The Crystal and Molecular Structure of a Paramagnetic, Five-co-ordinate Cobalt(III) Compound: {*NN*′-Bis[α-(2-amino-5-chlorophenyl)benzylidene]-ethane-1,2-diaminato(2-)-*NN*′*N*″*N*‴}chlorocobalt(III)–Chloroform–Dichloromethane (1/0.5/0.5)

By **Neil A. Bailey,* E. Donald McKenzie,** and **James M. Worthington,** Chemistry Department, The University, Sheffield S3 7HF

Crystals of the title compound are monoclinic, $a = 6.92(2)$, $b = 16.19(5)$, $c = 26.69(8)$ Å, $\beta = 95.3(1)°$, space group $P2_1/c$. A three dimensional *X*-ray analysis of the structure was made with counter data (1 303 independent reflections). The structure was solved by conventional Patterson and Fourier methods and refined by block-diagonal least squares to R 0.088. The [Co(N_4)Cl] co-ordination polyhedron is square pyramidal (Co–N 1.84—1.92 Å); the cobalt atom lies 0.19 Å out of the N_4 plane in the direction of the axial chlorine atom; there is an unusually long Co–Cl bond [2.507(2) Å]. The quadridentate ligand has a stepped conformation with the phenylene moieties approximately parallel and inclined at 173.9 and 172.6° to the N_4 plane; the central chelate ring has a symmetrical *gauche* conformation.

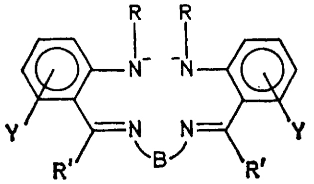
WE have recently reported [1,2] the preparations and some properties of paramagnetic cobalt(III) compounds of general type [Co(N_4)X] [where (N_4) represents the quadridentate dianionic ligands (1), and X is a halogen] in which the $S = 1$ state is thermally populated.[2] The initial assumption that these compounds were five-co-ordinate has now been established by an *X*-ray structural

---

[1] B. M. Higson and E. D. McKenzie, *J.C.S. Dalton*, 1972, **269**; E. D. McKenzie and J. M. Worthington, *Inorg. Chim. Acta*, 1976, **16**, 9.

[2] M. Gerloch, B. M. Higson, and E. D. McKenzie, *Chem. Comm.*, 1971, 1149.

analysis. A preliminary communication has appeared,[3] and here we report the full details.



(1) R = H, R′ = Ph, B = $CH_2 \cdot CH_2$, Y = 5-Cl

EXPERIMENTAL

Considerable difficulty was encountered in obtaining reasonable crystals of any of the paramagnetic compounds. The compound chosen, because it gave the best crystals, was [Co(cadmi)Cl] [cadmi = (1); R = H, R^1 = Ph, B = $(CH_2)_2$ and Y = 5-Cl]. Opaque, green, needle-shaped crystals were obtained by oxidising the cobalt(II) compound[4] in dichloromethane with chloroform. Decay of crystallinity with solvent loss was prevented by mounting them direct from the mother-liquor in thin-walled glass capillaries and then coating them with ' Formvar ' (polyvinylformal) to act as both adhesive and protective film; the crystal eventually used for data collection (dimensions *ca.* 0.68 × 0.14 × 0.10 mm) was still rather imperfect, and each diffraction maximum was split into two major peaks, the separation of which was dependent on the crystal orientation. This markedly affected the precision to which the cell constants could be determined, but data were obtained which were adequate for the determination of the molecular structure.

Crystal Data.—$C_{28}H_{22}CoCl_3N_4 \cdot \frac{1}{2}CHCl_3 \cdot \frac{1}{2}CH_2Cl_2$, M = 682.1, Monoclinic, a = 6.92(2), b = 16.19(5), c = 26.69(8) Å, β = 95.3(1)°, U = 2 977(15) Å^3, D_m = 1.50 g cm^{-3} (by flotation), Z = 4, D_c = 1.52 g cm^{-3}, $F(000)$ = 1 360. Space group $P2_1/c$ (C^5_{2h}, No. 14) from systematic absences. Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 24.7 cm^{-1}.

