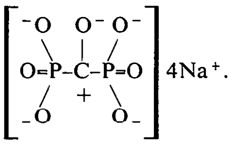
coordinate) bonds (Naqvi *et al.*, 1971). Long P–C bond lengths have also been reported for trisodium phosphonoformate (1·869 Å) (Naqvi *et al.*, 1971) and tetramethyl formadinium phosphonic anhydride (1·880 Å) (Sanz & Daly, 1972) and its parent acid (1·890 Å) (Daly, 1972). As was done by Naqvi *et al.* (1971) for phosphonoformate, we tend to attribute this lengthening of the P–C bond to repulsions between the negatively charged phosphonate groups. It is interesting to note that for the series of diphosphonates studied to date (H_4MDP, H_4EHDP, CaH_4EHDP and Na_4CDP), the trend in P–C bond lengths directly correlates with the extent and direction of distortion away from ideal tetrahedral angles about the P atoms. The length of the P–C bond in Na_4CDP, particularly when compared to the methylene and substituted methylene diphosphonates where only single P–C bonds are possible, suggests that multiple P–C binding (*e.g.* due to contribution of $p\pi$–$d\pi$ interaction) is not significant in this molecule.* The carbonyl distance of 1·263 Å is significantly longer than is normally found in ketones. This lengthening is consistent with the suggestion made by Quimby *et al.*, that CDP^{4-} may be stabilized by a significant contribution of a resonance form such as



$$\left[\begin{array}{c} {}^{-}O\quad O^{-}\,O^{-} \\ O{=}P{-}C{-}P{=}O \\ {}_{-}O\quad +\quad O_{-} \end{array}\right]4Na^{+}.$$

Also consistent with this observation is the unusually low infrared carbonyl stretching frequency of 1612 cm^{-1}.

We would like to acknowledge the experimental assistance of R. A. Gloss and M. R. Webb, as well as helpful discussions with Dr B. H. Wiers.

---

* This conclusion is also supported by the relative orientation of the carbonyl group and the PO_3 groups, since B. H. Wiers has shown (unpublished results) that $p\pi$–$d\pi$ orbital overlap is at a maximum when the molecule is in an eclipsed, planar 'W' (for an OPCPO chain of atoms) configuration. Also, Raman spectra results (W. Yellin, unpublished results) suggest an absence of coupling of the carbonyl frequencies with the symmetric PO_3 stretching mode.

References

DALY, J. J. (1972). *J. Chem. Soc. Dalton*, pp. 1048–1051.

DELAMATTER, D., MCCULLOUGH, J. J. & CALVO, C. (1973). *J. Phys. Chem.* **77**, 1146–1148.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.

LEUNG, K. Y. & CALVO, C. (1972). *Canad. J. Chem.* **50**, 2519–2526.

NAQVI, R. R., WHEATLEY, P. J. & FORESTI-SERANTONI, E. (1971). *J. Chem. Soc.* (*A*), pp. 2751–2754.

QUIMBY, O. T., PRENTICE, J. B. & NICHOLSON, D. A. (1967). *J. Org. Chem.* **32**, 4111–4114.

SANZ, F. & DALY, J. J. (1972). *J. Chem. Soc. Dalton*, pp. 2267–2269.

STEWART, J. M. (1967). Technical Report 67-58, Dec. 1967, Computer Science Center, Univ. of Maryland.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, pp. 454–458. New York: Macmillan.

UCHTMAN, V. A. (1972). *J. Phys. Chem.* **76**, 1304–1310.

UCHTMAN, V. A. & GLOSS, R. A. (1972). *J. Phys. Chem.* **76**, 1298–1304.

