comparable with 1·81 (1) and 1·73 (1) Å for the nitromethane complex. The Ir atom lies in the mirror plane (Plane III). The results of the calculations show that the methyl groups of the cyclopentadienyl and benzene rings are bent away from their calculated mean planes. The cyclopentadienyl and benzene rings are tilted to each other, the dihedral angle being 14·4 (2)°. They are perpendicular to the plane of the connecting side chain by symmetry.

The molecular packing of the compound in the unit cell was also studied (Fig. 2). In the structure the components may be considered to form distinct units. The cations, anions and solvent molecules form separate columns in the **c** direction. The disorder of the anions and solvent molecules should also be considered. There seems, however, to be one intramolecular H bond C(4)–H···F(3) [C(4)···F(3) = 3·18 (5) Å] and five intermolecular H bonds O(1)–H···F(6$^{\rm i}$), O(1)–H···F(8$^{\rm ii}$), C(5$^{\rm iii}$)–H···F(5), C(5$^{\rm iv}$)–H···F(7) and C(11$^{\rm v}$)–H···F(4), because the heavy-atom distances are 2·90 (7), 3·03 (7), 3·09 (5), 3·18 (5) and 3·00 (4) Å, respectively. The symmetry codes are: (i) $0{\cdot}5-x$, $-y$, $0{\cdot}5+z$; (ii) $0{\cdot}5+x$, $0{\cdot}5-y$, $0{\cdot}5-z$; (iii) $-x$, $0{\cdot}5+y$, $-z$; (iv) $-x$, $-y$, $-z$; (v) $-0{\cdot}5-x, y-0{\cdot}5, z-0{\cdot}5$.

Because of the lack of a general H-bond net in the structure, it is held together mainly through van der Waals forces. These circumstances may account for the lability of the complex. The exchange of the solvent molecule $MeNO_2$ for MeOH affects the molecular packing in the crystal structure and increases the H-bond formation to some extent as is to be expected. The present results confirm the conclusions drawn concerning the structure of the Ir cation and the products of the syntheses described earlier (Kaganovich *et al.*, 1987).

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Cobaloximes Containing Planar Neutral Ligands. Structures of *trans*-(Cyanoethyl)bis(dimethylglyoximato)(1-methylimidazole)cobalt(III) and *trans*-(Alkyl)bis(dimethylglyoximato)(1,2-dimethylimidazole)cobalt(III) with Alkyl = Nitromethyl and Cyanopropyl

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Abstract. (I) *trans*-(Cyanoethyl)bis(dimethylglyoximato)(1-methylimidazole)cobalt(III), $[Co(C_4H_7N_2O_2)_2(C_3H_4N)(C_4H_6N_2)]$, $M_r = 425{\cdot}3$, monoclinic, $P2_1/c$, $a = 10{\cdot}904$ (2), $b = 11{\cdot}676$ (2), $c = 15{\cdot}738$ (2) Å, $\beta = 102{\cdot}31$ (1)°, $V = 1957{\cdot}5$ (3) Å^3, $Z = 4$, $D_x = 1{\cdot}44$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 9{\cdot}1$ cm^{-1}, $F(000) = 888$, $T = 295$ (1) K, $R = 0{\cdot}042$ for 2619 unique observed reflections. (II) *trans*-Bis(dimethylglyoximato)(1,2-dimethylimidazole)(nitromethyl)cobalt(III), $[Co(C_4H_7N_2O_2)_2(CH_2NO_2)(C_5H_8N_2)]$,

