

***trans*-Chloro(dimethylamine-*N*)bis[dimethylglyoximato(1-)-*N,N'*]cobalt(III),  
[CoCl(C<sub>4</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>{NH(CH<sub>3</sub>)<sub>2</sub>}]**

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**Abstract.**  $M_r = 369.8$ , orthorhombic,  $P2_1nb$  (equivalent positions:  $x, y, z; \frac{1}{2} + x, -y, -z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z; x, \frac{1}{2} + y, \frac{1}{2} - z$ ),  $Z = 4$ ,  $a = 9.136$  (2),  $b = 12.650$  (3),  $c = 13.981$  (2) Å,  $V = 1615.8$  Å<sup>3</sup>,  $D_x = 1.52$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu(\text{Mo } K\alpha) = 1.291$  mm<sup>-1</sup>,  $F(000) = 768$ , room temperature,  $R_w = 0.039$  for 1120 reflections. A comparison of the geometry of the title compound with other chloro-cobaloximes carrying *trans*-related N-donor ligands shows that the Co–Cl distance is rather insensitive to changes in the nature of the N-donor ligand. There are two short O··O hydrogen bridges of 2.45 (1) and 2.42 (1) Å.

**Introduction.** Our interest in cobaloximes – compounds containing the Co(Hdmg)<sub>2</sub> unit, where Hdmg is the monoanion of dimethylglyoxime – is stimulated by their similarity to vitamin B<sub>12</sub>. Like vitamin B<sub>12</sub>, they show catalytic properties in hydrogenation processes. In terms of structural properties cobaloximes are interesting, because the octahedral Co coordination in *trans*-Co(Hdmg)<sub>2</sub>XY is strongly dependent upon the electronic and steric properties of the X and Y ligands. Electronic interactions between Co<sup>III</sup> and X and Y reveal themselves in such a way that, for example, Co–X lengths increase with the  $\sigma$ -donor ability of the *trans*-situated ligand Y. Steric interactions, introduced, for example, by the bulkiness of Y, cause a further lengthening of the Co–X bond as well as distortions in the octahedral symmetry (Bresciani-Pahor, Randaccio, Toscano, Sandercock & Marzilli, 1982). In order to obtain reference values for the Co–Cl length we investigated the title compound Co(Hdmg)<sub>2</sub>Cl(NHMe<sub>2</sub>) and compared its geometry with those of six other chloro-cobaloximes having axial N-donor ligands.

**Experimental.** The title compound was prepared by dissolving 3.00 g (0.0083 mol) dichlorocobaloxime [Co(Hdmg)<sub>2</sub>Cl.HCl], upon gentle heating, in 400 ml absolute ethanol. Then 0.75 g (0.0166 mol) dimethylamine in 50 ml ethanol was added dropwise. After cooling, and evaporating ca 300 ml solvent, the crude product precipitated. It was recrystallized from

methanol/water (1/1). Crystals suitable for X-ray analysis were obtained after two days storage in a refrigerator.

Crystal 0.15 × 0.2 × 0.15 mm, cell dimensions (from setting angles of 25 reflections) and subsequent collection of intensity data ( $\omega$  scan) performed on an Enraf–Nonius CAD-4 diffractometer; three intensity- and orientation-control reflections measured every 120 min and every 200 reflections, respectively, showed no significant drift in intensity; 1512 independent intensity data,  $\theta_{\text{max}} = 25^\circ$ , 1120 unique reflections with  $I > 2\sigma(I)$ , no correction for absorption effects in view of the small size of the crystal and low  $\mu$ . Systematic extinctions indicated  $Pmnb$  and  $P2_1nb$  as possible space groups. The latter, chosen because of the acentric  $E$  distribution and the density of the compound, was corroborated by the analysis. Structure solved from Patterson and heavy-atom Fourier maps; most of the H atoms found from difference electron density calculations, the remainder located at expected positions. Positional and anisotropic thermal parameters of non-hydrogen atoms refined on  $F$  with weights based on counting statistics, coordinates of H atoms and their Debye–Waller temperature parameters (4 Å<sup>2</sup>) kept fixed.  $R = 0.042$ ,  $R_w = 0.039$ ,  $S = 3.12$ ,  $(\Delta/\sigma)_{\text{max}} = 0.15$ , maximum noise level in the final difference Fourier map 0.3 e Å<sup>-3</sup>. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974), all calculations performed with the *SDP* program series (Frenz, 1978).

