

of atoms in $K_{0.55}Rb_{0.45}HSO_4$ is then necessary for the alignment of sulphate groups and alkali metals which is found in $RbHSO_4$.

Comparable structure dissimilarities have been observed previously between such compounds as $BaSO_4$ and $BaHPO_4$ (Bengtsson, 1941). These differences may derive from the influence of the hydrogen atom on the mutual orientation and distances in the sulphate (and phosphate) tetrahedral groupings in these compounds.

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The Crystal and Molecular Structure of Bis-(*N*-benzylidiphenylphosphinic amide)-dichlorocobalt(II)

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The crystal and molecular structure of bis-(*N*-benzylidiphenylphosphinic amide)dichlorocobalt(II), $[(C_6H_5)_2PONHCH_2C_6H_5]_2CoCl_2$, has been elucidated by single-crystal X-ray diffraction. The crystals are monoclinic, space group *Cc* or *C2/c*, with unit-cell dimensions $a = 12.767$ (4), $b = 14.038$ (3), $c = 20.811$ (6) Å, $\beta = 101.7$ (1)°, and $Z = 4$. The conventional discrepancy index is 0.119 for 1669 visually estimated reflexions. The molecule contains a cobalt atom which is bonded in almost regular tetrahedral directions to two chlorine atoms and two oxygen atoms, one each from the *N*-benzylidiphenylphosphinic amide ligands.

Introduction

The reflux reaction between *p,p*-diphenyl-*N*-benzylphosphinothioic amide and a large excess of cyclohexene (Ibrahim, 1968) gives a number of products, one of which, a viscous colourless liquid, can be extracted by thin layer chromatography from the residue obtained by distilling off the excess cyclohexene. Treatment of an ethereal solution of this liquid with anhydrous cobalt chloride in alcohol, followed by evaporation of the solvents and extraction of the residue with anhydrous ether, yields a blue solution from which deep blue crystals of a cobalt complex can be obtained. On the basis of the above method of preparation and the partial chemical analysis figures for batch (1) shown in Table 1, a chemical formula of $[(C_6H_5)_2PNHCH_2C_6H_5]CoCl$ was assigned to the complex. An approximate molecular weight, measured in 1,2-dichloroethane using a vapour pressure osmometer, was found to be 668; the above formula requires a molecular weight of 385. It was suggested that the

molecule could be a dimer (molecular weight = 770) containing two cobalt atoms with the additional possibility of chlorine bridging between these two atoms.

The crystal structure analysis of this cobalt complex was undertaken in order to determine the atomic arrangement and the molecular geometry. In the course of this investigation the original formula was found to be incorrect and the correct formula, $[(C_6H_5)_2PONHCH_2C_6H_5]_2CoCl_2$, obtained. The corrected formula was checked by reparing the complex by the reaction of pure crystalline $(C_6H_5)_2PONH.CH_2.C_6H_5$ directly with anhydrous cobalt chloride; the blue crystals obtained (m.p. 164.5–165.5°C, Thakur, 1970) were shown to have identical X-ray diffraction spectra to the initial batch. An analysis of these crystals [Table 1, batch (2)] confirmed the new formula.

Experimental

Crystal data

All crystallographic observations were made at $20 \pm 5^\circ C$ and are recorded according to the recom-

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mendations prepared on behalf of the Commission on Crystallographic Data, I.U.Cr. (Kennard, Speakman & Donnay, 1967).

Bis-(*N*-benzylidiphenylphosphinic amide)dichlorocobalt(II), $[(C_6H_5)_2PONH \cdot CH_2 \cdot C_6H_5]_2CoCl_2$, M.W. 744.5, m.p. = 164°C. Monoclinic crystals, habit equant; $a = 12.767 \pm 4$, $b = 14.038 \pm 3$, $c = 20.811 \pm 6$ Å, $\beta = 101.7 \pm 1^\circ$, $V = 3646 \pm 8$ Å³. Unit-cell dimensions were obtained using the method described by Farquhar & Lipson (1946). Because of the focusing effect on back reflexions, especially of highly absorbing crystals, accurate measurements were possible in spite of the rather large size of the crystals. $D_m = 1.346 \pm 3$ g cm⁻³ (by flotation), $Z = 4$, $D_c = 1.356$ g cm⁻³ (the value of D_c for the original formula, 1.410, is 4% more than the measured value; the discrepancy on the basis of the errors of measurement should be 0.5%. $\mu = 65$ cm⁻¹ (Cu $K\alpha$). The systematic absences, hkl absent for $h+k=2n+1$, $h0l$ absent for $l=2n+1$ ($h=2n+1$), (and $0k0$ absent for $k=2n+1$) imply space groups Cc or $C2/c$; a piezo-electric test gave a negative result. The crystals are optically positive and biaxial.