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$M_r = 445{\cdot}3$, monoclinic, $P2_1/c$, $a = 9{\cdot}212\,(1)$, $b = 14{\cdot}929\,(3)$, $c = 14{\cdot}391\,(2)$ Å, $\beta = 106{\cdot}87\,(1)°$, $V = 1894{\cdot}0\,(5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}56$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}7107$ Å, $\mu = 9{\cdot}5$ cm^{-1}, $F(000) = 928$, $T = 295\,(1)$ K, $R = 0{\cdot}037$ for 3085 unique observed reflections. (III) *trans*-(Cyanopropyl)bis(dimethylglyoximato)(1,2-dimethylimidazole)cobalt(III), $[\text{Co}(C_4H_7N_2O_2)_2(C_4H_6N)(C_5H_8N_2)]$, $M_r = 453{\cdot}4$, monoclinic, $P2_1/c$, $a = 9{\cdot}043\,(1)$, $b = 25{\cdot}777\,(3)$, $c = 8{\cdot}952\,(1)$ Å, $\beta = 94{\cdot}23\,(1)°$, $V = 2081{\cdot}0\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}45$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}7107$ Å, $\mu = 8{\cdot}58$ cm^{-1}, $F(000) = 952$, $T = 295\,(1)$ K, $R = 0{\cdot}041$ for 2986 unique observed reflections. The axial fragment of the distorted octahedral polyhedron of Co is characterized by Co—C and Co—N distances of 1·989 (5) and 2·037 (3) Å in (I), 2·001 (3) and 2·086 (1) Å in (II), and 2·023 (3) and 2·083 (2) Å in (III). Large angular distortions are detected in the coordination to Co of 1,2-dimethylimidazole (1,2-Me$_2$Im), while an orientation of the planar 1-methylimidazole (1-MeIm) with respect to the equatorial moiety different from that of planar L ligands, such as pyridine (py), 1,2-Me$_2$Im, 1,5,6-trimethylbenzimidazole (Me$_3$Bzm), is found. Comparison with strictly related cobaloximes indicates the following order of increasing Co—N(ax) distance: Im $\simeq$ 1-MeIm < py $\simeq$ Me$_3$Bzm < 1,2-Me$_2$Im, which is the same as that of increasing bulk of the neutral L ligand.

Introduction. Our previous studies on organocobaloximes, $L\text{Co(DH)}_2R$ where DH = monoanion of dimethylglyoxime, L = neutral ligand and R = alkyl group (Bresciani Pahor, Forcolin, Marzilli, Randaccio, Summers & Toscano, 1985; Zangrando, Bresciani Pahor, Randaccio, Charland & Marzilli, 1986; Bresciani Pahor, Attia, Randaccio, Lopez & Charland, 1987; Geremia, 1988) have shown that a knowledge of the structural parameters, namely the Co—L, Co—C distances and the bonding geometry of R and L to Co, is of fundamental importance to rationalize reactivity and solution properties of this class of complex, a model of the vitamin B$_{12}$ system. Furthermore, the study of the influence of steric and electronic features of various R and L on the Co—C bond has given support to the mechanism proposed for the Co—C cleavage, one of the most important steps in the enzymic action of the B$_{12}$ coenzyme (Halpern, 1985). On the one hand, the systematic solution and solid-state studies have furnished a large amount of kinetic, NMR and structural data, which have allowed interpretation of subtle details of the behaviour, determined by difference in bulk and in σ-donor ability, of the axial ligands (Marzilli, Bayo, Summers, Thomas, Zangrando, Bresciani Pahor, Mari & Randaccio, 1987). On the other hand, since most of the complexes studied contained planar L ligands such as py and Me$_3$Bzm, having relatively medium bulk, there are some aspects dealing with the Co—N bond still to be clarified, especially when the L bulk is both smaller and larger than that of the two above ligands. Therefore, we have decided to study the series LCo(DH)$_2R$ with L = 1-MeIm and 1,2-Me$_2$Im, because the latter is expected to have a bulk larger, and the former a bulk smaller, than that of py and Me$_3$Bzm. Here we report the crystal structure determination of 1-MeImCo(DH)$_2$(CH$_2$)$_2$CN (I), 1,2-Me$_2$ImCo(DH)$_2R$ with R = CH$_2$NO$_2$ (II) and (CH$_2$)$_3$CN (III).