Acta Cryst. (1976). B**32**, 492

The Crystal and Molecular Structure of 5,5-Dimethyl-2-oxo-2-aminobenzo-1,3,2-dioxaphosphorinane

BY T. STANLEY CAMERON

Chemistry Department, The New University of Ulster, Coleraine, Co. Londonderry, N. Ireland

AND ZDZISLAW GALDECKI AND JANINA KAROLAK-WOJCIECHOWSKA*

Technical University, Łódź, Poland

(*Received* 11 *June* 1975; *accepted* 23 *June* 1975)

$C_{11}H_{16}NO_3P$, orthorhombic, $a = 11{\cdot}48$ (3), $b = 11{\cdot}37$ (3), $c = 9{\cdot}71$ (2) Å, space group $P2_12_12_1$, $Z = 4$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations with 1200 independent reflexions to R 0·12. The dioxaphosphorinane ring has the chair configuration with the phosphoryl O atom, despite predictions to the contrary, in the equatorial position.

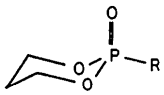
Introduction

In the chair form of 2-oxo-2-R-1,3,2-dioxaphosphorinanes the phosphoryl O atom can assume either an equatorial (I*a*) or an axial (I*b*) position. In most of the structures determined (Silver & Rudman, 1972; Drew & Rodgers, 1972; Wagner, Jensen & Wadsworth, 1973: and references therein) the O atom is equatorial though Galdecki & Karolak-Wojciechowska (1971) report a structure (II) where the O atom is axial. Mosbo & Verkade (1973) suggest from ¹H n.m.r. and dipole

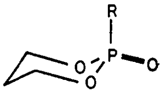
---

* Present address: The New University of Ulster, Coleraine, N. Ireland.

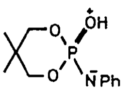
measurements that when R is NMe_2 the O atom will also be axial and explain this in terms of the steric requirements of N–P π bonding. To examine the possible effect of π bonding on the molecular conformation, this structure, where R is NHPh, has been determined.



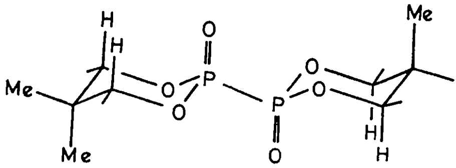
(I*a*)



(I*b*)



(I*c*)



(II)

Experimental

The crystals were provided by W. J. Stec, Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Łódź, Poland.

Crystal data

$C_{11}H_{16}NO_3P$, $M=241{\cdot}2$, $F(000)=128$. Orthorhombic, $a=11{\cdot}48$ (3), $b=11{\cdot}37$ (3), $c=9{\cdot}71$ (2) Å. $D_m=1{\cdot}24$, $D_c=1{\cdot}23$ g cm^{-3}, $Z=4$, Cu $K\alpha$ radiation, $\mu=11{\cdot}9$ cm^{-1}, $\lambda=1{\cdot}54178$ Å. Space group $P2_12_12_1$ (D_2^4, No. 19); systematic extinctions $h00$, $h=2n+1$; $0k0$, $k=2n+1$; $00l$, $l=2n+1$.

The crystals are thin shiny needles extended along [001], and 1200 independent reflexions were estimated visually from equi-inclination Weissenberg photographs, $hk0$–$hk7$. The data were corrected for Lorentz and polarization effects, but not for absorption.

A position for the P atom in space group $P2_12_12_1$ was determined from a sharpened three-dimensional Patterson function, and the positions of the other non-hydrogen atoms were located from an F_o synthesis phased on the P atom position.

The trial structure was refined by full-matrix least-squares calculations. After three cycles with individual isotropic temperature factors and unit weights, and subsequently two cycles with anisotropic temperature factors on all atoms, R was 0·12. While the temperature factors were isotropic the individual layer scale factors ($l=1$–7) were included among the parameters that were refined. A difference synthesis calculated when R was 0·12 clearly showed the position of the H atom [H(1)] bonded to the N atom (see below), and less clearly that of several other H atoms. Therefore fractional coordinates were calculated for all the H atoms, except H(1), with positions defined by the geometry of the molecule. These H atoms were assigned the same isotropic temperature factor as the atom to which they were bonded and their parameters were included in, but not altered by, the two final cycles of refinement, which converged at R 0·12. There were no unusual features in a difference synthesis, calculated at this stage. All calculations used Cameron's (1973) CRYSTALS or Sheldrick's (1972) computing system.

