Structural Study of Octahedral Cobalt(III) Complexes. Crystal and Molecular Structure of *trans*-Chlorobis(dimethylglyoximato)(triphenylphosphine)cobalt(III) and *trans*-Chlorobis(dimethylglyoximato)(ammine)cobalt(III) Monohydrate

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The crystal structures of the title compounds have been determined from three-dimensional X-ray diffractometer data by conventional Patterson and Fourier methods. Both compounds crystallize in the orthorhombic space group $P2_12_12_1$, with $Z = 4$; cell parameters for the ammonia derivative (II) are: a = 10·540(5), b = 13·147(6), and c = 10·443(5) Å; those of the triphenylphosphine derivative (I) are: a = 17·211(8), b = 14·225(6), and c = 10·656(5) Å. The structures were refined by least-squares methods to R 0·038 [(II), 1651 observed reflections] and 0·049 [(I), 1429 observed reflections]. Evidence for *trans*-influence in this type of octahedral cobalt(III) complex is discussed.

BIS(DIMETHYLGLYOXIMATO)COBALT(III) complexes have been extensively studied [1] in solution. Kinetic, thermodynamic, and ground-state *cis*- and *trans*-effects [2] have been related to the σ-donor power of the influencing ligands and to transmission of electronic effects from each ligand to the other through the cobalt atom. However, few structural results [3,4] on such systems have been reported. Knowledge of the bond lengths and of the overall geometry of the molecules would give useful information about ground-state effects and about steric factors influencing the reactivity of such complexes.

We now report the crystal and molecular structure of *trans*-chlorobis(dimethylglyoximato)(triphenylphosphine)cobalt(III), (I), and *trans*-chlorobis(dimethylglyoximato)(ammine) cobalt(III) (II).

EXPERIMENTAL

Crystal Data.—(*a*) $C_{26}H_{29}ClCoN_4O_4P$, (I), M = 586·9, Orthorhombic, a = 17·211(8), b = 14·225(6), c = 10·656(5), U = 2608·9 Å^3, D_m = 1·50, Z = 4, D_c = 1·495. μ(Mo-K_α) = 8·9 cm^{-1}. Space group $P2_12_12_1$.

(*b*) $C_8H_{17}ClCoN_5O_4,(H_2O)$, (II), M = 359·7, Orthorhombic, a = 10·540(5), b = 13·147(6), c = 10·433(5), U = 1447·1 Å^3, D_m = 1·65, Z = 4, D_c = 1·652. μ(Mo-K_α) = 6·0 cm^{-1}. Space group $P2_12_12_1$.

Cell parameters were determined from Weissenberg photographs taken with Co-K_α radiation and refined with an on-line automated single-crystal Siemens diffractometer with Mo-K_α radiation, λ = 0·7107 Å.

Intensity Measurements.—Three-dimensional intensity data were collected for both compounds on a Siemens diffractometer by means of the θ—2θ scan technique and Mo-K_α radiation for maximum 2θ 50° for (I) and 60° for (II). Reflections having $I_0 < 3\sigma(I_0)$ were rejected, the remainder being corrected for Lorentz-polarization factors. A total of 1429 for (I) and 1651 for (II) were used in the subsequent calculations. No correction for absorption or anomalous dispersion of the cobalt atom was applied.

Structure Determination and Refinement.—Both structures were solved by conventional Patterson and Fourier methods. After least-squares isotropic refinement R was 0·070 for (I) and 0·060 for (II). After three cycles of anisotropic block-diagonal least-squares refinement, three-dimensional difference Fourier syntheses were calculated to enable location of the hydrogen atoms. Calculated positions of these atoms all occurred in regions of positive electron density. However, the methyl groups of (I) did not appear clearly on the map, and the contributions of these hydrogen atoms were not therefore included. Final anisotropic block-diagonal least-squares refinement gave R 0·049 for (I) and 0·038 for (II). The co-ordinates and the temperature factors of the hydrogen atoms [set at B 5·5 Å^2 for (I) and 5·0 Å^2 for (II)] were not allowed to vary. The final weighting schemes were $w = 1/(A + B|F_o| + C|F_o|^2)$, where for (I) A = 10·0, B = 1·0, and C = 0·004, and for (II) A = 5, B = 1·0, and C = 0·008, chosen to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and $(\sin\theta/\lambda)$. Final atomic parameters are listed in Tables 1 and 2, together with their estimated standard deviations, calculated from the residuals and the diagonal elements of the inverse matrix of the last least-squares cycle. The numbering schemes of the atoms are shown in Figures 1 and 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20943 (10 pp., 1 microfiche).† Atomic scattering factors were calculated according to ref. 5.

