Structural Chemistry of Alkylcobaloximes. Structural Evidence for a Hydroxocobaloxime and Molecular Structure of *trans*-Bis(dimethylglyoximato)methylpyridinecobalt(III) and *trans*-Bis(dimethylglyoximato)-methyl(3-*N*-methylimidazole)cobalt(III)

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The structure of methylcobaloximes containing pyridine, (I), and 3-*N*-methylimidazole, (II), are reported together with a single-crystal i.r. study of the 3-*N*-methylimidazole derivative. Structural evidence for a hydroxocobaloxime with 3-*N*-methylimidazole, (III), is also reported. Crystals of (I) are triclinic, space group $P\bar{1}$, with cell parameters: a = 14.38(1), b = 10.02(1), c = 9.41(1) Å, α = 56.3(1), β = 127.3(1), γ = 106.6(1)°. Crystals of (II) and (III) are both monoclinic, space group $P2_1/c$, with cell parameters: (II) a = 9.25(1), b = 11.77(1), c = 19.80(1) Å, β = 124.4(1)°; and (III) a = 9.24(1), b = 11.55(1), c = 19.80(1) Å, β = 124.3(1)°. A total of 3 083 (I), 1 801 (II), and 1 739 (III) independent reflexions were used; the structures were solved from diffractometer data by the heavy-atom method and refined by least squares to final R factors of 0.064 (I), 0.051 (II), and 0.043 (III). Evidence of structural *trans*- and *cis*-effects is reported. Possible correlations between the structural features and chemical behaviour of cobaloximes and analogous quadridentate Schiff-base complexes are discussed.

THE chemistry of cobaloximes has excited much interest since Shrauzer [1] suggested them as a model for vitamin B_{12}. However as Drago pointed out [2] cobaloximes also merit study for their unusual chemical behaviour. Although a great number of chemical and physicochemical investigations have been performed there are very few structural data. These appear of interest because of the possibility of correlating structural aspects with other properties. For example geometric deformation, which may arise from steric interaction between equatorial and axial ligands, should influence chemical behaviour.

Structural investigations of dimethylglyoximate compounds allow an analysis of the structural *cis*- and *trans*-effects in cobalt(III) octahedral complexes, as already suggested for similar compounds with quadridentate Schiff bases.[3]

Here we report the crystal and molecular structure of *trans*-bis(dimethylglyoximato)methylpyridinecobalt(III) and *trans*-bis(dimethylglyoximato)methyl(3-*N*-methylimidazole)cobalt(III), $MeCo(dmg)_2(py)$, (I), and $MeCo(dmg)_2(nmeim)$ (II). A preliminary account of the structure determination of (I) has already appeared.[4] Single-crystal i.r. pleochroism of (II) is also reported.

During the crystallization of compound (II) some crystals were obtained which gave a diffraction pattern corresponding to the formulation $(OH)Co(dmg)_2(nmeim)$. The crystal structure results for such a hydroxo-compound, (III), are also reported.

EXPERIMENTAL

Preparation of Crystals.—Both (I) and (II) were prepared according to the method of ref. 1(*b*). (I) was recrystallized from acetone and (II) from ethanol [preparation (*A*)] to give well formed stable crystals. A crystal chosen from the latter crystallization was used for the crystal structure analysis of (II) but the final results were not in perfect agreement with the expected formulation, rather suggesting the presence of a hydroxo-compound (*vide infra*). At this stage a new series of crystals (*B*) were prepared from $MeCo(dmg)(H_2O)$ by substitution of water with *N*-methylimidazole. The results of the crystal structure analysis from these crystals were in agreement with the expected formulation $MeCo(dmg)_2(nmeim)$. Unfortunately, it was not possible to obtain again crystals of the former type (*A*) in order to characterize them by elemental analysis. How-

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[1] (*a*) G. N. Shrauzer, *Accounts Chem. Res.*, 1968, **1**, 97; G. N. Shrauzer, P. See, and J. W. Sibert, *J. Amer. Chem. Soc.*, 1970, **92**, 2997 and refs. therein; (*b*) G. N. Shrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, 1966, **88**, 3738.

[2] R. L. Courtright, R. S. Drago, J. A. Nusz, and M. S. Nozani, *Inorg. Chem.*, 1973, **12**, 2809.

[3] M. Calligaris, G. Nardin, and L. Randaccio, *J.C.S. Dalton*, 1972, 1433; M. Calligaris, G. Nardin, and L. Randaccio, *Coordination Chem. Rev.*, 1972, **7**, 385.

[4] L. Randaccio and E. Zangrando, *Cryst. Struct. Comm.*, 1974, **3**, 565.

ever, i.r. spectra (Figure 1) obtained from the powdered crystals (*A*) suggested the presence of some amount of OH because of the weak band at *ca.* 3 400 cm^{-1}, in agreement with the structure analysis results. On the other hand the n.m.r. spectra of both (*A*) and (*B*) compounds were in agreement with the formulation of an alkylcobaloxime, except for the presence of a resonance at *ca.* τ 2.45 for preparation (*A*). It seems likely that in the crystallization of (II) from ethanol a mixture of the methyl- and hydroxo-derivatives was obtained and that by chance a crystal of the second compound was chosen for the structure analysis.

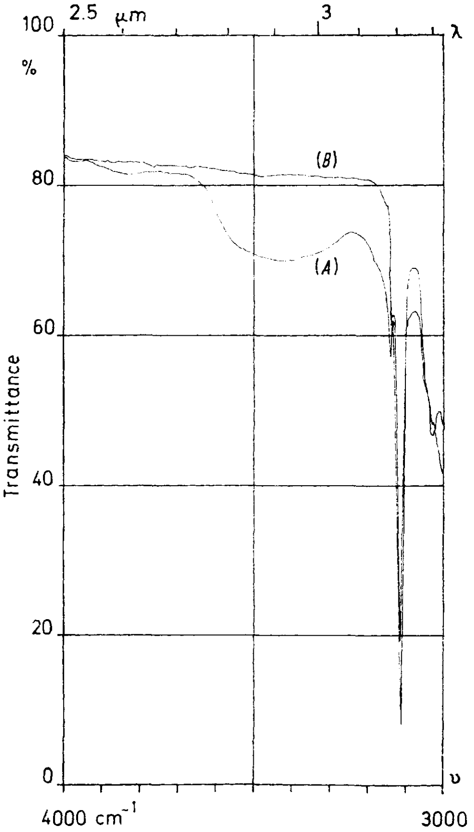

FIGURE 1 Comparison of i.r. spectra of compounds prepared according to method (*A*) and (*B*)

Crystal Data.—(*a*) $C_{14}H_{22}CoN_5O_4$, (I), $M = 383.4$, Triclinic, $a = 14.38(1)$, $b = 10.02(1)$, $c = 9.41(1)$ Å, $\alpha = 56.3(1)$, $\beta = 127.3(1)$, and $\gamma = 106.6(1)°$, $U = 894.8$ Å^3, $D_m = 1.418$, $Z = 2$, $D_c = 1.420$, $\mu(\text{Mo-}K_\alpha) = 10.1$ cm^{-1}, $\mu.r = 0.29$. Space group $P\bar{1}$ (from final refinement). (*b*) $C_{13}H_{23}CoN_6O_4$, (II), $M = 386.3$, Monoclinic, $a = 9.25(1)$, $b = 11.77(1)$, $c = 19.80(1)$ Å, $\beta = 124.4(1)°$, $U = 1\,778.3$ Å^3, $D_m = 1.46$, $Z = 4$, $D_c = 1.44$. $\mu(\text{Mo-}K_\alpha) = 10.4$ cm^{-1}, $\mu.r = 0.20$. Space group $P2_1/c$. (*c*) $C_{12}H_{21}CoN_6O_5$, (III), $M = 388.3$, Monoclinic, $a = 9.24(1)$, $b = 11.55(1)$, $c = 19.80(1)$ Å, $\beta = 124.3(1)°$, $U = 1\,745.8$ Å^3, $D_m = 1.47$, $Z = 4$, $D_c = 1.47$. $\mu(\text{Mo-}K_\alpha) = 10.6$ cm^{-1}, $\mu.r = 0.23$. Space group $P2_1/c$.