The observed structure amplitudes, and structure factors calculated from the final atomic parameters, given in Table 1, are available.* The interatomic distances and interbond angles are given in Table 2. Fig. 1 is a stereoscopic projection along **c**, showing the packing of the molecules in the unit cell, and Fig. 2 shows a single molecule projected along **b**.

Results and discussion

The dioxaphosphorinane ring was found to have the chair configuration with the phosphoryl O(1) not in the axial position (I*a*) but the equatorial (I*b*). There is

Table 1. *Atomic parameters* (× 10^4) *with e.s.d.'s in parentheses*

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P(1)	1693 (3)	460 (3)	1985 (4)	539	606	758	−36	21	−8
N(1)	2749 (8)	817 (8)	3066 (12)	616	622	801	−11	−106	−78
O(1)	2050 (9)	307 (10)	535 (11)	908	1368	848	−343	225	−168
O(2)	1143 (7)	−663 (6)	2662 (9)	624	545	1057	−33	−50	−72
O(3)	682 (7)	1428 (7)	2062 (11)	656	699	820	152	50	167
C(1)	3719 (8)	1537 (7)	2693 (11)	768	613	602	−18	118	−10
C(2)	3714 (9)	2334 (10)	1644 (15)	1068	647	589	−54	90	−16
C(3)	4719 (13)	3024 (9)	1363 (12)	1574	781	814	−31	56	−96
C(4)	5729 (8)	2916 (7)	2131 (11)	1293	1165	1229	−86	451	−584
C(5)	5734 (9)	2118 (10)	3181 (15)	800	1178	1349	−334	−30	26
C(6)	4729 (13)	1429 (9)	3461 (12)	609	842	1110	−9	−64	−73
C(7)	369 (10)	−563 (10)	3857 (15)	757	700	851	−4	−6	−126
C(8)	−607 (9)	329 (12)	3636 (15)	578	816	1036	32	173	41
C(9)	10 (11)	1516 (10)	3301 (14)	859	680	925	145	42	172
C(10)	−1250 (12)	432 (16)	5077 (17)	820	1387	1278	−176	436	28
C(11)	−1420 (10)	20 (13)	2446 (13)	585	1410	703	−91	−90	−98

---

* Catalogue number QD 921. C34. Copies may be obtained on application to the Librarian for Science, The New University of Ulster, Coleraine, Nr. Ireland. This table has also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31219 (5 pp.) and copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1 (*cont.*)

	x	*y*	*z*	*U*
H(1)	3000	150	3970	651
H(2)	2995	2490	998	752
H(3)	4457	3633	627	1144
H(4)	6431	3397	1817	987
H(5)	6489	1957	3787	952
H(6)	4751	894	4297	739
H(19)	−590	2162	3191	802
H(29)	546	1759	4073	802
H(17)	830	−366	4726	699
H(27)	−5	−1378	4082	699

a hydrogen bond between this O atom and the N atom of a second molecule. The -N-H···O-P-N-H··· O-P- systems form helices around the twofold screw axes in the zone of the *c* axis (Fig. 1). The unit cell is therefore constructed from columns of molecules with the O, N and P atoms in the centre of the columns and the two methyl groups in particular protruding on the outside. The methyl groups of two adjacent columns pack, apparently none too closely, in the obvious interstices between the columns. The marked cleavage plane, parallel to the needle axis (*c*) of the crystals, is probably the consequence of the weak crystal forces holding the columns of molecules together.