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† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

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TABLE 1

Fractional co-ordinates ($\times 10^4$) and thermal parameters for (I), with estimated standard deviations in parentheses. Anisotropic temperature factors * are $\times 10^4$

	x	y	z	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Co	839(1)	1595(1)	870(2)	17(1)	2(1)	1(1)	27(1)	1(2)	41(1)
Cl	1124(2)	2711(2)	2331(3)	46(1)	−10(3)	−17(4)	37(2)	−12(4)	59(3)
P	495(2)	518(2)	−677(3)	17(1)	0(2)	5(3)	32(1)	0(4)	49(3)
O(1)	1997(5)	412(7)	1923(10)	27(3)	42(8)	−54(10)	67(6)	21(14)	116(11)
O(2)	−748(5)	1757(7)	1598(9)	24(3)	18(8)	27(10)	68(6)	−38(14)	101(10)
O(3)	−307(6)	2841(7)	−100(10)	39(4)	43(8)	−8(11)	60(6)	−5(15)	96(11)
O(4)	2445(5)	1491(9)	232(10)	19(3)	−7(10)	−26(10)	84(7)	−5(17)	110(11)
N(1)	1253(6)	691(7)	1955(9)	37(4)	1(8)	−24(11)	30(5)	3(12)	57(10)
N(2)	−68(6)	1299(7)	1783(10)	22(4)	−4(8)	6(11)	37(5)	−19(13)	89(10)
N(3)	442(6)	2561(7)	−161(11)	27(4)	13(8)	−20(12)	39(5)	−23(13)	76(11)
N(4)	1767(6)	1920(8)	33(11)	23(3)	−11(8)	0(11)	45(6)	−8(14)	78(11)
C(1)	1057(12)	−401(10)	3734(15)	86(10)	15(16)	−22(21)	45(8)	66(17)	85(15)
C(2)	803(9)	300(9)	2786(12)	45(6)	−10(12)	21(16)	43(7)	2(15)	45(11)
C(3)	12(9)	675(8)	2651(13)	43(5)	−13(10)	45(14)	28(6)	2(15)	62(13)
C(4)	−673(10)	304(12)	3405(15)	49(6)	−34(14)	92(16)	73(10)	0(23)	111(16)
C(5)	686(12)	3832(12)	−1664(15)	90(10)	42(19)	3(22)	80(10)	73(21)	74(15)
C(6)	923(8)	3014(9)	−861(14)	44(5)	−13(12)	−41(17)	41(6)	9(19)	74(12)
C(7)	1731(8)	2633(9)	−752(14)	32(5)	−36(10)	26(15)	62(7)	−43(18)	59(13)
C(8)	2398(10)	3015(15)	−1498(16)	62(7)	−89(16)	75(18)	114(14)	−18(26)	86(16)

	x	y	z	B/Å^2		x	y	x	B/Å^2
C(9)	776(7)	933(8)	−2220(11)	2·6(2)	C(18)	1553(9)	−2440(12)	−441(15)	4·9(4)
C(10)	264(8)	1307(10)	−3144(13)	3·4(3)	C(19)	1600(10)	−1990(12)	−1507(18)	5·2(4)
C(11)	533(8)	1646(11)	−4290(15)	4·2(3)	C(20)	1264(8)	−1073(10)	−1615(14)	4·2(3)
C(12)	1317(9)	1633(12)	−4528(15)	4·6(3)	C(21)	−558(7)	302(8)	−664(12)	2·4(2)
C(13)	1864(8)	1296(9)	−3616(13)	3·5(3)	C(22)	−1065(8)	993(9)	−1075(13)	3·7(3)
C(14)	1574(7)	951(8)	−2494(12)	2·7(2)	C(23)	−1858(8)	816(10)	−1130(13)	4·0(3)
C(15)	920(7)	−676(8)	−592(11)	2·5(2)	C(24)	−2133(10)	−16(12)	−635(17)	5·2(4)
C(16)	893(8)	−1185(9)	519(12)	3·4(2)	C(25)	−1661(9)	−689(11)	−175(16)	4·8(3)
C(17)	1181(8)	−2074(10)	515(14)	4·0(3)	C(26)	−857(8)	−533(9)	−212(13)	3·7(3)