X-Ray data with $6.5 < 2\theta < 50°$ were collected from a crystal mounted up the a axis on a Stoe Stadi-2 automatic diffractometer in stationary-counter–moving-crystal mode using graphite-monochromated Mo-K_α radiation.

For each reflection, angular step-scan ranges were systematically varied to allow for variations in peak-width, and a counting time of 1.0 s was used for each 0.01° increment of the scan. Background counts were accumulated for 30 s at each extremity of the scan.

Reflections with intensity $I < 3\sigma(I)$ were ignored, as were those with background difference $\Delta > 4\sigma_B$. Lorentz and polarisation corrections were applied, but no allowance was made for absorption or extinction, and 1 303 independent reflections were used in the final refinement.

The positions of the atoms in the [Co(cadmi)Cl] molecule were found by conventional Patterson and Fourier methods and refined by block-diagonal least squares with, eventually, anisotropic thermal vibrations for cobalt and chlorine and refined inter-layer scale-factors to R 0.155.

From Fourier syntheses it was clear that the solvent system was disordered and comprised a $CHCl_3$ and a CH_2Cl_2 molecule each with a population of approximately 0.5 and having the carbon and one chlorine atom in common; the other chlorine atoms were located in an extended region of electron density. Refinement of the solvent with constrained geometry (C–Cl 1.77 Å, Cl–C–Cl

TABLE 1

Atomic positional and thermal parameters with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	B/Å^2
(a) Fractional co-ordinates (× 10^4) of the non-hydrogen atoms with isotropic thermal parameters where appropriate				
Co	−2 294(4)	792(2)	424(1)	
Cl(1)	−831(10)	−3 187(4)	1 612(3)	
Cl(2)	−4 045(10)	3 967(4)	−1 481(3)	
Cl(3)	−5 408(8)	879(5)	832(2)	
N(1)	−2 286(27)	−339(11)	295(6)	2.73(6)
C(1)	−1 799(28)	−995(13)	600(7)	1.92(7)
C(2)	−2 138(35)	−1 790(14)	394(9)	3.01(7)
C(3)	−1 800(33)	−2 447(14)	722(8)	2.72(8)
C(4)	−1 144(34)	−2 317(15)	1 236(9)	3.08(8)
C(5)	−791(33)	−1 580(14)	1 421(8)	2.82(8)
C(6)	−1 176(29)	−883(15)	1 108(8)	2.57(7)
C(7)	−624(31)	−65(13)	1 322(8)	2.20(7)
N(2)	−896(24)	612(11)	1 063(6)	2.50(6)
C(8)	−179(35)	1 397(16)	1 285(9)	3.35(8)
C(9)	−1 202(42)	2 098(18)	1 069(11)	5.09(11)
N(3)	−1 803(27)	1 953(12)	518(7)	3.45(7)
C(10)	−2 043(30)	2 549(14)	208(8)	2.17(7)
C(11)	−2 824(33)	2 454(14)	−301(8)	2.58(7)
C(12)	−3 091(32)	3 180(15)	−609(8)	2.79(8)
C(13)	−3 727(36)	3 073(16)	−1 108(9)	3.63(9)
C(14)	−4 078(35)	2 305(15)	−1 342(9)	3.18(8)
C(15)	−3 876(31)	1 640(14)	−1 036(8)	2.46(7)
C(16)	−3 219(29)	1 650(13)	−522(8)	2.09(7)
N(4)	−3 106(23)	979(11)	−244(6)	2.12(6)
C(17)	272(30)	−30(13)	1 853(8)	1.81(7)
C(18)	2 218(33)	−14(15)	1 972(9)	2.86(8)
C(19)	3 040(38)	−28(17)	2 462(10)	3.94(9)
C(20)	1 844(39)	−77(18)	2 836(10)	4.45(10)
C(21)	−122(43)	−112(19)	2 740(11)	5.37(11)
C(22)	−961(40)	−66(18)	2 239(10)	4.51(10)
C(23)	−1 564(32)	3 428(14)	398(8)	2.70(8)
C(24)	377(39)	3 687(17)	439(10)	4.22(10)
C(25)	810(44)	4 462(19)	620(12)	6.09(12)
C(26)	−519(43)	4 963(18)	741(11)	5.00(11)
C(27)	−2 484(43)	4 766(18)	702(11)	5.25(11)
C(28)	−3 039(38)	3 945(16)	515(10)	4.38(10)
Cl(4)	−3 268(23)	2 382(11)	2 281(6)	15.4(4)
C(29)	−5 614(26)	2 409(19)	1 956(10)	15.4(4)
Cl(5)	−7 430(25)	2 406(26)	2 381(15)	15.4(4)
Cl(6)	−5 875(48)	3 272(27)	1 548(14)	15.4(4)
Cl(7)	−7 177(52)	3 064(24)	2 011(14)	15.4(4)
(b) Calculated hydrogen atom positions (× 10^3) with estimated isotropic thermal parameters				
H[N(1)]	−272	−47	−1	3.3
H[C(2)]	−254	−187	4	3.5
H[C(3)]	−204	−300	60	3.3
H[C(5)]	−26	−151	177	3.5
H[C(12)]	−282	373	−47	3.3
H[C(14)]	−442	226	−170	3.8
H[C(15)]	−416	110	−118	2.9
H[N(4)]	−350	53	−41	2.8
H′[C(8)]	118	146	123	3.6
H″[C(8)]	−26	140	164	3.6
H′[C(9)]	−36	258	111	5.2
H″[C(9)]	−230	220	125	5.2
H[C(18]	309	2	170	3.4
H[C(19)]	445	−4	254	4.3
H[C(20]	241	−11	319	5.0
H[C(21)]	−100	−12	301	6.2
H[C(22)]	−236	−7	216	5.2
H[C(24)]	139	332	35	5.0
H[C(25)]	214	465	66	6.5
H[C(26)]	−16	552	87	5.9
H[C(27)]	−350	515	79	6.1
H[C(28)]	−439	376	48	5.1