The P coordination sphere is not very different from that found in similar dioxaphosphorinanes. The phosphoryl P(1)=O(1) bond length [1·476 (10) Å] lies within the range (1·39–1·51 Å) observed for these compounds. The single P–O bond lengths 1·567 (7) [O(2)] and 1·597 (7) Å [O(3)], mean 1·582 (7) Å, are slightly but not significantly longer than those normally observed which are in the range 1·522–1·584 Å (Galdecki & Karolak-Wojciechowska, 1973). The P–N bond length of 1·649 (10) Å is shorter than a single bond (1·77 Å)

Table 2. *Interatomic distances* (Å) *and interbond angles* (°) *with e.s.d.'s in parentheses*

P(1)——N(1)	1·649 (10)	O(1)—P(1)–N(1)	115·7 (0·6)
P(1)——O(1)	1·476 (10)	O(2)—P(1)–N(1)	103·1 (0·7)
P(1)——O(2)	1·567 (07)	O(2)—P(1)–O(1)	114·5 (0·6)
P(1)——O(3)	1·597 (07)	O(3)—P(1)–N(1)	109·2 (0·5)
N(1)——C(1)	1·424 (09)	O(3)—P(1)–O(2)	104·6 (0·4)
O(2)——C(7)	1·464 (13)	O(3)—P(1)–O(1)	109·0 (0·6)
O(3)——C(9)	1·431 (12)	C(1)—N(1)-P(1)	123·2 (0·4)
C(1)——C(2)	1·363 (17)	H(1)—N(1)-P(1)	119·1 (0·6)
C(2)——C(3)	1·417 (16)	H(1)—N(1)-C(1)	111·4 (0·4)
C(3)——C(4)	1·379 (16)	C(7)—O(2)-P(1)	120·8 (0·4)
C(4)——C(5)	1·365 (16)	C(9)—O(3)-P(1)	118·4 (0·4)
C(5)——C(6)	1·416 (16)	C(2)—C(1)-N(1)	124·7 (0·9)
C(6)——C(1)	1·379 (16)	C(6)—C(1)-N(1)	117·5 (0·9)
C(8)——C(7)	1·522 (15)	C(6)—C(1)-C(2)	117·8 (0·9)
C(8)——C(9)	1·557 (16)	C(3)—C(2)-C(1)	120·6 (1·2)
C(8)——C(10)	1·585 (18)	C(4)—C(3)-C(2)	121·6 (1·2)
C(8)——C(11)	1·522 (16)	C(5)—C(4)-C(3)	117·8 (0·9)
N(1)——H(1)	1·195 (10)	C(6)—C(5)-C(4)	120·5 (1·2)
O(1)···H(1)	1·607	C(5)—C(6)-C(1)	121·7 (1·2)
N(1)···O(1)	2·726	C(8)—C(7)-O(2)	112·5 (1·0)
		C(9)—C(8)-C(7)	106·0 (0·8)
		C(10)-C(8)-C(7)	105·3 (1·1)
		C(10)-C(8)-C(9)	109·2 (1·1)
		C(11)-C(8)-C(7)	113·6 (1·1)
		C(11)-C(8)-C(9)	108·5 (1·1)
		C(11)-C(8)-C(10)	113·9 (0·9)
		C(8)—C(9)-O(3)	110·9 (0·9)

