the hexagonal motif of the metallic plane. α -Co₂P₂O₇ [space group *B2₁/c*, non-standard setting of *P2₁/c*, reported by Krishnamachari & Calvo (1972), or space group *P2₁/c*, from neutron data, reported by Forsyth, Wilkinson, Paster & Wanklyn (1989)] shows a disruption of this regular hexagon with one Co··Co distance of 4.228 (4) Å and no bridging atoms across this distance (Fig. 2a). The unbridged Co atoms are five-coordinate (square-pyramidal geometry) with a distance of 3.409 (4) Å to a sixth (would-be bridging) O atom. The

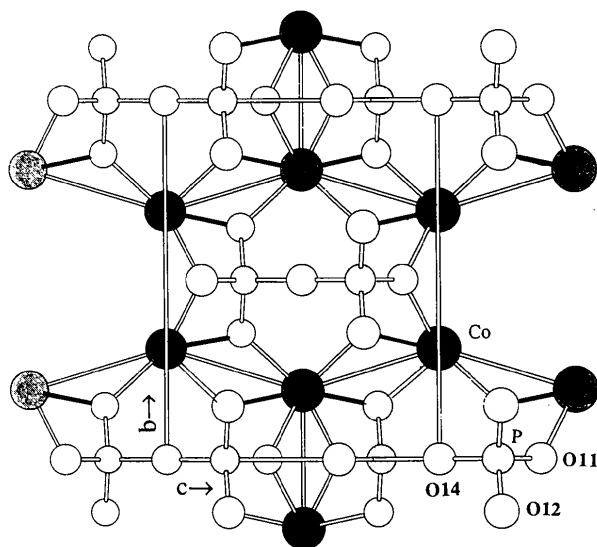


Fig. 1. Projection view of β -Co₂P₂O₇. Elongated axial Co—O distances are shown in black, Co atoms have dark shading, P atoms have light shading and O atoms are unshaded.

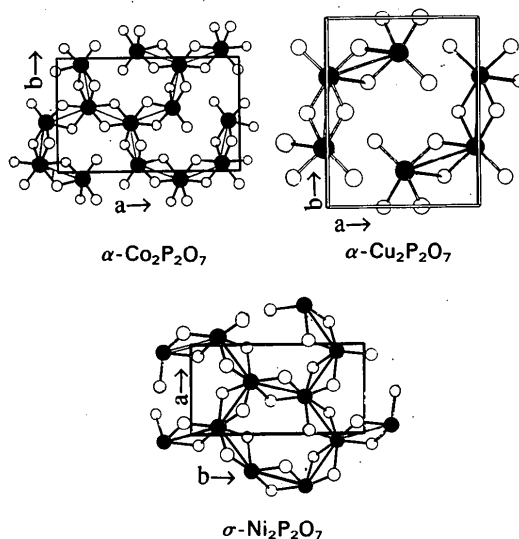


Fig. 2. Projection views of α -Co₂P₂O₇ (α -Ni₂P₂O₇ is isostructural), α -Cu₂P₂O₇ (with elongated axial Cu—O distances shown in black) and σ -Ni₂P₂O₇. In all three projections the P atoms have been omitted for clarity.

second Co-atom site in the unit cell shows octahedral geometry. Neither Co atom shows elongation of the Co—O bonds. Thus the α and β forms differ in the closing of the hexagon and axial distortions. These structural changes between the α and β forms are mirrored by Ni₂P₂O₇ (Lukaszewicz, 1967).

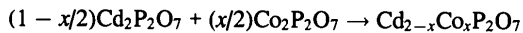
Cu shows a slightly different pattern: α -Cu₂P₂O₇ [space group *C2/c* (Robertson & Calvo, 1967)] crystallizes with a single five-coordinate metal site of fivefold (square-pyramidal) coordination resulting in disruption of the symmetry of the hexagon in two places; the unbridged Cu···Cu distance is 3.869 (4) Å (Fig. 2*b*). The axial Cu—O distance is elongated and a potential sixth bonding O atom is at a distance of 2.947 Å. Cu···Cu distances are 3.047 (4) Å when the bridging O atoms are equatorial to Cu and 3.313 (4) Å when they are axial.

