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***trans*-Bis[dimethylglyoximato(1-)-*N,N'*]bis(pyrrolidine-*N*)cobalt(III) Chloride, *trans*-Chlorobis[dimethylglyoximato(1-)-*N,N'*](pyrrolidine-*N*)cobalt(III) and *trans*-(Benzyl)bis[dimethylglyoximato(1-)-*N,N'*](pyrrolidine-*N*)cobalt(III)\***

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**Abstract.** (I):  $[\text{Co}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_4\text{H}_9\text{N})_2]\text{Cl}$ ,  $M_r = 466.8$ ,  $C2/c$ ,  $a = 18.474(4)$ ,  $b = 12.751(1)$ ,  $c = 9.380(1)$  Å,  $\beta = 107.90(1)^\circ$ ,  $V = 2103(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.48$  Mg m<sup>-3</sup>,  $\text{Mo } K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 1.01$  mm<sup>-1</sup>,  $F(000) = 984$ , room temperature,  $wR = 0.041$  for 1569 reflections. (II):  $[\text{Co}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2\text{Cl}(\text{C}_4\text{H}_9\text{N})]$ ,  $M_r = 395.7$ ,  $P2_12_12_1$ ,  $a = 9.489(3)$ ,  $b = 12.411(4)$ ,  $c = 14.595(4)$  Å,  $V = 1719(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.53$  Mg m<sup>-3</sup>,  $\text{Mo } K\alpha$ ,  $\mu = 1.22$  mm<sup>-1</sup>,  $F(000) = 824$ , room temperature,  $wR = 0.044$  for 1329 reflections. (III):  $[\text{Co}(\text{C}_7\text{H}_7)(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_4\text{H}_9\text{N})]$ ,  $M_r = 451.4(1)$ ,  $P2_12_12_1$ ,  $a = 11.546(3)$ ,  $b = 11.724(4)$ ,  $c = 15.694(4)$  Å,  $V = 2124(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.41$  Mg m<sup>-3</sup>,  $\text{Mo } K\alpha$ ,  $\mu = 0.88$  mm<sup>-1</sup>,  $F(000) = 952$ , room temperature,  $wR = 0.039$  for 1080 reflections. Ground-state *trans* effects are observed. With the Co–N(pyr) distance in (I) as reference, the Co–N(pyr) in (II) is only slightly larger, but in (III) it is significantly elongated, in keeping with the weak  $\sigma$ -donor ability of the chlorine compared to the benzyl ligand. Comparison of the title compounds with other

cobaloximes shows indications of ground-state *cis* effects, namely in the correlation between the larger Co–N(axial) and the smaller Co–N(equatorial) and in the shifts of the Co atoms from the plane of the four equatorial N atoms. The possibility of a ligand-induced proton shift in (II) and (III) is discussed.

**Introduction.** Transformation of, for example, an octahedral complex  $ML_6$  ( $M$ : metal;  $L$ : ligand) into  $ML_5X$  causes a change in the properties of the ligands  $L$ , whilst the substituent effects of  $X$  on  $L$  are different for *trans*- and *cis*-positioned ligands  $L$  relative to  $X$ . Such *cis* and *trans* interactions influence ground-state properties as well as thermodynamic and kinetic characteristics. Unfortunately there is an excessive number of terms used in the literature to correlate the mutual influence of ligands on the properties concerned. We will follow the recommendations of Buchler, Kokisch & Smith (1978) and adhere to the terminology used by Hill, Pratt & Williams (see e.g. Philips & Williams, 1966), i.e. we will use the term ground-state *trans/cis* effect in connection with geometrical and spectroscopic properties.

Cobaloximes –  $\text{Co}(\text{Hdmg})_2\text{LX}$ , with Hdmg the monoanion of dimethylglyoxime – are studied because they can be considered as model compounds for vitamin  $B_{12}$  and because by analogy with vitamin  $B_{12}$

\* Dimethylglyoxime is 2,3-butanedione dioxime.