Hydrogen atom co-ordinates ($\times 10^3$)

	x	y	z		x	y	z		x	y	z
HA	−70	240	50	H(5)	198	69	−176	H(11)	−87	160	−139
HB	244	100	140	H(6)	62	−90	131	H(12)	−224	130	−150
H(1)	−29	133	−310	H(7)	116	−241	131	H(13)	−272	−16	−66
H(2)	12	196	−497	H(8)	178	−315	−69	H(14)	−183	−127	12
H(3)	145	185	−530	H(9)	187	−225	−230	H(15)	−49	−102	13
H(4)	238	130	−351	H(10)	128	−74	−240				

* In the form: $T = \exp[-(\beta_{11}h^2 + \beta_{12}hk + \beta_{13}hl + \beta_{22}k^2 + \beta_{23}kl + \beta_{33}l^2)]$

TABLE 2

Fractional co-ordinates ($\times 10^4$) and anisotropic temperature parameters ($\times 10^4$)* for (II), with estimated standard deviations in parentheses

	x	y	z	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Co	1697(1)	1120(1)	1352(1)	39·4(4)	1(1)	−9(1)	32·6(3)	0(1)	53·4(5)
Cl	1028(1)	994(1)	3393(1)	79(1)	−20(2)	17(2)	50(1)	−4(2)	59(1)
N(5)	2359(5)	1222(4)	−402(4)	74(4)	4(7)	11(7)	54(3)	−1(6)	50(3)
O(1)	4214(4)	1280(4)	2320(5)	56(3)	7(5)	−53(7)	55(3)	30(6)	113(4)
O(2)	−64(4)	2704(4)	841(6)	56(3)	40(5)	−40(8)	52(3)	4(7)	147(6)
O(3)	−856(4)	952(3)	475(5)	46(3)	12(5)	−42(6)	59(3)	−1(6)	101(4)
O(4)	3460(4)	−476(4)	1848(5)	49(3)	30(5)	−4(7)	58(2)	34(6)	116(5)
N(1)	3168(4)	1782(4)	1946(5)	49(3)	0(6)	−21(7)	50(3)	8(6)	71(4)
N(2)	1106(4)	2470(4)	1262(5)	56(3)	15(5)	−6(8)	30(2)	6(6)	84(4)
N(3)	210(4)	446(4)	743(5)	41(3)	−14(5)	−13(7)	44(2)	−5(6)	76(4)
N(4)	2276(4)	−237(4)	1423(5)	58(4)	−4(5)	−5(7)	45(2)	−8(6)	62(4)
C(1)	4148(7)	3417(6)	2561(7)	81(5)	−62(8)	−45(10)	64(4)	−2(9)	94(6)
C(2)	3112(5)	2748(5)	2049(6)	54(4)	−17(7)	−5(8)	48(3)	−4(7)	69(4)
C(3)	1879(6)	3170(4)	1598(6)	71(5)	−13(6)	20(8)	41(3)	12(6)	69(5)
C(4)	1597(7)	4287(5)	1516(8)	99(6)	−9(8)	19(13)	38(3)	−10(8)	118(7)
C(5)	−785(6)	−1193(5)	148(7)	76(5)	2(8)	−14(10)	48(3)	−16(9)	104(6)
C(6)	274(5)	−529(4)	612(5)	67(5)	0(6)	13(8)	36(3)	0(6)	62(4)
C(7)	1518(6)	−932(4)	1019(6)	78(5)	−23(7)	23(8)	44(3)	6(6)	66(4)
C(8)	1870(8)	−2038(5)	960(8)	114(7)	8(9)	20(13)	38(3)	6(8)	120(7)
O(W)	3206(5)	6747(5)	3379(6)	96(4)	13(9)	33(11)	93(4)	−8(11)	146(6)

Hydrogen atom co-ordinates ($\times 10^3$); hydrogen atoms are numbered according to the carbon atom to which they are bonded

	x	y	z		x	y	z		x	y	z
1-H(1)	497	295	284	2-H(8)	182	−229	−2	2-H(N5)	193	70	−96
2-H(1)	381	382	341	3-H(8)	125	−247	156	3-H(N5)	330	111	−40
3-H(1)	444	396	184	1-H(5)	−49	−198	15	HA	385	60	220
1-H(4)	243	471	183	2-H(5)	−103	−97	−83	HB	−30	205	50
2-H(4)	79	447	211	3-H(5)	−161	−108	76	1-H(OW)	270	620	360
3-H(4)	139	449	52	1-H(N5)	217	193	−75	2-H(OW)	420	635	350
1-H(8)	286	−210	129								

* See footnote to Table 1.

