Note on the Crystal Structure of Co₃(PO₄)₂

ANDERS G. NORD

Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-104 05 Stockholm 50, Sweden

Co₃(PO₄)₂ crystallizes in the monoclinic space group $P2_1/n$ with Z=2 and the cell constants $a=7.5557\pm0.0007$ Å, $b=8.3736\pm0.0006$ Å, $c=5.0615\pm0.0006$ Å, $\beta=94.03\pm0.02^\circ$. The isomorphism between Co₃(PO₄)₂ and γ -Zn₃(PO₄)₂ has been verified through a rigid group least-squares refinement based on X-ray powder data.

A comparison of the X-ray powder data for the orthophosphates of zinc $(\gamma\text{-phase})$, magnesium, and cobalt indicates isomorphism between these three phases, a fact which has been reported earlier in the literature. However, in $\gamma\text{-Zn}_3(PO_4)_2$ the zinc atoms may be regarded as 4- and 6-coordinated, whereas in $Mg_3(PO_4)_2$ the magnesium atoms would rather be described as 5- and 6-coordinated. In order to find out which of these two orthophosphates $Co_3(PO_4)_2$ resembles a structure investigation of cobalt orthophosphate was carried out.

EXPERIMENTAL

Cobalt orthophosphate was prepared according to the method of Sarver, i.e. mixing $CoCO_3$ and $(NH_4)H_2PO_4$ under ethyl alcohol, whereupon drying and slow heating to 900° C yields deep purple crystals of $Co_3(PO_4)_2$. However, all attempts to produce crystals big enough for single crystal work proved fruitless and powder data, therefore, had to be used. Powder photographs were taken with strictly monochromatized Fe $K\alpha_1$ radiation (λ =1.9360 Å) in a Guinier-Hägg focusing camera using different exposure times (6, 12, 15, 24 h). Potassium chloride (α =6.29288 Å) was used as an internal standard. The intensities and positions of the reflections on the photographs were determined with a SAAB film scanner and the programs by Malmros and Werner. Corrections for multiplicity and the Lorentz-polarization effects were applied to the intensities, and

the $|F_{\rm obs}|$ values thus arrived at are listed in Table 1.

COMPUTING METHODS AND RESULTS

The lattice parameters were refined from the $\sin^2 \theta$ values of 34 distinct reflections measured on the 12h powder photograph. Twentyone other reflections could thereafter be unambiguously indexed, cf. Table 1. The cell constants are: $a = 7.5557 \pm 0.0007$ Å, $b = 8.3736 \pm 0.0006$ Å, $c = 5.0615 \pm 0.0006$ Å, and $\beta = 94.03 \pm 0.02^{\circ}$. The space group is $P2_1/n$ with two formula units per unit cell. In a conventional least-squares refinement of this structure with isotropic temperature factors there would be 26 parameters to refine. However, with the rigid group least-squares program system developed by Scheringer,8 the number of parameters can be reduced to ten by assuming the phosphate group to be a rigid regular tetrahedron with P-O distances of 1.53 Å, and by keeping the isotropic temperature factors fixed. The average value of the isotropic temperature factors from the structure of magnesium orthophosphate,2 B=0.41 Å², was used. The weights applied by the refinement program were $w=1/(\Delta^2+4)$. Twelve cycles of refinement reduced the conventional reliability index R to 14 %. The structure factors for all non-extinct reflections with $\sin^2 \theta < 0.4$ were then calculated with the final atomic parameters, cf. Table 1.