Experimental. The synthesis and crystallization of the three complexes have been performed with usual techniques (Bresciani Pahor *et al.*, 1985) and will be published elsewhere. Red-yellow crystals having approximate dimensions 0·30 × 0·30 × 0·35 mm (I), 0·30 × 0·30 × 0·40 mm (II) and 0·5 × 0·5 × 0·6 mm (III). Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$, lattice constants by least-squares refinement of 25 setting angle reflections ($11 \le \theta \le 17$, $15 \le \theta \le 18$, $14 \le \theta \le 18°$ respectively). Three standard reflections measured every 4000 s of X-ray exposure [($\bar{2}27$, $\bar{4}64$, $\bar{5}\bar{1}6$) ($4\bar{3}\overline{10}$, $7\bar{3}\bar{8}$, 159) (365, 295, $5\bar{3}\bar{5}$) respectively], no significant variations for the three crystals; $\omega/2\theta$ scan, scan speed 0·87–4° min^{-1} in ω, scan width $(1{\cdot}3 + 0{\cdot}35\tan\theta)°$ for (I) and (III), $(1{\cdot}2 + 0{\cdot}35\tan\theta)°$ for (II), in the range $3 \le \theta \le 28°$ for the three crystals, 5112, 4912 and 5424 reflections measured in the range ($-14 \le h \le 14$, $0 \le k \le 15$, $0 \le l \le 20$), ($-12 \le h \le 12$, $0 \le k \le 19$, $0 \le l \le 19$) and ($-12 \le h \le 12$, $0 \le k \le 36$, $0 \le l \le 12$) respectively, 2619, 3085 and 2986 observed reflections [$I > 3\sigma(I)$] for (I), (II) and (III) used for structure determinations; space group from systematic absences; intensities corrected for Lorentz–polarization effects, corrected for absorption *via* ψ scan, max./min. transmission 0·998/0·889 for (III) only. The structures solved by Patterson method, F synthesis and full-matrix least squares on F, 244, 253 and 262 parameters refined for the three structures respectively. Fourier maps of (II) clearly indicated that 1,2-Me$_2$Im was disordered. The disorder was interpreted assuming two orientations, related by a rotation of about 180° around an axis passing through Co and normal to the equatorial coordination plane, with occupancies of 0·8 and 0·2, respectively. Atoms of the latter were held constant at $B = 4{\cdot}0$ Å^2 in the final refinement and the contribution of their H atoms was not included. Anisotropic temperature factors for all non-H atoms, H atoms fixed at calculated positions with $B = 5$ Å^2 for (III), $B = 1{\cdot}3 \times B_{\text{eq}}$ of the corresponding C atom for (I) and (II). $R = 0{\cdot}042$, 0·037 and 0·041 respectively, $wR = 0{\cdot}051$ for the three structures, $S = 1{\cdot}16$, 1·11 and 1·25, function minimized $\sum w(|F_o| - |F_c|)^2$, $w = 1/[\sigma(F_o)^2 + (0{\cdot}02F_o)^2 + 1]$ for (I) and (III), $w = 1/[\sigma(F_o)^2 + (0{\cdot}03F_o)^2 + 1]$ for (II), max. $\Delta/\sigma = 0{\cdot}1$ for (II) and (III), 0·03 for (I), the final difference maps had max. of 0·511, 0·38 and 0·33 e Å^{-3}, the min. were

Table 1. *Positional parameters and their estimated standard deviations for compound* (I)

	x	*y*	*z*	*B*(Å^2)
Co	0·23620 (4)	0·16381 (4)	0·23492 (3)	2·681 (8)
O1	0·4049 (3)	0·1478 (3)	0·1200 (2)	5·18 (7)
O2	0·1299 (3)	0·3637 (2)	0·2912 (2)	4·42 (6)
O3	0·0792 (3)	0·1815 (3)	0·3585 (2)	4·71 (7)
O4	0·3461 (3)	−0·0362 (3)	0·1809 (2)	5·00 (7)
N1	0·3366 (3)	0·2178 (3)	0·1605 (2)	3·54 (7)
N2	0·2052 (3)	0·3221 (3)	0·2426 (2)	3·32 (6)
N3	0·1430 (3)	0·1109 (3)	0·3151 (2)	3·21 (6)
N4	0·2725 (3)	0·0056 (3)	0·2312 (2)	3·56 (7)
N5	0·0862 (3)	0·1467 (2)	0·1335 (2)	2·85 (6)
N6	−0·0971 (3)	0·0921 (3)	0·0578 (2)	3·56 (7)
N7	0·6563 (4)	0·2101 (4)	0·4765 (3)	6·4 (1)
C1	0·4125 (5)	0·3836 (5)	0·0902 (3)	6·4 (1)
C2	0·3387 (4)	0·3271 (4)	0·1481 (3)	3·95 (8)
C3	0·2606 (4)	0·3891 (3)	0·1969 (3)	3·67 (8)
C4	0·2502 (5)	0·5170 (4)	0·1979 (4)	6·0 (1)
C5	0·0867 (5)	−0·0522 (4)	0·3981 (3)	5·8 (1)
C6	0·1466 (4)	0·0022 (3)	0·3317 (2)	3·56 (8)
C7	0·2206 (4)	−0·0610 (3)	0·2799 (3)	3·81 (8)
C8	0·2338 (5)	−0·1881 (4)	0·2817 (4)	6·0 (1)
C9	0·3832 (5)	0·1716 (5)	0·3343 (3)	6·2 (1)
C10	0·4652 (6)	0·2555 (6)	0·3544 (5)	15·1 (2)
C11	0·5743 (5)	0·2329 (5)	0·4241 (4)	6·7 (1)
C12	−0·0150 (4)	0·0849 (3)	0·1344 (2)	3·37 (8)
C13	−0·0469 (4)	0·1616 (4)	0·0054 (2)	4·07 (8)
C14	0·0665 (4)	0·1951 (3)	0·0518 (2)	3·63 (8)
C15	−0·2195 (4)	0·0346 (4)	0·0370 (3)	5·3 (1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(\frac{4}{3})[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