Calculations.—All calculations were carried out on a CDC 6200 computer, with programs described in ref. 6. A local program was used to obtain best molecular planes, whose equations were calculated according to ref. 7.

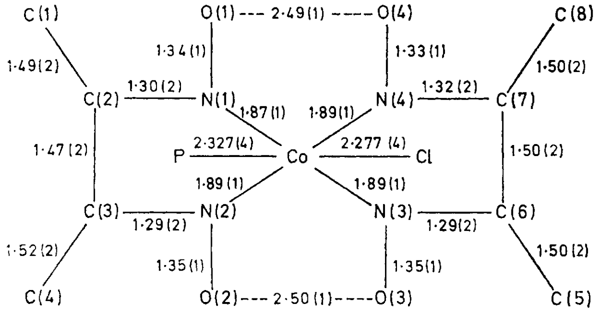

FIGURE 1 Numbering scheme for the atoms of CoCl(dmg)$_2$-(PPh$_3$), (I), with the most significant bond lengths; estimated standard deviations are in parentheses. The numbering scheme for the triphenylphosphine carbon atoms is given in Figure 3

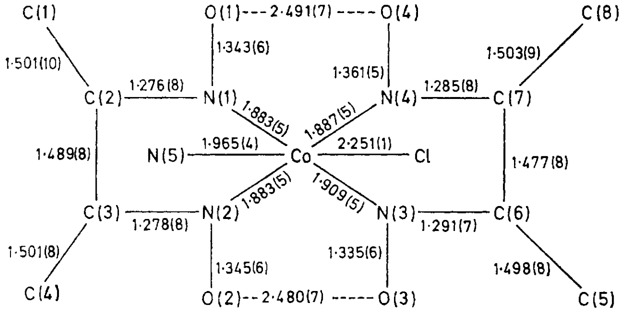

FIGURE 2 Numbering scheme for the atoms of Cl(dmg)$_2$Co(NH$_3$), (II), with the bond lengths; estimated standard deviations are in parentheses

RESULTS AND DISCUSSION

cis-*Influence and Equatorial Ligand.*—The overall molecular structures reveal no surprises, confirming the expected *trans*-geometry of both molecules. The most significant bond lengths are shown in Figures 1 and 2. As far as the equatorial ligand (dmg)$_2$ (dmg = dimethylglyoximato) is concerned, no significant differences are found between the two molecules. The mean values of chemically equivalent bond lengths and the corresponding calculated bond order according to the Bernstein equation [8] are given in Table 3 together with those of the related [Co^{III}(dmg)$_2$(PhNH$_2$)$_2$]Cl [4] and (CH$_3$CO$_2$CH$_2$)Co^{III}(dmg)$_2$(py) compounds.[3] The values of C–C bond lengths found in the first two molecules correspond to a nearly single bond order, *cf.* the mean value of 1·482 Å from recent accurate measurement for the single C(sp^2)–C(sp^2) bond,[9] whereas the C–N bond order is >1·5. This result is in agreement with that found in Cu(dmg)$_2$.[10] As the σ-donor power of the axial ligand increases (for dianiline and then to organometallic derivatives) the C–C bond lengths appear to shorten and finally, in the organometallic derivative, the N–O bond to lengthen, whereas the N–C bond length does not change significantly. This may imply a significant (at bond-length level) influence of an axial σ-bonded ligand on the equatorial (dmg)$_2$ group. An analogously shorter C–C bond length [1·452(9) Å] is found [11] for a similar equatorial ligand in Me$_2$Co^{III}L where L = 1,3-bis-(diacetylmonoximeimino)propane mono-anion.

If such differences are significant, the structural results would be in agreement with those of theoretical calculations carried out [12] on such molecules having axial substituents with different σ-donor power. These calculations lead us to conclude that the electronic charge donated by the axial ligand on the metal is partly spread over the atoms of chelate rings, essentially by delocalized π-orbitals. We suggest that here delocalization may also be extended to the rings containing the hydrogen bonds. This idea may be supported by the results for [ClRh^{III}(dmgH)(dmg)(PPh$_3$)]Cl,[13] where one O · · · H · · · O bridge is broken by protonation and the corresponding Rh–N distances are 2·094(3) and 2·091(4), whereas they are 1·993 Å on the side of the other O · · · H · · · O bridge.

Unfortunately, the accuracy and the number of structural data do not allow any conclusion to be made, but further data on σ-carbon-bonded dimethylglyoximate compounds may give an answer.

