

Note on the Crystal Structure of $\text{Co}_3(\text{PO}_4)_2$

ANDERS G. NORD

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

$\text{Co}_3(\text{PO}_4)_2$ crystallizes in the monoclinic space group $P2_1/n$ with $Z=2$ and the cell constants $a=7.5557 \pm 0.0007 \text{ \AA}$, $b=8.3736 \pm 0.0006 \text{ \AA}$, $c=5.0615 \pm 0.0006 \text{ \AA}$, $\beta=94.03 \pm 0.02^\circ$. The isomorphism between $\text{Co}_3(\text{PO}_4)_2$ and $\gamma\text{-Zn}_3(\text{PO}_4)_2$ 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 (γ -phase),¹ magnesium,² and cobalt³ indicates isomorphism between these three phases, a fact which has been reported earlier in the literature.^{1,2} However, in $\gamma\text{-Zn}_3(\text{PO}_4)_2$ the zinc atoms may be regarded as 4- and 6-coordinated, whereas in $\text{Mg}_3(\text{PO}_4)_2$ the magnesium atoms would rather be described as 5- and 6-coordinated.² In order to find out which of these two orthophosphates $\text{Co}_3(\text{PO}_4)_2$ resembles a structure investigation of cobalt orthophosphate was carried out.

EXPERIMENTAL

Cobalt orthophosphate was prepared according to the method of Sarver,⁴ *i.e.* mixing CoCO_3 and $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ under ethyl alcohol, whereupon drying and slow heating to 900°C yields deep purple crystals of $\text{Co}_3(\text{PO}_4)_2$. 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 $\text{FeK}\alpha_1$ radiation ($\lambda=1.9360 \text{ \AA}$) in a Guinier-Hägg focusing camera using different exposure times (6, 12, 15, 24 h). Potassium chloride ($a=6.29288 \text{ \AA}$)⁵ 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.⁶ Corrections for multiplicity and the Lorentz-polarization effects were applied to the intensities, and

the $|F_{\text{obs}}|$ 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.⁷ Twentyone other reflections could thereafter be unambiguously indexed, *cf.* Table 1. The cell constants are: $a=7.5557 \pm 0.0007 \text{ \AA}$, $b=8.3736 \pm 0.0006 \text{ \AA}$, $c=5.0615 \pm 0.0006 \text{ \AA}$, 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 \AA , and by keeping the isotropic temperature factors fixed. The average value of the isotropic temperature factors from the structure of magnesium orthophosphate,² $B=0.41 \text{ \AA}^2$, 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 $\text{Mg}_3(\text{PO}_4)_2$ 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_{obs} , d_{obs} , d_{calc} , $|F_{\text{obs}}|$, and

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 $\text{Co}_3(\text{PO}_4)_2$ are probably ± 0.05 Å.

Compound: $\text{Co}_3(\text{PO}_4)_2^a$ $\gamma\text{-Zn}_3(\text{PO}_4)_2^b$ $\text{Mg}_3(\text{PO}_4)_2^c$

6-coordinated metal atoms			
$\text{M}_2 - 2 \text{O}_1$	2.02	2.010	2.034
2O_2	2.16	2.201	2.179
2O_3	2.21	2.227	2.150
Average:	2.13	2.146	2.121
4- and 5-coordinated metal atoms			
$\text{M}_1 - \text{O}_1$	(2.38)	(2.396)	2.142
O_2	1.94	1.934	1.965
O_3	2.05	1.984	2.063
O_4	2.01	1.955	1.961
O_4'	2.02	2.007	2.012

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

Acknowledgements. The author sincerely thanks Professor Peder Kierkegaard for his encouraging and stimulating interest in this work. This investigation has been performed with financial support from the *Swedish Natural Science Research Council* and from the *Tri-Centennial Fund of the Bank of Sweden*.

REFERENCES

1. Calvo, C. J. *Phys. Chem. Solids* 24 (1963) 141.
2. Nord, A. G. and Kierkegaard, P. *Acta Chem. Scand.* 22 (1968) 1466.
3. de Wolff, P. *ASTM X-Ray Powder Data File*, Card 13-503.
4. Sarver, J. F. *Trans. Brit. Ceram. Soc.* 65 (1966) 191.
5. Hambling, P. G. *Acta Crystallogr.* 6 (1953) 98.
6. Malmros, G. and Werner, P. E. *Acta Chem. Scand.* 27 (1973) 493.
7. Werner, P. E. *Ark. Kemi* 31 (1969) 513.
8. Scheringer, C. *Acta Crystallogr.* 16 (1963) 546.
9. Calvo, C. (1973) *Private communication*.

Received September 24, 1973.