Ni₂P₂O₇ shows a further σ form [space group *P2₁/a* (Masse, Guitel & Durif, 1979)] in which octahedral Ni atoms with little or no axial distortion form planes of unbroken hexagons with two different Ni···Ni distances (Fig. 2*c*). Two opposite sides of the hexagon show Ni···Ni distances of 3.370 Å, whereas the other Ni···Ni distances are 3.197 Å. This elongation is achieved by a small opening of the Ni—O—Ni angle from 101.27 to 104.53°.

In β -Co₂P₂O₇, the P₂O₄²⁻ group is in a staggered configuration (thortveitite). The P—O—P angle of 180° is ordained by the positioning of the bridging O atom on a site of *2/m* symmetry. The high *U*₂₂ temperature factor of the bridging O atom, O14, may indicate some slight disorder in this atom's position; however, no significant satellite peaks were observed near this atom in a difference Fourier synthesis. The linear P—O—P angle has been the subject of discussion for other diphosphate complexes. For example, Stefanidis & Nord (1984) have refined the structure of Mn₂P₂O₇ in a variety of space groups: *C2/m*, with disorder of the bridging O atom, *C2* and *Cm*; they concluded the refinement in space group *C2/m* to be the best. P—O distances and angles appear normal in β -Co₂P₂O₇.

Experimental

The synthesis of materials of the type Cd_{2-x}Co_xP₂O₇ according to the equation



led to isolation of β -Co₂P₂O₇. Mixtures of appropriate stoichiometries were ground together, heated to 873 K, then to 1173 K for 72 h periods with intermediate grinding. Crystalline material was obtained by fusion in the presence of an excess of P₂O₅ (fusion point 1373 K) in a platinum crucible. Slow cooling (4 K h⁻¹ to 1173 K, then 10 K h⁻¹ to 473 K) followed by cessation of heating of the furnace led to the formation of violet crystals (CdCoP₂O₇), blue crystals of β -Co₂P₂O₇ and rose-colored crystals (Co₃CdP₄O₁₂).

Crystal data

Co ₂ P ₂ O ₇	Mo <i>K</i> α radiation
<i>M_r</i> = 291.8	λ = 0.71069 Å

Monoclinic

<i>A2/m</i>
<i>a</i> = 4.524 (2) Å
<i>b</i> = 8.526 (4) Å
<i>c</i> = 6.640 (3) Å
β = 102.59 (3)°
<i>V</i> = 250.0 (2) Å ³
<i>Z</i> = 2
<i>D_x</i> = 3.876 Mg m ⁻³

Data collection

Syntex <i>P3</i> automated diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
<i>T_{min}</i> = 0.78, <i>T_{max}</i> = 0.85
382 measured reflections
382 independent reflections
254 observed reflections
$[I > 3.0\sigma(I)]$

Refinement

Refinement on <i>F</i>
<i>R</i> = 0.057
<i>wR</i> = 0.073
<i>S</i> = 0.98
254 reflections
31 parameters
<i>w</i> = 1/ $\sigma^2(F)$
$(\Delta/\sigma)_{\text{max}}$ = 0.008

Cell parameters from 15 reflections

θ = 6.60–12.71°
μ = 7.239 mm ⁻¹
<i>T</i> = 298 K
Chunk
0.1 × 0.1 × 0.1 mm
Blue-purple

θ_{max} = 30.0°
<i>h</i> = -8 → 8
<i>k</i> = 0 → 12
<i>l</i> = 0 → 11
3 standard reflections monitored every 97 reflections
intensity variation: <5%

$\Delta\rho_{\text{max}}$ = 0.65 e Å ⁻³
$\Delta\rho_{\text{min}}$ = 0.05 e Å ⁻³
Atomic scattering factors from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Table 2.2B)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
Co1	1/2	-0.3074 (2)	0	0.98
P1	-0.0880 (8)	1/2	-0.2870 (6)	2.0
O11	0.214 (3)	0	0.369 (2)	2.4
O12	0.728 (2)	-0.352 (1)	0.725 (2)	3.4
O14	0	0	0	9.8