−0·45, −0·43 and −0·25 e Å^{-3} respectively, complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974), no correction for secondary extinction, all computer programs used were those in the Enraf–Nonius *SDP* (Frenz, 1983) on PDP 11/44.

The atomic parameters are listed in Tables 1–3 for (I), (II) and (III), respectively.* In (II), parameters for the 1,2-Me$_2$Im orientation with occupancy 0·8 are reported.

Discussion. The *ORTEP* (Johnson, 1965) drawings for non-H atoms of the crystallographically independent molecules of (I), (II) and (III) are shown in Figs. 1, 2 and 3 together with their respective numbering schemes. In all three complexes, Co has a distorted octahedral coordination, the DH ligands occupying the equatorial positions. The four equatorial N donors are coplanar within 0·008 (2) Å in (I), 0·030 (2) Å in (II) and 0·001 (5) Å in (III), and the displacement of Co from their mean plane is 0·05, 0·03 and 0·06 Å towards *L*, respectively. The slight deviation from

Table 2. *Positional parameters and their estimated standard deviations for compound* (II)

	x	*y*	*z*	*B*(Å^2)
Co	0·22403 (4)	0·08848 (2)	0·80086 (2)	2·643 (6)
O1	0·3458 (2)	0·1432 (2)	0·6489 (1)	4·41 (5)
O2	0·1555 (2)	0·1971 (2)	0·9452 (1)	4·26 (4)
O3	0·1475 (2)	0·0335 (2)	0·9705 (1)	4·32 (5)
O4	0·2954 (3)	−0·0207 (2)	0·6581 (1)	4·62 (5)
O5	0·5761 (3)	0·2010 (2)	0·8901 (2)	6·10 (6)
O6	0·5150 (3)	0·1496 (2)	1·0136 (2)	5·50 (6)
N1	0·2877 (3)	0·1704 (2)	0·7208 (1)	3·32 (5)
N2	0·2044 (2)	0·1956 (2)	0·8661 (2)	3·17 (4)
N3	0·1741 (2)	0·0073 (2)	0·8865 (2)	3·25 (4)
N4	0·2439 (2)	−0·0190 (2)	0·7361 (2)	3·37 (5)
N5	−0·0039 (3)	0·0953 (2)	0·7318 (2)	3·03 (5)
N6	−0·2301 (3)	0·1052 (2)	0·6285 (2)	3·15 (6)
N7	0·5165 (3)	0·1449 (2)	0·9294 (2)	3·93 (5)
C1	0·3462 (4)	0·3275 (3)	0·6923 (3)	5·31 (8)
C2	0·2887 (3)	0·2543 (2)	0·7434 (2)	3·57 (6)
C3	0·2361 (3)	0·2697 (2)	0·8290 (2)	3·47 (6)
C4	0·2250 (5)	0·3594 (2)	0·8712 (3)	5·17 (8)
C5	0·1085 (4)	−0·1477 (3)	0·9148 (3)	5·26 (8)
C6	0·1612 (3)	−0·0758 (2)	0·8605 (2)	3·63 (6)
C7	0·2051 (3)	−0·0917 (2)	0·7712 (2)	3·83 (6)
C8	0·2110 (4)	−0·1824 (2)	0·7306 (3)	5·53 (9)
C9	0·4428 (3)	0·0686 (2)	0·8717 (2)	3·53 (6)
C10	−0·0821 (4)	0·1041 (2)	0·6386 (2)	2·98 (6)
C11	−0·2514 (4)	0·0933 (3)	0·7190 (3)	3·78 (7)
C12	−0·1129 (4)	0·0887 (3)	0·7819 (2)	3·70 (7)
C13	−0·0204 (4)	0·1133 (3)	0·5551 (2)	4·12 (8)
C14	−0·3576 (4)	0·1127 (3)	0·5396 (3)	4·66 (9)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(\frac{4}{3})[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 3. *Positional parameters and their estimated standard deviations for compound* (III)