**Discussion.** Refined parameters are listed in Table 1, the numbering of atoms is given in Fig. 1.†

The Co<sup>III</sup> ion is coordinated by four N atoms of two Hdmg ligands, one N atom of the dimethylamine and a chlorine. Contact distances and corresponding angles of the resulting, slightly distorted octahedron are tabulated in Table 2. Relevant bond lengths and angles of the ligands are given in Table 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 39145 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Positional parameters in fractions of the cell edges and isotropic temperature factors (Å<sup>2</sup>)

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

	x	y	z	B <sub>iso</sub>
Co	0.00000	0.39059 (9)	0.29708 (8)	2.56
Cl	0.0960 (4)	0.2365 (2)	0.2471 (2)	4.07
O(1A)	0.1134 (9)	0.3448 (5)	0.4814 (4)	5.54
O(2A)	-0.2740 (7)	0.3350 (5)	0.2162 (5)	5.01
N(1A)	-0.0014 (12)	0.3371 (5)	0.4215 (5)	3.44
N(2A)	-0.1884 (8)	0.3283 (5)	0.2960 (5)	2.97
C(1A)	-0.140 (2)	0.245 (1)	0.5460 (8)	6.94
C(2A)	-0.118 (1)	0.2919 (7)	0.4510 (7)	3.82
C(3A)	-0.231 (1)	0.2868 (7)	0.3766 (8)	3.45
C(4A)	-0.375 (1)	0.238 (1)	0.3863 (9)	5.87
O(1B)	-0.1089 (8)	-0.0668 (6)	0.3895 (4)	4.79
O(2B)	0.2787 (8)	-0.0623 (5)	0.1244 (5)	3.86
N(1B)	0.001 (1)	-0.0594 (5)	0.3277 (4)	3.25
N(2B)	0.1963 (8)	-0.0512 (5)	0.2029 (5)	2.65
C(1B)	0.143 (1)	0.0410 (8)	0.4486 (7)	5.50
C(2B)	0.119 (1)	-0.0121 (8)	0.3551 (6)	3.41
C(3B)	0.236 (1)	-0.0098 (6)	0.2834 (6)	2.22
C(4B)	0.382 (1)	0.0377 (6)	0.2959 (8)	5.46
N(1D)	0.4289 (8)	0.4679 (6)	0.6607 (5)	3.08
C(1D)	0.464 (1)	0.4355 (7)	0.5656 (6)	3.69
C(2D)	0.273 (1)	0.4426 (8)	0.6810 (8)	5.35

Table 2. Distances (Å) and angles (°) in the cobalt coordination

Co-Cl	2.248 (2)	Co-N(1B <sup>II</sup> )	1.855 (5)
Co-N(1D <sup>I</sup> )	1.994 (5)	Co-N(1A)	1.866 (5)
Co-N(2B <sup>II</sup> )	1.939 (5)	Co-N(2A)	1.893 (6)
Cl-Co-N(1D <sup>I</sup> )	175.8 (2)	N(1D <sup>I</sup> )-Co-N(2A)	94.6 (2)
Cl-Co-N(1B <sup>II</sup> )	90.1 (2)	N(1B <sup>II</sup> )-Co-N(2B <sup>II</sup> )	82.4 (3)
Cl-Co-N(2B <sup>II</sup> )	88.2 (2)	N(1B <sup>II</sup> )-Co-N(1A)	178.7 (2)
Cl-Co-N(1A)	88.8 (2)	N(1B <sup>II</sup> )-Co-N(2A)	97.9 (4)
Cl-Co-N(2A)	89.5 (2)	N(2B <sup>II</sup> )-Co-N(1A)	98.3 (4)
N(1D <sup>I</sup> )-Co-N(1B <sup>II</sup> )	88.5 (2)	N(2B <sup>II</sup> )-Co-N(2A)	177.7 (3)
N(1D <sup>I</sup> )-Co-N(2B <sup>II</sup> )	87.7 (2)	N(1A)-Co-N(2A)	81.4 (3)
N(1D <sup>I</sup> )-Co-N(1A)	92.7 (2)		

Symmetry code: (i)  $-\frac{1}{2} + x, 1 - y, 1 - z$ . (ii)  $x, \frac{1}{2} + y, \frac{1}{2} - z$ .