Intensity measurement

Nickel-filtered copper radiation was used for all purposes. Intensity data were collected from non-integrated Weissenberg photographs of layers 0–12 about the b axis using multiple-film recording and eye estimation against a standard scale. The crystal was equant with an average cross-sectional diameter of 0.38 mm; spherical crystal absorption corrections were applied. 1836 reflexions were observed out of a possible 4177 in the Cu $K\alpha$ sphere, (500 were not recorded in layers 13 upwards). Very weak but visible reflexions below the minimum value on the standard scale were given the minimum value; unobserved reflexions were taken as zero. As far as possible symmetry related reflexions on the top and bottom of the film were averaged to reduce the error caused by spot extension and contraction.

Structure analysis

In the early stages of the analysis the space group was taken as Cc and the complex was assumed to con-

tain two cobalt atoms in the asymmetric unit; positions for the cobalt atoms were obtained from a three-dimensional Patterson synthesis. Some 35 possible atomic positions which roughly fitted the proposed formula were obtained from iterative Fourier syntheses. The least-squares refinement of this partial model, however, terminated at the high discrepancy index of 24%. The value of the isotropic temperature parameter for one of the cobalt atoms implied that this atom should be re-assigned as a phosphorus atom and similarly the substitution of one of the phosphorus atoms by a carbon atom was also indicated. Further, the excessively large values of the isotropic thermal parameters for five of the carbon atoms in the model suggested that these were incorrectly placed. The

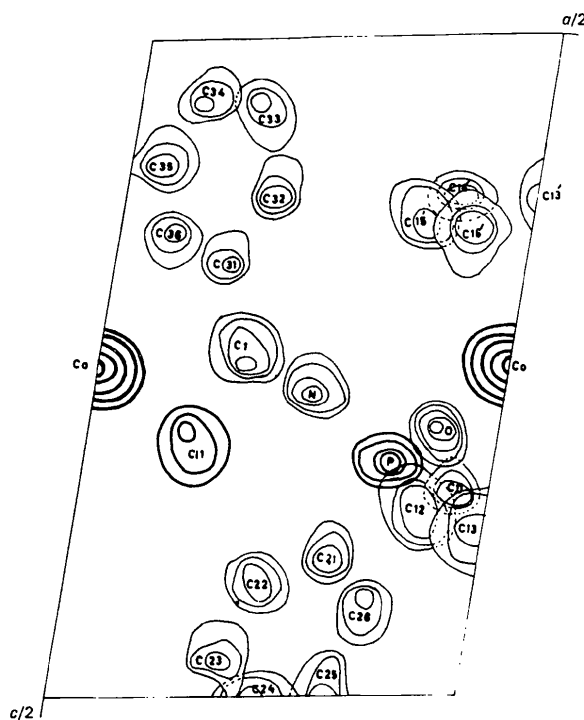


Fig. 1. A composite Fourier synthesis map through the atomic peaks viewed along the b axis.

Table 1. Analysis results (% by weight) for bis-(*N*-benzylidiphenylphosphinic amide)dichlorocobalt(II)

Element	Batch (1)		Batch (2)	
	Observed	Calculated from empirical formula $[(C_6H_5)_2PNH \cdot CH_2(C_6H_5) \cdot CoCl]$	Observed	Calculated from empirical formula $[(C_6H_5)_2PNO \cdot CH_2(C_6H_5)]_2CoCl_2$
Co	n.d.	15.28	8.24	7.92
Cl	9.6	9.19	9.85	9.53
P	7.8	8.03	8.26	8.32
O	n.d.	0.00	n.d.	4.30
N	3.5	3.63	3.90	3.76
C	59.5	59.16	60.69	61.30
H	4.8	4.70	4.93	4.87
Remainder†	14.8	—	4.13	—

n.d. Not determined.

