

The Crystal Structure of Cobalt Orthophosphate $\text{Co}_3(\text{PO}_4)_2$

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Received October 25, 1974

The crystal structure of cobalt orthophosphate has been refined by full-matrix least-squares procedures using automatic diffractometer data to a residual $R = 0.039$ ($R_w = 0.058$). The space group is $P2_1/c$, with $a = 5.063(1)$, $b = 8.361(2)$, $c = 8.788(2)$ Å, and $\beta = 121.00(2)^\circ$. $\text{Co}_3(\text{PO}_4)_2$ is isotopic with the previously reported $\gamma\text{-Zn}_3(\text{PO}_4)_2$ and $\text{Mg}_3(\text{PO}_4)_2$. Cobalt ions occupy two distinct coordination polyhedra, one five and one six-coordinated, in a ratio of two to one. The structure is described in detail.

Introduction

$\text{Co}_3(\text{PO}_4)_2$ has recently been reported (1) to crystallize in the space group $P2_1/n$ isotopic with two known orthophosphates, $\gamma\text{-Zn}_3(\text{PO}_4)_2$ (2) and $\text{Mg}_3(\text{PO}_4)_2$ (3). Due to the unavailability of single crystals, the published refinement was carried out on powder diffractometer data within a rigid group approximation. In the light of the inherent inaccuracy of such a refinement and of the reported four-coordination for one of the divalent cobalt ions we decided to refine this structure with data taken on a single crystal produced by flux techniques. This paper reports the results of this refinement and describes the structure in detail.

Experimental

Since it was found that $\text{Co}_3(\text{PO}_4)_2$ attacked quartz under the necessary growth conditions with the formation of crystals of Co_2SiO_4 , crystal growth was carried out by packing the charge into a gold tube (5 mm in diameter, 40 mm long) which had been welded shut at one end. This capsule was then crimped at the other end and sealed under vacuum in a quartz tube. Small submillimeter-size bur-

gundy crystals of $\text{Co}_3(\text{PO}_4)_2$ were produced in the melt of approximately 75 w/o $\text{CoCl}_2\cdot 25$ w/o $\text{Co}_3(\text{PO}_4)_2$ which was cooled from 960° to 600°C at a rate of 17°C/hr .

A sphere was ground to a radius of $0.021(1)$ cm; precision photographs confirmed the space group as $P2_1/c$. [Nord reports the space group of both $\text{Co}_3(\text{PO}_4)_2$ (1) and $\text{Mg}_3(\text{PO}_4)_2$ (3) as $P2_1/n$; we have chosen the equivalent conventional space group $P2_1/c$ and will refer to this space group for all three compounds throughout the remainder of this paper.]

The lattice parameters were determined in a PICK-II least-squares refinement program of 46 reflections in the angular range $33^\circ < 2\theta < 46^\circ$, each automatically centered on a Picker FACS-I four-circle diffractometer using $\text{Mo K}_{\alpha 1}$ radiation. At 25°C the lattice parameters for the monoclinic unit cell are $a = 5.063(1)$, $b = 8.361(2)$, $c = 8.788(2)$, $\beta = 121.00(2)^\circ$. The figures in parentheses represent the standard deviations in the last reported figure. These parameters are in good agreement with those derived from the refined powder diffraction data (1). The calculated density with $Z = 2$ is 3.813 g/cc ($V = 319.4$ Å³).

Diffraction intensities were measured using Zr filtered Mo K_{α} radiation at a take-off angle of 2.0° with the diffractometer operating in the θ - 2θ scan mode. Scans were made at

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TABLE I
FRACTIONAL ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS^a

	10 ⁴ x	10 ⁴ y	10 ⁴ z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Co(1)	0	0	0	0.66(3)	0.49(3)	0.60(3)	0	0.28(2)	0
Co(2)	202(1)	3591(1)	1142(1)	0.83(2)	0.49(2)	0.65(2)	-0.02(1)	0.38(2)	-0.02(1)
P	3404(2)	6938(1)	3024(1)	0.50(3)	0.40(3)	0.45(3)	-0.01(2)	0.14(3)	-0.02(2)
O(1)	2729(6)	6422(3)	4455(4)	0.97(10)	0.89(10)	0.62(9)	0.01(7)	0.39(8)	0.10(7)
O(2)	6881(6)	6958(3)	3750(3)	0.57(9)	0.73(9)	0.83(10)	0.00(7)	0.26(7)	-0.01(7)
O(3)	1902(6)	5786(3)	1432(4)	1.14(9)	0.52(8)	0.55(9)	-0.14(7)	0.23(7)	-0.13(7)
O(4)	1903(6)	8618(3)	2435(4)	0.89(9)	0.65(9)	0.63(9)	0.12(7)	0.31(7)	0.03(7)

^a Numbers in parentheses are estimated standard deviations in the last significant figure.

