Crystal Structure of Chloro[dodeca(dimethylamino)cyclohexaphosphazene-*NNNN*]cobalt(II) Di-μ-chloro-bis[dichlorocobaltate(II)]–Bischloroform

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Crystals of the title compound are monoclinic, a = 13·017, b = 17·439, c = 23·879 Å, β = 93·89°, Z = 2, space group $P2_1/c$. The structure was determined from diffractometer data by a combination of direct and Patterson methods, and refined by full-matrix least-squares procedures to R 0·093 for 2695 observed reflexions. The cation is similar to that in a related copper complex, cobalt being bonded to four nitrogen atoms of the phosphazene ring and to one chlorine atom in a configuration between a square pyramid and trigonal bipyramid. The anionic cobalt is present as the hitherto unrecognized centrosymmetrical $Co_2Cl_6^{2-}$ ion, in which two chlorine bridges complete tetrahedral co-ordination about the cobalt atoms.

THE copper chloride complex of dodeca(dimethylamino)cyclohexaphosphazene of composition LCu_2Cl_3 contains the ion $[N_6P_6(NMe)_{12}CuCl]^+$, with the copper atom bonded to four nitrogen atoms of the phosphazene ring and to a chlorine atom, in a configuration between a square pyramid and a trigonal bipyramid.[1] Complexes of the general formula $L(2MCl_2)$ have been obtained,[2] and we describe the structure of the compound with M = Co.

EXPERIMENTAL

Dark blue crystals of the cobalt complex were obtained from chloroform–carbon tetrachloride as the chloroform solvate of composition $L,2CoCl_2,CHCl_3$; the structure analysis later gave the formula as $[N_6P_6(NMe_2)_{12}CoCl^+]_2$-$[Co_2Cl_6{}^{2-}]$,$2CHCl_3$.

Crystal Data.—$C_{50}H_{146}Cl_{14}Co_4N_{36}P_{12}$, M = 2355·7, Monoclinic, a = 13·017, b = 17·439, c = 23·879 Å, β = 93·89°, U = 5408·1 Å^3, Z = 2. D_c = 1·446, $F(000)$ = 2448. Mo-$K\alpha$ radiation, λ = 0·7107 Å, μ(Mo-K_α) = 12 cm^{-1}. Space group $P2_1/c$ (C_2^5).

The intensities of the reflexions were measured by diffractometer methods as for the copper complex.[1] Of 4870 reflexions with $2\theta \leqslant 40°$, 2695 were classified as observed.

Structure Analysis.—The analysis was complicated by the weakness of k odd reflexions. In the initial stages, by both Patterson and direct methods, the cation was located lying on either a two-fold axis in $P2/c$, with an identically oriented cation displaced by $b/2$, or on a two-fold screw axis in $P2_1/c$· The unit cell is rather similar to that of the copper complex,[1] but with a doubled b axis. The pseudo-symmetrical electron-density maps could not be interpreted in terms of a reasonable anion; the difficulty was later shown to be a result of the presence of chloroform molecules so situated and oriented in the cell that their chlorine atom positions were related by a pseudo-two-fold axis to some of those of the anion (Figure 1). The structure was finally solved from a difference Patterson function, computed with coefficients $[F_0 - F(\text{cation})]^2$, and the presence of the $Co_2Cl_6{}^{2-}$ anion and chloroform solvent in space group $P2_1/c$ was established.

Refinement by full-matrix least-squares methods gave a final R of 0·093 for the 2695 observed reflexions. Scattering factors were from ref. 3, and the weighting scheme was adjusted to give constant average values of $w(F_o - F_c)^2$; $\sqrt{w} = 1$ when $|F_o| \leqslant 60$, $\sqrt{w} = 60/|F_o|$ when $|F_o| > 60$, $\sqrt{w} = 0·1$ for unobserved reflexions (with $|F_o|$ taken as

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[1] W. C. Marsh and J. Trotter, *J. Chem. Soc.* (*A*), 1971, 1482.

[2] W. Harrison, N. L. Paddock, J. Trotter, and J. N. Wingfield, *J.C.S. Chem. Comm.*, 1972, 23.