Cell parameters were determined from Weissenberg photographs taken with Co-K_α radiation and refined with an on-line automatic single-crystal Siemens diffractometer by use of Mo-K_α radiation ($\lambda = 0.7107$ Å).

Intensity Measurements.—Three-dimensional intensity data were collected on a Siemens diffractometer by means of the θ—2θ scan technique and Mo-K_α radiation for 2θ max. 60° for (I), and 50° for (II) and (III). Reflexions having $I_o < 3\sigma(I_o)$ were rejected, the remainder being corrected for the Lorentz-polarization factor. A total of 3 083 (I), 1 801 (II), and 1 739 (III) independent reflexions were used in the subsequent calculations. No correction for absorption and anomalous dispersion of cobalt was applied.

Structure Determination and Refinement.—All the structures were solved by the conventional heavy-atom method. The final anisotropic refinement, including the contribution of the hydrogen atoms held constant (B 5.0 Å^2), reduced R to 0.064 (I), 0.051 (II), and 0.045 (III). Final weighting schemes were $w = 1/(A + B|F_o| + C|F_o|^2)$, where $A = 0.8, B = 1.0, C = 0.032$ for (I), and $A = 10.0$, $B = 1.0$, and $C = 0.004$ for (II) and (III), the values of the constant being chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and $(\sin\theta/\lambda)$.

Previous refinement of (III), still assumed to be the methyl derivative, led to a higher value of R (0.057) and to a value of the isotropic temperature factor (B 0.88 Å^2) for the carbon atom, particularly low when compared with the B factors of the other atoms. Furthermore the final difference-Fourier synthesis gave a residual of positive electron density (2 eÅ^{-3}) at the carbon atom position.

Refinement carried out for (II) assuming an oxygen atom axially bonded to the cobalt atom gave a final R of 0.055 with a B value for the oxygen atom three times those of the remaining atoms. These results are in agreement with the formulation of a methyl- and hydroxo-structure for (II) and (III) respectively. When final co-ordinates of all the atoms of these compounds are compared, the only significant difference relates to atoms C(13) and O(5).

Final atomic parameters are listed in Tables **1**—**3**, together with their estimated standard deviations calculated from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle. The numbering schemes for the atoms are shown in Figure 2 for (I) and Figure 3 for (II) and (III). Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21535 (23 pp., 1 microfiche).* Atomic scattering factors were calculated according to ref. 5.

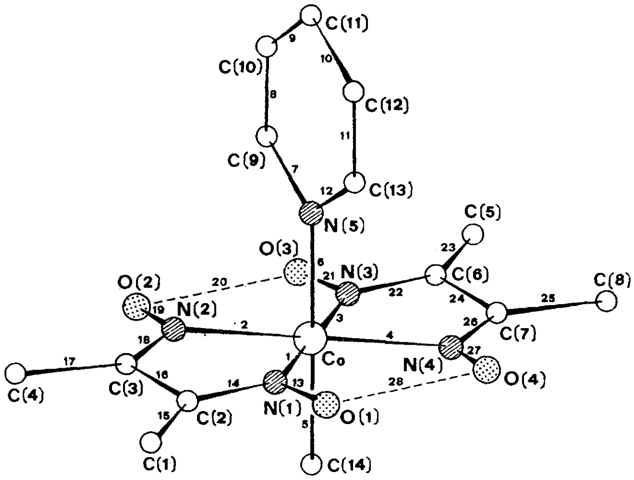

FIGURE 2 Numbering scheme for non-hydrogen atoms of (I)

Calculations.—All calculations were carried out on a CDC

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* For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue.

[5] F. H. Moore, *Acta Cryst.*, 1963, **16**, 1169.

Table 1

Positional and thermal parameters ($\times 10^4$) for (I), with estimated standard deviations in parentheses

	x	y	z	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Co	2 230(0)	2 037(1)	3 747(1)	43(0)	−44(1)	126(1)	118(0)	−160(1)	199(1)
O(1)	77(2)	1 592(4)	3 378(4)	61(2)	−41(4)	197(4)	203(4)	−241(6)	326(4)
O(2)	2 633(2)	2 677(4)	781(4)	105(2)	−61(5)	302(3)	233(5)	−222(6)	324(4)
O(3)	4 361(3)	2 695(4)	3 961(4)	76(2)	−101(5)	276(4)	288(5)	−354(7)	402(5)
O(4)	1 795(2)	1 635(4)	6 561(4)	95(2)	−55(4)	270(3)	250(4)	−346(5)	349(4)
N(1)	611(2)	1 831(3)	2 484(4)	56(2)	−24(4)	142(4)	122(3)	−156(5)	249(4)
N(2)	1 835(3)	2 339(4)	1 235(4)	57(2)	−3(4)	148(4)	141(4)	−128(6)	246(5)
N(3)	3 839(3)	2 375(4)	4 919(4)	53(2)	−67(4)	192(4)	171(4)	−241(6)	308(5)
N(4)	2 608(3)	1 864(4)	6 167(4)	63(2)	−16(4)	143(4)	137(4)	−189(5)	261(5)
N(5)	2 551(2)	−423(3)	5 251(4)	45(2)	−33(3)	136(3)	135(3)	−164(5)	213(4)
C(1)	−1 265(4)	1 638(5)	−423(7)	56(3)	−23(6)	88(8)	174(5)	−278(9)	354(8)
C(2)	20(3)	1 888(4)	699(5)	65(3)	−17(5)	112(5)	109(4)	−148(7)	242(6)
C(3)	748(4)	2 232(4)	−75(5)	88(3)	−3(5)	140(5)	131(4)	−157(6)	221(5)
C(4)	286(5)	2 559(6)	−2 184(6)	124(4)	37(8)	140(7)	233(6)	−239(9)	241(6)
C(5)	5 681(5)	2 646(7)	7 784(9)	65(4)	−107(9)	164(11)	298(9)	−456(15)	473(13)
C(6)	4 417(4)	2 339(5)	6 674(6)	63(3)	−46(6)	132(6)	174(5)	−266(8)	304(7)
C(7)	3 686(4)	2 029(5)	7 441(5)	75(3)	−31(6)	140(6)	163(4)	−248(7)	273(6)
C(8)	4 111(5)	1 937(6)	9 422(6)	124(4)	37(8)	109(8)	255(6)	−336(8)	278(6)
C(9)	3 237(4)	−1 071(5)	5 224(5)	70(3)	−12(5)	175(5)	165(5)	−210(7)	285(6)
C(10)	3 447(4)	−2 706(5)	6 203(6)	98(3)	16(6)	190(6)	185(5)	−252(8)	339(7)
C(11)	2 902(4)	−3 729(5)	7 232(7)	111(4)	9(7)	179(7)	144(5)	−150(9)	305(8)
C(12)	2 215(4)	−3 085(5)	7 285(6)	87(3)	−32(6)	189(6)	144(5)	−163(8)	272(8)
C(13)	2 047(3)	−1 435(5)	6 281(5)	72(3)	−37(5)	180(5)	145(4)	−155(7)	240(5)
C(14)	1 875(4)	4 400(5)	2 311(6)	94(3)	−46(6)	195(7)	134(5)	−184(9)	320(8)