1°/min over 1.1° with allowance for dispersion and with 20-sec background counts taken at both ends of the scan. Of the 1160 independent data investigated on the angular range $2\theta < 62^\circ$, 1032 were considered observable according to the criterion $|F_o| > 1.58\sigma_F$; where σ_F is defined as $0.02|F_o| + [C + k^2 B]^{1/2} / 2|F_o|L_p$; the total scan count is C ; k is the ratio of scanning time to the total background time; and B is the total background count. Three reflections were systematically monitored and no random variations in intensity greater than 4% were observed over the data collection period; the mean variation was smaller.

Intensity data were corrected for Lorentz and polarization effects, and absorption corrections (4) were applied for a spherical crystal with $\mu R = 0.89$. The maximum absorption correction applied was 2.2% of $|F_o|$.

Four cycles of full-matrix least-squares refinement (5) using the positional parameters for $\gamma\text{-Zn}_3(\text{PO}_4)_2$ as a trial structure, a $1/\sigma^2$ weighting scheme, zerovalent scattering factors for Co, P, and O (6), isotropic temperature factors, and corrections for secondary extinction and anomalous dispersion, yielded a residual $R = 0.052$ and a weighted residual $R_w = 0.085$. The anisotropic refinement, based on a data: parameter ratio of 17 to 1 with 60 independently varied parameters, yielded a final $R = 0.039$ and $R_w = 0.058$ for the observed data.¹ In the final refinement, the maximum

extinction correction (7) was 40% of $|F_c|$ for the 100 reflection.

Table I presents the final atomic coordinates and anisotropic thermal parameters.

Discussion

$\text{Co}_3(\text{PO}_4)_2$ is isotypic with $\gamma\text{-Zn}_3(\text{PO}_4)_2$ and $\text{Mg}_3(\text{PO}_4)_2$. Table II lists the bond distances and angles for the two cation polyhedra. The standard deviations for all bond lengths were computed by the function and error program ORFFE (8). Co(1) lies at the origin in the center of a distorted octahedron of oxygen atoms with an average Co(1)-O distance of 2.125 Å. Co(2) is irregularly coordinated by five oxygen atoms at an average Co(2)-O distance of 2.045 Å. The unit cell contains four Co(2) and two Co(1) atoms. In his refinement of the structure of $\text{Co}_3(\text{PO}_4)_2$, Nord (1) assumed that the fifth oxygen atom surrounding Co(2) [O(1)], which he found at a distance of 2.38(5) Å, was not near enough to be considered as part of the primary coordination sphere. Our

¹ A table of observed and calculated structure factors (6 pp) has been deposited as an NAPS Document, 02522. Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Ave. South, New York, N.Y. 10006. Remit in advance for each NAPS accession number \$1.50 for microfiche or \$5.00 for photocopies up to 30 pages, 15 cents for each additional page. Make checks payable to Microfiche Publications.

TABLE II
BOND DISTANCES, POLYHEDRAL EDGE LENGTHS,
AND BOND ANGLES FOR COBALT POLYHEDRA

(i) Interatomic distances (Å) ^a	
Co(1)–O(1) 2x 2.058	Co(2)–O(2) 1.978
Co(1)–O(2) 2x 2.144	Co(2)–O(3) 1.988
Co(1)–O(4) 2x 2.174	Co(2)–O(3') 2.012
	Co(2)–O(4) 2.109
	Co(2)–O(1) 2.229
Co(1) polyhedron	Co(2) polyhedron
O(1)–O(2) 2.732	O(2)–O(3) 3.280
O(1)–O(2') 3.195	O(2)–O(3') 3.069
O(1)–O(4) 2.859	O(2)–O(4) 3.572
O(1)–O(4') 3.123	O(2)–O(1) 2.732
O(2)–O(4) 2.953	O(3)–O(3') 2.606
O(2)–O(4') 3.151	O(3)–O(4) 3.157
	O(3)–O(1) 4.189
	O(3')–O(4) 3.551
	O(3')–O(1) 3.066
	O(4)–O(1) 2.437
(ii) Angles (°) ^b	
Co(1) polyhedron	Co(2) polyhedron
O(1)–Co(1)–O(2) 81.1	O(2)–Co(2)–O(3) 111.6
O(1)–Co(1)–O(2') 98.9	O(2)–Co(2)–O(3') 100.5
O(1)–Co(1)–O(4) 84.9	O(2)–Co(2)–O(4) 126.7
O(1)–Co(1)–O(4') 95.1	O(2)–Co(2)–O(1) 80.8
O(2)–Co(1)–O(4) 86.3	O(3)–Co(2)–O(3') 81.3
O(2)–Co(1)–O(4') 93.7	O(3)–Co(2)–O(4) 104.0
	O(3)–Co(2)–O(1) 166.9
	O(3')–Co(2)–O(4) 123.5
	O(3')–Co(2)–O(1) 92.5
	O(4)–Co(2)–O(1) 69.8

^a e.s.d. for Co–O distances 0.003 Å; for O–O distances 0.004 Å.