---

[3] N. A. Bailey, E. D. McKenzie, and J. M. Worthington, *Inorg. Chim. Acta*, 1975, **12**, L31.

[4] E. D. McKenzie, R. D. Moore, and J. M. Worthington, *Inorg. Chim. Acta*, 1975, **14**, 37.

TABLE 1 (*Continued*)

(*c*) Anisotropic thermal parameters ($\times 10^5$)*

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Co	933(8)	148(2)	61(1)	−18(3)	−27(4)	−154(11)
Cl(1)	2 272(28)	240(4)	153(2)	109(5)	106(13)	245(21)
Cl(2)	2 246(28)	322(5)	145(2)	168(5)	−52(12)	509(20)
Cl(3)	1 505(21)	370(5)	102(1)	−57(5)	110(9)	−152(22)

* The expression for the temperature factor is $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + klb_{23} + hlb_{13} + hkb_{12})]$.

111°[5] for the $CHCl_3$ molecule, with co-ordinates for the non-common Cl atom of the CH_2Cl_2 molecule refined independently) and an overall isotropic vibrational parameter reduced R to 0.106 when parameter shifts were $<0.5\sigma$. This model for the solvent was included, but not varied, in block-diagonal least-squares refinement of the [Co(cadmi)Cl] molecule, with anisotropic thermal parameters for Co and Cl, to R 0.094. (An attempt to refine anisotropic thermal parameters for C and N atoms gave unacceptable results, and the attempt was discontinued.) A difference-Fourier synthesis using low-angle data ($\sin\theta/\lambda \leqslant 0.3$) revealed most of the hydrogen atoms close to calculated positions (C–H 0.95, N–H 0.85 Å);[6] these were included, but not varied, in further block-diagonal least-squares refinement with isotropic thermal parameters 0.5 Å^2 in excess of those of the atoms to which they were attached. A further adjustment of the inter-layer scaling followed by refinement of the [Co(cadmi)Cl] molecule with anisotropic thermal parameters for Co and Cl only, reduced R to 0.088 when parameter shifts were less than one-sixth of their estimated standard deviations.