Hydrogen atom co-ordinates ($\times 10^4$)

H(1,1) *	−1 551	1 736	−1 867	H(8,3)	3 670	2 876	9 080
H(1,2)	−1 759	2 537	−790	H(14,1)	2 460	5 064	1 810
H(1,3)	−1 410	436	531	H(14,2)	1 994	4 700	3 361
H(4,1)	−668	2 392	−2 980	H(14,3)	967	4 737	965
H(4,2)	723	1 743	−2 039	H(9)	3 631	−259	4 411
H(4,3)	402	3 802	−3 094	H(10)	4 017	−3 199	6 164
H(5,1)	5 967	2 580	9 190	H(11)	3 026	−5 037	7 983
H(5,2)	5 802	3 883	6 771	H(12)	1 811	−3 860	8 112
H(5,3)	6 214	1 799	8 137	H(13)	1 503	−931	6 334
H(8,1)	5 078	2 162	10 162	H(A)	3 600	3 000	2 200
H(8,2)	4 030	772	10 455	H(B)	800	1 400	5 000

* Hydrogen atoms are numbered according to the C atom to which they are bonded.

6 200 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.

I.r. Spectral Measurements.—I.r. spectra were recorded on a Perkin-Elmer 225 spectrophotometer. Powder spectra were run as Nujol mulls. Single crystals of (II) were best used for i.r. measurements as thin platelets. The orientation and identification of the crystallographic axes were performed by X-ray methods. It was shown by Weissenberg photographs that the plane developed in our samples contained the a and b axes. Because of their small dimensions, single crystals used in these experiments were mounted at the focus of a Perkin-Elmer mirror beam-condenser. Polarized spectra were obtained by use of a wire-grid polarizer, with the electric vector oriented parallel to the a and b axes of the sample.

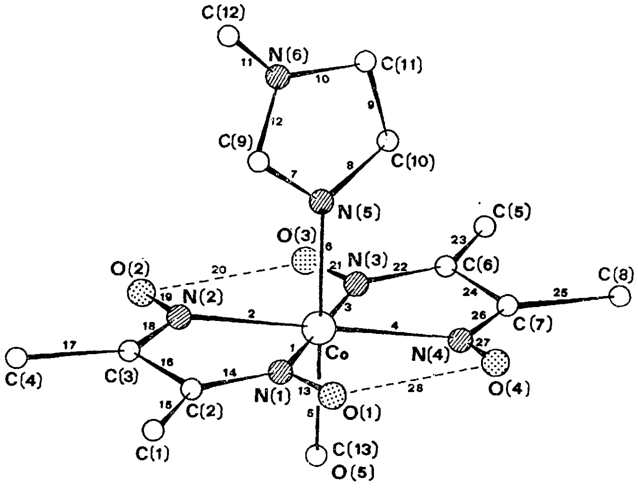

Figure 3 Numbering scheme for non-hydrogen atoms of (II) and (III)

RESULTS AND DISCUSSION

Description of the Structures.—The structure of (I) consists of discrete molecules held together by van der Waals forces. The co-ordination around the cobalt atom is nearly octahedral. The four equatorial nitrogen atoms are coplanar to within ±0.01 Å, the cobalt atom being slightly displaced (0.043 Å) from their mean plane towards the pyridine molecule. The planes passing through the atoms of the two dmg units are bent away from the axially bonded pyridine molecule at 3.2°.

The pyridine molecule is nearly planar (±0.008 Å) and its plane is nearly perpendicular (90.8°) to the equatorial co-ordination plane, bisecting the angles N(1)–Co–N(4) and N(2)–Co–N(3). This orientation is

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[6] V. Albano, A. Domenicano, and A. Vaciago, *Gazzetta*, 1966, **96**, 922.

[7] V. Schomaker, J. Waser, R. F. Marsh, and G. Bergmann, *Acta Cryst.*, 1959, **12**, 600.

similar to that found in other cobaloximes.[8,9] The Co–N(py) bond length [2.068(3) Å] is in good agreement with the reported value [2.040(6) Å].[8] The Co–CH_3 bond length [1.998(5) Å] is very close to that reported[10] for $MeCo(dmg)_2(H_2O)$ [1.990(5) Å] and for (II) [2.009(7) Å]. Other bond lengths are as expected and are reported in Table 4, together with relevant bond angles.

The structures of (II) and (III) are practically identical, with the exception of the exchange between the C(13) and O(5) atoms. In fact the co-ordinates of these atoms are significantly different, whereas those of all other corresponding atoms are the same, within 3σ.

TABLE 2

Positional and thermal parameters (× 10^4) for (II), with estimated standard deviations in parentheses

	x	y	z	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Co	1 200(1)	2 133(1)	1 540(0)	92(1)	10(1)	50(1)	42(1)	−2(1)	21(0)
O(1)	−1 906(6)	1 878(5)	1 520(3)	134(6)	−10(9)	101(4)	91(5)	−6(5)	48(2)
O(2)	2 584(6)	4 185(5)	1 312(3)	275(8)	−55(9)	183(5)	64(4)	3(4)	58(2)
O(3)	4 150(5)	2 394(5)	1 453(3)	159(6)	−40(9)	112(4)	99(5)	−6(4)	37(1)
O(4)	−237(5)	79(4)	1 726(3)	166(6)	−41(9)	121(4)	64(4)	−1(4)	50(2)
N(1)	−836(6)	2 622(5)	1 458(3)	101(6)	15(9)	58(4)	69(5)	−4(4)	26(2)
N(2)	1 289(7)	3 722(5)	1 355(3)	196(9)	−8(10)	87(5)	55(4)	0(4)	28(2)
N(3)	3 139(6)	1 651(5)	1 539(3)	119(6)	13(9)	64(4)	77(5)	−1(4)	21(1)
N(4)	1 017(6)	545(4)	1 656(3)	112(7)	−20(9)	55(5)	45(4)	−16(4)	29(2)
N(5)	2 723(5)	2 326(4)	2 792(3)	106(5)	6(8)	60(4)	43(4)	10(4)	24(1)
N(6)	3 595(7)	2 817(5)	4 036(3)	151(8)	−43(11)	68(5)	74(5)	−11(5)	25(2)
C(1)	−2 831(10)	4 214(8)	1 235(5)	204(12)	196(14)	59(8)	137(8)	−17(7)	34(3)
C(2)	−1 225(8)	3 710(6)	1 325(4)	152(9)	90(12)	53(6)	74(6)	−6(6)	25(2)
C(3)	57(10)	4 366(6)	1 276(4)	226(12)	64(14)	98(7)	58(6)	9(6)	35(2)
C(4)	−49(13)	5 648(8)	1 144(6)	393(19)	78(19)	222(12)	58(7)	27(9)	83(4)
C(5)	4 954(9)	30(8)	1 626(4)	206(9)	153(14)	123(6)	117(7)	26(7)	38(2)
C(6)	3 464(8)	556(6)	1 615(4)	138(9)	43(11)	59(6)	68(6)	−7(5)	23(2)
C(7)	2 218(8)	−117(6)	1 689(4)	156(9)	41(12)	60(6)	53(5)	4(5)	24(2)
C(8)	2 277(10)	−1 399(7)	1 787(4)	270(13)	83(14)	124(8)	61(6)	17(6)	42(2)
C(9)	2 334(7)	2 901(6)	3 240(3)	139(8)	−25(12)	73(5)	65(5)	10(5)	25(2)
C(10)	4 347(8)	1 820(6)	3 349(4)	109(8)	−7(11)	52(6)	70(6)	4(5)	27(2)
C(11)	4 880(8)	2 124(7)	4 116(4)	135(9)	−2(14)	64(6)	84(6)	19(6)	29(2)
C(12)	3 600(11)	3 341(9)	4 719(5)	286(14)	−10(19)	138(8)	127(9)	−25(8)	39(2)
C(13)	−300(9)	1 888(7)	323(4)	161(10)	37(13)	58(7)	85(7)	−8(6)	26(2)