† Undetermined elements plus errors.

substitutions indicated above gave a model in which the lone cobalt atom in the asymmetric unit was approximately 2.2 Å from two atoms which were assigned as chlorine and 3.4 Å distant from two atoms which were assigned as phosphorus in a distorted tetrahedral environment; all the significant peaks in the three-dimensional Patterson synthesis could be explained in terms of this arrangement. Iterative three-dimensional Fourier syntheses starting with phases computed from this new model, combined with the suggestion that oxidation had occurred during the preparation of the complex, enabled all non-hydrogen atoms to be located, including peaks between Co and P corresponding to the two oxygen atoms not included in the original formula. The molecule showed almost precise twofold symmetry and the remainder of the analysis was carried out within the symmetry of space group $C2/c$ with the cobalt atom in the special position $0, y, \frac{1}{4}$.

The structure was refined by the method of full-matrix least squares to a discrepancy index (R) of 11.9% when all the shifts in the parameters varied were less than $\frac{1}{4}$ of the corresponding estimated standard deviations. 167 reflexions from layers 11 and 12 (9% of the total) which showed discrepancies much greater than the other layers (probably because of inadequate correction for spot extension) were omitted from the refinement. In the initial cycles of the refinement all the atoms were treated isotropically and the layer scale factors were refined. In the final cycles the layer scale factors were held constant and the cobalt, chlorine and phosphorus atoms were treated anisotropically. Hydrogen atoms, with positions calculated from the molecular geometry, were included in a final cycle of refinement but their positional and thermal parameters, the latter arbitrarily assessed at 6.0 \AA^2 , were not refined. The R value fell to 11.3%. Relative weights were assigned to the observed structure factors according to the function, $w^{-1} = (2.5 + 0.008|F_o|^2 +$

$0.0000002|F_o|^4)$. The analysis of this weighting scheme is shown in Table 2.

Table 2. Analysis of weighting scheme

$ F_o $	n	$\sum w \Delta^2$	$\sum w \Delta^2/n$
4.0- 8.0	4	1.65	0.41
8.0- 16.0	336	227.76	0.68
16.0- 32.0	595	325.48	0.55
32.0- 64.0	461	309.53	0.67
64.0-128.0	205	145.03	0.71
128.0-256.0	39	25.01	0.64
256.0-512.0	4	2.35	0.59
sin θ/λ			
0.05-0.10	6	11.62	1.94
0.10-0.15	30	26.99	0.90
0.15-0.20	68	79.24	1.17
0.20-0.25	105	107.79	1.03
0.25-0.30	156	100.70	0.65
0.30-0.35	217	119.38	0.55
0.35-0.40	243	131.31	0.54
0.40-0.45	251	128.98	0.51
0.45-0.50	228	147.76	0.65
0.50-0.55	184	117.05	0.64
0.55-0.60	115	54.63	0.48
0.60-0.65	41	11.36	0.28
Layer (k)			
0	109	111.15	1.02
1	183	111.72	0.61
2	190	103.65	0.55
3	175	171.63	0.98
4	173	94.61	0.55
5	158	92.46	0.59
6	134	81.36	0.61
7	133	67.07	0.50
8	139	95.93	0.69
9	112	45.28	0.40
10	138	61.94	0.45

An attempt to improve the refinement by reverting to space group Cc produced a reduction of only 0.2 in the discrepancy index. Since this change almost doubled the number of variable parameters it is clear that there can only be insignificant departures from the centrosymmetric space group.

A final difference Fourier synthesis showed no feature of any significance, thus confirming the correctness of the structure. Throughout the structure factor calculations the atomic scattering factors listed by Hanson, Herman, Lee & Skillman (1964) were used.

Structural data

A composite Fourier synthesis map through the atomic peaks is shown in Fig. 1. The atom numbering for space group Cc has been retained. Fig. 2 is a schematic drawing of the molecule as viewed along the b axis and Fig. 3 shows the packing of the molecules in the unit cell.