To test the reliability of this method, powder data of $Mg_3(PO_4)_2$ were treated in the same way. 59 reflections were refined to R=15% and the final parameters arrived at were close to those obtained from Weissenberg data.²

The values of $I_{\rm obs}$, $d_{\rm obs}$, $d_{\rm calc}$, $|F_{\rm obs}|$, and Acta Chem. Scand. A 28 (1974) No. 2

Table 1. X-Ray powder data for $\text{Co}_3(\text{PO}_4)_2$. Fe $K\alpha_1$ radiation. The 34 reflections marked with an asterisk were used to refine the cell constants. All $|F_{\text{obs}}|$ values listed below were used in the final refinement of the crystal structure of $\text{Co}_3(\text{PO}_4)_2$.

h	k l I _{obs} d _{obs}	dcalc	Fol Fc	'n	k l I _{obs} d _{obs}	d _{calc}	Fol Fc
1	1 0 9 5.5758	5.6021	22 23	2	2 -2 7* 1.9255	1.9260	50 40
ī	0 -1 94* 4.3381		11 -113	ī	4 -17 6 ~1.8847	1.8854	37
ō	1 1 9 4.3204	4.3238	25 36	4	0 0	1.8843	-41
ŏ	2 0 6* 4.1901	4.1869	28 -27	0	3 2 3 1.8719	1.8723	30 -26
ĭ	0 1 42* 4.0663	4.0648	78 -91	3	3 0 3 1.8676	1.8674	32 33
î	1 -1 42* 3.8532	3.8520	59 -60	í	4 1 2* 1.8611	1.8611	29 -38
2	0 0 -	3.7686	4	i	3 -2) 22 ~1.8396	1.8397	82
1	2 0] 3 ~3.6579	3.6601	15	4	1 0	1.8383	3
i	1 1	3.6567	-6	ż	4 07 21 ~1.8287	1.8301	31
2	1 0 100* 3.4381		05 -127	2	2 2	1.8284	75
ō	2 1 35* 3.2242	3.2229	67 -64	3	1 -2 -	1.8036	-6
ĭ	2 -1 70 3.0137	3.0127	98 -55	í	3 2 2 1.7949	1.7953	30 31
2	1-1 1 2.9309	2.9297	12 -13	3	3 -1 1 1.7821	1.7820	23 24
1	2 1 8* 2.9173	2.9164	36 -35	4	1 -1 30* 1.7668	1.7668	108 -92
2	2 0 28* 2.8017	2.8011	69 70	ż	4 -1 16* 1.7397	1.7397	80 56
2	1 1 21* 2.7603	2.7599	61 -52	3	3 1 1 1.7227	1.7224	16 -17
ì	3 0 14* 2.6180	2.6175	53 53	4	2 0 2 1.7187	1.7183	31 43
ō	0 2 36* 2.5241		23 125	ż	3 -2 -	1.7127	8
2	2 -1 41* 2.5056	2.5055	95 -93	2	4 1 5 1.7019	1.7020	46 47
õ	3 1 62* 2.4432		20 -122	4	1 1 23 ~1.6902	1.6905	-79
ŏ	1 2 8* 2.4171	2.4170	43 -47	3	2 -2	1.6898	58
3	1 0 28* 2.4064	2.4064	83 78	3	1 2 28* 1.6858	1.6861	108 90
ž	2 1 9* 2.3971	2.3968	47 -46	ī	0 -3 3 1.6674	1.6677	50 -49
ĩ	1 -2) 6 ~2.3477	2.3480	-4	4	2 -1 4* 1.6591	1.6595	36 -46
ī	3 -1	2.3474	-39	0	1 3 3 1.6498	1.6500	39 -41
3	0 -1 6* 2.3155	2.3152	57 -35	2	3 2 -	1.6430	2
1	3 1 11* 2.3014	2.3010	53 49	1	1 -3 28 ~1.6353	1.6356	-84
ì	1 2 2 2.2589	2.2578	24 25	1	5 0	1.6349	67
2	3 0 -	2.2430	-1	1	0 3 -	1.6185	1
3	1 -1 19* 2.2313	2.2315	74 69	0	4 2 -	1.6115	-2
3	0 1 3* 2.1889	2.1888	42 27	3	4 0 3 1.6078	1.6083	36 -28
2	0 -2 1 2.1695	2.1691	19 26	4	2 1 3 1.5962	1.5958	38 43
0	2 2 2 2.1627	2.1619	19 23	3	2 2]	1.5920	-6
3	2 0 5* 2.1534	2.1543	36 18	1	4 -2	1.5905	14
3	1 1 26* 2.1174	2.1176	89 75	0	5 1 4 ~1.5897	1.5896	-35
1	2 -2 27* 2.1126	2.1121	90 -64	1	1 3	1.5891	-6
2	1 -2 3 2.0994	2.0998	30 -33	4	0 -2 1	1.5637	9
0	4 0 11* 2.0938	2.0935	82 -68	1	5 -1	1.5624	15
2	3 -1 35* 2.0826	2.0824	.04 -89	4	3 0 23 ~1.5617	1.5618	-36
1	2 2 31* 2.0459	2.0457	97 91	0	2 3	1.5616	-95
2	0 2 8* 2.0324	2.0324	70 -55	1	4 2 🕽	1.5616	-11
3	2 -1 4* 2.0263	2.0261	34 -17	3	4 -17	1.5528	-35
2	3 1) 1 ~2.0184	2.0188	11	2	1 -3 13 ~1.5500	1.5513	-12
1	ره 4	2.0171	8	1	2 -3	1.5493	-47
2	1 2	1.9750	-4	1	ر 1 5	1.5485	-45
3	2 1 1 1.9400	1.9397	17 -16	3	3 -2 7 30 ~1.5392	1.5403	112
0	4 1 5 1.9333	1.9338	40 39	4	1 -2]	1.5371	-15