Hydrogen atom co-ordinates (× 10^4)

H(1,1)	−2 857	5 142	1 133	H(8,3)	2 136	−1 810	1 257
H(1,2)	−2 775	4 084	1 796	H(12,1)	2 388	3 852	4 467
H(1,3)	−4 016	3 842	721	H(12,2)	4 721	3 885	5 078
H(4,1)	1 041	5 941	1 122	H(12,3)	3 598	2 675	5 103
H(4,2)	−4	6 080	1 646	H(13,1)	−161	2 617	12
H(4,3)	−1 285	5 873	567	H(13,2)	−1 683	1 827	104
H(5,1)	4 940	−900	1 686	H(13,3)	86	1 120	162
H(5,2)	6 211	352	2 143	H(9)	1 126	3 382	2 988
H(5,3)	4 856	215	1 058	H(10)	5 062	1 265	3 200
H(8,1)	1 224	−1 687	1 841	H(11)	6 068	1 888	4 689
H(8,2)	3 539	−1 657	2 340	H(A)	3 360	3 300	1 380
				H(B)	−1 080	1 100	1 650

The planes through the two dmg units are bent away from the nmeim molecule, at 4.4°. The nmeim molecule is planar within ±0.014 Å and nearly perpendicular to the co-ordination plane (86.9°).

The four nitrogen atoms of the dmg units are planar within ±0.02 Å, the cobalt atom being displaced towards the nmeim ligand by *ca.* 0.05 Å.

The Co–OH distance [2.190(3) Å] in (III) is significantly longer than that [2.05 Å] for the Co–OH_2 bond in $MeCo(dmg)_2(H_2O)$. Since a value of 1.894(8) Å for Co–OMe has been reported[11] in MeO·Co(salen)(py) [salen = bis(salicylaldehyde)ethylenedi-iminato(2−)] a value <2.00 Å might be expected. This result is the only one at odds with the foregoing experimental evidence, which suggests a hydroxo-compound (see Experimental section). No hydrogen bond has been detected in the crystal packing, because the molecules are arranged so that the OH groups are related by the crystallographic symmetry centres, with O · · · O intermolecular distances slightly >4.0 Å.

Table 5 lists equations of least-squares planes.

trans-*Influence*.—Recently there has been some evidence to suggest the existence of a *trans*-influence in octahedral derivatives of cobaloximes.[12] All structural data so far available (Table 6) definitely confirm this suggestion. The trend of the Co–N bond lengths suggests that the *trans*-influencing ability of a group increases with the increasing σ-donor power. Thus values of the Co–N distances support the hypothesis of Hill *et al.*,[13] who attributed to a lengthening of the Co–N(py) distance the lowering of the chemical shifts of the α-protons of the pyridine molecule from X = halogen to X = alkyl in the series $XCo(dmg)_2(py)$. Furthermore, although too few data are at present available for Co–P and Co–Cl

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[8] G. P. Lenhert, *Chem. Comm.*, 1967, 980.

[9] W. W. Adams and G. P. Lenhert, *Acta Cryst.*, 1973, **B29**, 2412.

[10] D. L. McFadden and A. T. McPhail, *J.C.S. Dalton*, 1974, 363.

[11] M. Cesari, C. Neri, G. Perego, E. Perotti, and A. Zazzetta, *Chem. Comm.*, 1970, 276.

[12] S. Brückner and L. Randaccio, *J.C.S. Dalton*, 1974, 1017.

[13] H. A. O. Hill and K. G. Morallee, *J. Chem. Soc.* (*A*), 1969, 544.

distances, it appears that the lower is the tendency of a group to be *trans*-influenced the higher is its *trans*-influencing power. In fact the variation in Co–N distances is larger than that observed for the Co–P distance.

cis-*Influence*.—The ability of an equatorial ligand in octahedral complexes to influence the axial ligands or *vice versa* may be called *cis*-influence. However, in the case of chelate equatorial ligands we can extend such a definition, assuming that any variation of the structural parameters in one kind of equatorial ligand by varying the axial groups is indicative of *cis*-influence.

TABLE 3

Positional and thermal parameters (× 10^4) for (III), with estimated standard deviations in parentheses

	x	y	z	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Co	1 205(1)	2 133(1)	1 547(0)	101(1)	13(1)	59(1)	35(0)	1(1)	24(0)
O(1)	−1 903(5)	1 880(5)	1 527(3)	148(5)	−5(8)	142(4)	84(5)	−2(5)	62(2)
O(2)	2 603(6)	4 196(4)	1 329(3)	288(7)	−38(9)	195(4)	54(4)	9(4)	62(2)
O(3)	4 147(5)	2 393(5)	1 454(2)	165(5)	−39(8)	123(4)	88(5)	−3(4)	49(1)
O(4)	−210(5)	83(4)	1 736(3)	175(6)	−35(8)	123(4)	56(4)	1(4)	53(2)
O(5)	−424(5)	1 826(4)	226(2)	162(6)	101(7)	85(4)	66(4)	28(4)	37(1)
N(1)	−830(6)	2 631(5)	1 466(3)	125(6)	17(9)	66(4)	52(4)	−1(4)	32(2)
N(2)	1 331(7)	3 733(5)	1 376(3)	224(8)	18(10)	99(5)	49(4)	9(4)	32(2)
N(3)	3 139(5)	1 650(5)	1 543(3)	130(6)	18(9)	85(4)	71(4)	−4(4)	30(1)
N(4)	1 018(5)	530(4)	1 664(2)	117(6)	−31(8)	67(4)	46(4)	−5(4)	28(1)
N(5)	2 717(5)	2 327(4)	2 788(2)	106(6)	−8(8)	57(4)	39(3)	3(4)	25(1)
N(6)	3 560(6)	2 821(5)	4 031(3)	176(7)	−15(11)	89(4)	69(4)	−6(5)	28(1)
C(1)	−2 802(8)	4 243(7)	1 246(4)	228(10)	145(13)	139(6)	99(7)	−8(7)	55(2)
C(2)	−1 203(8)	3 717(6)	1 344(4)	177(10)	101(12)	60(6)	69(5)	2(6)	30(2)
C(3)	83(9)	4 373(6)	1 287(4)	243(11)	50(12)	124(6)	42(5)	7(5)	41(2)
C(4)	−34(12)	5 661(7)	1 148(5)	393(17)	85(17)	201(10)	54(6)	25(8)	71(3)
C(5)	4 959(8)	31(7)	1 620(4)	206(10)	125(14)	111(6)	102(7)	23(7)	43(2)
C(6)	3 463(7)	553(6)	1 618(3)	145(8)	45(10)	78(5)	61(5)	−3(5)	28(2)
C(7)	2 216(7)	−111(5)	1 693(3)	164(9)	33(11)	69(5)	46(4)	−4(5)	27(2)
C(8)	2 301(10)	−1 398(6)	1 801(4)	287(13)	54(14)	129(7)	43(5)	−1(6)	47(2)
C(9)	2 299(7)	2 912(6)	3 236(3)	148(7)	−12(11)	69(4)	53(4)	2(5)	25(2)
C(10)	4 345(7)	1 831(6)	3 353(3)	119(7)	−13(10)	88(5)	58(5)	8(5)	38(2)
C(11)	4 858(7)	2 140(6)	4 107(3)	145(8)	−43(12)	65(5)	71(5)	15(6)	29(2)
C(12)	3 598(11)	3 378(9)	4 707(4)	311(13)	−27(19)	128(7)	129(8)	−47(7)	34(2)