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

the actual measured value, minimum zero). Final positional and thermal parameters are given in Table 1, bond lengths and angles in Table 2, and measured and calculated structure factors are listed in Supplementary Publication No. SUP 20499 (6 pp., 1 microfiche).*

DISCUSSION

The complex is ionic, and the crystal contains cobalt bonded to the phosphazene ring in the cation, the previously unrecognized $Co_2Cl_6^{2-}$ anion, and chloroform solvent (Figure 1).

TABLE 1

Final positional parameters (fractional × 10^4), with standard deviations in parentheses, and thermal parameters *

(*a*) Cation

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Co(1)	4986(1)	0983(1)	2542(1)	467	227	113	−6	2	18
Cl(1)	4984(3)	−0318(2)	2544(2)	987	210	291	−3	135	−2
P(1)	3011(3)	1579(2)	2340(1)	442	267	149	12	15	−3
P(2)	3521(3)	1454(2)	3558(1)	596	299	115	−5	45	13
P(3)	5675(3)	1883(2)	3722(1)	584	276	141	−25	−7	−5
P(4)	6967(3)	1567(2)	2738(1)	483	295	146	−10	−21	35
P(5)	6445(3)	1385(3)	1524(2)	446	438	142	10	75	1
P(6)	4314(3)	1851(2)	1352(1)	607	270	112	51	−12	20
N(1)	3461(7)	1189(6)	2917(4)	437	280	163	−29	34	21
N(2)	4475(8)	1942(7)	3764(4)	663	416	133	−1	−25	−82
N(3)	5954(7)	1582(6)	3106(4)	443	274	105	40	26	−23
N(4)	6508(7)	1152(7)	2182(4)	362	516	115	31	4	87
N(5)	5510(8)	1915(7)	1319(4)	775	418	120	−127	47	31
N(6)	4023(7)	1558(6)	1971(4)	546	261	115	5	−23	−13

	x	y	z	B/Å^2		x	y	z	B/Å^2
N(7)	2029(11)	1065(9)	2106(6)	4·6	C(8)	3436(17)	0725(14)	4546(9)	7·5
N(8)	2563(12)	2462(9)	2351(6)	4·5	C(9)	3335(16)	−0151(13)	3683(9)	6·0
N(9)	2495(12)	1955(10)	3704(6)	5·0	C(10)	6145(17)	1476(13)	4803(9)	6·5
N(10)	3486(11)	0636(10)	3904(6)	5·2	C(11)	6317(15)	0462(13)	4075(8)	6·1
N(11)	6277(11)	1298(10)	4186(6)	4·9	C(12)	5510(16)	3430(13)	3869(8)	6·0
N(12)	6149(12)	2731(9)	3914(6)	4·8	C(13)	7243(17)	2872(13)	4093(9)	7·1
N(13)	7938(12)	1052(9)	2988(6)	5·2	C(14)	8585(17)	1309(14)	3509(10)	7·4
N(14)	7424(12)	2441(9)	2706(6)	4·6	C(15)	8063(17)	0215(15)	2843(10)	7·1
N(15)	7488(12)	1847(10)	1367(6)	5·2	C(16)	8505(17)	2631(13)	2572(9)	7·2
N(16)	6381(11)	0553(9)	1188(6)	5·2	C(17)	6692(16)	3093(13)	2570(8)	6·0
N(17)	3703(11)	1269(10)	0900(6)	4·6	C(18)	8483(17)	1412(14)	1406(9)	6·8
N(18)	3859(12)	2697(9)	1153(6)	4·8	C(19)	7458(18)	2516(16)	0965(10)	8·3
C(2)	1405(17)	1254(14)	1566(10)	7·3	C(20)	6330(16)	0618(14)	0548(9)	7·1
C(3)	1893(16)	0239(14)	2267(9)	6·7	C(21)	6730(17)	−0194(14)	1414(9)	6·6
C(4)	3296(16)	3106(13)	2489(8)	6·0	C(22)	3674(16)	1441(13)	0287(9)	6·1
C(5)	1475(17)	2645(13)	2475(9)	7·0	C(23)	3651(15)	0426(13)	1032(8)	5·8
C(6)	1460(18)	1575(14)	3675(10)	6·7	C(24)	45191(6)	3379(13)	1177(9)	6·3
C(7)	2524(16)	2665(14)	4064(9)	7·1	C(25)	2775(16)	2835(12)	0968(8)	5·6

