Crystal Structure of Chloro{bis-[2-(diethylamino)ethyl]-2-(diphenylphosphino)ethylamine}cobalt(II) Perchlorate

By **P. Dapporto** * and **Giovanna Fallani**, Laboratorio C.N.R. and Istituto di Chimica Generale e Inorganica dell'Università di Firenze, 39 Via J. Nardi, 50132 Firenze, Italy

The structure of the title complex has been determined by three-dimensional *X*-ray analysis from photographic data. The crystals are monoclinic, space group *Cc*, with $Z = 4$ in a unit cell of dimensions: $a = 8{\cdot}952 \pm 0{\cdot}003$, $b = 22{\cdot}812 \pm 0{\cdot}011$, $c = 15{\cdot}096 \pm 0{\cdot}004$ Å, $\beta = 104^\circ\ 50' \pm 2'$. The structure has been solved by Patterson and Fourier syntheses and refined by least-squares techniques to R 0·097 over 1115 independent observed reflections.

The complex consists of discrete cations and $\mathrm{ClO_4^-}$ anions. The cobalt atoms are five-co-ordinate, with an $\mathrm{N_3PCl}$ donor set. The geometry of the co-ordination polyhedron can be described as a remarkably distorted trigonal bipyramid. This geometry can be better considered as a ' capped tetrahedron ' with the central nitrogen atom of the tripod ligand unusually distant from the metal [Co–N(1) 2·30(3) Å]. Other distances in the co-ordination polyhedron are: Co–P 2·42(1), Co–N(2) 2·17(3), Co–N(3) 2·15(2), and Co–Cl = 2·28(1) Å.

DURING a study on nickel(II) and cobalt(II) complexes with quadridentate tripod ligands, a series of complexes having general formula $[\mathrm{M(n_3p)X]Y}$ was synthesised, where $\mathrm{n_3p}$ is the ligand bis-[2-(diethylamino)ethyl]-2-(diphenylphosphino)ethylamine $[\mathrm{Et_2N{\cdot}CH_2{\cdot}CH_2}]_2\mathrm{N{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2}$, M is $\mathrm{Ni^{II}}$ or $\mathrm{Co^{II}}$, X is Cl, Br, I, or NCS, and Y is I, $\mathrm{BPh_4}$, or $\mathrm{ClO_4}$.[1]

The complexes $[\mathrm{Ni(n_3p)X]BPh_4}$ (X = Cl or Br) were isolated either as paramagnetic trigonal bipyramidal or planar diamagnetic with one nitrogen atom of a chain nonbonded to the metal.[1,2]

All the complexes of cobalt(II) with this ligand are high-spin and their spectra are characteristic of a trigonal bipyramidal geometry.[1]

Recently the structures of the complexes of cobalt(II) with the quadridentate tripod ligands $\mathrm{np_3}$ [3] {tris-[2-(diphenylphosphino)ethyl]amine} and $\mathrm{nop_2}$ [4] {*NN*-bis-[2-(diphenylphosphino)ethyl]-2-methoxyethylamine}, containing three and two phosphorus atoms respectively, have been studied; they showed trigonal bipyramidal geometries remarkably distorted toward a ' capped tetrahedron '. Since the complex of cobalt(II) with the $\mathrm{Me_6tren}$ ligand {tris-[2-(dimethylamino)ethyl]amine}, having four nitrogens as donor atoms, $[\mathrm{Co(Me_6tren)Br]Br}$,[5] shows only a small distortion of this type, this distortion seems to be related to the presence of the phosphorus atoms. For this reason it seemed of interest to investigate whether the complexes of cobalt(II) with the ligand $\mathrm{n_3p}$, containing only one phosphorus atom, are also distorted toward a ' capped tetrahedron '. We have therefore undertaken the *X*-ray analysis of the complex $[\mathrm{Co(n_3p)Cl]ClO_4}$.