Hydrogen atom co-ordinates (× 10^4)

H(1,1)	−3 567	3 559	1 289	H(8,2)	3 546	−1 628	2 379
H(1,2)	−3 600	4 661	652	H(8,3)	2 219	−1 831	1 301
H(1,3)	−2 409	4 876	1 728	H(9)	1 084	3 395	2 985
H(4,1)	1 066	5 956	1 127	H(10)	5 081	1 279	3 208
H(4,2)	−30	6 124	1 626	H(11)	6 077	1 890	4 678
H(4,3)	−1 260	5 866	554	H(12,1)	2 379	3 862	4 466
H(5,1)	5 684	693	1 546	H(12,2)	4 706	3 945	5 039
H(5,2)	4 442	−598	1 113	H(12,3)	3 676	2 699	5 119
H(5,3)	5 840	−438	2 194	H(A)	3 500	3 400	1 400
H(8,1)	1 224	−1 678	1 847	H(B)	−1 150	1 200	1 650
				H[O(5)]	−1 100	2 500	0

The available Co–C bond lengths are compared in Table 7 for the ocahedral complexes of formula L·Co^{III}-(chel)R, where chel = $(dmg)_2$, salen, or acacen [bis(acetylacetone)ethylenedi-iminato(2—)], R = alkyl or aryl, and L = Lewis base. Table 7 also lists the Co–C distances corrected for the different σ-covalent radii of the hybridized carbon atom. As already suggested [10] these values do not indicate a significant *cis*-influence since all the Co–C distances are almost equal if the vinyl derivatives are excluded in which a π-bonding contribution in the Co–C bond is present. On the contrary, if the axial Co–N and Co–O distances are compared a significant increase of bond lengths is observed in the order $(dmg)_2$ < salen < acacen (Table 8). Since the experimental values for the Co–N distances can be affected by other factors, such as the different hybridization of the N atom and the influence of the *trans*-ligand, they have been corrected by attempting to take into account these effects. According to Ibers *et al.*[14] it has been assumed that the covalent radii of N(sp^2) and N(sp^3) differ by *ca.* 0.05 Å. The lengthening due to a strong *trans*-influencing group, with respect to a non-influencing ligand, may be assumed to be *ca.* 0.12 Å (see Table 6 and the foregoing section).

It may be argued that the observed *cis*-influence may derive from steric rather than electronic effects. Obviously these factors cannot be easily separated but we believe that the latter are the most important, mainly because no significant difference has been observed for the Co–C bond lengths reported in Table 7. Furthermore the higher flexibility [3] of salen and acacen ligands with respect to the $(dmg)_2$ ligand [12] would suggest an opposite trend of the axial bond lengths.

The trend of bond lengths correlates with that of other physicochemical properties. Recently Costa [15] has found that the electrochemical properties for the reduction:

$$[RCo(chel)]^{n+} + e^- \longrightarrow [RCo(chel)]^{(n-1)+}$$

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[14] R. G. Little and J. A. Ibers, *J. Amer. Chem. Soc.*, 1974, **96**, 4440, and refs. therein.

[15] G. Costa, *Co-ordination Chem. Rev.*, 1972, **8**, 63, and refs. therein.

(where R = alkyl group) suggest the order of increasing ease of reduction: acacen < salen < $(dmg)_2$. This is in agreement with the recent conclusion [16] that $RCo(dmg)_2$ is a stronger acid than is RCo(acacen). Thus assuming the formation of the octahedral compounds MeCo(chel)L as a reaction between the MeCo(chel) acid and the Lewis base L, the Co–L bond is expected to be stronger, and the corresponding bond length shorter, with dmg ligands than with Schiff bases.

TABLE 4

Relevant bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) For (I)

(i) Distances

(1) 1.877(2)	(11) 1.379(6)	(20) 2.481(4)
(2) 1.918(5)	(12) 1.354(6)	(21) 1.357(7)
(3) 1.887(4)	(13) 1.345(6)	(22) 1.307(7)
(4) 1.905(5)	(14) 1.319(6)	(23) 1.492(7)
(5) 1.998(5)	(15) 1.503(6)	(24) 1.486(10)
(6) 2.068(3)	(16) 1.478(9)	(25) 1.523(9)
(7) 1.345(8)	(17) 1.514(8)	(26) 1.300(5)
(8) 1.376(6)	(18) 1.301(5)	(27) 1.355(6)
(9) 1.401(8)	(19) 1.351(6)	(28) 2.489(4)
(10) 1.362(11)		

(ii) Angles

(1)–(2) 81.0(2)	(2)–(6) 92.5(2)
(1)–(3) 176.7(1)	(3)–(4) 81.4(2)
(1)–(4) 99.1(2)	(3)–(5) 89.3(2)
(1)–(5) 87.4(2)	(3)–(6) 92.3(1)
(1)–(6) 91.0(1)	(4)–(5) 88.3(2)
(2)–(3) 98.4(2)	(4)–(6) 90.7(2)
(2)–(4) 176.8(2)	(5)–(6) 178.0(2)
(2)–(5) 88.5(2)	

(*b*) For (II)

(i) Distances

(1) 1.886(6)	(11) 1.484(13)	(20) 2.483(8)
(2) 1.917(6)	(12) 1.333(6)	(21) 1.359(9)
(3) 1.882(7)	(13) 1.378(9)	(22) 1.313(9)
(4) 1.903(5)	(14) 1.316(9)	(23) 1.499(13)
(5) 2.009(7)	(15) 1.513(13)	(24) 1.472(12)
(6) 2.058(5)	(16) 1.463(13)	(25) 1.519(1)
(7) 1.317(10)	(17) 1.525(12)	(26) 1.328(10)
(8) 1.398(7)	(18) 1.302(11)	(27) 1.359(9)
(9) 1.353(11)	(19) 1.361(10)	(28) 2.514(8)
(10) 1.375(11)		