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they show catalytic properties in homogeneous processes. Obviously with their nearly flat rigid Hdmg units in the equatorial plane cobaloximes are ideally suited to show *trans* effects, the influencing ligand *X* and the influenced one *L* being *a priori* in *trans* positions. Since the detailed geometry of the Co octahedral coordination depends upon the electronic and steric properties of *X* and *L*, we study in this work three complexes with fixed *L*, the secondary amine pyrrolidine, and variable *X*, which is pyrrolidine (compound I), chlorine (compound II) and benzyl (compound III). (I) serves as the point of reference for the Co–N(pyrrolidine) bond, while (II) and (III) are at opposite ends of the covalency scale in Co–*X*.

**Experimental.** Preparation of (I): *trans*-bis(dimethylglyoximato(1–)-*N,N'*)bis(pyrrolidine-*N*)cobalt(III) chloride. 3.58 g (9.92 mmol) of *trans*-dichloro[*trans*-bis(dimethylglyoximato(1–)-*N,N'*)]cobalt(III), [Co(H<sub>2</sub>dmg)(Hdmg)Cl<sub>2</sub>], was suspended in 50 ml ethanol. A solution of 4.23 g (59.52 mmol) pyrrolidine in 20 ml ethanol was added dropwise. The clear and transparent solution obtained was left to crystallize for 3 d to give (I). Elemental analysis, found: C 41.92, H 7.08, N 18.42, Cl 7.82; calculated for CoClC<sub>16</sub>H<sub>32</sub>N<sub>6</sub>O<sub>4</sub>: C 41.16, H 6.86, N 18.0, Cl 7.60%. Crystals suitable for X-ray diffraction were grown from a solution of 2.0 g (I) in 40 ml warm ethanol.

Preparation of (II): *trans*-chlorobis[*trans*-bis(dimethylglyoximato(1–)-*N,N'*)](pyrrolidine-*N*)cobalt(III). 2.03 g (5.56 mmol) of *trans*-dichloro[*trans*-bis(dimethylglyoximato(1–)-*N,N'*)]cobalt(III) were suspended in 50 ml ethanol, to which 0.71 g (9.95 mmol) pyrrolidine in 20 ml ethanol was added dropwise. After 1 h a first crop of crystals appeared, which were a mixture of Co(Hdmg)<sub>2</sub>(pyr)Cl and Co(Hdmg)<sub>2</sub>(pyr)<sub>2</sub>Cl. These crystals were filtered off and the filtrate was left to evaporate in an open beaker. The next day 0.8 g (yield 36%) of crystalline (II) was obtained. Elemental analysis, found: C 36.69, H 5.85, N 17.93, Cl 9.54, calculated for CoClC<sub>12</sub>H<sub>23</sub>N<sub>5</sub>O<sub>4</sub>: C 36.41, H 5.81, N 17.70, Cl 8.96%.

Preparation of (III): *trans*-(benzyl)bis[*trans*-bis(dimethylglyoximato(1–)-*N,N'*)](pyrrolidine-*N*)cobalt(III). 2.0 g (6.10 mmol) of diaquacobaloxime was dissolved in 240 ml acetone under argon. Then 0.85 g (12 mmol) of pyrrolidine in 10 ml acetone was added whilst stirring. After about 30 min, to the nearly transparent solution 0.68 g (3.1 mmol) of benzyl bromide was slowly added dropwise and the reaction mixture was agitated for 24 h. The precipitate consisting of 1.15 g (yield 85%) *trans*-bromobis[*trans*-bis(dimethylglyoximato(1–)-*N,N'*)](pyrrolidine-*N*)cobalt(III) was filtered off and the filtrate evaporated to a volume of about 20 ml. Soon 1.05 g (yield 76%) crystalline (III) appeared. Crystals suitable for X-ray analysis were grown from a solution

of 0.56 g (III) in 4 ml CHCl<sub>3</sub> by slow evaporation in air. Elemental analysis, found: C 50.32, H 6.41, N 15.65%; calculated for CoC<sub>19</sub>H<sub>30</sub>N<sub>5</sub>O<sub>4</sub>: C 50.56, H 6.65, N 15.52%.

The structure of the products was confirmed by NMR spectroscopy independently of the X-ray crystallographic measurements. The <sup>13</sup>C and <sup>1</sup>H NMR chemical shift data for (I), (II) and (III) are gathered in Tables 1 and 2.

