Acta Cryst. (1972). B**28**, 2883

The Crystal Structure of Cobalt Diphosphate

BY N. KRISHNAMACHARI AND C. CALVO

Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada

(*Received* 10 *April* 1972 *and in revised form* 12 *May* 1972)

Abstract. $Co_2P_2O_7$, monoclinic, $B2_1/c$ (convenient unconventional setting of $P2_1/c$), $a=13{\cdot}248$ (6), $b=8{\cdot}345$ (3), $c=9{\cdot}004$ (3) Å, $\beta=104{\cdot}60$ (6)°, $Z=8$, $D_x=3{\cdot}595$ g.cm^{-3}. Crystals were grown from a melt of $Co_2P_2O_7$. The anion shows significant deviations from C_2 symmetry caused by six strong Co–O bonds on one side and only five on the other. All the terminal oxygen atoms save one are bonded to two Co^{2+} and a P ion. The remaining one, bonded to only one Co^{2+} and one P ion, shows both the shortest P–O and Co–O bonds in the structure.

Introduction. The intensities and cell dimensions were obtained from a crystal of 0·03 mm average linear dimension utilizing a General Electric quarter circle semi-automatic diffractometer (Mo $K\alpha$, Zr-filtered, θ–2θ scan, scintillation counter with pulse height discrimination, four check reflexions measured after every fifty). 2129 reflexions in a hemisphere up to $2\theta=78°$ were measured, of which 1123 had significant intensity. The systematic absences were hkl for $h+k$ odd, $h0l$ for h or l odd and $0k0$ for k odd. The trial-structure atomic parameters corresponded to those of α-$Mg_2P_2O_7$ (Calvo, 1967). Full-matrix least-squares refinement with anisotropic thermal parameters and weights chosen so that $\omega(|F_o|-|F_c|)^2$ would be independent of F_o yielded a final R value of 0·056 and the parameters listed in Tables 1 and 2. A table of observed and calculated structure factors is obtainable as Supplementary Publication No. SUP 30012 (11 pp.). The bond lengths and angles are in Table 3.

* This table has been deposited with the National Lending Library, England. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic parameters, with estimated standard errors, in* α-$Co_2P_2O_7$

	x	y	z
Co(1)	0·3665 (1)	0·9287 (1)	0·2571 (2)
Co(2)	0·3999 (1)	0·5580 (1)	0·2253 (1)
P(1)	0·2798 (2)	0·2324 (3)	0·0386 (3)
P(2)	0·4847 (2)	0·2257 (3)	−0·0479 (2)
O_I	0·3763 (4)	0·1717 (6)	−0·0236 (7)
$O_{II}(2)$	0·5607 (5)	0·2353 (7)	0·1095 (8)
$O_{II}(1)$	0·1902 (5)	0·2411 (8)	−0·1065 (7)
$O_{III}(1c)$	0·2625 (5)	0·0986 (7)	0·1439 (7)
$O_{III}(1t)$	0·3065 (6)	0·3900 (8)	0·1186 (8)
$O_{III}(2c)$	0·5089 (5)	0·0916 (7)	−0·1458 (7)
$O_{III}(2t)$	0·4745 (6)	0·3861 (8)	−0·1290 (8)

Discussion. The structure is nearly identical with that of α-$Mg_2P_2O_7$ with the anion in a nearly eclipsed configuration. The P–O–P bond angle is 142·6°. The P–O bond, involving the bridging oxygen atom on the side of the anion where each terminal oxygen atom is bonded to two Co^{2+} ions, is 1·566 (8) Å long. In contrast the analogous bond on the side of the anion where one of the three terminal oxygen atoms is bonded to only one Co^{2+} ion is 1·600 (8) Å long. This side of the anion also has the shortest terminal P–O bond length at 1·499 (7) Å. One cation shows octahedral coordination with an average Co–O bond length of 2·116 Å, while the other cation is fivefold coordinated as a result of a broken sixth interaction (3·398 Å) when compared with the thortvietite structure (Cruickshank, Lynton & Barclay, 1962). The latter cobalt has an average Co–O bond length of 2·049 Å with a bond length of 1·957 (7) Å to the same oxygen atom showing the short terminal P–O bond.