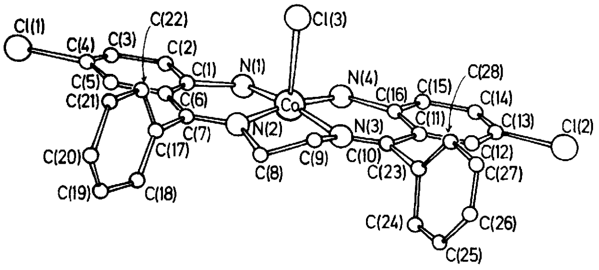


FIGURE 1 The [Co(cadmi)Cl] molecule viewed perpendicular to the [N(2),N(3),Cl(3)] plane

A difference-Fourier synthesis indicated that although a better model for the disordered solvent system might be possible, the quality of the data would make this an unjustifiable elaboration.

Atomic scattering factors were taken from ref. 7. Programs used are part of the Sheffield *X*-ray system, and calculations were performed on the Sheffield University ICL 1907 computer. The final structural parameters, with estimated standard deviations, are listed in Table 1. Structure factors are listed in Supplementary Publication No. SUP 21888 (10 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Figure 1 shows the molecule with the atom numbering scheme; C(5)—(7) and C(29) are atoms of the disordered solvent system (see above). Interatomic distances and angles with estimated standard deviations are listed in Table 2, and equations of least-squares planes, with atom deviations and interplanar angles, are listed in Table 3.

TABLE 2

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) The co-ordination sphere of the metal

Co–N(1)	1.86(2)	Co–N(4)	1.84(2)
Co–N(2)	1.90(2)	Co–Cl(3)	2.507(7)
Co–N(3)	1.92(2)		
N(1)–Co–N(2)	90.3(8)	N(2)–Co–N(4)	167.3(7)
N(1)–Co–N(4)	89.3(8)	N(1)–Co–Cl(3)	98 8(6)
N(2)–Co–N(3)	87.9(8)	N(2)–Co–Cl(3)	90.3(5)
N(3)–Co–N(4)	90.1(8)	N(3)–Co–Cl(3)	92.1(6)
N(1)–Co–N(3)	169.0(8)	N(4)–Co–Cl(3)	102.3(5)