^b e.s.d. for O–Co–O angles 0.1°.

refined Co(2)–O(1) distance is 2.229(3) Å and, although this is a rather long M–O distance for Co²⁺, we consider it to be within the coordinating polyhedron. Calculation of the individual bond strengths using Brown and Shannon's formula (9) $s = s_0(R/R_0)^{-N}$; where s is the strength in valence units (v.u.) of a bond of length R ; s_0 is the ideal strength of a bond of length R_0 ; and N is a characteristic constant, using empirically-fit values (9) of 0.333, 2.118, and 5.0 for s_0 , R_0 , and N , respectively, gives a value of 2.037 v.u. for

five-coordination about Co(2) as compared to 1.780 v.u. for four-coordination. Since the bond strength sum in v.u. should be equal in magnitude to the charge on the ion, five-coordination is definitely favored. Furthermore, the next larger M–O distance is 3.32 Å, certainly outside of a bonding distance. We therefore choose five and six-coordination for the cations.

The phosphate tetrahedron is fairly regular with an average bond length of 1.539 Å (–0.013, +0.015 Å) and an average angle of

109.5° (−4.9, +3.4°). Table III lists the bond lengths and angles for the phosphate tetrahedron. Finally, each oxygen is bonded to one phosphorus and two cobalt atoms. Table IV presents the bond distances and angles for the polyhedra surrounding each oxygen atom.

Since we feel that none of the previously mentioned papers (1–3) adequately describe the polyhedral linkages in this structure, we present two drawings of the structure prepared by a local modification of the program ORTEP (10). Fig. 1 is a projection of a part of the structure onto the *b*–*c* plane centered about the Co(1) atom at 0 1/2 1/2. Chains of edge-sharing polyhedra are formed running parallel to the *b*-axis by linking the Co(1) polyhedra (centered at the origin) with a pair of Co(2) polyhedra that share an edge O(3)–O(3') across a center of symmetry. These chains are crosslinked in the *b*–*c* plane by Co(2) polyhedra corner-sharing O(4)'s. Within the chains parallel to *b*, the Co(2)–Co(2) distance across the shared edge O(3)–O(3')

TABLE III

BOND DISTANCES, POLYHEDRAL
EDGE LENGTHS, AND BOND ANGLES
FOR THE PHOSPHATE TETRAHEDRON^a

(i) Interatomic distances (Å) ^a	
P–O(1) 1.526	O(1)–O(2) 2.520
P–O(2) 1.533	O(1)–O(3) 2.525
P–O(3) 1.540	O(1)–O(4) 2.437
P–O(4) 1.554	O(2)–O(3) 2.486
	O(2)–O(4) 2.573
	O(3)–O(4) 2.528
(ii) Angles (°) ^b	
O(1)–P–O(2) 110.9	
O(1)–P–O(3) 110.9	
O(1)–P–O(4) 104.6	
O(2)–P–O(3) 108.0	
O(2)–P–O(4) 112.9	
O(3)–P–O(4) 109.6	

^a e.s.d. for P–O distances 0.003 Å:
for O–O distances 0.004 Å.

^b e.s.d. for O–P–O angles 0.2°.

TABLE IV

BOND DISTANCES, BOND ANGLES, AND POLYHEDRAL
EDGE LENGTHS FOR OXYGEN POLYHEDRA

	Distance (Å) ^a	Angle (°) ^b	Edge length (Å) ^c
(i) O(1) polyhedron			
O(1)–P	1.526		
O(1)–Co(1)	2.058		
O(1)–Co(2)	2.229		
P–O(1)–Co(1)		144.8	3.421
P–O(1)–Co(2)		88.9	2.676
Co(1)–O(1)–Co(2)		94.6	3.152
(ii) O(2) polyhedron			
O(2)–P	1.533		
O(2)–Co(2)	1.978		
O(2)–Co(1)	2.144		
P–O(2)–Co(2)		134.2	3.239
P–O(2)–Co(1)		126.2	2.391
Co(2)–O(2)–Co(1)		99.7	3.151
(iii) O(3) polyhedron			
O(3)–P	1.540		
O(3)–Co(2)	1.988		
O(3)–Co(2')	2.012		
P–O(3)–Co(2)		132.3	3.232
P–O(3)–Co(2')		126.1	3.173
Co(2)–O(3)–Co(2')		98.7	3.035
(iv) O(4) polyhedron			
O(4)–P	1.554		
O(4)–Co(2)	2.019		
O(4)–Co(1)	2.174		
P–O(4)–Co(2)		96.1	2.676
P–O(4)–Co(1)		134.6	3.448
Co(2)–O(4)–Co(1)		120.6	3.642

^a e.s.d. 0.003 Å.