Cell dimensions determined from setting angles of 25 high-order reflections. Enraf–Nonius CAD-4 diffractometer, Zr-filtered Mo radiation,  $\omega$  scan. Three intensity- and orientation-control reflections measured every 120 min and 200 reflections, respectively, no significant drift noted. Intensities not corrected for absorption because of small crystal size. Further details in Table 3. Structures solved by Patterson and Fourier methods. Least-squares refinement on *F*<sup>2</sup>s in which each individual reflection was given a weight based on counting statistics. Non-hydrogen atoms refined anisotropically. H atoms fixed at calculated positions with fixed isotropic *B* set equal to overall Wilson *B*. No extinction correction applied. Atomic scattering factors from *International Tables for X-ray Crystallography*

Table 1. <sup>13</sup>C NMR chemical shifts  $\delta$  (p.p.m., Me<sub>4</sub>Si)

The numbering of the atoms is given in Figs. 1–3.

Compound	Solvent	C(1P)	C(2P)	C(1A)	C(2A)	Others
(I)	D <sub>2</sub> O	50.16	22.75	13.79	158.80	
(II)	Me <sub>2</sub> SO	48.17	22.00	12.50	151.94	
(III)	CDCl <sub>3</sub>	47.88	24.25	11.88	149.19	C <sub>1(ipsi)</sub> 147.43 C <sub>ortho</sub> 127.38 C <sub>meta</sub> 128.48 C <sub>para</sub> 124.09 C(7T) not observed

Table 2. <sup>1</sup>H NMR chemical shifts  $\delta$  (p.p.m., Me<sub>4</sub>Si).

H(*X*) are H atoms attached to carbon *X*, numbered as in Figs. 1–3.

Compound	Solvent	H(1P)	H(2P)	CH <sub>3</sub> (Hdmg)	Others
(I)	D <sub>2</sub> O	2.60	1.64	2.60	
(II)	Me <sub>2</sub> SO	2.41	1.44	2.36	
(III)	CDCl <sub>3</sub>	2.68	1.60	2.04	H(7T) 2.70 aromatic H: 6.8–7.2

Table 3. Crystallographic details of Co(Hdmg)<sub>2</sub>(pyrrolidine)*X* with *X* = pyrrolidine (I), *X* = chlorine (II) and *X* = benzyl (III)

	(I)	(II)	(III)
Empirical formula	CoClC <sub>16</sub> H <sub>32</sub> N <sub>6</sub> O <sub>4</sub>	CoClC <sub>12</sub> H <sub>23</sub> N <sub>5</sub> O <sub>4</sub>	CoC <sub>19</sub> H <sub>30</sub> N <sub>5</sub> O <sub>4</sub>
Crystal size (mm)	0.2 × 0.2 × 0.1	0.1 × 0.1 × 0.2	0.1 × 0.2 × 0.15
$\theta_{max}$ (°)	25	25	25
<i>h</i> range	–21 to 20	0 to 11	0 to 13
<i>k</i> range	0 to 15	0 to 14	0 to 13
<i>l</i> range	0 to 11	0 to 17	0 to 17
Number of reflections measured	1963	1744	2128
Number of reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	1569	1329	1080
<i>wR</i> final	0.041	0.044	0.039
Max. noise in final difference Fourier map (e Å <sup>–3</sup> )	0.25	0.3	0.3
Max. shift/e.s.d. in last cycle of LS refinement	0.03	0.02	0.05

Table 4. Positional parameters in fractions of the cell edges and isotropic temperature factors ( $\text{\AA}^2$ )

The e.s.d.'s given in parentheses refer to the last significant digit. Isotropic temperature factors are calculated from anisotropic temperature parameters assuming equal volume of the 50% probability region.  $B(\text{iso})$  for non-hydrogen atoms were calculated according to Lipson & Cochran (1968):  $B_{\text{iso}} = 8\pi^2(U_{11}^{\circ}U_{22}^{\circ}U_{33}^{\circ})^{1/3}$ . All but one anisotropic temperature parameters were physically acceptable.