No significant differences in O · · · O distances are detectable between (I) and (II), in both of which the hydrogen bridge appears to be asymmetric, from an analysis of the difference-Fourier synthesis, although the N–O distances are all similar. On the contrary the O · · · O distance is strongly dependent upon the metal–nitrogen distance, *i.e.* the nature of the metal atom, being 2·50 in Co^{III} complexes and 2·70 Å in Rh^{III} complexes.[14,15] Table 4 lists the O · · · O and M–N distances and the bond angles of the M(dmg)$_2$ unit for different metal atoms M. The bond angles are shown to be nearly independent of the nature of the metal, so that the strength (*i.e.* the length) of the O · · · H · · · O bridge appears to be related mainly to the length of the co-ordination distances.

trans-*Influence and Axial Ligands.*—As far as the axial distances are concerned, the *trans*-influence of the phosphine ligand on the *trans*-chlorine atom is significantly greater, although of little amount, than that of the ammonia molecule. However the *trans*-influencing power of these two ligands is far less than that of a σ-carbon-bonded group. In fact the Co–Cl distance

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in (II) is 2·251(1), nearly coincident with that of 2·256(3) reported for *trans*-dichlorobis(diarsine)cobalt(III) chloride,[16] whereas it is 2·277(3) Å for (I).

A larger value of 2·380(4) Å for the Co–Cl distance is found in the protonated cobaloxime $ClCo^{III}(dmg)(dmgH)Et$,[17] although this compound has a different equatorial ligand. However for this type of octahedral cobalt compound the equatorial ligand has little, if any, effect on the axial distance.[18] Such a strong influence of a σ-carbon-bonded group has already been found[19] in the dimeric $[Co^{III}(salen)X]_2$ [salen = dianion of bis(salicylaldehyde)ethylenedi-imine] where Co–O was 2·342(3) for $X = CH_2Me$ and 2·00(1) Å for X = Cl. The values of these distances follow the same trend as the pK_a values of reaction (1), which are 6·98 for

$$[H_2OCo(dmg)_2L]^+ \rightleftharpoons HO{\cdot}Co(dmg)_2L + H^+ \quad (1)$$

$L = NH_3$ and 7·10 for $L = PPh_3$.[2] On the other hand pK_a for ammonia is 9·27 whereas that for the phosphine ligand is 3·05.

TABLE 3

Mean values of chemically equivalent bond lengths (Å), with their standard deviations in parentheses, and in square brackets calculated C–C, C–N, and N–O bond orders* for the dmg moiety. Values for free glyoxime are reported for comparison

	(I)	(II)	$(CH_3CO_2CH_2)Co^{III}(dmg)_2(py)$	$[(PhNH_2)Co^{III}(dmg)_2(NH_2Ph)]Cl$	Glyoxime †
C–C	1·485(15) [1·05]	1·483(6) [1·06]	1·460(10) [1·15]	1·470(14) [1·11]	1·449(6) [1·20]
C–N	1·300(14) [1·68]	1·282(4) [1·77]	1·285(12) [1·76]	1·295(7) [1·70]	1·284(5) [1·77]
N–O	1·343(9) [1·43]	1·346(10) [1·40]	1·373(12) [1·29]	1·340(14) [1·42]	1·397(5) [1·21]

* The equation used for calculating bond orders is $-4{\cdot}192 \log\left(\frac{3R}{R^1} - 2\right)$, where R is the actual distance and R^1 the single-bond distance, taken as C–N 1·45, C–C 1·50, and N–O 1·44 Å. † From M. Calleri, G. Ferraris, and D. Viterbo, *Acta Cryst.*, 1966, **20**, 73.

TABLE 4

O · · · O and M–N distances (Å) and ring bond angles (°) of some metal–glyoxime complexes. Estimated standard deviations of each individual measurement are given in parentheses. The numbering scheme is the same as that of Figure 1