(ii) Angles

(1)–(2) 80.5(3)	(2)–(3) 98.6(3)	(3)–(5) 88.1(3)
(1)–(3) 175.9(2)	(2)–(4) 176.6(2)	(3)–(6) 91.8(2)
(1)–(4) 99.1(3)	(2)–(5) 89.2(3)	(4)–(5) 87.4(3)
(1)–(5) 87.8(3)	(2)–(6) 92.8(2)	(4)–(6) 90.6(2)
(1)–(6) 92.3(2)	(3)–(4) 81.6(3)	(5)–(6) 178.0(3)

(*c*) For (III)

(i) Distances

(1) 1.884(6)	(11) 1.467(12)	(20) 2.457(7)
(2) 1.895(6)	(12) 1.334(6)	(21) 1.349(8)
(3) 1.875(6)	(13) 1.373(9)	(22) 1.292(9)
(4) 1.886(5)	(14) 1.288(9)	(23) 1.505(11)
(5) 2.190(3)	(15) 1.505(11)	(24) 1.459(10)
(6) 2.043(3)	(16) 1.466(12)	(25) 1.498(9)
(7) 1.333(9)	(17) 1.506(11)	(26) 1.305(8)
(8) 1.395(6)	(18) 1.295(11)	(27) 1.325(8)
(9) 1.336(9)	(19) 1.341(10)	(28) 2.490(7)
(10) 1.370(9)		

(ii) Angles

(1)–(2) 81.1(3)	(2)–(3) 97.8(3)	(3)–(5) 87.8(2)
(1)–(3) 175.7(2)	(2)–(4) 177.3(2)	(3)–(6) 91.7(2)
(1)–(4) 98.9(2)	(2)–(5) 90.8(2)	(4)–(5) 86.5(2)
(1)–(5) 88.0(2)	(2)–(6) 92.2(2)	(4)–(6) 90.4(2)
(1)–(6) 92.4(2)	(3)–(4) 82.0(2)	(5)–(6) 176.9(2)

TABLE 5

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

(*a*) For (I)

Plane (1): Co, N(1)—(4)

$$-2.418x + 8.839y + 1.231z = 1.765$$

[Co −0.043, N(1) 0.011, N(2) 0.010, N(3) 0.011, N(4) 0.011]

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

$$-2.632x + 8.935y + 1.443z = 1.811$$

[Co −0.037, O(1) 0.079, O(2) 0.001, N(1) 0.023, N(2) −0.025, C(1) −0.075, C(2) −0.028, C(3) −0.024, C(4) 0.086]

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

$$-2.619x + 8.6824y + 1.026z = 1.581$$

[Co −0.011, O(3) 0.024, O(4) 0.042, N(3) −0.019, N(4) −0.012, C(5) 0.028, C(6) −0.022, C(7) −0.021, C(8) −0.008]

Plane (4): N(5), C(9)—(13)

$$3.847x + 3.838y + 5.691z = 3.809$$

[N(5) −0.002, C(9) −0.002, C(10) 0.008, C(11) −0.009, C(12) 0.004, C(13) 0.001]

(*b*) For (II)

Plane (1): Co, N(1)—(4)

$$0.044x + 1.527y + 16.146z = 2.768$$

[Co 0.049, N(1) −0.018, N(2) −0.006, N(3) −0.018, N(4) −0.007]

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

$$-0.223x + 1.810y + 16.408z = 2.875$$

[Co 0.011, O(1) 0.001, O(2) −0.023, N(1) 0.010, N(2) −0.007, C(1) −0.023, C(2) −0.002, C(3) 0.007, C(4) 0.025]

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

$$0.315x + 1.222y + 15.857z = 2.735$$

[Co 0.005, O(3) −0.008, O(4) 0.004, N(3) 0.006, N(4) −0.011, C(5) 0.003, C(6) 0.003, C(7) −0.001, C(8) −0.001]

Plane (4): N(5), N(6), C(9)—(12)

$$5.486x + 9.4564y - 7.512z = 1.594$$

[N(5) 0.002, N(6) 0.010, C(9) −0.004, C(10) −0.004, C(11) 0.000, C(12) −0.004]

(*c*) For (III)

Plane (1): Co, N(1)—(4)

$$0.045x + 1.452y + 16.180z = 2.773$$

[Co 0.045, N(1) −0.023, N(2) 0.001, N(3) −0.023, N(4) 0.001]

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

$$-0.237x + 1.800y + 16.441z = 2.897$$

[Co 0.002, O(1) −0.003, O(2) −0.018, N(1) 0.007, N(2) 0.006, C(1) −0.018, C(2) 0.010, C(3) 0.004, C(4) 0.010]

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

$$0.357x + 1.240y + 15.830z = 2.750$$

[Co 0.006, O(3) −0.004, O(4) 0.001, N(3) 0.009, N(4) −0.014, C(5) −0.005, C(6) 0.003, C(7) −0.005, C(8) 0.009]

Plane (4): N(5), N(6), C(9)—(12)

$$5.436x + 9.354y - 7.611z = 1.520$$

[N(5) 0.011, N(6) −0.014, C(9) −0.009, C(10) 0.003, C(11) −0.003, C(12) 0.013]

As already stated above, the *cis*-influence can provoke a variation in the chelate ligand bond lengths.[12] Analysis of Co–N, C–C, C–N, N–O, and C–CH_3 chemically independent bond lengths for all reported structures of dimethylglyoximates (data relating to alkylcobaloximes grouped and averaged separately from those of other

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[16] R. J. Gushl and T. L. Brown, *Inorg. Chem.*, 1973, **12**, 2815.

cobaloximes in order to distinguish compounds with strong σ-donor axial ligands) is shown in Figure 4.

Although the ranges are too large for discussion of the differences found in the two groups, it may be observed that the C=C, Co–N, and C–N bond lengths appear to be different on the basis of their σ values. This observation, if confirmed by further data, will support the conclusion obtained by semiempirical calculations for cobaloximes with axial substitutents of different σ-donor power. In fact De Alti *et al.*[17] have suggested that the electronic charge donated by the axial ligands on the metal is partly spread out over the atoms of the chelate rings, essentially through delocalized π-orbitals causing a slight change in bond lengths.

TABLE 6

The *trans*-influence in octahedral cobaloxime derivatives; distances in Å

	Co–N	*trans* to
$ClCo(dmg)_2(NH_3)$ [a]	1.965(4)	Cl
$(PhNH_2)Co(dmg)_2(NH_2Ph)$ [b]	2.001(5)	N(sp^3)
$MeCo(dmg)_2(nmeim)$ [c]	2.058(5)	C(sp^3)
$(MeCO_2{\cdot}H_2C)Co(dmg)_2(py)$ [d]	2.040(6)	C(sp^3)
$MeCo(dmg)_2(py)$ [c]	2.068(3)	C(sp^3)
	Co–P	
$ClCo(dmg)_2(PPh_3)$ [a]	2.327(4)	Cl
$(N[CH]_4C)Co(dmg)_2(PBu_3)$ [e]	2.342(1)	C(sp^2)
	Co–Cl	
$(H_3N)Co(dmg)_2Cl$ [a]	2.251(1)	N(sp^3)
$(Ph_3P)Co(dmg)_2Cl$ [a]	2.277(4)	P

[a] Ref. 12. [b] L. P. Battaglia, A. Bonamartini Corradi, C. Grasselli Palmieri, M. Nardelli, and M. E. Vidoni Tani, *Acta Cryst.*, 1974, **B30**, 1114. [c] Present work. [d] Ref. 8. [e] Ref. 9.