EXPERIMENTAL

Crystal Data.—$\mathrm{C_{26}H_{42}O_4Cl_2CoN_3P}$, $M = 621{\cdot}45$, Monoclinic, $a = 8{\cdot}952 \pm 0{\cdot}003$, $b = 22{\cdot}812 \pm 0{\cdot}011$, $c = 15{\cdot}096$

---

[1] L. Sacconi and R. Morassi, *J. Chem. Soc.* (*A*), 1969, 2904.

[2] I. Bertini, P. Dapporto, G. Fallani, and L. Sacconi, *Inorg. Chem.*, 1971, **10**, 1703.

[3] L. Sacconi, M. Di Vaira, and A. Bianchi, *J. Amer. Chem. Soc.*, 1970, **92**, 4465.

[4] P. Dapporto, G. Fallani, and L. Sacconi, *J. Co-ordination Chem.*, 1971, **1**, 269.

[5] M. Di Vaira and P. L. Orioli, *Inorg. Chem.*, 1967, **6**, 955.

± 0·004 Å, $\beta = 104° \, 50' \pm 2'$, $U = 2980{\cdot}05$ Å^3, $D_m = 1{\cdot}40$, $Z = 4$, $D_c = 1{\cdot}393$, $F(000) = 1308$. Space group *Cc*. Fe-K_α radiation, $\lambda = 1{\cdot}9373$ Å, μ(Fe-K_α) = 62·5 cm^{-1}.

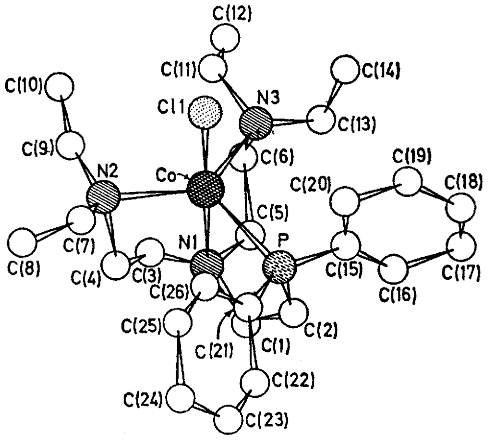
Data Collection.—Crystals of [Co(n$_3$p)Cl]ClO$_4$ were prepared from the ligand n$_3$p and CoCl$_2$ and Co(ClO$_4$)$_2$ salts in n-butyl alcohol. Cell parameters were determined by a least-squares refinement of 30 values of 2θ from *h0l* and *hk0* Weissenberg photographs. The crystal used for data collection had dimensions *ca.* 0·20 × 0·07 × 1·1 mm. The longest dimension was chosen as the rotation axis and doubly integrated Weissenberg photographs of the layers *hk*0—10 were taken on a Nonius camera by the multiple-film equi-inclination technique with manganese-filtered Fe-K_α radiation ($\lambda = 1{\cdot}9373$ Å). The intensities of 1115 reflections were measured on a Nonius microdensitometer, and corrected for Lorentz and polarization effects. No correction was made for absorption. Atomic scattering factors for cobalt, chlorine, phosphorus, oxygen, nitrogen, and carbon atoms were taken from ref. 6. For cobalt the real part of the anomalous dispersion correction was subtracted according to ref. 7. The hydrogen scattering factor was that of ref. 8.