	x	y	z	$B_{\text{iso}}$
<b>(I)</b>				
Co	0.2500	0.2500	0.0000	2.03
Cl	0.5000	0.1722 (1)	0.2500	3.83
O(1A)	0.1660 (1)	0.1458 (2)	0.1660 (3)	3.63
O(2A)	0.2339 (1)	0.4600 (2)	-0.1089 (3)	3.50
N(1A)	0.1764 (1)	0.2354 (2)	0.0997 (3)	2.88
N(2A)	0.2086 (2)	0.3869 (2)	-0.0318 (3)	2.63
N(1P)	0.3298 (2)	0.2937 (2)	0.1881 (3)	2.61
C(1A)	0.0711 (2)	0.3184 (5)	0.1645 (5)	4.91
C(2A)	0.1342 (2)	0.3167 (3)	0.0996 (5)	2.97
C(3A)	0.1550 (2)	0.4069 (3)	0.0241 (4)	2.74
C(4A)	0.1162 (2)	0.5096 (3)	0.0129 (5)	4.18
C(1P)	0.3137 (2)	0.2918 (4)	0.3325 (5)	4.25
C(2P)	0.3812 (3)	0.3387 (4)	0.4457 (5)	4.77
C(3P)	0.4169 (2)	0.4088 (3)	0.3567 (6)	4.25
C(4P)	0.3684 (2)	0.3974 (3)	0.1952 (5)	3.89
<b>(II)</b>				
Co	0.1128 (1)	0.1772 (1)	0.29331 (9)	2.41
Cl	0.0490 (3)	0.0111 (2)	0.2512 (2)	3.69
O(1A)	0.0103 (7)	0.1318 (5)	0.4696 (4)	4.22
O(2A)	0.3846 (7)	0.1357 (5)	0.2195 (5)	3.78
O(1B)	-0.1652 (7)	0.2078 (5)	0.3633 (4)	4.47
O(2B)	0.2143 (8)	0.2196 (5)	0.1122 (4)	4.67
N(1A)	0.1205 (9)	0.1282 (5)	0.4156 (5)	3.00
N(2A)	0.3036 (7)	0.1301 (5)	0.2915 (5)	2.67
N(1B)	-0.0738 (7)	0.2186 (5)	0.2891 (5)	2.88
N(2B)	0.0981 (9)	0.2267 (5)	0.1686 (4)	2.20
N(1P)	0.1641 (7)	0.3284 (6)	0.3281 (4)	2.08
C(1A)	0.265 (1)	0.0409 (8)	0.5341 (7)	4.58
C(2A)	0.242 (1)	0.0875 (8)	0.4410 (7)	3.73
C(3A)	0.347 (1)	0.0864 (8)	0.3684 (6)	2.75
C(4A)	0.489 (1)	0.0407 (9)	0.3792 (8)	4.68
C(1B)	-0.275 (1)	0.2884 (9)	0.1198 (8)	4.80
C(2B)	-0.124 (1)	0.2548 (8)	0.2159 (7)	3.24
C(3B)	-0.018 (1)	0.2615 (7)	0.1425 (6)	2.26
C(4B)	-0.045 (1)	0.3031 (9)	0.0487 (7)	5.56
C(1P)	0.169 (1)	0.3573 (8)	0.4229 (7)	4.17
C(2P)	0.226 (1)	0.4718 (8)	0.4273 (7)	3.57
C(3P)	0.315 (1)	0.4797 (8)	0.3428 (7)	4.33
C(4P)	0.300 (1)	0.3721 (8)	0.2960 (9)	5.12
<b>(III)</b>				
Co	0.0870 (2)	0.0638 (1)	0.1618 (1)	2.85
O(1A)	0.1856 (7)	0.2855 (6)	0.1517 (6)	3.89
O(2A)	0.1991 (7)	-0.1470 (6)	0.1925 (5)	3.60
O(1B)	-0.0076 (7)	-0.1578 (6)	0.1696 (6)	3.18
O(2B)	-0.0235 (7)	0.2728 (6)	0.1195 (5)	3.39
N(1A)	0.2046 (7)	0.1730 (7)	0.1691 (6)	2.81
N(2A)	0.2164 (7)	-0.0337 (6)	0.1840 (6)	*
N(1B)	-0.0285 (6)	-0.0479 (8)	0.1568 (6)	3.04
N(2B)	-0.0368 (8)	0.1586 (8)	0.1334 (5)	2.77
N(1P)	0.0576 (7)	0.0926 (7)	0.2930 (5)	2.89
C(1A)	0.415 (1)	0.207 (1)	0.1875 (9)	4.54
C(2A)	0.3062 (9)	0.1320 (9)	0.1842 (7)	2.02
C(3A)	0.3131 (9)	0.0117 (9)	0.1915 (8)	2.94
C(4A)	0.417 (1)	-0.0498 (9)	0.2196 (7)	3.26
C(1B)	-0.233 (1)	-0.090 (1)	0.1331 (9)	3.57
C(2B)	-0.1303 (8)	-0.0136 (8)	0.1377 (7)	2.47
C(3B)	-0.1373 (9)	0.110 (1)	0.1228 (7)	2.01
C(4B)	-0.240 (1)	0.171 (1)	0.105 (1)	5.63
C(1P)	-0.0556 (9)	0.063 (1)	0.3267 (7)	3.76
C(2P)	-0.0438 (9)	0.070 (1)	0.4247 (7)	3.73
C(3P)	0.084 (1)	0.067 (1)	0.4400 (7)	3.94
C(4P)	0.1348 (9)	0.050 (1)	0.3539 (8)	4.43
C(1T)	0.049 (1)	-0.0068 (9)	-0.0207 (7)	2.89
C(2T)	-0.050 (1)	0.039 (1)	-0.0549 (7)	3.80
C(3T)	-0.130 (1)	-0.025 (1)	-0.0994 (8)	5.56
C(4T)	-0.106 (1)	-0.135 (1)	-0.1146 (9)	5.38
C(5T)	-0.008 (2)	-0.186 (1)	-0.0835 (8)	4.95
C(6T)	0.066 (1)	-0.122 (1)	-0.0370 (8)	5.21
C(7T)	0.1248 (9)	0.055 (1)	0.0293 (8)	2.64