As can be seen in Table 4 the other low-temperature divalent metal ion pyrophosphates of this series show anion distortions paralleling those in α-$Co_2P_2O_7$. Only

Table 2. *Mean square atomic vibrations in* Å^2 ($\times 10^4$) *with estimated standard deviations*

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	78 (4)	55 (4)	73 (4)	−2 (5)	18 (3)	−6 (5)
Co(2)	83 (4)	53 (4)	67 (4)	6 (4)	−4 (3)	−2 (4)
P(1)	45 (8)	43 (8)	23 (8)	−2 (7)	−1 (7)	16 (6)
P(2)	27 (8)	47 (7)	36 (9)	6 (7)	12 (7)	7 (6)
O_I	65 (22)	110 (21)	141 (30)	−30 (21)	53 (22)	23 (21)
$O_{II}(2)$	92 (23)	64 (22)	31 (24)	−32 (19)	34 (20)	−31 (17)
$O_{II}(1)$	85 (23)	67 (22)	11 (23)	37 (19)	−9 (19)	17 (17)
$O_{III}(1c)$	89 (28)	63 (23)	62 (27)	5 (20)	49 (22)	21 (19)
$O_{III}(1t)$	133 (26)	103 (24)	60 (24)	−54 (21)	−38 (22)	−26 (19)
$O_{III}(2c)$	33 (21)	81 (24)	85 (23)	−7 (18)	10 (18)	−6 (19)
$O_{III}(2t)$	104 (30)	74 (26)	122 (31)	36 (21)	17 (24)	71 (22)

Table 3. *Interatomic distances and angles in* α-$Co_2P_2O_7$ (*uncorrected for the effects of thermal motion*)

$P_2O_7^{4-}$ group

Bond distances (Å)

P(1)–P(2)	2·998 (3)
P(1)–O_I	1·600 (8)
P(2)–O_I	1·566 (8)
P(1)–O_{II}(1)	1·535 (6)
P(2)–O_{II}(2)	1·527 (5)
P(1)–O_{III}(1*c*)	1·519 (7)
P(2)–O_{III}(2*c*)	1·510 (7)
P(1)–O_{III}(1*t*)	1·499 (7)
P(2)–O_{III}(2*t*)	1·514 (7)

	Side 1	Side 2
O_I——O_{II}	2·469 (2)	2·498 (9)
O_I——O_{III}(*t*)	2·530 (10)	2·531 (10)
O_I——O_{III}(*c*)	2·459 (11)	2·388 (10)
O_{II}——O_{III}(*c*)	2·519 (9)	2·532 (9)
O_{II}——O_{III}(*t*)	2·547 (8)	2·506 (9)
O_{III}(*c*)–O_{III}(*t*)	2·524 (9)	2·511 (9)

Angles (°)

P(1)–O_I–P(2)	143·1 (6)

	Side 1	Side 2
O_I——P–O_{II}	103·5 (4)	107·7 (4)
O_I——P–O_{III}(*t*)	109·4 (4)	110·5 (4)
O_I——P–O_{III}(*c*)	104·1 (4)	101·9 (4)
O_{II}——P–O_{III}(*t*)	114·1 (4)	111·0 (4)
O_{II}——P–O_{III}(*c*)	111·2 (4)	113·0 (4)
O_{III}(*c*)–P–O_{III}(*t*)	113·5 (5)	112·3 (4)

$Co(1)–O_6$ group

Bond distances (Å)