TABLE 1

Positional parameters (×10^4) and anisotropic temperature factors [a] (×10^4) with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0	1665(2)	0	74(7)	8(1)	25(3)	−2(3)	10(4)	0(1)
Cl(1)	2175(14)	2010(5)	1011(9)	106(15)	14(2)	38(7)	−4(6)	6(8)	−1(3)
Cl(2) [b]	2010(13)	4434(4)	1078(8)	101(14)	11(2)	31(6)	−5(5)	14(7)	0(3)
P	−1793(14)	1726(5)	964(9)	92(15)	11(2)	29(6)	−2(5)	13(7)	−4(3)
O(1) [b]	1646(58)	3842(20)	927(36)	283(88)	28(11)	110(32)	6(27)	36(42)	2(16)
O(2) [b]	3611(50)	4502(20)	1715(32)	190(64)	38(12)	92(30)	−38(23)	19(34)	−1(15)
O(3) [b]	956(44)	4691(22)	1587(28)	158(51)	51(13)	61(23)	6(22)	63(25)	2(14)
O(4) [b]	1788(44)	4710(17)	227(24)	185(58)	28(9)	37(20)	−4(19)	21(27)	7(10)
N(1)	−2238(34)	1324(13)	−979(20)	68(40)	12(6)	4(16) [c]	−7(14)	9(19)	6(8)
N(2)	−308(38)	2342(14)	−1040(25)	72(47)	10(7)	44(21)	4(16)	4(25)	−4(10)
N(3)	693(40)	783(15)	−226(25)	101(44)	12(7)	29(18)	−9(16)	26(21)	−1(9)

[a] Anisotropic thermal factors are of the form: $\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$. [b] Atoms of the perchlorate ion. [c] This low value of β_{33} seems to be scarcely significant.



A perspective view of the configuration of the complex cation

Structure Determination.—The positions of the cobalt and the two chlorine atoms were obtained from a three-dimensional Patterson synthesis. Three three-dimensional Fourier syntheses showed the positions of all non-hydrogen atoms; *R* was then 0·22. Refinement was continued with the full-matrix least-squares programme of Busing and Levy adapted by Stewart for the IBM 7090 computer.[9]

TABLE 2

Positional parameters (×10^3) and isotropic temperature factors with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*	*B*/Å^2
C(1)	−368(5)	142(2)	−68(3)	3·2(0·9)
C(2)	−337(5)	129(2)	31(3)	2·7(0·9)
C(3)	−240(5)	165(2)	−184(3)	3·5(1·0)
C(4)	−198(5)	231(2)	−167(3)	3·5(1·0)
C(5)	−203(5)	67(2)	−109(3)	2·9(0·9)
C(6)	−34(6)	60(2)	−112(4)	4·1(1·0)
C(7)	−6(5)	290(2)	−65(3)	3·4(0·9)
C(8)	−38(6)	344(2)	−129(4)	4·4(1·1)
C(9)	77(5)	220(2)	−165(3)	2·7(0·8)
C(10)	252(6)	231(2)	−124(3)	3·8(1·0)
C(11)	225(6)	78(3)	−34(4)	4·8(1·2)
C(12)	288(7)	15(3)	−55(4)	5·0(1·2)
C(13)	45(6)	41(2)	56(4)	4·4(1·1)
C(14)	166(6)	46(2)	150(4)	4·7(1·2)
C(15)	−256(5)	248(2)	105(3)	2·7(0·9)
C(16)	−413(5)	259(2)	98(3)	2·8(0·8)
C(17)	−461(6)	318(2)	112(4)	4·5(1·1)
C(18)	−337(5)	360(2)	137(3)	3·5(1·0)
C(19)	−187(5)	348(2)	143(4)	3·9(1·0)
C(20)	−139(6)	291(2)	134(4)	4·8(1·2)
C(21)	−139(5)	143(2)	207(3)	2·5(0·8)
C(22)	−244(5)	105(2)	240(4)	4·3(1·1)
C(23)	−206(5)	88(2)	332(3)	3·7(1·0)
C(24)	−84(7)	101(3)	399(4)	5·1(1·3)
C(25)	24(6)	146(2)	368(4)	4·0(1·1)
C(26)	1(5)	163(2)	278(3)	3·1(0·9)

The weighting scheme used was $w = 1$ for reflections with $F_o \leqslant 70$ and $\sqrt{w} = 70/F_o$ for $F_o > 70$. A difference-Fourier synthesis calculated in an intermediate stage of refinement showed the positions of 20 hydrogen atoms (eleven of these atoms belong to methylene groups, five to methyl groups, and four to phenyl groups). These

---

[6] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[7] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[8] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 202.