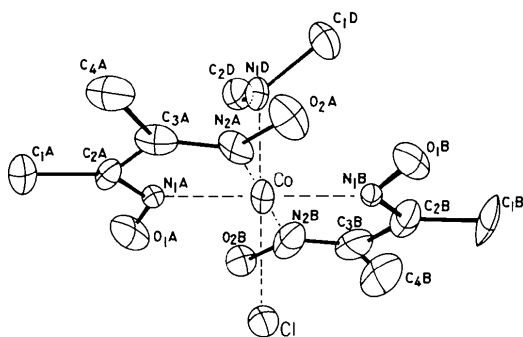


Fig. 1. ORTEP drawing (Johnson, 1965) of the title compound with atomic numbering.

Table 3. Bond distances (Å) and valence angles (°) in the dimethylglyoximate and dimethylamine ligands

The e.s.d.'s are ca 0.01 Å and 0.8°, respectively.

	Hdmg Ligand A	Hdmg Ligand B	
N(1)-O(1)	1.33	1.35	
C(1)-C(2)	1.48	1.47	
C(2)-C(3)	1.46	1.47	
C(2)-N(1)	1.29	1.28	
C(3)-C(4)	1.47	1.46	
C(3)-N(2)	1.29	1.30	
N(2)-O(2)	1.34	1.37	
O(1)-N(1)-C(2)	118.1	118.7	
N(1)-C(2)-C(1)	126.2	126.0	
N(1)-C(2)-C(3)	114.5	112.2	
C(1)-C(2)-C(3)	119.3	121.8	
C(2)-C(3)-C(4)	125.9	126.0	
C(2)-C(3)-N(2)	112.5	112.8	
N(2)-C(3)-C(4)	121.5	121.1	
C(3)-N(2)-O(2)	126.8	124.3	
N(1D)-C(1D)	1.43	C(1D)-N(1D)-C(2D)	109.2
N(1D)-C(2D)	1.48		

Table 4. Comparison of complexes Co(Hdmg)<sub>2</sub>ClY

*d* represents the distance of the Co atom from the N(1A)-N(2A)N(1B)N(2B) plane;  $\alpha$  is the angle between the N(1A)-C(2A)C(3A)N(2A) and N(1B)C(2B)C(3B)N(2B) planes; the two torsion angles N=C(2)-C(3)=N are denoted by  $\phi$ . mor is morpholine and pyr is pyrrolidine.

Y	Reference	Co-Cl (Å)	Co-N(axial) (Å)	<i>d</i> (Å)	$\alpha$ (°)	$\phi$ (°)
NH <sub>3</sub>	1	2.251 (1)	1.965 (4)	0.006	2	3.0
Me <sub>2</sub> NH	2	2.248 (2)	1.994 (5)	0.029 (5)	2	1.4
mor	3	2.256 (1)	2.022 (3)	0.046 (4)	7	3.4
pyr	4	2.235 (1)	2.004 (4)	0.025 (4)	4	3.2
C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>	5	2.261 (1)	2.019 (2)	0.004	7	3.1
ClC <sub>2</sub> H <sub>4</sub> NH <sub>2</sub>	6	2.257 (2)	1.999 (6)	0.008	4	1.1
H <sub>2</sub> NSO <sub>2</sub> C <sub>2</sub> H <sub>4</sub> NH <sub>2</sub>	6	2.235 (3)	2.023 (8)	0.005	6	1.2

References: (1) Brückner & Randaccio (1974); (2) this work; (3) Lenstra, Van Loock, Tyrlik & Stąpowska (1982); (4) Tyrlik, Van Loock, Lenstra & Geise (1982); (5) Botoshanskii, Simonov, Malinovskii, Ablov & Bologna (1975); (6) Palenik, Sullivan & Naik (1976).

The main distortion in the octahedron is introduced by the rigidity of the N=C-C=N fragments of the Hdmg anions. Both N(1)-Co-N(2) angles of the five-membered rings Co-N(1)=C(2)-C(3)-N(2) are decreased from 90° to ca 81°, while the complementary angles N(A)-Co-N(B) are increased to ca 98°, in order to keep the four equatorial N atoms coplanar: they are coplanar to within 0.01 Å. The Co atom is shifted over  $d = 0.029(5)$  Å from the N(1A)N(2A)-N(1B)N(2B) plane towards the dimethylamine. As judged by the values of the torsion angles  $\phi$  [N=C(2)-C(3)=N], being 1 and 4° for ligands A and B, respectively, the Hdmg units are individually planar. 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, amounts to 2°.