	O · · · O	M–N	N(1)–M–N(4)	N(1)–M–N(2)	M–N(1)–C(1)	N(1)–C(1)–C(2)	M–N(1)–O(1)	O(1)–N(1)–C(1)	d_M/Å
$ClCo^{III}(dmg)_2(NH_3)$ [a]	2·491(7) 2·480(7)	1·890(5)	98·9(2)	81·2(2)	117·0(3)	112·4(4)	122·3(4)	120·6(5)	0·005
$ClCo^{III}(dmg)_2(PPh_3)$ [a]	2·49(1) 2·50(1)	1·89(1)	98·7(2)	81·3(5)	117·4(9)	112(1)	122·9(8)	120(1)	0·050
$(CH_3CO_2CH_2)Co^{III}(dmg)_2(py)$ [b]	2·51(1) 2·49(1)	1·880(6)	99·7(3)	80·3(3)	117·7(6)	111·8(6)	122·2(6)	120·6(6)	
$(PhNH_2)Co^{III}(dmg)_2(NH_2Ph)$ [c]	2·488(7)	1·887(5)	99·2(3)	80·8(3)	117·3(9)	112·3(9)	122·1(6)	121(1)	
$Cu^{II}(dmg)_2$ [d]	2·526(5) 2·694(5)	1·953(5)	97·7(2)	80·5(2)	116·2(3)	113·4(4)	123·3(3)	120·4(4)	0
$(im)Fe^{II}(dmg)_2(im)$ [e]	2·588(8)	1·905(6)	99·6(2)	80·4(6)	117·6(5)	112·1(8)	123·5(5)	118·8(6)	0·310
$ClRh^{III}(dmg)_2(PPh_3)$ [f]	2·709(6) 2·618(6)	1·992(4)	100·5(2)	79·6(2)	115·9(2)	114·2(2)	121·1(3)		0·126
$ClRh^{III}(dmg)_2(SbPh_3)$ [g]	2·70(1) 2·61(1)	1·98(1)	100·4(4)	79·5(4)	116·4(8)	114(1)	121·2(8)	123(1)	
$Ni^{II}(EtMeg)_2$ [h]	2·454(5)	1·962(4)	97·5(2)	82·5(2)	116·3(3)	112·5(4)	123·9(4)	119·9(4)	0
$Ni^{II}(g)_2$ [i]	2·453(6)	1·874(5)	97·8(2)	82·2(2)	115·4(3)	113·6(5)	123·3(6)	121·4(7)	
$Pd^{II}(g)_2$ [j]	2·60(1)	1·955(8)	99·7(4)	80·3(4)	115·8(7)	113·4(9)	121·9(7)	122·4(9)	0
	2·66(1)	1·970(8)	99·7(4)	80·3(4)	115·7(7)	114·2(9)	122·3(7)	122·2(9)	0

[a] Present work. [b] Ref. 3. [c] Ref. 4. [d] Ref. 10. [e] K. Bowman, A. P. Gaughan, and Z. Dori, *J.Amer. Chem. Soc.*, 1972, **94**, 727. [f] Ref. 14. [g] Ref. 15. [h] R. H. Bowers, C. V. Banks, and R. A. Jacobson, *Acta Cryst.*, 1972, **B28**, 2318. [i] M. Calleri, G. Ferraris, and D. Viterbo, *Acta Cryst.*, 1967, **22**, 468. [j] M. Calleri, G. Ferraris, and D. Viterbo, *Inorg. Chim. Acta*, 1967, **1**, 297; in this paper the two crystallographically non-independent molecules appear to have significantly different geometries.

Ligand abbreviations: im = imidazole, g = glyoximato, EtMeg = ethylmethylglyoximato.

The $Co-NH_3$ distance [1·965(4) Å] does not differ from the less accurate Co–N(py) value [1·97(2) Å] found for *cis*-[1,12-bis(methylglyoximato)dodecane]chloro(pyridine)cobalt(III),[20] a chlorine atom being *trans* to the nitrogen base in both cases. However, they differ significantly from the values for Co–N(py) [2·040(6)][3] and $Co-NH_2Ph$ [2·001Å],[4] in which, respectively, a σ-carbon-bonded group and a $NH_2{\cdot}Ph$ base are present in the *trans* position. The following trend is obtained,

	trans to	Distance/Å
Co–N(*sp*³)	Cl	1·965(4)
Co–N(*sp*²)	Cl	1·97(2)
Co–N(*sp*³)	NH_2Ph	2·001(5)
Co–N(*sp*²)	$-CH_2R$	2·040(6)

which follows that of the increasing σ-donor power of the *trans*-influencing ligand, on changing from Cl to an organic group. In the last two compounds, making allowance for the different σ-covalent radii of the hybridized nitrogen atom, the particularly strong *trans*-influence of the σ-bonded organic group again appears.