(*b*) The cadmi ligand

N(1)–C(1)	1.36(3)	C(15)–C(16)	1.40(3)
C(1)–C(2)	1.41(3)	C(16)–C(11)	1.44(3)
C(1)–C(6)	1.40(3)	C(16)–N(4)	1.31(3)
C(2)–C(3)	1.38(3)	C(13)–Cl(2)	1.76(3)
C(3)–C(4)	1.42(3)	C(7)–C(17)	1.49(3)
C(4)–C(5)	1.30(3)	C(17)–C(18)	1.36(3)
C(5)–C(6)	1.42(3)	C(18)–C(19)	1.38(4)
C(4)–Cl(1)	1.73(2)	C(19)–C(20)	1.36(4)
C(6)–C(7)	1.48(3)	C(20)–C(21)	1.36(4)
C(7)–N(2)	1.30(3)	C(21)–C(22)	1.41(4)
N(2)–C(8)	1.47(3)	C(22)–C(17)	1.40(3)
C(8)–C(9)	1.43(4)	C(10)–C(23)	1.54(3)
C(9)–N(3)	1.51(3)	C(23)–C(24)	1.40(3)
N(3)–C(10)	1.27(3)	C(24)–C(25)	1.37(4)
C(10)–C(11)	1.42(3)	C(25)–C(26)	1.29(4)
C(11)–C(12)	1.44(3)	C(26)–C(27)	1.39(4)
C(12)–C(13)	1.37(3)	C(27)–C(28)	1.46(4)
C(13)–C(14)	1.40(3)	C(28)–C(23)	1.38(3)
C(14)–C(15)	1.35(3)		
Co–N(1)–C(1)	131(1)	C(10)–C(11)–C(12)	118(2)
Co–N(2)–C(7)	130(1)	C(10)–C(11)–C(16)	122(2)
Co–N(2)–C(8)	111(1)	C(12)–C(11)–C(16)	120(2)
Co–N(3)–C(9)	108(2)	C(11)–C(12)–C(13)	118(2)
Co–N(3)–C(10)	130(2)	C(12)–C(13)–C(14)	125(2)
Co–N(4)–C(16)	133(1)	Cl(2)–C(13)–C(12)	117(2)
N(1)–C(1)–C(2)	117(2)	Cl(2)–C(13)–C(14)	118(2)
N(1)–C(1)–C(6)	121(2)	C(13)–C(14)–C(15)	116(2)
C(2)–C(1)–C(6)	122(2)	C(14)–C(15)–C(16)	126(2)
C(1)–C(2)–N(3)	116(2)	C(15)–C(16)–N(4)	123(2)
C(2)–C(3)–C(4)	121(2)	N(4)–C(16)–C(11)	121(2)
C(3)–C(4)–C(5)	122(2)	C(7)–C(17)–C(18)	123(2)
C(3)–C(4)–Cl(1)	117(2)	C(7)–C(17)–C(22)	118(2)
Cl(1)–C(4)–C(5)	121(2)	C(18)–C(17)–C(22)	119(2)
C(4)–C(5)–C(6)	119(2)	C(17)–C(18)–C(19)	122(2)
C(5)–C(6)–C(1)	120(2)	C(18)–C(19)–C(20)	118(2)
C(5)–C(6)–C(7)	117(2)	C(19)–C(20)–C(21)	122(3)
C(1)–C(6)–C(7)	123(2)	C(20)–C(21)–C(22)	120(3)
C(6)–C(7)–N(2)	122(2)	C(21)–C(22)–C(17)	118(2)
C(6)–C(7)–C(17)	118(2)	C(10)–C(23)–C(24)	119(2)
N(2)–C(7)–C(17)	120(2)	C(10)–C(23)–C(28)	120(2)
C(7)–N(2)–C(8)	119(2)	C(24)–C(23)–C(28)	122(2)
N(2)–C(8)–C(9)	113(2)	C(23)–C(24)–C(25)	119(2)
C(8)–C(9)–N(3)	111(2)	C(24)–C(25)–C(26)	122(3)
C(9)–N(3)–C(10)	122(2)	C(25)–C(26)–C(27)	123(3)
N(3)–C(10)–C(11)	124(2)	C(26)–C(27)–C(28)	117(3)
N(3)–C(10)–C(23)	118(2)	C(27)–C(28)–C(23)	117(2)
C(11)–C(10)–C(23)	118(2)	C(15)–C(16)–C(11)	116(2)

The Cobalt(III) *Co-ordination Polyhedron.*—The co-odination geometry of the metal is square pyramidal. The nitrogen atoms of the quadridentate ligand are coplanar within 0.01 Å and the cobalt atom lies 0.19 Å

---

* For details, see Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

[5] Microwave studies: S. N. Ghosh, R. Trambarulo, and W. Gordy, *J. Chem. Phys.*, 1952, **20**, 605 ($CHCl_3$); R. J. Meyers and W. D. Gwinn, *ibid.*, 1420 (CH_2Cl_2).

[6] M. R. Churchill, *Inorg. Chem.*, 1973, **12**, 1213.