	x	*y*	*z*	*B*(Å^2)
Co	0·21371 (6)	0·12308 (2)	0·20562 (6)	2·430 (8)
O1	0·1307 (4)	0·1413 (1)	0·5019 (3)	4·60 (8)
O2	0·4755 (4)	0·1560 (2)	0·0747 (5)	6·5 (1)
O3	0·2921 (4)	0·1076 (2)	−0·0924 (4)	5·30 (8)
O4	−0·0604 (3)	0·0993 (1)	0·3307 (3)	4·10 (7)
N1	0·2359 (4)	0·1477 (1)	0·4053 (4)	3·47 (7)
N2	0·4017 (4)	0·1544 (2)	0·2000 (5)	4·34 (9)
N3	0·1878 (4)	0·1014 (1)	0·0043 (4)	3·36 (7)
N4	0·0202 (4)	0·0971 (1)	0·2085 (4)	2·84 (7)
N5	0·3160 (4)	0·0524 (1)	0·2593 (4)	2·73 (6)
N6	0·3870 (4)	−0·0241 (1)	0·3450 (4)	3·86 (8)
N7	−0·2055 (6)	0·3244 (2)	0·3118 (7)	6·8 (1)
C1	0·3953 (8)	0·1913 (2)	0·5998 (7)	7·8 (2)
C2	0·3592 (6)	0·1704 (2)	0·4463 (6)	4·7 (1)
C3	0·4567 (5)	0·1745 (2)	0·3267 (7)	5·0 (1)
C4	0·6070 (7)	0·2000 (3)	0·340 (1)	8·5 (2)
C5	0·0191 (8)	0·0640 (2)	−0·1942 (6)	6·2 (1)
C6	0·0597 (5)	0·0811 (2)	−0·0366 (5)	3·72 (9)
C7	−0·0400 (5)	0·0791 (2)	0·0843 (5)	3·38 (9)
C8	−0·1974 (6)	0·0611 (2)	0·0640 (8)	5·9 (1)
C9	0·1217 (5)	0·1909 (2)	0·1328 (5)	3·65 (9)
C10	0·0340 (6)	0·2219 (2)	0·2350 (5)	4·0 (1)
C11	−0·0481 (6)	0·2655 (2)	0·1537 (6)	4·9 (1)
C12	−0·1361 (6)	0·2985 (2)	0·2440 (6)	4·2 (1)
C13	0·2957 (5)	0·0166 (2)	0·3590 (5)	3·30 (9)
C14	0·4737 (5)	−0·0122 (2)	0·2269 (6)	4·5 (1)
C15	0·4297 (5)	0·0338 (2)	0·1764 (5)	3·70 (9)
C16	0·1924 (6)	0·0177 (2)	0·4761 (6)	4·8 (1)
C17	0·3966 (7)	−0·0724 (2)	0·4295 (7)	6·0 (1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(\frac{4}{3})[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

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* Lists of structure factors, anisotropic thermal parameters for non-H atoms, atomic parameters for H atoms and for atoms of compound (II) with 0·2 occupancy, bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51504 (51 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

planarity of the equatorial moiety is measured by the dihedral angle between the two DH units, which is 4·9° in (I), 3·4° in (II) and 5·9° in (III). In (I) the 1-MeIm ligand, planar within 0·001 (2) Å, is nearly perpendicular to the equatorial plane oriented in such a way that its plane crosses the five-membered chelate rings (orientation *A* in Fig. 4). The 1,2-Me$_2$Im is planar within 0·016 (5) Å in (II) and 0·020 (5) Å in (III) and in both (II) and (III) has the usual orientation found in all cobaloximes containing planar ligands (orientation *B* in Fig. 4) if the orientation *A* found in 1-MeIm-Co(DH)$_2$Me is excluded (Bresciani Pahor *et al.*, 1985).