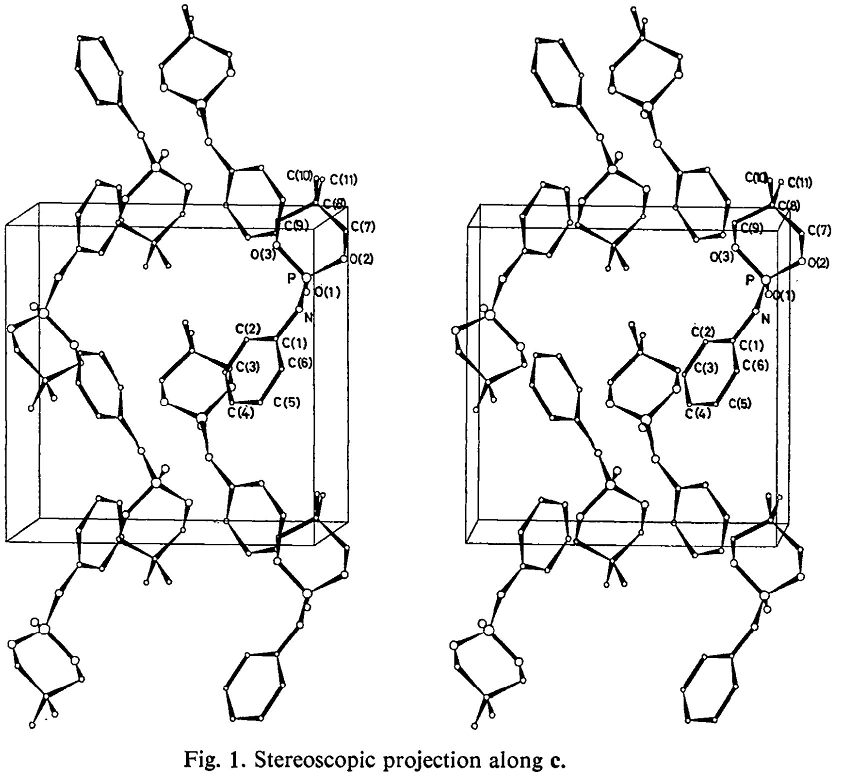
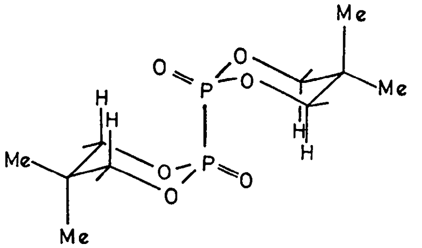
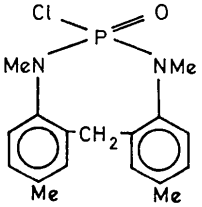


Fig. 1. Stereoscopic projection along **c**.

(Cruickshank, 1961), but longer than the lengths 1·52–1·60 Å normally found in cyclotriphosphazenes (Corbridge, 1974) where there is thought to be a strong *pπ–dπ* delocalization along the P–N bond. The angles between the plane of the three atoms bonded to the N atom and the planes through atoms O(1)=P(1)–O(2) and O(1)=P(1)–O(3) are 129 and 105° respectively. In 6-chloro-5,6,7,12-tetrahydro-2,5,7,10-tetramethyldibenzo[*d*,*g*] [1,3,2]diazaphosphocine 6-oxide (IV), the angles between the planes through the atoms bonded to each of the two N atoms and the plane through the Cl–P=O fragment of the molecule are 91° and 127° with the corresponding P–N distances 1·637 (6) and 1·650 (6) Å respectively (Cameron, 1972, 1975). For (IV) a *dπ–pπ* interaction along the P–N bond was suggested. In the present compound, with a similar configuration around the phosphoryl bond and similar P–N bond length there may also be a π interaction along the P–N bond. In this context it is significant that the N atom is only 0·19 Å from the plane of the three atoms bonded to it.



(III)



(IV)