(*b*) Anion

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Co(2)	0107(2)	4202(2)	4647(1)	827	778	306	103	95	156
Cl(2)	0162(5)	4124(5)	3714(2)	1708	1381	321	476	23	37
Cl(3)	−1276(3)	4927(4)	4920(2)	569	1105	441	100	113	120
Cl(4)	0298(6)	3098(4)	5111(3)	2874	785	581	314	409	309

(*c*) Chloroform solvent

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	−0034(11)	3760(11)	0569(7)	491	873	312	−135	1	−21
Cl(5)	0988(5)	4248(5)	0392(4)	1272	1365	950	68	310	418
Cl(6)	−1121(6)	3919(5)	0213(4)	1715	1493	762	−285	−254	479
Cl(7)	−0157(7)	3882(6)	1300(3)	2205	1962	546	−685	−24	−61

* Anisotropic thermal parameters are in the form: $\exp -10^{-5} (b_{11}h^2 + b_{21}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)$.

The cation is similar to that in the related copper complex.[1] The cobalt atom, Co(1), is co-ordinated to four nitrogen atoms of the phosphazene ring and to a chlorine atom. The five-fold co-ordination can be described as a distorted square pyramid (chlorine apical), or as a distorted trigonal bipyramid, with N(1) and N(4) axial. The latter is perhaps a closer description, since all the equatorial angles are very close to 120°, with N(ax)–Co–N(ax) 163° (Table 2). The Co(1)–Cl bond distance, 2·268(4) Å, is close to the corresponding distance in the copper compound. The Co–N bond lengths are 2·064(10) and 2·051(10) Å for the equatorial bonds of the trigonal bipyramid, and 2·262(10) and 2·233(9) Å for the axial bonds. The difference of 0·19 Å between the mean axial and equatorial bond lengths is highly significant, and larger than and in the opposite sense to the difference in the copper compound (Figure 2). There is no immediate explanation for these variations.

The phosphazene ring has very nearly C_2 symmetry

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* 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).

(crystallographically required in the copper complex[1]), and the mean ring parameters are summarized in Figure 3. All of the features noted for the copper compound are confirmed, and established more definitely since the accuracy is much better in the present analysis. The P–N ring bonds involving nitrogen atoms bonded to cobalt, 1·594—1·634, mean 1·618(6) Å, are longer than those involving nitrogen atoms not bonded to cobalt, 1·557—1·579, mean 1·570(6) Å, the mean values differing by 6σ. The N–P–N angles are all smaller than in the parent phosphazene,[4] the reduction being most marked at P(1) and P(4), mean 100·9°, as are the P–N–P angles mean 135·0°. The exocyclic P–N bonds are all shorter than single bonds, with those at P(1) and P(4), mean 1·637(5), slightly shorter than those at the other phosphorus atoms, mean 1·652(2) Å. All these details are explicable in terms of π-bonding theories, as for the copper complex.[1]

TABLE 2

Bond lengths (Å) and valency angles (°), with standard deviations in parentheses (σ for the mean values is the larger of the least-squares value and the r.m.s. deviation from the mean)

(*a*) Cation

(i) Co(1) co-ordination

Co(1)–N(1)	2·262(9)	N(1)–Co(1)–N(4)	163·3(4)
Co(1)–N(4)	2·233(10)		
Co(1)–N(3)	2·064(10)		
Co(1)–N(6)	2·051(10)	N(1)–Co(1)–N(3)	100·1(3)
Co(1)–Cl(1)	2·268(4)	N(1)–Co(1)–N(6)	70·9(4)
		N(1)–Co(1)–Cl(1)	99·0(3)
N(3)–Co(1)–N(6)	120·3(4)	N(4)–Co(1)–N(6)	101·4(4)
N(3)–Co(1)–Cl(1)	120·4(3)	N(4)–Co(1)–N(3)	70·5(4)
N(6)–Co(1)–Cl(1)	119·3(3)	N(4)–Co(1)–Cl(1)	97·7(3)