\* N(2A) has an imaginary amplitude of vibration.

(1974). Computer calculations with Enraf-Nonius CAD-4 SDP (Frenz, 1978). No attempt to determine absolute configuration for (II) and (III). Further LS particulars in Table 3. Refined parameters\* in Table 4, numbering schemes of atoms in Figs. 1, 2 and 3.

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42711 (53 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

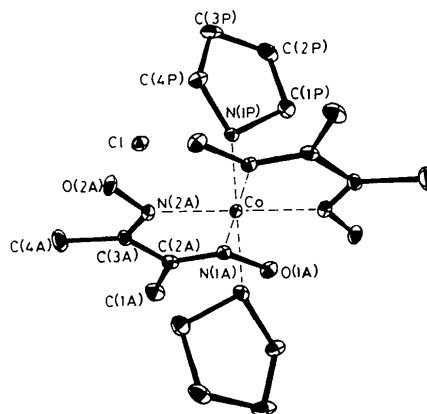


Fig. 1. Structural formula of (I) with numbering scheme.

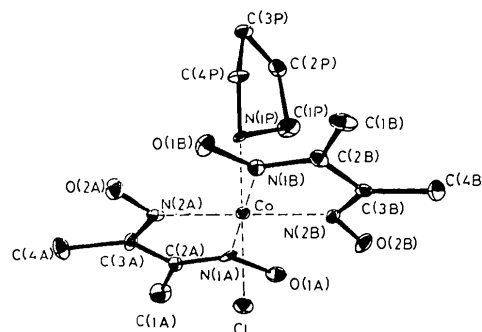


Fig. 2. Structural formula of (II) with numbering scheme.

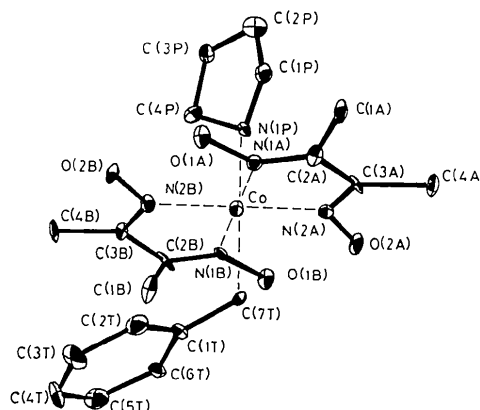


Fig. 3. Structural formula of (III) with numbering scheme.