[9] J. M. Stewart, Technical Report TR 64 6, University of Maryland, Computer Science Centre, 1964.

atoms were introduced in the subsequent calculations in fixed positions with an overall temperature factor of 5·0 Å^2. Individual isotropic temperature factors were used for the carbon atoms, whereas heavier atoms were allowed to vibrate anisotropically. Several cycles of refinement on positional and thermal parameters, and scale factors gave R 0·097. A final difference Fourier synthesis did not show any remarkable features.

The designation of atoms is shown in the Figure. The final values of the parameters and their standard deviations are reported in Tables 1—3.*

TABLE 3

Positional parameters ($\times 10^3$) of the hydrogen atoms

Atom	x/a	y/b	z/c
H(1,1)	−480	117	−90
H(2,1)	−381	145	81
H(3,1)	−375	170	−210
H(3,2)	−164	178	−213
H(5,1)	−195	60	−20
H(5,2)	−250	54	−161
H(6,1)	0	20	−130
H(8,1)	−150	353	−144
H(8,2)	39	347	−151
H(9,1)	80	184	−177
H(9,2)	66	260	−206
H(10,1)	294	289	−93
H(10,2)	310	215	−200
H(11,1)	300	90	30
H(12,1)	278	−45	−51
H(13,1)	−44	47	61
H(17)	−600	327	110
H(20)	−22	294	133
H(22)	−335	90	190
H(26)	35	200	295

Hydrogen atoms are numbered according to the carbon atom to which they are attached.

DISCUSSION

The structure consists of discrete [Co(n$_3$p)Cl]$^+$ and ClO$_4^-$ ions. The cobalt atoms are five-co-ordinate, linked to the four donor atoms of the n$_3$p ligand and to the chlorine atom. The central nitrogen atom of the tripod ligand lies at the apex of a distorted trigonal bipyramid, the phosphorus and the other two nitrogen atoms being in the equatorial positions. The other apex is occupied by the chlorine atom (Figure).

TABLE 4

Bond lengths (Å) and angles (°) about the metal atom, with estimated standard deviations in parentheses

(*a*) Distances

Co–Cl(1)	2·28(1)	Co–N(1)	2·30(3)
Co–P	2·42(1)	Co–N(2)	2·17(3)
		Co–N(3)	2·15(2)

(*b*) Angles

Cl(1)–Co–P	99·2(0·4)	P–Co–N(2)	114·2(0·9)
Cl(1)–Co–N(1)	177·8(0·8)	P–Co–N(3)	114·2(0·9)
Cl(1)–Co–N(2)	99·3(0·9)	N(1)–Co–N(2)	81·2(1·0)
Cl(1)–Co–N(3)	101·7(0·9)	N(1)–Co–N(3)	79·7(1·1)
P–Co–N(1)	78·6(0·7)	N(2)–Co–N(3)	122·5(1·0)

TABLE 5

Bond lengths (Å) and angles (°) in the perchlorate ion and in the ligand molecule with their estimated standard deviations

(*a*) Distances

Cl(2)–O(1)	1·39(5)	C(5)–C(6)	1·53(7)
Cl(2)–O(2)	1·51(4)	C(7)–C(8)	1·55(7)
Cl(2)–O(3)	1·49(4)	C(9)–C(10)	1·55(7)
Cl(2)–O(4)	1·40(4)	C(11)–C(12)	1·60(9)
P–C(2)	1·79(5)	C(13)–C(14)	1·55(8)
P–C(15)	1·88(5)	C(15)–C(16)	1·40(6)
P–C(21)	1·75(5)	C(15)–C(20)	1·42(7)
N(1)–C(1)	1·49(5)	C(16)–C(17)	1·44(7)
N(1)–C(3)	1·48(5)	C(17)–C(18)	1·44(7)
N(1)–C(5)	1·51(5)	C(18)–C(19)	1·35(6)
N(2)–C(4)	1·55(5)	C(19)–C(20)	1·39(7)
N(2)–C(7)	1·40(5)	C(21)–C(22)	1·46(6)
N(2)–C(9)	1·53(5)	C(21)–C(26)	1·50(6)
N(3)–C(6)	1·48(6)	C(22)–C(23)	1·40(7)
N(3)–C(11)	1·45(6)	C(23)–C(24)	1·32(7)
N(3)–C(13)	1·52(6)	C(24)–C(25)	1·56(8)
C(1)–C(2)	1·48(6)	C(25)–C(26)	1·38(7)
C(3)–C(4)	1·56(6)		