An examination of space filling models of the compound in the chair configuration with either the phosphoryl O or the amine N atom in the axial position shows that the dominant steric interaction would occur between the axial O atom and the axial H atoms H(17) and H(29) at C(7) and C(9). This is the result of the short P=O bond length which brings the O and H atoms close together and also of the large volume occupied by electrons of a double bond (Gillespie & Nyholm, 1957). When the N atom is axial its steric interaction is less since the contact distance to the axial H atoms is increased (the P–N bond length is 0·17 Å longer than the P=O), and the interaction with the bonding electrons should decrease as the π-bond order in the P–N bond is probably significantly less than 1 (Alcock, 1972). The atoms bonded at N are apparently accommodated without further strain with contact distances H(1)···H(17) 2·65 Å and C(1)···C(29) 3·35 Å, greater than the sum of the van der Waals radii. In the bisdioxaphosphorinane (II) where the O atom is in the axial position, an examination of a model shows that the axial steric interaction will be less than the interaction between an equatorial phosphoryl O atom of one phosphorinane ring and the axial H atoms of the second ring (III) (Galdecki & Karolak-Wojciechowska, 1973). Since substituents such as CPh_3 and Br occupy the axial position in similar dioxaphosphorinanes (Drew & Rogers, 1972; Beinecke, 1969) it seems that the structure with the axial interaction between the phosphoryl O and the H atoms is the least favoured, and this is not affected by π bonding between the P atom and the other substituents at the P atom.

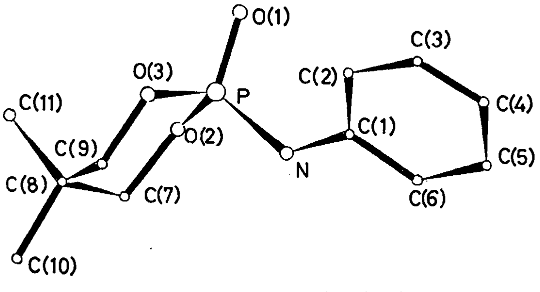


Fig. 2. Projection of the molecule along **b**.

The configuration and dimensions of the dioxaphosphorinane ring are unexceptional. The angle between the planes through P(1), O(2), O(3) and O(2), O(3), C(7), C(9) is 34·2° and that between this second plane and the plane through C(7), C(8), C(9) is 55·6° so that the chair configuration, as in similar compounds, is flattened at the P end.

The hydrogen bond between O(1) and N(1) of another molecule is strong with the O···N distance short for this type of bond (Corbridge, 1974). The H atom of the bond was clearly indicated in the difference map (see above) and was closer to the N atom (1·195 Å) than the O (1·607 Å). Formula (I*c*) makes little contribution to the structure and this is reflected in the short P=O bond length.

The N–C(phenyl) bond length, 1·424 (8) Å, is short [*cf.* C–N in acetanilide 1·43 Å (Brown, 1966)]. The torsional angle about the N–C bond of the P–N bond and the plane of the benzene ring is 23·8°, so with the effectively planar configuration about the N atom the π system of the benzene ring can be conjugated with the phosphoryl O atom and this might explain the shortening of the N–C bond.

Apart from the hydrogen bond, there are no unusually short intermolecular contacts.

We thank the Polish Ministry of Education and Technology for a scholarship to J.K.-W. and The New University of Ulster Computing Centre for facilities.

References

ALCOCK, H. R. (1972). *Chem. Rev.* **72**, 315–356.
BEINECKE, T. A. (1969). *Acta Cryst.* B**25**, 413–419.
BROWN, C. J. (1966). *Acta Cryst.* **21**, 442–445.
CAMERON, T. S. (1972). *J. Chem. Soc. Perkin* II, pp. 491–593.
CAMERON, T. S. (1973). New Univ. of Ulster, Internal Report I.
CAMERON, T. S. (1975). *Acta Cryst.* B**31**, 2331–2333.
CORBRIDGE, D. E. C. (1974). *The Structural Chemistry of Phophorus*, p. 333. Amsterdam: Elsevier.
CRUICKSHANK, D. W. J. (1961). *J. Chem. Soc.* pp. 5486–5507.
DREW, M. G. B. & RODGERS, J. (1972). *Acta Cryst.* B**28**, 924–929.
GALDECKI, Z. & KAROLAK-WOJCIECHOWSKA, J. (1971). *Bull. Acad. Polon. Sci. Ser. Sci. Chim.* **19**, 257–261.
GALDECKI, Z. & KAROLAK-WOJCIECHOWSKA, J. (1973). *Lodz. Towarz. Nauk. Wydzial.* III, *Acta Chim.* **115**, 1–55.
GILLESPIE, R. J. & NYHOLM, R. S. (1957). *Quart. Rev.* **11**, 339–381.
MOSBO, J. A. & VERKADE, J. G. (1973). *J. Amer. Chem. Soc.* **95**, 4659–4665.
SHELDRICK, G. M. (1972). Personal communication.
SILVER, J. & RUDMAN, R. (1972). *Acta Cryst.* B**28**, 574–577.
WAGNER, R., JENSEN, W. & WADSWORTH, W. (1973). *Cryst. Struct. Commun.* **3**, 507–509.