The geometry of the (CH$_2$)$_2$CN group in (I) is close to that found in the py analogue, *i.e.* the C—N residue is away from the equatorial ligand with a torsion angle Co—C—C—CN of −171·9° (Fig. 1). In contrast, in the 4-Mepy analogue (Ukida, Sasada & Ohashi, 1988) the C—N group lies nearly parallel to one of the two equatorial five-membered rings, with a torsion angle Co—C—C—CN of 82·5°. In (II), the CH$_2$NO$_2$ group is oriented in such a way that the C9—N7 bond lies above the equatorial bond Co—N2. On the other hand, in (III) the alkyl group in a planar zigzag

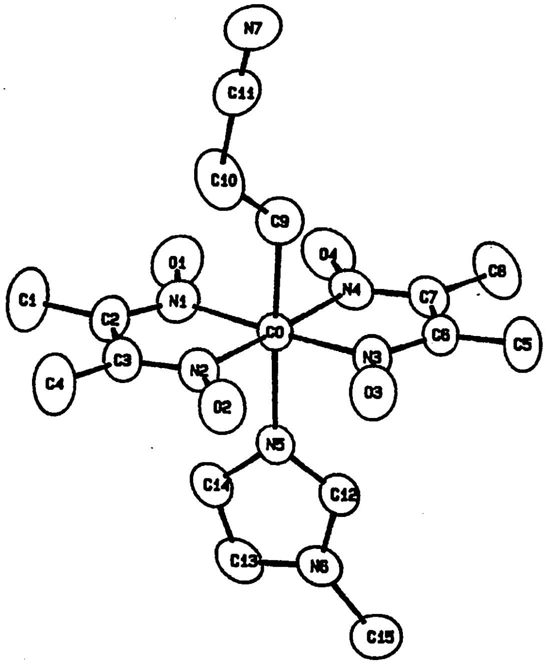

Fig. 1. *ORTEP* drawing and atom-numbering scheme for the molecule of (I).

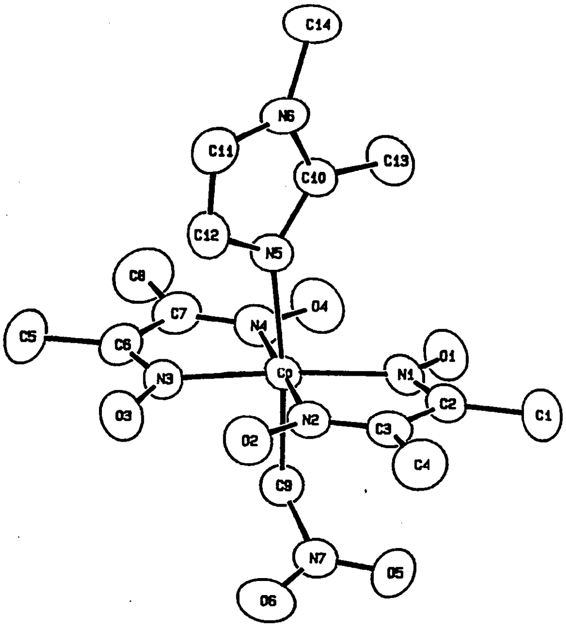

Fig. 2. *ORTEP* drawing and atom-numbering scheme for the molecule of (II). The reported 1,2-Me$_2$Im is that in the orientation with the occupancy 0·8.

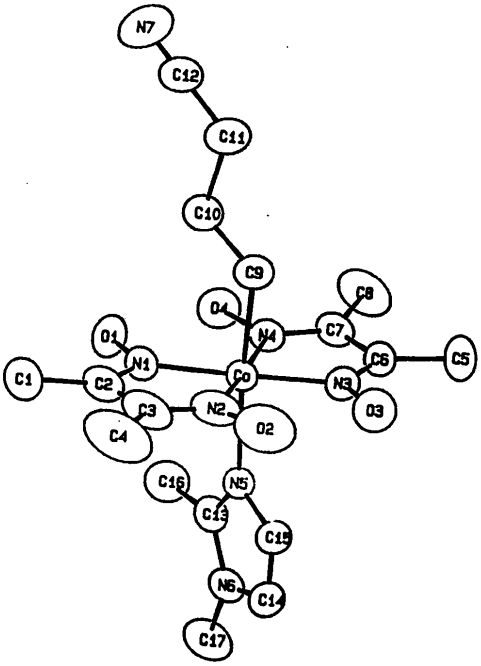

Fig. 3. *ORTEP* drawing and atom-numbering scheme for the crystallographically independent molecule of (III).

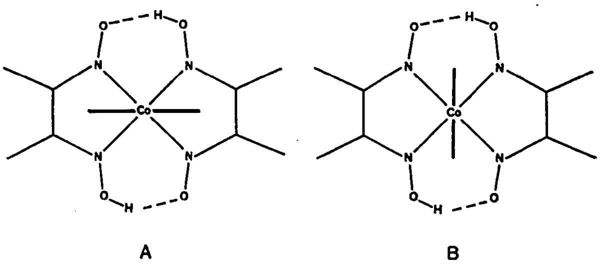

Fig. 4. Sketch of the two limiting orientations *A* and *B* of the planar *L* ligand with respect to the equatorial moiety.

conformation lies in a plane which crosses the O1—O4 oxime bridge.