[7] 'International Tables for *X*-Ray Crystallography,' vol. IV Kynoch Press, Birmingham, 1974.

above this plane, towards Cl(3). The angles of 90.2(8), 87.9(8), and 90.1(8)°, for N(1)–Co–N(2), N(2)–Co–N(3), and N(3)–Co–N(4), respectively, are a reflection of the relative sizes of the chelate rings. The Co–N bond lengths, 1.84—1.92 Å, are in the same range as found for low-spin octahedral cobalt(III) compounds (1.85—1.96 Å) [8] but bond lengths to N(1) and N(4), 1.86(2) and 1.84(2) Å respectively, are significantly shorter than those to N(2) and N(3), 1.90(2) and 1.92(2) Å, respectively; this reflects the different formal electronic characters of these atoms as anionic and azomethine nitrogen atoms.

TABLE 3

Equations of important least-squares planes given in the form $lX + mY + nZ = d$ (where X, Y, and Z are co-ordinates in Å referred to the axes a, b, and c^*). Deviations (Å) of various atoms from these planes are listed in parentheses. Angles between some of these planes are listed at the end of the Table

	l	m	n	d
Plane (1): N(1)–N(4)	−0.9434	0.0179	0.0311	1.7976
[Co 0.194, N(1) 0.013, N(2) −0.013, N(3) 0.013, N(4) −0.013]				
Plane (2): C(1)–C(6)	0.9720	−0.0410	−0.2312	−1.6613
[C(1) 0.005, C(2) 0.006, C(3) −0.003, C(4) −0.010, C(5) 0.020, C(6) −0.017, N(1) −0.106, Cl(1) −0.063, C(7) 0.117]				
Plane (3): C(11)–C(16)	0.9742	−0.0656	−0.2158	−1.9253
[C(11) 0.005, C(12) −0.001, C(13) −0.013, C(14) 0.023, C(15) −0.019, C(16) 0.005, N(4) −0.074, Cl(2) −0.018, C(10) 0.108]				
Plane (4): C(17)–C(22)	0.0349	−0.9985	−0.0428	−0.1743
[C(17) 0.003, C(18) 0.009, C(19) −0.009, C(20) −0.004, C(21) 0.017, C(22) −0.016, C(7) 0.102]				
Plane (5): C(23)–C(28)	0.0160	−0.3507	0.9364	−0.9871
[C(23) 0.014, C(24) −0.011, C(25) 0.002, C(26) 0.005, C(27) −0.002, C(28) −0.007, C(10) 0.034]				

Angles between planes (°)

(1)–(2)	173.9	(1)–(5)	73.2
(1)–(3)	172.6	(2)–(3)	1.7

The Co–Cl bond-axis is tilted at 6.7° to the normal to the N_4 plane (see later) and the Co–Cl bond-length, 2.507(7) Å, is very long. A survey of Co–Cl bond-lengths in octahedral cobalt(III) compounds [8] gives a common range of 2.25—2.27 Å and the only other published example of an anomalously long Co–Cl bond is observed [9] for *trans*-$[Co(en)_2(NO)Cl][ClO_4]$, 2.575(3) Å, and this is attributed to the structural *trans* influence of the strong σ-donor NO^- (in 'bent' co-ordination). The lengthening in the present case may be an effect of the presence of an unpaired electron in the d_{z^2} orbital of the cobalt atom; [2] the effect is reminiscent of that found for the differences in bond lengths between high- and low-spin iron compounds.[10]

The Quadridentate Ligand.—Bond lengths and angles within the ligand skeleton are normal, and comparable with corresponding ones in the analogous N_2O_2 ligands.[11] The dimethylene fragment has a *gauche* conformation with respect to the N_4 plane, C(8) and C(9) lying 0.23 and 0.24 Å, respectively, below and above this plane.

The overall ligand skeleton is very similar to that in many planar [M(salen)] species [salen = 1,2-bis(salicylideneimino)ethane dianion].[12] In the present compound, the closely planar phenylene moieties, C(1)—(6) and C(11)—(16), are almost parallel, at an angle of 1.7° to one another, and make angles of 173.9 and 172.6°, respectively, with the mean N_4 plane so that the ligand has a 'stepped' conformation.[13] By contrast, the analogous [Fe(salen)Cl] and $[Co(3\text{-}OMe\text{-}salen)(OH_2)]$ [14] molecules have the oblique conformation, with the quadridentate ligand convex as viewed from the axial substituent.