Table 3 gives the final parameters of the atoms in the asymmetric unit. The intramolecular distances and angles, together with the molecular geometry, are given in Table 4. The list of observed and calculated structure factors is given in Table 58 of Roy (1969).

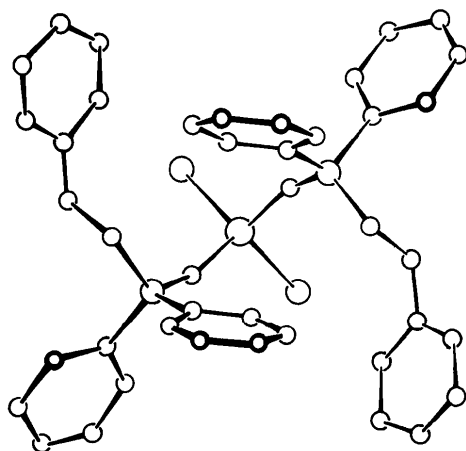


Fig. 2. A schematic drawing of bis-(*N*-benzyl)diphenylphosphinic amide)dichlorocobalt(II).

Table 3. Atomic parameters

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (Å ²)
Co	0.0000	0.0048 (2)	0.2500	*
Cl(1)	-0.1331 (3)	-0.0788 (3)	0.1892 (2)	*
P(1)	-0.1269 (2)	0.1678 (3)	0.3257 (1)	*
O(1)	-0.0649 (7)	0.0873 (7)	0.3049 (4)	6.8 (2)
C(11)	-0.1771 (8)	0.1278 (8)	0.3954 (5)	4.3 (2)
C(12)	-0.2631 (9)	0.1729 (9)	0.4134 (6)	4.9 (2)
C(13)	-0.2995 (11)	0.1425 (11)	0.4684 (7)	6.4 (3)
C(14)	-0.2482 (12)	0.0697 (11)	0.5057 (7)	6.9 (3)
C(15)	-0.1633 (12)	0.0226 (12)	0.4878 (7)	7.3 (3)
C(16)	-0.1262 (10)	0.0499 (11)	0.4323 (7)	6.2 (3)
C(21)	-0.0471 (9)	0.2687 (9)	0.3450 (5)	4.6 (2)
C(22)	-0.0830 (12)	0.3547 (12)	0.3621 (7)	7.1 (3)
C(23)	-0.0168 (14)	0.4348 (14)	0.3761 (9)	8.9 (4)
C(24)	0.0917 (13)	0.4266 (13)	0.3727 (8)	7.7 (4)
C(25)	0.1337 (12)	0.3403 (13)	0.3625 (8)	7.4 (3)
C(26)	0.0654 (11)	0.2608 (11)	0.3474 (7)	6.9 (3)
C(31)	-0.3561 (8)	0.1798 (8)	0.1693 (5)	4.1 (2)
C(32)	-0.3136 (10)	0.1390 (10)	0.1196 (7)	6.0 (3)
C(33)	-0.3421 (12)	0.1719 (11)	0.0563 (7)	6.9 (3)
C(34)	-0.4195 (11)	0.2441 (11)	0.0419 (7)	7.0 (3)
C(35)	-0.4616 (11)	0.2852 (11)	0.0906 (7)	6.4 (3)
C(36)	-0.4286 (10)	0.2505 (10)	0.1549 (6)	5.5 (3)
N(1)	-0.2265 (8)	0.2068 (8)	0.2707 (5)	5.2 (2)
C(1)	-0.3172 (10)	0.1479 (10)	0.2378 (6)	5.5 (3)
H(12)	-0.3020	0.2345	0.3845	6.0
H(13)	-0.3652	0.1795	0.4849	6.0
H(14)	-0.2728	0.0455	0.5516	6.0
H(15)	-0.1204	-0.0368	0.5191	6.0
H(16)	-0.0567	0.0158	0.4171	6.0
H(22)	-0.1696	0.3614	0.3644	6.0
H(23)	-0.0475	0.5026	0.3877	6.0
H(24)	0.1408	0.4896	0.3772	6.0
H(25)	0.2234	0.3291	0.3653	6.0
H(26)	0.0990	0.1915	0.3365	6.0
H(32)	-0.2561	0.0796	0.1311	6.0
H(33)	-0.3100	0.1425	0.0149	6.0
H(34)	-0.4438	0.2688	-0.0084	6.0
H(35)	-0.5189	0.3453	0.0789	6.0
H(36)	-0.4632	0.2870	0.1930	6.0
H(1)	-0.2263	0.2783	0.2560	6.0
H(2)	-0.3809	0.1485	0.2664	6.0
H(3)	-0.2886	0.0721	0.2379	6.0