**Discussion.** As was expected, Co is coordinated in the equatorial plane by four N atoms of the dimethylglyoximate units and axially by one N atom of pyrrolidine and by one N, Cl or C atom depending upon the compound. The coordination is a distorted octahedron in all cases; the geometrical details are presented in Table 5. A ground-state *trans* effect is clearly visible: the strong  $\sigma$ -donor benzyl ligand causes a marked elongation of the *trans*-positioned Co–N(pyrrolidine) bond [2.114 Å in (III)] with respect to the 'internal' standard Co–N (pyrrolidine) [1.999 Å in (I)], whereas the weak  $\sigma$ -donor Cl ligand has hardly any effect [2.004 Å in (II)]. Even though the variation in individual Co–N(equatorial) bond lengths is rather

large (see, however, below), the average Co–N(equatorial) bond lengths reveal a small accompanying ground-state *cis* effect in the sense that the larger Co–N(axial) accompanies the smaller Co–N(equatorial). The correlation observed in (I), (II) and (III) fits well into a series of 13 cobaloximes containing axial N-bonded ligands (see Table 6).

Furthermore, one notes that the angles N(1A)–Co–N(2A) and N(1B)–Co–N(2B) are about 80°, whereas the other N–Co–N angles in the equatorial plane are about 100°. This phenomenon has already been observed (Van Hooste, Lenstra, Kwiecinski & Tyrlik, 1982; Lenstra, Van Loock, Tyrlik & Stapowska, 1982; Lenstra, Geise & Tyrlik, 1984) and is undoubtedly introduced by the geometrical demands of the Hdmg ligands.

The Co atom is in the N(1A)N(1B)N(2A)N(2B) plane in (I), but shifted towards N(1P) by a distance (*d*) 0.025 (1) Å in (II) and 0.021 (2) Å in (III). Observed *d* values are similar to those reported for cobaloximes with other secondary amines as axial ligands and may be regarded as further indications of the existence of a ground-state *cis* effect (Lenstra, Geise & Tyrlik, 1984).

The Hdmg units can be considered planar because of the small values of the torsion angle  $\phi$ [N=C–C=N], actual numbers being 3 and 3° for ligands *A* and *B* in (I), 2 and 3° in (II) and 1 and 2° in (III), all with e.s.d.'s of about 1°. With planar Hdmg units one may consider the interplanar angle  $\alpha$ , defined as the angle between the N(1A)C(2A)C(3A)N(2A) and N(1B)C(2B)C(3B)–N(2B) planes, as a measure of the difference in steric demands of the axial ligands. The values are 0 (I), 4 (II) and 4° (III), suggesting a small difference between pyrrolidine on the one hand and chlorine or benzyl on the other.

Geometrical features of the individual organic ligands are presented in Tables 7 through 9. Valence angles indicate a planar benzyl ligand in (III) (Table 7), and decidedly puckered pyrrolidine rings in all three compounds (Table 8). Individual lengths and angles in the Hdmg moieties (Table 9) show a rather large scatter, particularly in (II) and (III). On the other hand, the summary of average bond distances, given in Table 10, reveals an excellent agreement with similar values put forward by Palenik, Sullivan & Naik (1976). A possible explanation for the scatter in (II) and (III) could be ligand-induced proton shift (LIPS), *i.e.* an asymmetrical positioning of the axial ligands causing the two protons in the equatorial plane to be on one dimethylglyoxime unit, rather than to be distributed over both (Fig. 4).

LIPS would lead to C<sub>2v</sub> symmetry in the equatorial plane and would allow the *A* and *B* dimethylglyoxime ligands to be different. The presence of an inversion center in (I) rules out C<sub>2v</sub> symmetry, and thus excludes the presence of LIPS and proves that (I) must be formulated as (Hdmg)<sub>2</sub>(pyr)<sub>2</sub>Co. Trends indicating how

Table 5. The Co coordination: bond lengths (Å) and angles (°), with e.s.d.'s in parentheses