(*b*) Angles

O(1)–Cl(2)–O(2)	110(3)	C(11)–N(3)–C(13)	115(4)
O(1)–Cl(2)–O(3)	109(3)	C(6)–N(3)–C(13)	112(3)
O(1)–Cl(2)–O(4)	109(3)	N(1)–C(1)–C(2)	109(3)
O(2)–Cl(2)· O(3)	105(2)	P–C(2)–C(1)	111(3)
O(2)–Cl(2)· O(4)	115(2)	N(1)–C(3)–C(4)	113(3)
O(3)–Cl(2)· O(4)	109(2)	N(2)–C(4)–C(3)	107(3)
Co–P–C(2)	101(2)	N(1)–C(5)–C(6)	105(3)
Co–P–C(15)	114(1)	N(3)–C(6)–C(5)	110(4)
Co–P–C(21)	123(1)	N(2)–C(7)–C(8)	119(4)
C(2)–P–C(15)	107(2)	N(2)–C(9)–C(10)	117(3)
C(2)–P–C(21)	105(2)	N(3)–C(11)–C(12)	115(5)
C(15)–P–C(21)	106(2)	N(3)–C(13)–C(14)	118(4)
Co–N(1)–C(1)	116(2)	P–C(15)–C(16)	122(3)
Co–N(1)–C(3)	105(2)	P–C(15)–C(20)	114(3)
Co–N(1)–C(5)	107(2)	C(16)–C(15)–C(20)	123(4)
C(1)–N(1)–C(3)	107(3)	C(15)–C(16)–C(17)	119(4)
C(1)–N(1)–C(5)	109(3)	C(16)–C(17)–C(18)	115(4)
C(3)–N(1)–C(5)	113(3)	C(17)–C(18)–C(19)	125(4)
Co–N(2)–C(4)	110(2)	C(18)–C(19)–C(20)	121(4)
Co–N(2)–C(7)	112(2)	C(15)–C(20)–C(19)	117(4)
Co–N(2)–C(9)	108(2)	P–C(21)–C(22)	124(3)
C(4)–N(2)–C(7)	109(3)	P–C(21)–C(26)	120(3)
C(4)–N(2)–C(9)	106(3)	C(22)–C(21)–C(26)	116(4)
C(7)–N(2)–C(9)	113(3)	C(21)–C(22)–C(23)	119(4)
Co–N(3)–C(6)	105(2)	C(22)–C(23)–C(24)	130(5)
Co–N(3)–C(11)	110(3)	C(23)–C(24)–C(25)	112(5)
Co–N(3)–C(13)	107(2)	C(24)–C(25)–C(26)	122(5)
C(6)–N(3)–C(11)	107(4)	C(21)–C(26)–C(25)	120(4)

Tables 4 and 5 list intramolecular distances and angles in the complex cation and in the ClO$_4^-$ ion with their standard deviations.

The geometry of the co-ordination polyhedron of this complex shows a remarkable distortion toward a ' capped tetrahedron ', as already found in other five-co-ordinate cobalt(II) complexes.[3,4] In fact, the cobalt atom is displaced from the equatorial plane, which has equation $7{\cdot}216x + 8{\cdot}817y + 8{\cdot}073z = 1$ (monoclinic co-ordinates), by 0·39 Å toward the chlorine atom. Consequently the Cl–Co–L(eq) angles (L = donor atom) are all larger than 90° [Cl–Co–N(2) 99·3(0·9), Cl–Co–N(3) 101·7(0·9), and Cl–Co–P 99·2(0·4)°], and the Co–N(1) distance [2·30(3) Å] is unusually long for a Co–N bond.