The $Co^{III}-P$ distance [2·327(4) Å] compares well with the sum of the radii (2·32 Å) assuming[21] cobalt(III) atom to have the normal octahedral radius of 1·22 and phosphorus the tetrahedral radius of 1·10 Å. It is comparable with values reported for a series of five-co-ordinate cobalt(II) complexes[22] in which Co–P ranges from 2·31 to 2·40 Å. Surprisingly the $Co^{III}-P$ distance has the same value [2·327(1) Å] as the Rh–P distance in

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[19] M. Calligaris, G. Nardin, and L. Randaccio, *Co-ordination Chem. Rev.*, 1972, **7**, 385.

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the analogous $ClRh^{III}(dmg)_2(PPh_3)$,[14] whereas the corresponding Co–Cl and Rh–Cl distances are 2·277(4) and 2·381(1) Å respectively. Such a comparison suggests that the Co–P bond has little double-bond character. In addition, the steric interaction of the phosphine ligand with the rigid equatorial ligand may be responsible for the lengthening of the Co–P bond.

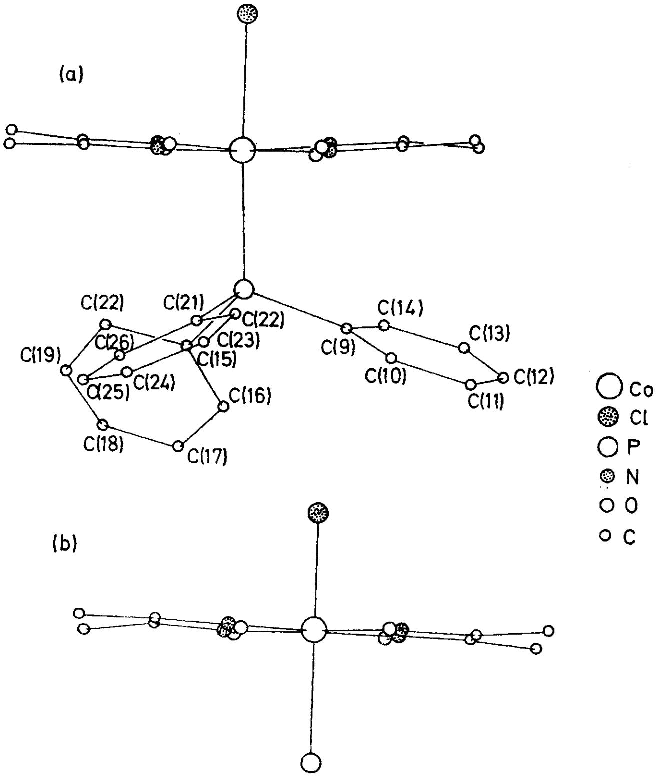

FIGURE 3 A side view of molecules of (a) (I) and (b) (II), showing the numbering scheme for the phosphine carbon atoms

Conformational Aspects.—Figure 3 shows a side view of the molecules of (I) and (II). The $Co(dmg)_2$ units are both nearly planar, with only slight differences in the fine points of their geometry. In (II) the four nitrogen donor atoms are coplanar (±0·002 Å) with Co essentially in their mean plane, being displaced from it by only 0·005 Å, whereas in (I) the cobalt atom is displaced 0·05 Å towards the P atom from the plane of the four coplanar nitrogen atoms (±0·004 Å). In both molecules the cobalt atom has a slightly distorted octahedral stereochemistry. The $ClRh^{III}(dmg)_2(PPh_3)$ analogue[14] show a more marked displacement of the rhodium atom (0·126 Å) from the plane of its four nitrogen donor atoms. Furthermore the planes passing through the atoms of the two dmg units make an angle of 17·1, their angles with the plane of the four nitrogen donor atoms being 10·6 and 7·1 * in the rhodium compound. For the cobalt complex the corresponding values are 6·0, 4·3, and 1·6°, which do not differ from the corresponding values for (II) which are 3·7, 3·0, and 1·3°. The weighted least-squares planes are listed in Table 5. The slight distortion from planarity in all these compounds may be described as an asymmetric ‘ umbrella-shaped ’ conformation. The larger co-ordination bond lengths involving the Rh atom, as compared with those of the

TABLE 5

Equation of least-squares planes and, in square brackets, distances (Å) of atoms from the planes. The equations are referred to the crystal axes and *x*, *y*, *z* are fractional co-ordinates

(*a*) $ClCo(dmg)_2(PPh_3)$, (I)

Plane (1): Co, O(1), O(2), N(1), N(2), C(1)—(4)

$$3{\cdot}742x + 10{\cdot}141y + 7{\cdot}105z = 2{\cdot}568$$

[Co −0·018, O(1) −0·036, O(2) 0·070, N(1) −0·009, N(2) −0·009, C(1) 0·074, C(2) 0·016, C(3) 0·005, C(4) −0·092]