	(I)	(II)	(III)
Co–N(1A)	1.881 (2)	1.887 (5)	1.870 (9)
Co–N(2A)	1.893 (2)	1.902 (5)	1.865 (10)
Co–N(1B)	1.881	1.926 (5)	1.870 (8)
Co–N(2B)	1.893	1.845 (5)	1.912 (8)
Co–N(1P)	1.999 (2)	2.004 (4)	2.114 (8)
Co–X*	1.999	2.235 (1)	2.128 (8)
N(1A)–Co–N(2A)	81.4 (1)	82.9 (2)	82.0 (4)
N(1A)–Co–N(1B)	180.0	178.1 (3)	178.4 (5)
N(1A)–Co–N(2B)	98.6	99.1 (3)	98.4 (4)
N(1A)–Co–N(1P)	92.2 (1)	93.0 (2)	92.2 (4)
N(1A)–Co–X	87.8	88.5 (1)	94.1 (4)
N(2A)–Co–N(1B)	98.6	98.9 (2)	99.4 (4)
N(2A)–Co–N(2B)	180.0	176.8 (2)	176.6 (5)
N(2A)–Co–N(1P)	92.0 (1)	93.4 (2)	90.8 (4)
N(2A)–Co–X	88.0	88.3 (1)	87.3 (4)
N(1B)–Co–N(2B)	81.4	79.1 (2)	80.3 (3)
N(1B)–Co–N(1P)	87.8	87.6 (2)	87.0 (4)
N(1B)–Co–X	92.2	90.9 (1)	86.8 (4)
N(2B)–Co–N(1P)	88.0	88.9 (2)	92.5 (4)
N(2B)–Co–X	92.0	89.3 (1)	89.4 (5)
N(1P)–Co–X	180.0	177.8 (1)	173.1 (4)

\* X is N(1P)' related to N(1P) by the inversion center in (I), X is Cl in (II) and X is C(7T) in (III).

Table 6. Summary of average bond distances (Å) in some cobaloximes XYCo(Hdmg)<sub>2</sub> with Y a nitrogen-bonded ligand

Abbreviations used: pyr pyrrolidine, mor morpholine, sulfa sulfanilamide, clan 4-chloroaniline, an aniline, benz benzyl.

X	Y	References	Co–Y	Co–N(eq.)
NO <sub>2</sub>	NO <sub>2</sub>	(1)	1.946 (2)	1.910 (2)
Cl	pyr	(2)	2.004 (5)	1.890 (6)
Cl	mor	(3)	2.022 (3)	1.892 (4)
Cl	NH <sub>2</sub>	(4)	1.965 (4)	1.890 (5)
Cl	(CH <sub>3</sub> ) <sub>2</sub> NH	(5)	1.994 (5)	1.888 (6)
Cl	sulfa	(6)	2.023 (8)	1.889 (15)
Cl	clan	(6)	1.999 (6)	1.893 (5)
Cl	an	(7)	2.019 (5)	1.892 (5)
pyr	pyr	(2)	1.999 (2)	1.887 (2)
an	an	(8)	2.001 (5)	1.887 (6)
benz	pyr	(2)	2.114 (8)	1.879 (8)
benz	mor	(9)	2.11 (1)	1.88 (1)
CH <sub>2</sub> COOCH <sub>3</sub>	pyr	(10)	2.04	1.88

References: (1) Bresciani-Pahor, Calligaris & Randaccio (1978); (2) this work; (3) Lenstra, Van Loock, Tyrlik & Stapowska (1982); (4) Brückner & Randaccio (1974); (5) Lenstra, Geise & Tyrlik (1984); (6) Palenik, Sullivan & Naik (1976); (7) Botoshanskii, Simonov, Malinowskii, Ablov & Bologna (1975); (8) Battaglia, Corradi, Palmieri, Nardelli & Tani (1974); (9) Van Hooste, Lenstra, Kwiecinski & Tyrlik (1982); (10) Lenhart (1967).

Table 7. Geometrical characteristics of the benzyl ligand in (III)

E.s.d.'s are *ca* 0.01 Å and 0.8°, respectively.

C(17)–C(77)	1.38	C(37)–C(47)	1.34
C(17)–C(27)	1.37	C(47)–C(57)	1.37
C(17)–C(67)	1.39	C(57)–C(67)	1.35
C(27)–C(37)	1.37		
C(27)–C(17)–C(77)	123	C(37)–C(47)–C(57)	122
C(67)–C(17)–C(77)	121	C(47)–C(57)–C(67)	118
C(17)–C(27)–C(37)	123	C(17)–C(67)–C(57)	123
C(27)–C(37)–C(47)	118	C(27)–C(17)–C(67)	115

Table 8. Geometrical characteristics of the pyrrolidine rings

E.s.d.'s are *ca* 0.01 Å and 0.9°, respectively.

