Inorganica Chimica Acta, *121* (1986) 71–75

Synthesis and Structure of Chloro(ligand)bis(glyoximato)cobalt(III) Complexes: Structural Evidence of an Electronic Effect on the Structure of the Dimethylpyrazine Ligand

CONCEPCIÓN LÓPEZ*, SANTIAGO ALVAREZ

Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona, 08028 Barcelona, Spain

XAVIER SOLANS and MANUEL FONT-ALTABA

Departament de Cristallografía, Facultat de Geología, Universitat de Barcelona, 08028 Barcelona, Spain

(Received May 2, 1986; revised June 25, 1986)

Abstract

The synthesis and characterization of *trans*-chloroligandbis(glyoximato)cobalt(III) complexes (ligand = 2,6-dimethylpyrazine, β-picoline and γ-picoline) are presented. X-ray crystal structure determination of the dimethylpyrazine derivative, [CoCl(gH)$_2$(Me$_2$pz)] (1), has been carried out, and two important structural features found: a significant change in bond distances within the aromatic nitrogen donor upon substitution of a methyl group of the equatorial dioximato ligand by a hydrogen, and a conformational preference for the axial ligand which appears to be oriented parallel to the equatorial C–C bonds, indicating that the substituents of the dioximato ligand are not important in determining that conformation. Changes in the bond angles of the glyoxime ligands upon coordination are due to chelation and hydrogen bond formation. Compound 1 is monoclinic, space group $P2_1/n$, with $Z = 4$ and unit cell parameters $a = 14.973(3)$, $b = 10.790(2)$ and $c = 10.844(2)$ Å and $\beta = 90.92(2)°$.

Introduction

The structural and spectral properties of bis(dimethylglyoximato)cobalt(III) complexes, [CoX(dmgH)$_2$L], have been the subject of a large number of studies in the last years [1–6]. However, much less is known about the structure and properties of the simpler bis(glyoximato) complexes [7–9], [CoX(gH)$_2$L], in which any steric influence of the equatorial substituents on the axial ligands are kept to a minimum. In-depth study of *trans*-bis(glyoximato)cobalt(III) compounds should provide useful information on the electronic *cis*- and *trans*-effects already detected in the dimethylglyoximato analogues, as well as on the relative importance of electronic and steric factors in the conformation of the axial ligands [10, 11].

Experimental

Elemental analyses were carried out at the Instituto de Química Bio-Orgánica (C.S.I.C., Barcelona) with a Carlo Erba 1106 microanalyzer. Infrared and ultraviolet (CH$_2$Cl$_2$) spectra were recorded with a Beckman IR-20A and a Beckman UV 2530 spectrophotometer, respectively. ^{1}H spectra were obtained at 20–25 °C on a Bruker WP-80-54 spectrometer using CDCl$_3$ (99.8%) as solvent, operating at 80.13 MHz and using TMS as an internal standard.

Conductivities of 10^{-3} M acetonic solutions of the new compounds were measured with a Radiometer CDM3 conductivity bridge. Weight losses were found by heating the compounds at 120 °C to constant weight. Glyoxime from standard sources moistened with 20% of water was used for the synthesis of the complexes.

Preparation of the Complexes

1.0 g (9.1 mmol) of glyoxime dissolved in ethanol was added to a solution of 1.08 g (4.53 mmol) of CoCl$_2$·6H$_2$O in 25 ml of ethanol. When the solution became dark blue (~45 min), 5.5 mmol of the ligand dissolved in 30 ml of ethanol were added. The resulting mixture was stirred at room temperature for 3 h. During this period the mixture turned brown. Slow evaporation of the solvent lead to dark brown needles which were collected by filtration and air dried. Yields: 54–70%.

Crystal Structure Determination and Refinement

Compound 1 was recrystallized in CH$_2$Cl$_2$ and a prismatic crystal (0.1 × 0.1 × 0.15 mm) was selected and mounted on a Philips PW-1100 four circle diffractometer. The unit-cell parameters were determined

---

*Author to whom correspondence should be addressed.