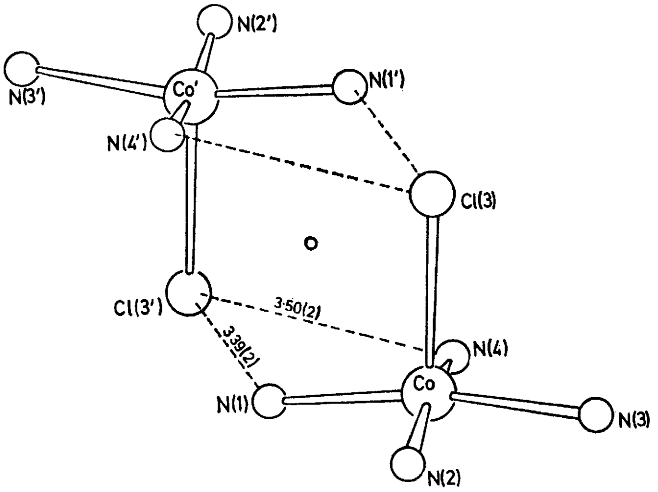


FIGURE 2 Two CoN_4Cl units related by the centre of symmetry at (−½,0,0) [shown as the small circle]. The distances marked are in Å

The phenyl substituents on C(7) and C(10) are planar within experimental error and make angles of 93.7 and 73.2°, respectively, with the N_4 plane. The resulting isolation of the conjugated π-electron systems of these phenyl groups is reflected in the 'long' bond lengths C(7)–C(17) 1.49(3) and C(10)–C(23) 1.54(3) Å. A similar situation exists, for example, in the metal tetraphenylporphinates.[15]

The Crystal Packing.—There is an association between molecules across the centre of symmetry at (−½,0,0), apparently with some hydrogen-bonding: N(1) · · · Cl(3')

---

[8] Survey sources: 'Molecular Structures and Dimensions,' vols. 1—5 (1969—1973), eds. O. Kennard, D. G. Watson, and W. G. Town, N. V. A. Oosthoek's Uitgevers Mij Utrecht; 'Bond Index to the Determinations of Inorganic Crystal Structures (BIDICS),' 1969—1974, compiled by I. D. Brown and P. Weiss, Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada.

[9] B. A. Snyder and D. L. Weaver, *Inorg. Chem.*, 1970, **9**, 2760.

[10] *E.g.* J. L. Hoard, *Science*, 1971, **174**, 1295.

[11] M. Calligaris, G. Nardin, and L. Randaccio, *Co-ordination Chem. Rev.*, 1971, **7**, 385.

[12] M. Gerloch and F. E. Mabbs, *J. Chem. Soc.* (*A*), 1967, 1598; M. Calligaris, G. Nardin, and L. Randaccio, *J.C.S. Dalton*, 1974, 1903.

[13] *E.g.* J. F. Kirmer and W. R. Scheidt, *Inorg. Chem.*, 1975, **14**, 2081, and refs. cited therein.

[14] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, 1970, p. 120.

[15] W. R. Schiedt and J. L. Hoard, *J. Amer. Chem. Soc.*, 1973, **95**, 8281.

3.39(2) and N(4) · · · Cl(3′) 3.50(2) Å. This may explain the tilt of the Co–Cl bond-axis with respect to the N_4 plane (see above). The situation is shown in Figure 2. The only other apparently short intermolecular contact is Cl(1) · · · Cl(5′) 3.19(4) Å (the prime denotes the symmetry operation $-1 - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$; the generally accepted van der Waals radius of chlorine is *ca.* 1.8 Å[14]), but since Cl(5) is part of the disordered solvent system, the reality of this short contract is uncertain.

We thank the S.R.C. for a grant (for the diffractometer) and a studentship (for J. M. W.).

[6/1224 *Received*, 24*th June*, 1976]