Table 2. Selected geometric parameters (Å, °)

Co1—O12 ⁱ	2.32 (1)	P1—O11 ^{iv}	1.52 (1)
Co1—O11 ⁱⁱⁱ	2.15 (1)	P1—O12 ^v	1.52 (1)
Co1—O12 ⁱⁱⁱ	2.12 (1)	P1—O14 ^{iv}	1.551 (4)
O12 ⁱ —Co1—O11 ⁱⁱⁱ	83.6 (4)	O11 ^{vi} —Co1—O12 ^{vii}	92.7 (3)
O12 ⁱ —Co1—O11 ^{vi}	81.9 (4)	O11 ^{vi} —Co1—O12 ^{viii}	83.6 (4)
O12 ⁱ —Co1—O12 ^{vi}	77.5 (4)	O12 ^{vi} —Co1—O12 ^{vii}	99.8 (4)
O12 ⁱ —Co1—O12 ^{vii}	115.4 (3)	O12 ^{vi} —Co1—O12 ^{viii}	115.4 (3)
O12 ⁱ —Co1—O12 ^{viii}	161.0 (3)	O12 ^{vii} —Co1—O12 ^{viii}	77.5 (4)
O11 ⁱⁱⁱ —Co1—O11 ^{vi}	80.7 (3)	O11 ^{iv} —P1—O12 ^v	112.6 (4)
O11 ⁱⁱⁱ —Co1—O12 ^{vi}	92.7 (3)	O11 ^{iv} —P1—O14 ^{iv}	104.5 (5)
O11 ⁱⁱⁱ —Co1—O12 ^{vii}	159.0 (4)	O12 ^{iv} —P1—O12 ^{ix}	111.8 (5)
O11 ⁱⁱⁱ —Co1—O12 ^{viii}	81.9 (4)	O12 ^{iv} —P1—O14 ^{iv}	107.4 (4)
O11 ^{vi} —Co1—O12 ^{vi}	159.0 (4)	P1—O14 ^{iv} —P1 ^a	180

Symmetry codes: (i) *x*, *y*, *z* - 1; (ii) *x*, *y* - ½, *z* - ½; (iii) 1 - *x*, ½ - *y*, - ½ - *z*; (iv) *x*, ½ + *y*, *z* - ½; (v) *x* - 1, *y*, *z* - 1; (vi) 1 - *x*, - ½ - *y*, ½ - *z*; (vii) *x*, - ½ - *y*, *z* - ½; (viii) 1 - *x*, *y*, 1 - *z*; (ix) *x* - 1, - *y*, *z* - 1; (x) - *x*, *y*, 1 - *z*.

Data collection: Syntex Nicolet *P3* data collection package. Variable scan rate with a scan width of 1.2% below *K* α ₁ and 1.2° above *K* α ₂ to a maximum 2θ value of 60°. Cell refinement: Syntex Nicolet *P3* data collection package. Data reduc-

tion: *DREAM* (Blessing, 1986). Program(s) used to solve structure: *MULTAN80* (Main *et al.*, 1980). Program(s) used to refine structure: *XRAY* (Stewart, 1978). Molecular graphics: *CHEM3D* (Rubenstein & Rubenstein, 1987).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71727 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1056]