* An anisotropic temperature factor of the form:
 $\exp[-10^{-5}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$
 was used for the cobalt, chlorine and phosphorus atoms with coefficients:

	<i>b</i> ₁₁	<i>b</i> ₂₂	<i>b</i> ₃₃	<i>b</i> ₁₂	<i>b</i> ₁₃	<i>b</i> ₂₃
Co	807 (16)	555 (17)	299 (6)	0	146 (8)	0
Cl(1)	821 (22)	655 (27)	401 (10)	59 (20)	-76 (12)	-117 (13)
P(1)	682 (21)	605 (25)	246 (8)	9 (18)	89 (10)	-122 (11)

Table 4. Molecular geometry

(a) Intramolecular distances (Å)*

Co—Cl(1)	2.235 (4)	C(25)—C(26)	1.42 (2)
Co—O(1)	1.92 (1)	C(26)—C(21)	1.44 (2)
O(1)—P(1)	1.50 (1)	P(1)—N(1)	1.62 (1)
P(1)—C(11)	1.78 (1)	N(1)—C(1)	1.47 (2)
C(11)—C(12)	1.39 (2)	C(1)—C(31)	1.48 (2)
C(12)—C(13)	1.39 (2)	C(31)—C(32)	1.39 (2)
C(13)—C(14)	1.36 (2)	C(32)—C(33)	1.38 (2)
C(14)—C(15)	1.38 (2)	C(33)—C(34)	1.39 (2)
C(15)—C(16)	1.39 (2)	C(34)—C(35)	1.38 (2)
C(16)—C(11)	1.41 (2)	C(35)—C(36)	1.41 (2)
P(1)—C(21)	1.74 (1)	C(36)—C(31)	1.35 (2)
C(21)—C(22)	1.38 (2)	Co—P(1)	3.373 (5)
C(22)—C(23)	1.39 (2)	O(1)—O(1')	3.08 (2)
C(23)—C(24)	1.39 (2)	O(1)—Cl(1)	3.37 (1)
C(24)—C(25)	1.34 (2)	O(1)—Cl(1')	3.42 (1)

Table 4 (cont.)

(b) Intramolecular angles (°)*

O(1)—Co—Cl(1)	106.4 (3)
O(1)—Co—Cl(1')	110.4 (3)
O(1)—Co—O(1')	106.6 (7)
Cl(1)—Co—Cl(1')	116.5 (2)
Co—O(1)—P(1)	160.3 (7)
O(1)—P(1)—C(11)	106.9 (6)
O(1)—P(1)—C(21)	111.1 (7)
O(1)—P(1)—N(1)	116.1 (6)
C(11)—P(1)—C(21)	110.8 (6)
C(11)—P(1)—N(1)	108.7 (6)
C(21)—P(1)—N(1)	103.3 (6)
P(1)—C(11)—C(12)	121.2 (10)
P(1)—C(11)—C(16)	119.3 (10)
C(12)—C(11)—C(16)	119.5 (12)
C(11)—C(12)—C(13)	120.9 (14)
C(12)—C(13)—C(14)	118.9 (15)
C(13)—C(14)—C(15)	121.5 (16)
C(14)—C(15)—C(16)	120.7 (17)
C(15)—C(16)—C(11)	118.4 (14)
P(1)—C(21)—C(22)	124.5 (11)
P(1)—C(21)—C(26)	119.5 (12)
C(22)—C(21)—C(26)	116.0 (14)
C(21)—C(22)—C(23)	122.2 (16)
C(22)—C(23)—C(24)	120.0 (19)
C(23)—C(24)—C(25)	120.9 (19)
C(24)—C(25)—C(26)	119.6 (17)
C(25)—C(26)—C(21)	120.8 (16)
P(1)—N(1)—C(1)	124.6 (10)
N(1)—C(1)—C(31)	111.6 (12)
C(1)—C(31)—C(32)	119.0 (13)
C(1)—C(31)—C(36)	121.2 (12)
C(32)—C(31)—C(36)	119.7 (12)
C(31)—C(32)—C(33)	120.2 (15)
C(32)—C(33)—C(34)	119.8 (16)
C(33)—C(34)—C(35)	120.5 (16)
C(34)—C(35)—C(36)	118.2 (16)
C(35)—C(36)—C(31)	121.5 (14)