Co(1)–O_{II}(1)^d	2·085 (6)
–O_{II}(2)^a	2·099 (6)
–O_{II}(2*c*)^b	2·139 (7)
–O_{III}(1*c*)^a	2·062 (7)
–O_{III}(2*t*)^c	2·183 (7)
–O_{III}(1*c*)^e	2·126 (8)

Angles (°)

O_{II}(1)^a—Co(1)–O_{II}(2)^a	80·5 (2)
–O_{II}(2*c*)^b	80·3 (3)
–O_{III}(1*c*)^a	96·1 (3)
–O_{III}(2*t*)^c	157·8 (4)
–O_{III}(1*c*)^e	89·7 (3)
O_{II}(2)^d—Co(1)–O_{II}(2*c*)^b	84·8 (3)
–O_{III}(1*c*)^a	165·4 (4)
–O_{III}(2*t*)^c	96·9 (3)
–O_{III}(1*c*)^e	88·9 (3)
O_{II}(2*c*)^b–Co(1)–O_{III}(1*c*)^a	108·8 (3)
–O_{III}(2*t*)^c	77·5 (3)
–O_{III}(1*c*)^e	168·9 (3)
O_{III}(1*c*)–Co(1)–O_{III}(2*t*)^c	91·5 (3)
–O_{III}(1*c*)^e	76·9 (3)
O_{III}(2*t*)^c–Co(1)–O_{III}(1*c*)^e	112·3 (3)

$Co(2)–O_5$ group

Bond distances (Å)

Co(2)–O_{II}(1)^d	2·067 (5)
–O_{II}(2)^a	2·072 (6)
–O_{III}(2*t*)^b	2·110 (8)
–O_{III}(1*t*)^a	1·957 (7)
–O_{III}(1*t*)^e	3·398 (12)
–O_{III}(2*c*)^c	2·040 (6)

Angles (°)

O_{II}(1)^d—Co(2)–O_{II}(2)^a	81·6 (2)
–O_{III}(2*t*)^b	92·1 (3)
–O_{III}(1*t*)^a	93·5 (3)
–O_{III}(2*c*)^c	169·6 (3)
O_{II}(2)^a—Co(2)–O_{III}(2*t*)^b	93·0 (3)
–O_{III}(1*t*)^a	151·7 (4)
–O_{III}(2*c*)^c	90·6 (2)
O_{III}(2*t*)^b–Co(2)–O_{III}(1*t*)^a	115·1 (3)
–O_{III}(2*c*)^c	77·5 (3)
O_{III}(1*t*)—Co(2)–O_{III}(2*c*)^c	96·5 (3)

Symmetry transformations: $a \equiv x,y,z$; $b \equiv -x,-y,z$; $c \equiv x,\frac{1}{2}-y,\frac{1}{2}+z$; $d \equiv \frac{1}{2}-x,\frac{1}{2}+y,z$; $e \equiv x,\frac{1}{2}-y,\frac{1}{2}+z$.

Table 4. *Comparison of pertinent bond distances in various* $M_2P_2O_7$ *systems* (Å)

	Mg	Co	Zn	Ni	Predicted*
Side 1					
P–O_I	1·612 (10)	1·600 (8)	1·599 (8)	1·598	1·595
–O_{II}	1·533 (10)	1·535 (6)	1·518 (5)	1·535	1·54
–O_{III}(*c*)	1·507 (10)	1·519 (7)	1·528 (9)	1·558	1·53
–O_{III}(*t*)	1·472 (10)	1·499 (7)	1·489 (10)	1·516	1·50
Side 2					
P–O_I	1·569 (10)	1·566 (8)	1·566 (7)	1·606	1·595
–O_{II}	1·539 (10)	1·527 (5)	1·520 (5)	1·541	1·54
–O_{III}(*c*)	1·527 (10)	1·510 (7)	1·518 (9)	1·545	1·54
–O_{III}(*t*)	1·521 (10)	1·514 (7)	1·531 (10)	1·527	1·54
M–O_{III}(*t*)	1·985 (10)	1·957 (7)	1·929 (9)	1·935	
⟨M–O(6)⟩	2·105	2·116	2·092	2·079	
⟨M–O(5)⟩	2·044	2·049	2·023	2·007	

* Calculated from P–O = 1·32 + 0·11 P_O where P_O is the sum of the electrostatic bond strength of the oxygen ion bonded to the phosphorus atom.