References

- Blessing, R. H. (1986). *Crystallogr. Rev.* **1**, 3–58.
 Calvo, C. (1968). *Bull. Soc. Chim. Fr.* pp. 1744–1747.
 Forsyth, J. B., Wilkinson, C., Paster, S. & Wanklyn, B. M. (1989). *J. Phys. Condens. Matter*, **1**, 169–178.
 Krishnamachari, N. & Calvo, C. (1972). *Acta Cryst.* **B28**, 2883–2885.
 Łukaszewicz, K. (1967). *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **15**, 47–51.
 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*. Univ. of York, England, and Louvain, Belgium.
 Masse, B., Guitel, A. & Durif, A. (1979). *Mater. Res. Bull.* **14**, 337–341.
 Pietraszko, A. & Łukaszewicz, K. (1968). *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **16**, 183–187.
 Robertson, B. E. & Calvo, C. (1967). *Acta Cryst.* **22**, 665–672.
 Robertson, B. E. & Calvo, C. (1968). *Can. J. Chem.* **46**, 605–612.
 Rubenstein, M. & Rubenstein, S. (1987). *CHEM3D. The Molecular Modeling System*. Cambridge Scientific Computing, Inc., Cambridge, Massachusetts, USA.
 Stefanidis, T. & Nord, A. G. (1984). *Acta Cryst.* **C40**, 1995–1998.
 Stewart, J. M. (1978). Editor. *The XRAY System of Crystallographic Programs*. (Version of 1980.) Technical Report TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

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Isomorphous Crystals: K₂HPO₄ and K₅Na(HPO₄)₃

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Abstract

The crystals of dipotassium hydrogenphosphate, K₂HPO₄, are almost isomorphous with crystals of pentapotassium sodium tris(hydrogenphosphate), K₅Na-

(HPO₄)₃. In both, the three crystallographically independent HPO₄²⁻ anions are held together by O11—H11···O33 and O31—H31···O23 hydrogen bonds, forming chains. These chains are joined by symmetry-related hydrogen bonds, O24—H24···O21ⁱ and O21—H21···O24ⁱⁱ in K₂HPO₄ and K₅Na(HPO₄)₃, respectively, forming infinite helical chains running parallel to the *c* axis. The K⁺ cations have different numbers of neighbours (from six to eleven) and the Na⁺ cations are six-coordinated. The P—O(H) distances range from 1.596 (5) to 1.625 (3) Å and the P—O(terminal) distances range from 1.502 (3) to 1.536 (3) Å.

Comment

Usually dipotassium hydrogenphosphate crystallizes from an aqueous solution in three forms depending on temperature (Galecki, 1964). It crystallizes as a hexahydrate (K₂HPO₄·6H₂O) below 287 K, as a trihydrate (K₂HPO₄·3H₂O) in the temperature range 287–322 K, and as an anhydrite (K₂HPO₄) above 322 K. Only the crystal structure of the trihydrate salt has been determined previously (Baran, Lis & Ratajczak, 1989). In this paper the structure of the anhydrous salt and the isomorphous K₅Na(HPO₄)₃ salt are reported.

The crystal of K₂HPO₄ consists of three crystallographically independent HPO₄²⁻ anions and K⁺ cations. The crystallographically independent HPO₄²⁻ anions are held together by O11—H11···O33 and O31—H31···O23 hydrogen bonds. These chains are joined by symmetry-related O24—H24···O21ⁱ hydrogen bonds to form infinite chains running parallel to the *c* axis. The crystal structure of K₂HPO₄ and the numbering scheme are shown in Fig. 1, views of the structure of K₅Na(HPO₄)₃ are presented in Figs. 2 and 3, and data for the hydrogen bonds for both crystals are summarized in Table 5.

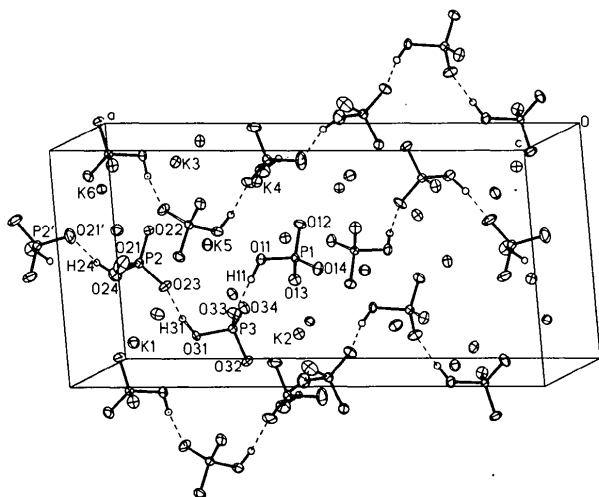


Fig. 1. The crystal structure and numbering scheme of K₂HPO₄.