(ii) Phosphazene ring

N(1)–P(1)	1·613(10)	P(1)–N(7)	1·629(4)
N(1)–P(2)	1·596(10)	P(1)–N(8)	1·648(4)
N(3)–P(3)	1·626(10)	P(4)–N(13)	1·630(4)
N(3)–P(4)	1·634(9)	P(4)–N(14)	1·640(4)
N(4)–P(4)	1·594(11)	Mean	1·637(5)
N(4)–P(5)	1·618(10)		
N(6)–P(6)	1·633(10)	P(2)–N(9)	1·653(4)
N(6)–P(1)	1·633(10)	P(2)–N(10)	1·651(4)
Mean	1·618(6)	P(3)–N(11)	1·661(4)
		P(3)–N(12)	1·656(4)
N(2)–P(2)	1·557(11)	P(5)–N(15)	1·643(4)
N(2)–P(3)	1·575(11)	P(5)–N(16)	1·658(4)
N(5)–P(5)	1·579(12)	P(6)–N(17)	1·647(4)
N(5)–P(6)	1·568(11)	P(6)–N(18)	1·648(4)
Mean	1·570(6)	Mean	1·652(2)
N(6)–P(1)–N(1)	101·1(5)	P(1)–N(1)–P(2)	133·6(7)
N(1)–P(2)–N(2)	116·6(5)	P(2)–N(2)–P(3)	135·8(7)
N(2)–P(3)–N(3)	111·2(5)	P(3)–N(3)–P(4)	136·9(7)
N(3)–P(4)–N(4)	100·7(5)	P(4)–N(4)–P(5)	133·4(7)
N(4)–P(5)–N(5)	115·7(5)	P(5)–N(5)–P(6)	133·6(8)
N(5)–P(6)–N(6)	111·1(5)	P(6)–N(6)–P(1)	136·6(7)
Co(1)–N(1)–P(1)	90·3(4)	Co(1)–N(4)–P(4)	91·7(4)
Co(1)–N(1)–P(2)	116·0(5)	Co(1)–N(4)–P(5)	114·8(5)
Co(1)–N(3)–P(3)	126·1(5)	Co(1)–N(6)–P(6)	125·9(6)
Co(1)–N(3)–P(4)	96·9(5)	Co(1)–N(6)–P(1)	97·6(5)

Exocyclic angles at P

	N(*exo*)-P-N(*exo*)	N(*exo*)-P-N(ring)
P(1)	104·4	107·0, 119·3, 116·5, 109·2
P(2)	107·5	111·5, 103·1, 106·5, 111·3
P(3)	102·4	115·0, 106·1, 106·3, 115·8
P(4)	104·7	116·5, 108·6, 107·1, 120·0
P(5)	109·5	110·8, 104·4, 105·9, 110·5
P(6)	102·3	116·5, 105·1, 105·6, 116·1

N–C 1·465—1·548, mean 1·499; P–N–C 114—129, mean 121; C–N–C 112—116, mean 114; sum of three angles at exocyclic N 349—360, mean 356

(*b*) Anion

See Figure 4

(*c*) Chloroform solvent

C(1)–Cl(5)	1·659(16)	Cl(5)–C(1)–Cl(6)	117·7(12)
C(1)–Cl(6)	1·625(16)	Cl(5)–C(1)–Cl(7)	108·5(10)
C(1)–Cl(7)	1·776(17)	Cl(6)–C(1)–Cl(7)	111·1(10)
Mean	1·69(5)	Mean	112(3)

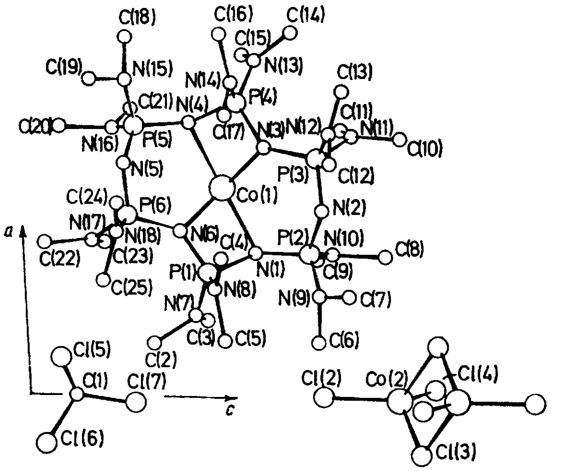

FIGURE 1 Structure viewed along *b*. Only atoms in the lower part of the cell are shown; Cl(1) is directly below Co(1)