Values of selected bond lengths and angles for (I), (II) and (III) are given in Table 4 together with the corresponding values for their methyl analogues and for some other strictly related cobaloximes containing py (Bresciani Pahor *et al.*, 1985) and Me_3Bzm (Charland, Zangrando, Bresciani Pahor, Randaccio & Marzilli, to be published). As expected, these data confirm (Bresciani Pahor *et al.*, 1985) that for the same *L* ligand the Co—N(ax) distance increases with the increase of the σ-donor power of the *trans* alkyl group. In addition, this axial distance is also determined by the bulk of the *L* ligand. In fact, it has been observed that the C—N(ax)—C angle of 105°, in the imidazole ligand, significantly narrower than that of 120° in py, allows a shorter axial bond length in the former. However, in Me_3Bzm the increased bulk due to the fused six-membered ring distorts the coordination around N as shown by the significantly different values of the two C—N(ax)—C angles (Table 4) and lengthens the Co—N bond. Thus, for the same *R* this bond length is almost the same in py and Me_3Bzm analogues (Parker, Zangrando, Bresciani Pahor, Marzilli, Randaccio & Marzilli, 1988). In 1,2-Me_2Im, the α-methyl group causes a similar, but more enhanced, lengthening. Therefore, for the same *R* and the same *L* orientation the Co—N(ax) distance increases in the order: Im $\simeq$ 1-MeIm < py $\simeq$ Me_3Bzm < 1,2-Me_2Im which follows the order of increasing bulk of *L*.

A third point must be stressed. The orientation *A* (see above and Fig. 4) is found only in 1-MeIm derivatives with $R = Me$ and $(CH_2)_2CN$ while in the others, including the Im analogue, it is always *B*. Since there is no reason to expect significant differences in the Co—N(ax) distances for Im and 1-MeIm methyl analogues, we suggested that orientation *A* leads to longer Co—N distances (Parker *et al.*, 1988). This is further supported by the relatively short bond length in 1-MeImCo$(DH)_2$adamantyl, where the orientation *B* is found, as compared with that in the Me_3Bzm analogue. It appears clear from Fig. 4 that the planar *L* ligand in orientation *A* should interact with the equatorial moiety more strongly than in orientation *B*, probably leading to longer axial distances. The reason why the less bulky imidazoles can assume both *A* and *B* orientations may reside in the difference in energy between the two orientations. Such a difference should be of the same order of magnitude as the crystal packing so that the latter is responsible for the ligand orientation, unless the bending of the equatorial ligands towards *L*, induced by bulky *R* groups, contributes to stabilize orientation *B*, as occurs in the adamantyl derivative.

The Co—C bond lengths and the Co—C—*X* angle increase with the increasing bulk of *R*. Data for $(CH_2)_2CN$ derivatives suggest that the geometry of the Co—C—*X* fragment is the result of the balance of a lengthening of the Co—C bond and a widening of the Co—C—*X* angle. As a consequence of the widening of the Co—C—C angle to 127·9 (5)° in (I), the C—C distance decreases to 1·329 (7) Å. On the contrary, in (III) the same angle is 119·4 (2)° and corresponds to a C—C distance of 1·488 (5) Å. Such a relationship between these bond lengths and angles has also been observed in ethylcobaloximes (Parker *et al.*, 1988), although the effect could be enhanced by the thermal motion, often high, of the terminal C atom.

Table 4. *Values of selected bond lengths* (Å) *and angles* (°) *for* $LCo(DH)_2R$ *complexes and orientation O* (*see* Fig. 4) *of L with respect to the equatorial moiety; the mean values of the* Co—C—*X angles are reported for adamantyl derivatives*