* Estimated standard deviations include cell parameter errors.

(c) Least-squares planes defined by atomic positions

In the following equations *X*, *Y* and *Z* refer to orthogonal coordinates obtained by the transformation:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a & 0 & c \cdot \cos \beta \\ 0 & b & 0 \\ 0 & 0 & c \cdot \sin \beta \end{bmatrix} \begin{bmatrix} x/a \\ y/b \\ z/c \end{bmatrix}$$

(i) Plane defined by C(11)—C(16)

$$0.5278X + 0.6416Y + 0.5566Z = 3.5478$$

Distances of atoms from plane (Å)

C(11), -0.01; C(12), 0.00; C(13), 0.02; C(14), -0.01; C(15), 0.00; C(16), 0.01; P(1), -0.08

(ii) Plane defined by C(21)—C(26)

$$-0.0174X - 0.2382Y + 0.9711Z = 6.0004$$

Distances of atoms from plane (Å)

C(21), 0.04; C(22), -0.02; C(23), -0.02; C(24), 0.05; C(25), -0.03; C(26), -0.01; P(1), 0.07

(iii) Plane defined by C(31)—C(36)

$$0.7192X + 0.6748Y + 0.1657Z = -1.5097$$

Distances of atoms from plane (Å)

C(31), 0.00; C(32), 0.01; C(33), -0.02; C(34), 0.01; C(35), 0.00; C(36), 0.00; C(1), -0.08

Description of the structure

The structure consists of discrete molecules of bis-(*N*-benzylidiphosphinic amide)dichlorocobalt(II).

The cobalt atom occupies the special fourfold position (on a twofold axis) of the space group $C2/c$ and the four bonds to chlorine and oxygen are in almost exactly tetrahedral directions.

The chlorine and oxygen atoms are close-packed, as is indicated by the fact that their interatomic distances are equal to the sum of the van der Waals radii. The tetrahedral angles, $\text{Cl}(1)\text{-Co-Cl}(1')$, $\text{O}(1)\text{-Co-O}(1')$, $\text{O}(1)\text{-Co-Cl}(1)$ and $\text{O}(1)\text{-Co-Cl}(1')$ are $116.5(2)$, $106.6(7)$, $106.4(3)$ and $110.4(3)^\circ$ respectively. (Atoms denoted by a prime are related to the atoms listed in Table 3 by the twofold axis.) The distortions in these angles from the tetrahedral value of $109^\circ 28'$ are due to the differences in the Co-O and Co-Cl bond lengths and in the van der Waals radii of chlorine and oxygen.

The interatomic distances Co-O and Co-Cl, found in this structure, are $1.92(1)$ and $2.235(4)$ Å respectively. The Co-O distances determined in the structures of the cobalt(II) diphenylmonothiothiophosphate polymer, $[\text{Co}(\text{Ph}_2\text{PSO})_2]_n$, (Bruckner, Calligaris, Nardin, Randaccio & Ripamonti, 1969) and the decammine- μ -peroxodicobalt cation, $[(\text{NH}_3)_5\text{CoO}_2\text{Co}(\text{NH}_3)_5]^{5+}$, (Schaefer & Marsh, 1966)

are $1.96(2)$ and $1.90(1)$ Å respectively, in reasonable agreement with the above value. The Co-Cl distance as found in di-*p*-toluidinedichlorocobalt(II), $(\text{H}_2\text{NC}_6\text{H}_4\text{CH}_3)_2\text{CoCl}_2$, (Malinovskii, 1957) is $2.26(1)$ Å. This value is within two standard deviations of the Co-Cl distance given above.