^b e.s.d. 0.1°.

^c e.s.d. 0.002 Å.

is 3.035(2) Å and the Co(1)–Co(2) distance across the shared edge O(1)–O(2) is 3.152(2) Å.

Figure 2 is a projection onto the *a*–*b* plane centered about 1/2 1/2 0 but rotated 10° about the *b*-axis for clarity. It illustrates the linking of the edge-sharing chains by the phosphate tetrahedra in the *a*–*b* plane. Each tetrahedron is edge-linked through O(1) and O(4) to a Co(2) polyhedron and corner-

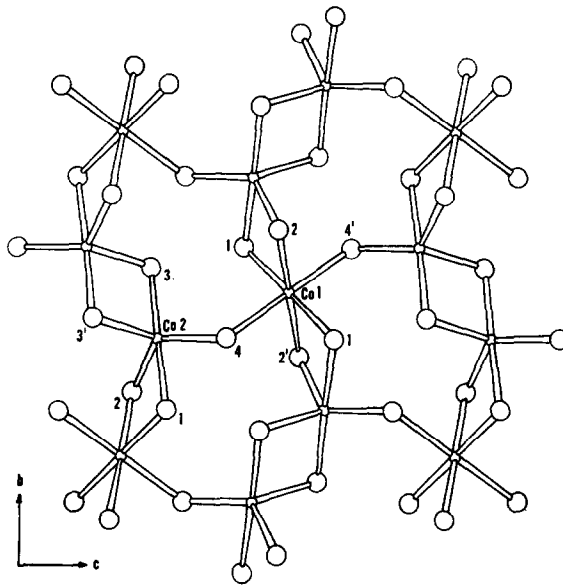


FIG. 1. A projection of a part of the structure onto the b - c plane centered about a Co(1) atom at $0\ 1/2\ 1/2$.

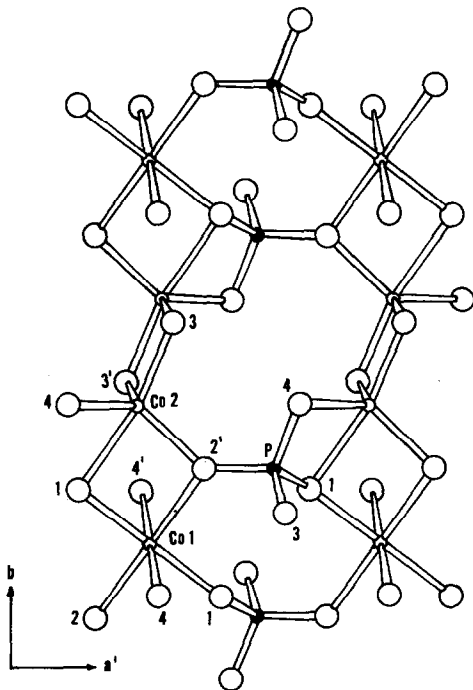


FIG. 2. A projection of the structure onto the a - b plane centered about $1/2\ 1/2\ 0$ but rotated 10° about the b -axis for clarity.

linked through O(1) to a Co(1) polyhedron in the same chain as well as corner-linked to a Co(1) and Co(2) in a parallel chain in the same (a - b) plane. These nets are connected by edge-sharing through O(3) to Co(2) atoms in nets above and below the plane of the figure. The shortest oxygen-oxygen distance is O(1)-O(4) at 2.437 Å and results from the edge-sharing by PO₄ and Co(2).

Nord (3) describes Mg₃(PO₄)₂ as having similar five and sixfold coordination about the metal ions with the Mg(2)-O(1) distance at 2.142(7) Å because of the smaller ionic radius of Mg²⁺. However, Calvo (2), in his description of the structure of γ -Zn₃(PO₄)₂, finds the Zn(2)-O(1) distance to be 2.39(5) Å and considers the cation coordination numbers to be 4 and 6. Using Brown and Shannon's bond strength formula for the Zn(2) site in γ -Zn₃(PO₄)₂ and with values of 0.5, 1.947, and 5.0 for s_o , R_o , and N , respectively, we calculate a bond strength sum of 1.89 v.u. for four-coordination and 2.07 for five-coordination. Again, the next closest oxygen to Zn(2) is at 3.29 Å. Our conclusion is that these three structures have essentially the same cation coordination.

Acknowledgments

This work was supported in part by the National Science Foundation. Computations were carried out at the University of Connecticut Computer Center.

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