	(I)	(II)	(III)
N(1P)–C(1P)	1.47	1.43	1.45
N(1P)–C(4P)	1.49	1.48	1.40
C(1P)–C(2P)	1.49	1.52	1.55
C(2P)–C(3P)	1.51	1.50	1.49
C(3P)–C(4P)	1.51	1.49	1.49
C(1P)–N(1P)–C(4P)	102	101	104
N(1P)–C(1P)–C(2P)	107	107	106
C(1P)–C(2P)–C(3P)	105	103	104
C(2P)–C(3P)–C(4P)	106	105	104
C(3P)–C(4P)–N(1P)	105	106	109

Table 9. Bond lengths (Å) and valence angles (°) of the Hdmg moieties

E.s.d.'s are *ca* 0.01 Å and 0.9°, respectively.

	(I)		(II)		(III)	
	A	B	A	B	A	B
O(1)–N(1)	1.34	1.31	1.39	1.37	1.33	1.36
O(2)–N(2)	1.35	1.30	1.38	1.35	1.36	1.36
N(1)–C(2)	1.30	1.31	1.25	1.29	1.28	1.28
N(2)–C(3)	1.28	1.31	1.25	1.24	1.30	1.30
C(2)–C(3)	1.46	1.45	1.47	1.42	1.47	1.47
C(1)–C(2)	1.47	1.49	1.52	1.53	1.49	1.49
C(4)–C(3)	1.48	1.47	1.48	1.46	1.41	1.41
O(1)–N(1)–C(2)	121	123	118	123	121	121
O(2)–N(2)–C(3)	121	122	123	123	120	120
N(1)–C(2)–C(3)	112	113	113	116	113	113
N(2)–C(3)–C(2)	113	114	111	112	111	111
N(1)–C(2)–C(1)	124	122	126	123	124	124
N(2)–C(3)–C(4)	124	122	123	123	124	124
C(1)–C(2)–C(3)	123	124	121	121	123	123
C(4)–C(3)–C(2)	122	124	125	124	124	124

Table 10. Summary of average bond lengths (Å) in the dimethylglyoxime ligands; ligands X and Y are normal to the plane of the dmg groups

Compound	X	Y	N–O	C=N	C–C	C–CH <sub>3</sub>
(I)	pyr	pyr	1.345	1.288	1.463	1.477
(II)	pyr	Cl	1.347	1.280	1.460	1.492
(III)	pyr	PhCH <sub>2</sub>	1.351	1.278	1.446	1.472

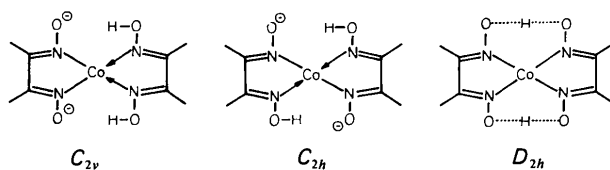


Fig. 4. Possible arrangements of protons in the equatorial plane with corresponding local symmetry.

bond lengths change when going from dmg(2–) to H<sub>2</sub>dmg have been published by Bresciani-Pahor, Calligaris & Randaccio (1978). Inspection of Tables 5 to 9 along these lines shows that the possibility of LIPS in (II) and (III) cannot be ruled out, although a firm statistically significant statement cannot be made.

Some of the conclusions drawn from the geometries revealed by the X-ray investigation are corroborated by the NMR behaviour of the compounds (Table 1), although the interpretation is hampered by the unfortunate solubility characteristics that force us to use different solvents. The variation in <sup>13</sup>C chemical shifts of C(1P) and C(2P) is in our opinion a reflection of the *trans* effect, while the variation of C(1A) and C(2A) is a reflection of the *cis* effect. Furthermore, the chemical shifts of C(1A) and C(2A) seem to confirm that the pyrrolidine derivative (I) can be set apart from the chlorine (II) and benzyl derivatives (III), as was also suggested by the comparison of interplanar angles  $\alpha$ . Of course, the origin for the grouping according to the  $\delta$  values need not be steric.

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