The Co-O-P angle is $160.3(7)^\circ$ whereas in $[\text{Co}(\text{Ph}_2\text{PSO})_2]_n$ these angles range between 139.9 and 153.3° . However, in the polymer the phosphinate groups are bridging groups, pairs of cobalt atoms being alternately singly and triply bridged, and this presumably accounts for the variation in the Co-O-P angles and the lower values compared to that found in the present complex.

The O-P bond distance, $1.50(1)$ Å, compares with $1.51(1)$ in $[\text{Co}(\text{Ph}_2\text{PSO})_2]_n$. The phosphorus atom in the molecule is tetrahedrally coordinated to two phenyl carbon atoms, one oxygen and one nitrogen atom, in a nearly regular arrangement; the third phenyl group is linked with the phosphorus atom through a $-\text{CH}_2\text{-NH}-$ linkage. The P-C bond distances, $1.78(1)$ and $1.74(1)$ Å, are marginally smaller than those found in *trans*-dimesitylbis(diethylphenylphosphine)cobalt(II), $1.835(17)$ and $1.817(15)$ Å (Owston & Rowe, 1963). The P-N distance, $1.62(1)$ Å, is comparable with that found in 6-chloro-5,6,7,12-tetrahydro-2,5,7,10-tetramethyldibenzo[*d.g.*] [1,3,2]diazophosphine 6-oxide, 1.644 Å (Cameron, 1972).

The phenyl C-C distances C(24)-C(25), $1.34(2)$ Å, and C(26)-C(21), $1.44(2)$ Å, show the largest divergences from the mean value, 1.39 Å; carbon atoms C(24), C(25) and C(26) have high isotropic thermal parameters compared with the other phenyl carbon atoms. It is probable that the reflexions to which these carbon atoms contribute most, have been affected by an accumulation of errors in the intensity measurements. The least-squares planes defined by the phenyl carbon atoms are given in Table 4. The planes defined by carbon atoms C(11)-C(16) inclusive and C(31)-C(36) inclusive are planar to within two estimated standard deviations, but the plane defined by C(21)-C(26) inclusive shows larger deviations presumably due to the same factors that give rise to the larger variations in the interatomic distances for these atoms.

In the crystal structure no two atoms in neighbouring molecules were found to be less than 3.5 Å apart indicating that the molecules are linked only by van der Waals forces. There was no indication of intramolecular hydrogen bonding, the N-Cl distances being greater than 3.5 Å.

Conclusion

Bis-(*N*-benzylidiphenylphosphinic amide)dichlorocobalt(II) contains a tetrahedrally coordinated Co(II) atom and the deep blue colour of the crystals is not therefore surprising. The absorption band of the $[\text{CoCl}_4]^{2-}$ anion, which is a representative tetrahedral species, is placed in the red part of the spectrum and is very