α-$Ni_2P_2O_7$ (Łukaszewicz, 1967) seems anomalous. In the case of α-$Zn_2P_2O_7$ only that anion not containing a crystallographic twofold axis is considered (Robertson & Calvo, 1970). Aside from α-$Ni_2P_2O_7$ the anion geometry does not deviate significantly with change of cation, although the size of the estimated standard deviations precludes any conclusion concerning the effects of electronegativity on the bond lengths. The predicted values, obtained from Baur's (1970) relationship, agree only qualitatively and, since it contains no distance dependency, fails to predict the characteristic distortions between the two halves of the anion.

This research was supported by the National Research Council of Canada.

References

BAUR, W. H. (1970). *Trans. Amer. Crystallogr. Assoc.* **6**, 129.
CALVO, C. (1967). *Acta Cryst.* **23**, 259
CRUICKSHANK, D. W. J., LYNTON, H. & BARCLAY, G. A. (1962). *Acta Cryst.* **15**, 491
ŁUKASZEWICZ, K. (1967). *Bull. Acad. Pol. Sci., Ser. Sci. Chem.* **15**(2), 47.
ROBERTSON, B. E. & CALVO, C. (1970). *J. Solid State Chem.* **1**, 120

Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1972). B**28**, 2885

Corrigendum: the crystal and molecular structure of bismuth trichloride.

By S. C. NYBURG, G. A. OZIN and J. T. SZYMAŃSKI,* *Lash-Miller Chemical Laboratories, University of Toronto, Toronto,* 181, *Ontario, Canada*

(*Received* 4 *May* 1972)

Corrected atomic fractional coordinates and thermal parameters are given for the structure of bismuth trichloride previously reported.

In the recent report on the structure of bismuth trichloride (Nyburg, Ozin & Szymański, 1971), an undetected error in a program which transformed coordinates within a unit cell resulted in an incorrect set of parameters being published, these being different from the ones used in the refinement. The corrected set is given here (Table 1).

* Present address: Mines Branch, Department of Energy, Mines and Resources, 555 Both Street, Ottawa K1A 0G1, Canada.

Reference

NYBURG, S. C., OZIN, G. A. & SZYMAŃSKI, J. T. (1971). *Acta Cryst.* B**27**, 2298.

Table 1. *Atomic fractional coordinates* (*e.s.d.'s in parentheses*)

	x	y	z
Bi	−0·04678 (5)	−0·25*	−0·02328 (7)
Cl(1)	0·0567 (4)	−0·2505 (15)	0·3484 (7)
Cl(2)	0·1762 (9)	−0·0647 (09)	−0·1382 (17)
Cl(3)	0·1750 (9)	−0·4332 (09)	−0·1509 (16)

* Defines origin.

Table 1 (*cont.*). *Thermal parameters* (*e.s.d.'s in parentheses*)

Temperature factor $= \exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Bi	0·00636 (7)	0·00683 (6)	0·01125 (12)	−0·00138 (13)	−0·00106 (5)	0·00180 (21)
Cl(1)	0·0083 (4)	0·0087 (5)	0·0124 (7)	−0·0003 (12)	−0·0009 (4)	−0·0011 (14)
Cl(2)	0·0108 (10)	0·0041 (6)	0·0177 (17)	0·0007 (6)	0·0012 (10)	−0·0011 (7)
Cl(3)	0·0103 (10)	0·0063 (8)	0·0137 (14)	−0·0012 (7)	0·0050 (9)	0·0002 (9)