Acta Cryst. (1976). B**32**, 496

Y_8Co_5, a New Monoclinic Phase with Co Centred Trigonal Prisms

BY J. M. MOREAU,* D. PACCARD* AND E. PARTHÉ

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 *Quai Ernest-Ansermet*, *CH*-1211 *Geneva* 4, *Switzerland*

(*Received* 23 *June* 1975; *accepted* 28 *June* 1975)

Y_8Co_5 crystallizes with a new monoclinic structure type. Space group $P2_1/c$ (No. 14), $a=7{\cdot}058$ (2), $b=7{\cdot}286$ (2), $c=24{\cdot}277$ (8)Å, $\beta=102{\cdot}11$ (7)°, $Z=4$. Symbolic addition method, counter technique, absorption correction, least-squares refinement. $R=0{\cdot}09$ for 725 reflexions. The structure is built up from structural units consisting of trigonal prisms formed by Y atoms and centred by Co atoms. These units are linked in different ways, some sharing faces, some edges and some corners. Nevertheless the value of $3\frac{3}{4}$ for the trigonal prism linkage coefficient is in agreement with the overall composition of the compound. The structure may be characterized by layers of double prisms with an arrangement related to FeB.

Introduction

Phase diagrams for the system Y–Co have been published by Buschow (1971), and by Ray (1974) who refers to an earlier proposal by Strnat, Ostertag, Adams & Olson (1965). There is general agreement that for stoichiometries ranging from 0 to 50 at.% Co at least two intermetallic phases exist: Y_3Co with the orthorhombic $Gd_3Ni(Fe_3C,NiAl_3)$ type (Buschow & van der Goot, 1969) and Y_4Co_3 with the hexagonal Ho_4Co_3 type (Lemaire, Schweizer & Yakinthos, 1969). Buschow, however, pointed out that close to Y_4Co_3 there are two other unidentified phases. One of these has been identified as orthorhombic Y_3Co_2 (Moreau, Parthé & Paccard, 1975) which crystallizes with a shift structure variation of the monoclinic Dy_3Ni_2 structure type (Moreau, Paccard & Parthé, 1974).

We present the results of our structure determination on the third phase existing in the region from 30 at.% to 50 at.% Co and for which the exact composition is Y_8Co_5 with 38 at.% Co.

Experimental

The alloys were made from commercially available elements of high purity: Y 99·9%, Co 99·99%. Samples were prepared by conventional arc melting techniques and were then heat treated in sealed quartz tubes at 700°C for two days. Initial stoichiometries were such that the Co content ranged from 30 at.% to 40 at.%. X-ray photographs from powdered samples were obtained on a Guinier camera with Cu $K\alpha$ radiation. Small crystals suitable for X-ray analysis were isolated by mechanical fragmentation from the sample containing 38 at.% Co. Weissenberg photographs showed the crystals to be monoclinic, space group $P2_1/c$ (systematic absences; $h0l$ with l odd and $0k0$ with k odd).

Lattice constants and intensities were measured with graphite-monochromated Mo $K\alpha$ radiation and a

---

* Present address: Centre Universitaire de Savoie, I.U.T. d'Annecy et Laboratoire de Magnétisme, CNRS Grenoble, France.