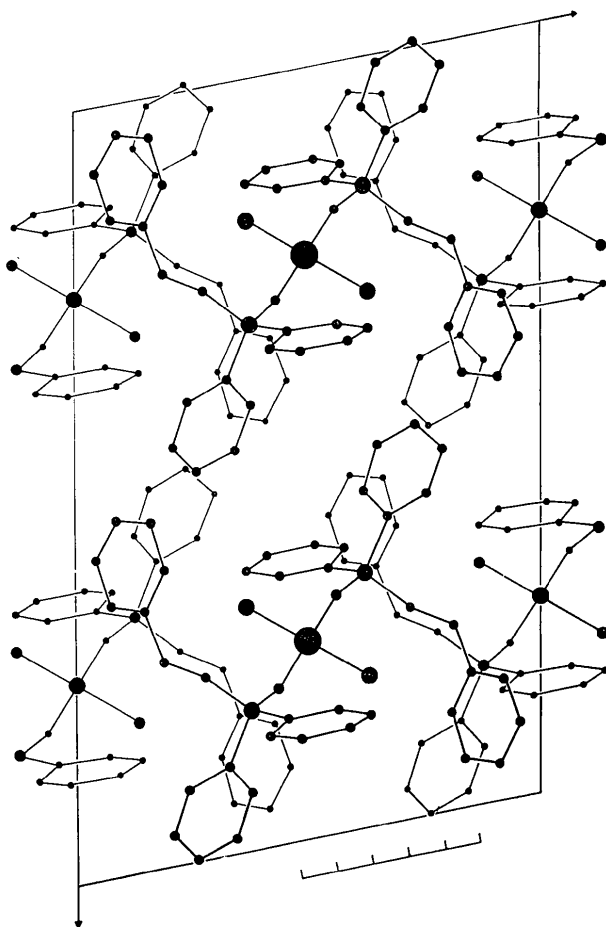


Fig. 3. The molecular packing as viewed along the *b* axis.

intense compared with the absorption of the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ cation (Cotton & Wilkinson, 1966). This accounts for the deep blue colour of this and most other tetrahedral Co(II) complexes.

The formation of the complex by Ibrahim can be explained by the initial removal of sulphur from the *p,p*-diphenyl-*N*-benzylphosphinothioic amide by cyclohexene (cyclohexene sulphide was found to be one of the products of the reaction), followed by the oxidation of the resultant trivalent phosphorus to give $(\text{C}_6\text{H}_5)_2\text{PONH}\cdot\text{CH}_2\text{C}_6\text{H}_5$. This ligand then binds *via* the oxygen atom to the cobalt to yield a tetrahedral complex of the type CoL_2X_2 where L is a monodentate neutral ligand and X a monodentate ionic ligand.

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Structure Cristalline et Moléculaire du Sel Complexe Thiocyanate de Plomb(II)–Tétraoxa-1,7,10,16-diaza-4,13-cyclooctadécane, $\text{Pb}(\text{SCN})_2\cdot\text{C}_{12}\text{H}_{26}\text{N}_2\text{O}_4$

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The determination of the crystal structure of the complex $\text{Pb}(\text{SCN})_2\cdot\text{C}_{12}\text{H}_{26}\text{N}_2\text{O}_4$ has shown that the lead ion lies in the plane of the four oxygen atoms, the two nitrogen atoms being on both sides. The coordination sphere of the lead ion is completed by the sulphur atoms of the thiocyanate anions, one above and one below the ring. The lead–nitrogen and lead–oxygen bonds are essentially electrostatic, whereas the lead–sulphur bonds have a covalent character. A direction in accordance with some experimental results is proposed for the orientation of the inert lone pair of the lead atom. The material crystallizes in space group *C2/c* with $a = 8.400$ (2) $b = 15.082$ (4) $c = 17.650$ (4) Å, $\beta = 106.33$ (3)°, $Z = 4$ and $D_m = 1.81 \pm 0.02$ g cm⁻³. The *R* value for 2180 reflexions is 0.047.

Introduction

Dans la suite le 1,7,10,16-tétraoxa-4,13-diazacyclooctadécane sera désigné par la nomenclature explicite (22). Le (22) est un macrocycle qui, par certaines de ses propriétés chimiques, ressemble aux polyéthers de Pedersen (1967). L'intérêt de ces macrocycles est considérable, car ils forment des complexes stables avec de nombreux cations, entre autres les cations alcalins et alcalino-terreux; ils présentent un comportement similaire aux produits naturels, notamment des antibiotiques du type cyclopeptide ou cyclodepsipeptide, d'où leur utilisation comme modèle. Nous avons déterminé la structure du complexe $(22)\text{Pb}(\text{SCN})_2$ afin d'étudier

l'influence de divers ions sur la conformation du cycle. L'étude structurale des complexes $(22)\text{KSCN}$ et $(22)\text{CuCl}_2$ a déjà été faite (Moras, Metz, Herceg & Weiss, 1972; Herceg & Weiss, 1973). Le remplacement de l'ion K^+ par l'ion Pb^{2+} de taille inférieure devrait produire un raccourcissement très net de la distance N–N, moins spectaculaire néanmoins que dans le complexe $(22)\text{CuCl}_2$.

Partie expérimentale

Le $(22)\text{Pb}(\text{SCN})_2$ a été préparé à partir d'une solution de thiocyanate de plomb et de (22) en quantités équimoléculaires dans un mélange méthanol–butanol. Il a