The more important geometrical data of the title compound are compared in Table 4 with those of other

cobaloximes having a chlorine and a N-donor ligand in *trans* relation. It follows that the Co—Cl distance is rather insensitive towards changes in the structure of the *trans* N-donor ligand. The values, ranging from 2.235 to 2.261 Å with an average of 2.249 (10) Å, are, however, significantly smaller than those reported (Marzilli, Toscano, Ramsden, Randaccio & Bresciani-Pahor, 1982) for chloro-cobaloximes with a *trans* P-donor ligand. In the latter complexes the range of Co—Cl is from 2.277 to 2.294 Å.

Turning to the Co—N(axial) distances (Table 4) one immediately notices much more variation. If only steric interactions were responsible, one would expect the Co—N to increase in the series Co(Hdmg)<sub>2</sub>ClY with Y = NH<sub>3</sub> < NH<sub>2</sub>R < NHR<sub>2</sub>. Indeed, the smallest Co—N is observed for Y = NH<sub>3</sub> but all other complexes fall in the same range. At first sight one concludes that none of the listed ligands is sterically demanding. A more detailed analysis, however, shows that local crowding around the central Co<sup>III</sup> exists and has consequences for the structures examined. *cis* effects are in operation as revealed by two indicators. The first indicator is the shift (*d*) of the Co<sup>III</sup> out of the least-squares plane through the four N atoms of the two Hdmg ligands; *d* is taken as positive when Co is shifted towards the axial N ligand, or in an alternative way of thinking when the *cis*-ligand plane (the Hdmg ligands) is pushed away from the axial N ligand. Examination of Table 4 shows that *d* is significantly larger for secondary amines than for primary amines or the NH<sub>3</sub> molecule. With primary amines or NH<sub>3</sub> as an axial ligand *d* is practically zero. The second indicator is the angle  $\alpha$  between the two Hdmg moieties, all of which can be considered planar as judged by the small values (0–4°) of the torsion angle  $\varphi(\text{N}=\text{C}-\text{C}=\text{N})$ . Crowding will increase  $\alpha$ . Table 4 shows that  $\alpha$  is small (*ca* 2°) for small axial ligands such as NH<sub>3</sub> and NH(CH<sub>3</sub>)<sub>2</sub>, but that  $\alpha$  is roughly three times larger for the more bulky ligands, irrespective of whether this is a secondary or a primary amine. We conclude that *cis* effects are operative in cobaloximes.

The title compound has two short hydrogen bridges, *viz* O(1B)···O(2A) at 2.45 (1) Å and O(1A)···O(2B) at

2.42 (1) Å. The accuracy of the data did not permit us to locate H atoms in these O···O bridges, nor could we infer information about the hydrogen positions from a comparison of Co—N(equatorial) and N—O bond lengths as indicated by Palenik, Sullivan & Naik (1976) and by Bresciani-Pahor, Calligaris & Randaccio (1978). Therefore the question whether the complex is truly Cl(Hdmg)<sub>2</sub>CoNH(CH<sub>3</sub>)<sub>2</sub> or should be formulated as Cl(dmg)(H<sub>2</sub>dmg)CoNH(CH<sub>3</sub>)<sub>2</sub> remains to be answered.

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## Structure of (5,10,15,20-Tetraphenyl-21*H*,23*H*-porphinato)platinum(II), C<sub>44</sub>H<sub>28</sub>N<sub>4</sub>Pt

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**Abstract.**  $M_r = 807.8$ , tetragonal,  $I\bar{4}2d$ ,  $a = 15.073$  (1),  $c = 13.988$  (1) Å,  $V = 3178.0$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.688$  (3) Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 8.632$  (1) mm<sup>-1</sup>,  $F(000) = 1592$ , room temper-

ature. Final  $R = 0.012$  for 1051 observed reflexions. The porphine nucleus is slightly ruffled, with N alternately 0.025 (3) Å above and below the plane. Pt—N is 2.008 (2) Å. The pyrrole ring is tilted at an

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