TABLE 7

Experimental and corrected values of Co–C distances (Å) in some cobalt(III) octahedral complexes with different equatorial ligands

	Found	Corr.
$(MeCO_2{\cdot}H_2C)Co(dmg)_2(py)$ [a]	2.040(6)	2.04
$(N[CH]_4C)Co(dmg)_2(PBu_3)$ [b]	1.983(1)	2.01
$MeCo(dmg)_2(OH_2)$ [c]	1.990(5)	2.00
$MeCo(dmg)_2(py)$ [d]	1.998(5)	2.00
$MeCo(dmg)_2{\cdot}(nmeim)$ [d]	2.009(7)	2.03
$(AcCH_2)Co(salen)(MeOH)$ [e]	2.019(14)	2.02
$[EtCo(salen)]_2$ [f]	1.990(7)	1.99
$[(CH_2CN)Co(salen)]_n$ [e]	1.988(22)	1.99
$(CH_2{:}CH)Co(salen)(py)$ [g]	1.930(20)	1.96
$PhCo(acacen)(OH_2)$ [h]	1.930(20)	1.96
$MeCo(acacen)(py)$ [i]	1.990(10)	1.99
$(CH_2{:}CH)Co(acacen)(OH_2)$ [j]	1.890(10)	1.92

[a] Ref. 8. [b] Ref. 9. [c] Ref. 10. [d] Present work. [e] Ref. 11. [f] Ref. 19. [g] Ref. 3. [h] S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, *Chem. Comm.*, 1970, 152. [i] M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 477. [j] S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, 1968, **2**, 416.

Conformational Aspects.—Some data relative to the geometry of the equatorial ligand and the stereochemistry around the cobalt atom are reported in Figure 5. It may be observed that when one axial ligand is bulkier than the other [Figure 5 (b)—(d)] the Co atom is slightly displaced from the equatorial plane towards the bulk ligand itself. If both axial ligands have little steric hindrance the Co atom is nearly coplanar with the four donor atoms [Figure 5(a), (e)]. In one case, in which they are the same, the molecule as a whole has a crystallographic centre of symmetry.[18] Finally if both ligands

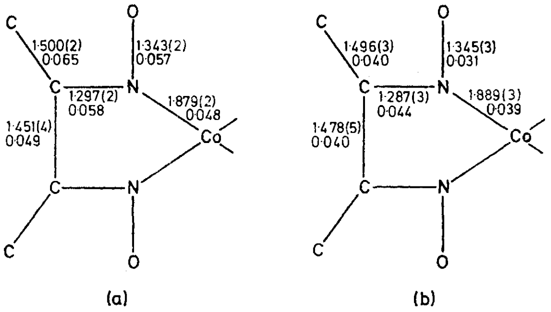

FIGURE 4 Mean values of $Co(dmg)_2$ chemically equivalent bond lengths (with estimated standard deviations in parentheses) and ranges, for (a) organometallic and (b) non-organometallic compounds

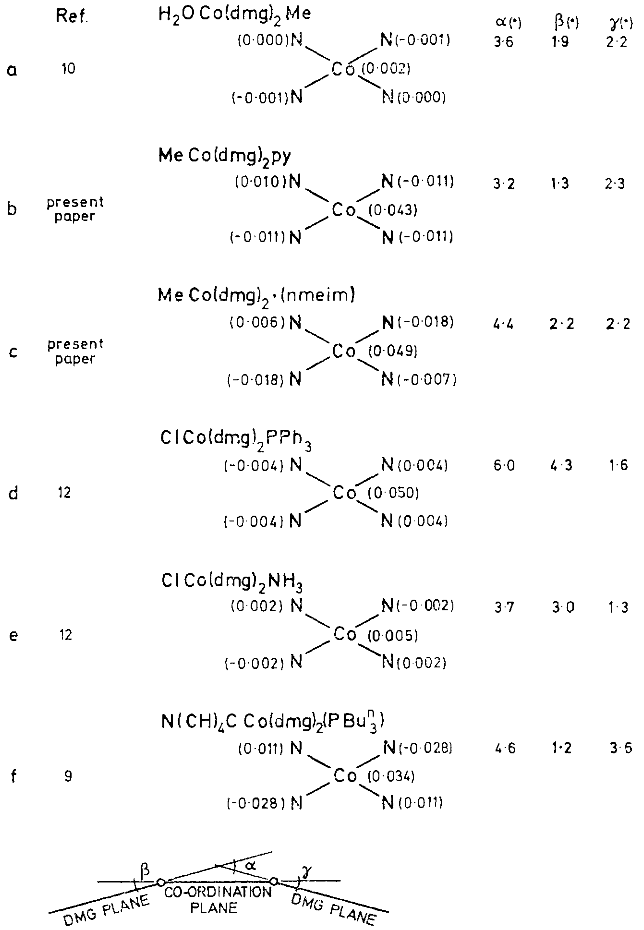

FIGURE 5 Comparison of the geometry of some cobaloxime derivatives. Displacements of the Co, N atoms from the best molecular plane are also reported, the cobalt atom being displaced towards the axial ligand on the right of the formula

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[17] G. De Alti, V. Galasso, A. Bigotto, and G. Costa, *Inorg. Chim. Acta*, 1969, **3**, 533.

[18] K. S. Viswanathan and N. R. Kunchur, *Acta Cryst.*, 1961, **14**, 675, and footnote (*b*) of Table 6.

have large steric hindrance, a significant distortion from planarity of the N atoms is observed [Figure 5(f)].

The dihedral angles between the co-ordination plane and the planes of the two dmg moieties do not exceed 6° with a slight deformation of the overall molecule towards an umbrella-shape, suggesting a noticeable rigidity of the $(dmg)_2$ equatorial ligand as compared with that of salen and acacen cobalt derivatives.[3] This rigidity may have an important role in determining the high stability of six-co-ordinate species of cobaloximes.[19]

Polarized I.r. Spectra of (II).—According to the *X*-ray measurements the crystal belongs to the space group $P2_1/c$ (C^5_{2h}) and the unit cell contains four molecules which occupy sites with C_1 symmetry. The molecular symmetry is also C_1 and according to the aforementioned site and space group the activities of the crystal vibrations should be as follows:

Molecular and site symmetry	Factor-group symmetry		
C_1	C_{2h}		
A(R, i.r.) 135	A_g (R)	141	(3 transl. + 3 tors.)
	B_g (R)	141	(3 transl. + 3 tors.)
	A_u (i.r.)	140	(2 transl. + 3 tors.) + T_b
	B_u (i.r.)	139	(1 transl. + 3 tors.) + $T_{a,c}$

A complicated crystal spectrum is expected from this correlation table, since all the vibrational modes of the complex are predicted to be i.r. active and moreover each mode should be split into two i.r.-active components in the crystal. This should make the interpretation of the observed spectrum very cumbersome. There are two facts, however, which allow a satisfactory interpretation of the i.r. spectra. Firstly it was observed that no extensive factor-group splitting is apparent, indicating that little interaction exists between the components of the crystal lattice. As a consequence the oriented-gas model can be adopted as a first approximation in the interpretation of the observed dichroism. Secondly the similarity between the spectra of the $M^{II}(dmg)_2$ complexes of skeletal symmetry D_{2h} and those of the octahedral complexes $L^1Co(dmg)_2L^2$, at least in that the low-frequency chelate ring vibrations are not concerned,[20] allows a sorting out, by comparison, of most of the bands due to axial ligands, and allows the vibrations of the chelate rings to be classified according to the symmetry group D_{2h}.