Table 2. Fractional atomic coordinates for Co₃(PO₄)₂. The estimated standard deviations given in parentheses refer to the last digit of the respective values.

\mathbf{Atom}	\boldsymbol{x}	\boldsymbol{y}	z
Co ₁	0.617(1)	0.141(1)	0.093(1)
Co2	0 `´	0 `´	į `´
P	0.197(2)	0.191(2)	0.042(1)
0,	0.058(4)	0.124(4)	-0.162(3)
O ₂	0.119(4)	0.201(4)	0.312(3)
O_3	0.253(4)	0.357(4)	-0.043(3)
O ₄	0.359(4)	0.080(4)	0.062(3)

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 $F_{\rm calc}$ from the present study of ${\rm Co_3(PO_4)_2}$ are listed in Table 1. The final atomic parameters are given in Table 2. Table 3 contains some interatomic metal-oxygen distances in the isomorphous orthophosphates of cobalt, zinc $(\gamma\text{-phase }^9)$, and magnesium.² The data for $\gamma\text{-Zn_3(PO_4)_2}$ refer to a later structure refinement of $\gamma\text{-(Zn_{0.97}Mn_{0.03})_3(PO_4)_2}$ by Calvo.⁹ It follows from the metal-oxygen bond distances in Table 3 that ${\rm Co_3(PO_4)_2}$ resembles $\gamma\text{-Zn_3(PO_4)_2}$ more than it resembles ${\rm Mg_3(PO_4)_2}$. This is probably due to the fact that the ${\rm Co^2}^+$ and ${\rm Zn^2}^+$ ions have similar ionic radii and electron configurations.

Table 3. Some metal-oxygen bond distances (Å) in three isomorphous orthophosphates. The atoms are numbered as in Table 2 (this work). The standard deviations of the distances in $Co_3(PO_4)_2$ are probably ± 0.05 Å.

Compound	d: Co ₃ (PO ₄	$_{1})_{2}^{a}$ γ - $\mathrm{Zn}_{3}(\mathrm{PO}_{4})$	$)_2{}^b \operatorname{Mg}_3(\mathrm{PO}_4)_2$
6-coording	ated metal	atoms	
$M_2 - 2 O_1$	2.02	2.010	2.034
2 0	2.16	2.201	2.179
$2 O_3$	2.21	2.227	2.150
Average:	2.13	2.146	2.121
4- and 5-c	oordinated	d metal atoms	
$\mathbf{M}_1 - \mathbf{O}_1$	(2.38)	(2.396)	2.142
0,	ì.94	ì.934	1.965
	2.05	1.984	2.063

1.955

2.007

1.961

2.012

2.01

2.02

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^aThis work. ^b Cf. Ref. 9. ^c Cf. Ref. 2.