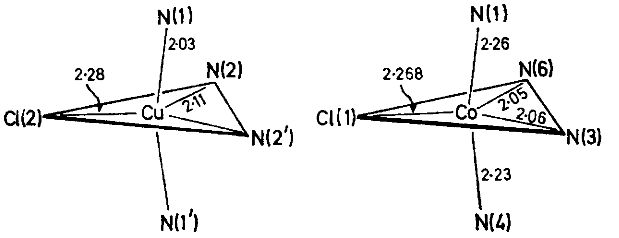

FIGURE 2 Metal atom co-ordinations in $N_6P_6(NMe_2)_{12}MCl^+$ ions, M = Cu and Co

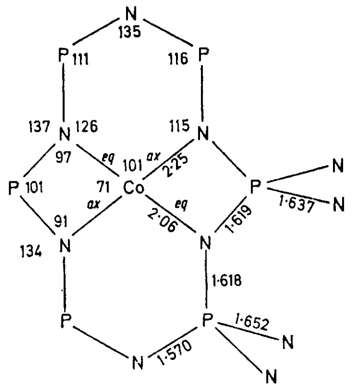

FIGURE 3 Mean dimensions of the phosphazene ring (Å and °)

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[4] A. J. Wagner and A. Vos, *Acta Cryst.*, 1971, **B24**, 1423.

The dimethylamino-groups are all not far from planar, the sums of the valency angles at the nitrogen atoms varying from 353—360°, except for 349° at N(11). The N–C bond lengths are in the range 1·465—1·548, mean 1·499 Å.

In the centrosymmetrical $Co_2Cl_6^{2-}$ anion (Figure 4) two chlorine bridges complete tetrahedral co-ordination about the cobalt atoms. The thermal parameters of the chlorine atoms are large, corresponding to a maximum root-mean-square displacement of *ca.* 0·5 Å. No interpretation in terms of disorder seems reasonable, and it is likely that this is a real thermal effect, the anion being rather loosely held in the structure, as is the $CuCl_2^-$ ion in the copper complex.[1] The Co–Cl(bridging) distances, mean 2·336 Å, are longer than the Co–Cl(terminal) lengths, mean 2·233 Å. The Cl(bridging)–Co–Cl(bridging) angle is 90·9°, with the other angles at the cobalt atom in the range 107·1—115·7°. The chloroform solvent molecule is also undergoing quite large thermal vibrations, and the bond lengths and angles show fairly wide variations, mean C–Cl 1·69(5) Å (with no librational correction) and mean Cl–C–Cl 112(3)°.

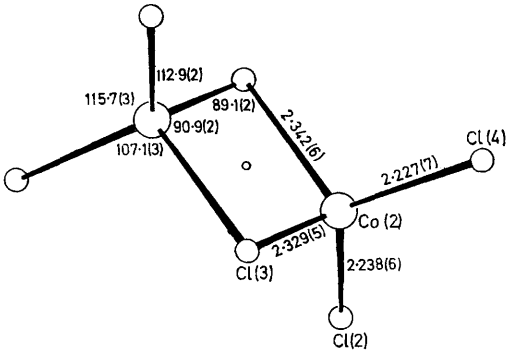

FIGURE 4 The $Co_2Cl_6^{2-}$ anion; angles not shown are Cl(2)–Co–Cl(3′) 114·5(3) and Cl(3)–Co–Cl(4) 113·1(2)°; Co (2) · · · Co(2′) is 3·277(6) Å

The packing in the structure is quite similar to that in the copper complex,[1] but in the cobalt compound alternate anions along *b* are replaced by two chloroform solvent molecules, resulting in a doubled *b* axis. Intermolecular distances correspond to van der Waals forces, as for the copper compound; the shortest contact between two chloroform molecules is Cl · · · Cl 3·52 Å.

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