TABLE 8

Axial Co–N and Co–O distances (Å) found in octahedral cobalt(III) complexes with different equatorial ligands

trans-Ligand	*N*-bonded ligand	Hybridization of N	Found	Corr.
			$(dmg)_2$	
Cl	NH_3	sp^3	1.965(4) [a]	2.04
$MeCO_2\cdot CH_2$–	py	sp^2	2.040(6) [b]	2.04
PhH_2N–	$PhNH_2$	sp^3	2.001(5) [c]	2.03
Me	py	sp^2	2.068(3) [d]	2.07
Me	nmeim	sp^2	2.058(5) [d]	2.06
			(salen)	
$CH_2{:}HC$–	py	sp^2	2.120(10) [e]	2.12
MeO–	py	sp^2	2.031(9) [f]	2.15
$NCCH_2$–	CH_2CN	sp	2.092(17) [g]	
			(acacen)	
Me	py	sp^2	2.160(10) [h]	
O_2–	py	sp^2	2.15(4) [i]	
trans-Ligand	*O*-Bonded ligand	Hybridization of O		
		$(dmg)_2$	Found	
Me	OH_2	sp^3	2.058(3) [j]	
		(salen)		
$AcCH_2$–	$OHCH_3$	sp^3	2.202(9) [g]	
O_2	$OCH{-}N(CH_3)_2$	sp^2	2.150(7) [k]	
		(acacen)		
$CH_2{:}HC$–	OH_2	sp^3	2.221(7) [h]	
Ph	OH_2	sp^3	2.330(20) [h]	

[a] Ref. 12. [b] Ref. 8. [c] See footnote (*b*) Table 6. [d] Present work. [e] Ref. 3. [f] Ref. 19. [g] Ref. 11. [h] Ref. 10. [i] See footnotes ([i]) and ([j]), Table 7. [j] M. Calligaris, G. Nardin, L. Randaccio, and G. Tauzher, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 419. [k] M. Calligaris, G. Nardin, L. Randaccio, and A. Ripamonti, *J. Chem. Soc.* (*A*), 1970, 1069.

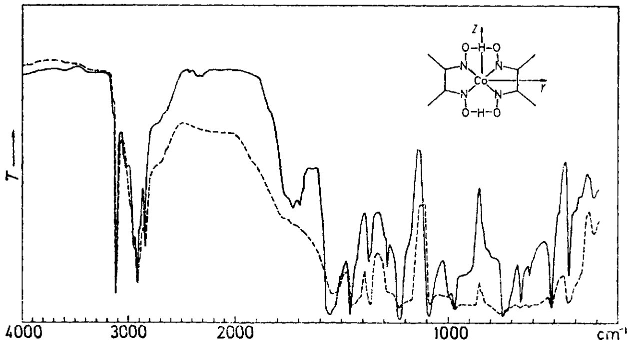

FIGURE 6 Polarized i.r. spectra of (II) in the (001) crystal plane; solid line, electric vector parallel to the *a* axis, broken line, electric vector parallel to *b* axis

The orientation of molecule axes used in the following discussion, performed according to the oriented-gas model, is shown in Figure 6. This orientation of the molecular axes is different from that of ref. 20. The *x* and *z* axes have been interchanged, and hence b_{1u} and b_{3u} species must be interchanged.

Squared values of the direction cosines between these axes and the crystallographic axes represent the proportionality factors for band intensities. Values calculated from the atomic co-ordinates are reported in Table 9.

TABLE 9

Proportionality factors for band intensities of chelate ring vibrations in (II)

	Molecular axes		
Crystal axes	$X(b_{3u})$	$Y(b_{2u})$	$Z(b_{1u})$
a	0.0000	0.3943	0.8043
b	0.0015	0.6048	0.1957
$c^*(\perp ab)$	0.9510	0.0012	0.0008

From this Table the following dichroic behaviour can be predicted for the skeletal bands in the polarized spectra recorded on the *ab* crystal plane. Out-of-plane vibrations with transition moments parallel to the *x* axis (b_{3u} modes) should not be observable with appreciable intensity, since they are almost completely polarized along the c^* direction. The in-plane vibrations of b_{2u} symmetry with transition moments parallel to the *y*

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axis should be polarized along the *b* crystal axis (parallel polarization) and those of b_{1u} species should appear with maximum intensity when the electric vector of the light is along the *a* axis (perpendicular polarization).

The most relevant features of the observed spectra can now be discussed. The strong band at 1 560 cm^{-1} is assigned to a skeletal stretching vibration of the chelate rings: its perpendicular polarization agrees well with the previous assignment [20] to the b_{1u} species. Another b_{1u} skeletal vibration having some NO stretching character was associated in previous investigations [20,21] with the strong band observed in the region 1 250—1 200 cm^{-1}. Indeed the band observed at 1 230 cm^{-1} shows the dichroic behaviour expected for a b_{1u} mode. Another skeletal band, assigned to NO stretching, is expected to belong to the b_{2u} species and was predicted by calculation [20] in the region 1 100 cm^{-1} according to the assignments of Blinc and Hadži.[21] Two bands are observed near 1 100 cm^{-1} in the present spectra. One, centred at *ca.* 1 085 cm^{-1}, is active when the electric vector is parallel to the *b* axis and hence can be assigned to the previously mentioned mode. The second absorption, according to its activity along the *a* axis, can be assigned to the b_{1u} mode predicted by the calculations as having mainly methyl rocking character. The dichroic activity of the band at 516 cm^{-1} is doubtful and does not allow a definite assignment. The band at 441 cm^{-1} shows a parallel character and can be assigned to a mode of b_{2u} symmetry. The feature at 325 cm^{-1} is also likely due to a b_{2u} mode because of the behaviour in the polarized spectrum. The latter assignment, however, has to be regarded with some caution because the band lies near to the limit of the working range of the polarizer. As regards the assignment of the vibrational modes associated with the hydrogen bonds, the polarized spectra provide some useful, although not conclusive data. A distinct band was not observed for this compound in the region 2 400—2 000 cm^{-1} where OHO stretching bands were previously assigned.[20-23] The absorption centred near 900 cm^{-1} is clearly polarized along the *b* axis and this behaviour is more consistent with its assignment to an in-plane mode of symmetry b_{2u} rather than to an out-of-plane mode as previously suggested.[21] This band makes a very strong contribution to the background absorption below 2 500 cm^{-1} in the spectrum recorded along the *b* axis and this makes somewhat unclear the dichroic behaviour of the band, which appears clearly resolved at 1 760 cm^{-1} in the spectrum recorded along the *a* axis. Hence the assignment of this band to a b_{1u} in-plane mode has to be considered tentative.

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