It is of interest to compare the size of this distortion

---

* Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20,398 (6 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

with that found in the complexes of cobalt(II) with the previously mentioned ligands Me_6tren,[5] nop_2,[4] and np_3.[3] Table 6 reports the value of the Co–N(ap) distance and the mean X–Co–L(eq) angle (X = halogen) for each of these structures; we can observe that both these values (therefore the tetrahedral distortion) increase with the number of equatorial phosphorus atoms.

TABLE 6

Compound	Donor set	Number of P atoms	Co–N(ap)	Mean angle X–Co–L(eq) *
$[Co(Me_6tren)Br]Br$	N_4		2·15 Å	99°
$[Co(n_3p)Cl]ClO_4$	N_3P	1	2·30	100
$[Co(nop_2)Cl]PF_6$	NOP_2	2	2·43	103
$[Co(np_3)Cl]PF_6$	NP_3	3	2·67	105

* X = Halogen.

The Co–P distance [2·41(1) Å] in the $[Co(n_3p)Cl]ClO_4$ complex is longer than the Co–P(eq) distances found in other trigonal bipyramidal cobalt(II) complexes {2·28 (mean) in $[CoCl(qp)]PPh_4$[10] and 2·18 Å in $Co(dpp)_3Br_2$,[11] where qp is the ligand tris-(*o*-diphenylphosphinophenyl)phosphine and dpp is diphenylphosphine}. The increase in the Co–P(eq) distance is not peculiar to the $[Co(n_3p)Cl]ClO_4$ complex, being common to all the five-co-ordinate complexes with tetrahedral distortion. The mean value of the Co–P(eq) distances is 2·37 in $[Co(np_3)Cl]PF_6$[3] and 2·42 Å in $[Co(nop_2)Cl]PF_6$.[4] The high-spin state of these complexes can be a factor contributing to these long distances.

The Co–Cl(1) distance [2·28(1) Å] is in the range of values (2·2—2·3 Å) found for Co–Cl distances in other five-co-ordinate complexes.[3,4,12,13] The distances and angles in the ligand molecule and in the ClO_4^- ion also appear to be normal within 3 σ.

There are some short contacts, especially between oxygen atoms of the ClO_4^- ions and carbon atoms of the n_3p ligand; those <3·5 Å are reported in Table 7.

TABLE 7

Intermolecular contacts <3·5 Å

O(1) ··· C(7)	3·28	O(1) ··· $C(3^{II})$	3·44
O(1) ··· C(8)	3·50	O(2) ··· $C(6^{II})$	3·18
O(2) ··· $C(13^{I})$	3·39	C(9) ··· $C(17^{III})$	3·41
O(4) ··· $C(5^{I})$	3·31		

Superscripts refer to the following equivalent positions relative to the reference molecule at *x*, *y*, *z*:

I $x + \frac{1}{2}, y + \frac{1}{2}, z$
II $x + \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$
III $x + \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$

We thank Professor L. Sacconi for his interest in the course of the investigation and for helpful discussions, and D. Masi for technical assistance.

[1/2485 *Received*, 29*th December*, 1971]

---

[10] T. L. Blundell, H. M. Powell, and L. M. Venanzi, *Chem. Comm.*, 1967, 763.

[11] J. A. Bertrand and D. L. Plymale, *Inorg. Chem.*, 1966, **5**, 879.

[12] Z. Dori, R. Eisenberg, and H. B. Gray, *Inorg. Chem.*, 1967, **6**, 483.

[13] M. Di Vaira and P. L. Orioli, *Inorg. Chem.*, 1969, **8**, 2729.