L	*R*	Co—C	Co—N	Co—N(ax)—C	Co—C—*X*	*O*	Ref.
Im	Me	1·985 (3)	2·019 (3)	129·7 (1) 124·8 (1)	—	*B*	(*a*)
1-MeIm	adamantyl	2·154 (4)	2·065 (4)	127·4 (3) 127·8 (3)	112·2 (4)	*B*	(*b*)
	Me	2·009 (7)	2·058 (4)	127·4 (3) 127·0 (5)	—	*A*	(*b*)
	$(CH_2)_2CN$	1·989 (5)	2·037 (3)	125·4 (2) 129·0 (2)	127·9 (5)	*A*	(*c*)
py	Me	1·998 (5)	2·068 (3)	122·3 (3) 119·7 (4)	—	*B*	(*b*)
	$(CH_2)_2CN$	2·002 (7)	2·050 (5)	121·9 (5) 120·7 (5)	123·6 (6)	*B*	(*d*)
	CH_2NO_2	2·002 (3)	2·028 (3)	121·2 (2) 121·2 (2)	113·7 (2)	*B*	(*b*)
Me_3Bzm	adamantyl	2·179 (5)	2·137 (4)	134·4 (3) 120·8 (4)	110·4 (3)	*B*	(*e*)
	Me	1·989 (2)	2·060 (2)	133·6 (1) 121·5 (2)	—	*B*	(*f*)
	CH_2NO_2	1·988 (5)	2·013 (3)	132·7 (3) 122·4 (3)	115·7 (4)	*B*	(*f*)
1,2-Me_2Im	Me	2·001 (2)	2·086 (1)	134·9 (1) 119·1 (1)	—	*B*	(*g*)
	$(CH_2)_3CN$	2·023 (3)	2·083 (2)	133·9 (2) 120·7 (2)	119·4 (2)	*B*	(*c*)
	CH_2NO_2	1·999 (3)	2·049 (3)	132·2 (2) 122·2 (2)	114·5 (1)	*B*	(*c*)

References: (*a*) Pattabhi, Nethaji, Gabe, Lee & Le Page (1984); (*b*) Bresciani Pahor *et al.* (1985); (*c*) present work; (*d*) Zangrando *et al.* (1986); (*e*) Bresciani Pahor *et al.* (1987); (*f*) Charland *et al.*, to be published; (*g*) Geremia (1988).

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Structure of [*N*,*N*-Bis(carboxymethyl)glycinato](1,3-propanediamine)cobalt(III) Monohydrate

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Abstract. $[Co(C_6H_6NO_6)(C_3H_{10}N_2)].H_2O$, $M_r = 338.90$, orthorhombic, $Pna2_1$, $a = 10.457$ (2), $b = 17.141$ (4), $c = 7.233$ (2) Å, $V = 1296.39$ Å^3, $Z = 4$, $D_x = 1.737$, D_m(by flotation) = 1.730 g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 12.83$ cm^{-1}, $F(000) = 692$, $T = 295$ K, $R = 0.0254$ for 1156 observed reflections. The two N atoms of the 1,3-propanediamine (pd) ligand, the N atom and three carboxyl O atoms of the *N*,*N*-bis(carboxymethyl)glycinato (nta) ligand give distorted octahedral coordination around Co. The Co—O(6) bond distance is shorter than the other axial Co—O(4) bond distance. The amine groups and the water molecule are involved in hydrogen bonding.

Introduction. In continuation of research on metal complexes involving tripod ligands (Swaminathan, Sinha, Chatterjee, Patel & Padmanabhan, 1988; Swaminathan, Sinha, Chatterjee, Yadava & Padmanabhan, 1989), the structural investigation of the title compound was undertaken to establish the details of coordination.

Experimental. The complex was synthesized by a similar method to that reported in the literature (Chatterjee, Singh, Phulambrikar & Das, 1988):

$$CoCO_3 + H_3nta + pd \xrightarrow{333\ K} [Co(pd)(nta)].H_2O.$$

Recrystallized from hot water, washed with water and ethanol and finally air-dried. Intensity data were first collected on an indigenously fabricated four-circle diffractometer at BARC, Bombay. As the number of reflections with $|F_o| > 5\sigma(|F_o|)$ was inadequate to locate the H atoms, data were again collected (crystal dimensions $0.35 \times 0.13 \times 0.15$ mm) on an Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω–2θ scan. Lattice parameters obtained by photographs were refined by least-squares analysis using 22 reflections, $7 < \theta < 11°$. Intensities of two standard reflections recorded for every 1800 s showed no significant changes. Range $2 < \theta < 25°$ (resolution $d = 0.84$ Å, $h_{max} = 12$, $k_{max} = 20$, $l_{max} = 8$). 1362 unique reflections were collected of which 1164 reflections had $|F_o| > 3\sigma(|F_o|)$. Lp corrections, no absorption correction. Structure was solved by Patterson method, *SHELXS*86 (Sheldrick,

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