Plane (2): Co, O(3), O(4), N(3), N(4), C(5)—(8)

$$3{\cdot}485x + 9{\cdot}115y + 7{\cdot}891z = 2{\cdot}400$$

[Co 0·032, O(3) 0·003, O(4) −0·006, N(3) −0·039, N(4) −0·009, C(6) −0·011, C(7) 0·009, C(5) 0·018, C(8) 0·001]

Plane (3): Co, N(1)—(4)

$$3{\cdot}648x + 9{\cdot}875y + 7{\cdot}330z = 2{\cdot}569$$

[Co −0·050, N(1) 0·004, N(3) −0·004, N(2) 0·004, N(4) −0·004]

Plane (4): C(9)—(14)

$$1{\cdot}339x + 12{\cdot}995y + 4{\cdot}255z = 0{\cdot}384$$

[C(9) −0·013, C(10) 0·012, C(11) 0·001, C(12) −0·012, C(13) 0·011, C(14) 0·001]

Plane (5): C(15)—(20)

$$15{\cdot}022x + 5{\cdot}562y + 3{\cdot}113z = 0{\cdot}819$$

[C(15) 0·003, C(16) 0·025, C(17) −0·038, C(18) 0·020, C(19) 0·009, C(20) −0·019]

Plane (6): C(21)—(26)

$$-1{\cdot}081x + 5{\cdot}699y + 9{\cdot}741z = -0{\cdot}402$$

[C(21) −0·012, C(22) 0·036, C(23) −0·033, C(24) 0·005, C(25) 0·019, C(26) −0·015]

(*b*) $ClCo(dmg)_2(NH_3)$, (II)

Plane (1): O(1), O(2), N(1), N(2), C(1)—(4)

$$-3{\cdot}764x - 0{\cdot}816y + 9{\cdot}733z = 0{\cdot}590$$

[Co −0·004, O(1) −0·023, O(2) 0·032, N(1) −0·034, N(2) 0·020, C(1) 0·062, C(2) 0·009, C(3) −0·001, C(4) −0·066]

Plane (2): O(3), O(4), N(3), N(4), C(5)—(8)

$$-3{\cdot}622x - 1{\cdot}639y + 9{\cdot}720z = 0{\cdot}600$$

[Co −0·084, O(3) 0·016, O(4) 0·022, N(3) −0·027, N(4) −0·002, C(5) 0·029, C(6) −0·017, C(7) −0·006, C(8) −0·010]

Plane (3): N(1)—(4)

$$-3{\cdot}556x - 0{\cdot}954y + 9{\cdot}801z = 0{\cdot}610$$

[Co 0·005, N(1) 0·002, N(2) −0·002, N(3) 0·002, N(4) −0·002]

TABLE 6

Intermolecular distances (Å) <3·5 Å in (II)

N(5) ··· $O(2^{IV})$	3·095(7)	O(3) ··· $C(4^{V})$	3·410(9)
N(5) ··· $O(W^{III})$	3·017(8)	O(4) ··· $N(5^{II})$	3·155(7)
O(1) ··· $C(5^{II})$	3·388(9)	N(2) ··· $O(W^{III})$	3·263(8)
O(2) ··· $O(W^{III})$	3·312(8)	C(1) ··· $O(4^{VII})$	2·976(9)
O(3) ··· $C(1^{V})$	3·277(9)	C(8) ··· $O(W^{I})$	3·303(10)
O(3) ··· $C(2^{V})$	3·324(8)	O(W) ··· $O(1^{VII})$	2·882(7)
O(3) ··· $C(3^{V})$	3·423(8)	O(W) ··· $O(3^{VI})$	2·943(7)

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

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

Co atom, appear to be responsible for the Rh being out-of-plane, the in-plane position requiring a too large shift of the two dmg units. If the reactivity were parallelled by such a distortion, the Rh analogue would be expected to have a greater ligand exchange rate than the corresponding cobalt compound.

The phenyl groups are nearly planar and the equations of the best planes passing through the atoms of each group are listed in Table 5.

Intermolecular contacts are as expected in (I). In (II) there are some particularly short van der Waals distances, in addition to those indicative of hydrogen-bond formation, involving the water molecule of crystallization, the ammonia molecule, and the oxygen atoms of the dmg units. Intermolecular distances $<3{\cdot}5$ Å are reported in Table 6.

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