0020-1693/86/$3.50

from 25 reflections ($4^\circ < \theta < 12^\circ$) and refined by least-squares. Intensities were collected with graphite monochromatized Mo Kα radiation, using the ω-scan technique, scan speed 0.03° s^{-1}, scan width 0.8°. 3797 independent reflections were measured in the range $2^\circ < \theta < 30.5^\circ$, and 3730 were considered as observed applying the condition $I \geqslant 2.5\sigma(I)$. Three reflections were measured every two hours as orientation and intensity control and no significant intensity decay was observed. Lorentz polarization corrections but no absorption corrections were made.

The Co atom was located from a Patterson synthesis and the remaining non-hydrogen atoms from a weighted Fourier synthesis. The structure was isotropically and anisotropically refined by full-matrix least-squares method, using the SHELX76 computer program [12]. The function minimized was $w(|F_o| - |F_c|)^2$, where $w = (\sigma^2(F_o) + 0.0054|F_o|^2)^{-1}$. Anomalous scattering factors, f, f' and f'' were taken from the literature [13]. Methyl hydrogen atoms were computed and remaining hydrogen atoms obtained from a difference synthesis and refined with an overall isotropic temperature factor; the remaining atoms were refined anisotropically. The final R was 0.053 ($R_w = 0.061$) for all observed reflections.

Final atomic parameters are listed in Table I together with their estimated standard deviations. See also 'Supplementary Material'.

Crystal data

$C_{10}H_{14}N_6O_4ClCo \cdot CH_2Cl_2$ (1), $M = 461.6$, monoclinic, $a = 14.973(3)$, $b = 10.790(2)$, $c = 10.844(2)$ Å, $\beta = 90.92(2)^\circ$, $V = 1751.1(10)$ Å^3, $P2_1/n$, $Z = 4$, $D_x = 1.643$ g cm^{-3}, $F(000) = 880$, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 14.94 cm^{-1}. Room temperature.

TABLE I. Atomic Coordinates and Thermal Parameters for $[CoCl(gH)_2(2,6\text{-}Me_2pz)] \cdot CH_2Cl_2$

	x/a	y/b	z/c	B_{eq}
Co	0.20072(3)	0.21730(4)	1.01161(4)	1.88(2)
Cl	0.32058(6)	0.11393(9)	1.08001(9)	3.13(4)
N1	0.0947(2)	0.3059(3)	0.9478(3)	2.01(10)
C2	0.0118(2)	0.2741(3)	0.9833(3)	2.37(13)
C3	−0.0628(2)	0.3385(3)	0.9387(3)	2.42(13)
N4	−0.0554(2)	0.4320(3)	0.8583(3)	2.49(11)
C5	0.0272(2)	0.4605(3)	0.8200(3)	2.49(13)
C6	0.1021(2)	0.3969(3)	0.8653(3)	2.28(12)
C7	−0.1550(3)	0.3020(4)	0.9779(5)	3.62(17)
C8	0.0360(3)	0.5618(4)	0.7267(4)	3.46(16)
O11	0.3137(2)	0.4272(3)	0.9633(3)	3.20(12)
N11	0.2610(2)	0.3693(3)	1.0444(3)	2.31(11)
C11	0.2504(3)	0.4139(3)	1.1531(4)	2.80(14)
C12	0.1935(3)	0.3401(4)	1.2301(3)	2.93(15)
N12	0.1637(2)	0.2409(3)	1.1779(3)	1.82(10)
O12	0.1119(2)	0.1593(3)	1.2370(3)	3.44(12)
O21	0.2922(2)	0.2755(3)	0.7917(3)	3.29(12)
N21	0.2397(2)	0.1943(3)	0.8475(3)	2.45(11)
C21	0.2088(3)	0.0959(4)	0.7943(4)	3.15(15)
C22	0.1540(3)	0.0189(4)	0.8732(4)	3.38(16)
N22	0.1429(2)	0.0640(3)	0.9829(3)	2.65(12)
O22	0.0970(2)	0.0032(3)	1.0676(3)	3.43(12)
C11	0.1119(1)	0.2896(1)	0.5538(1)	5.41(7)
C12	−0.0079(1)	0.1162(2)	0.6716(1)	5.91(7)
C	0.0221(4)	0.1860(6)	0.5328(5)	5.00(24)

Results and Discussion

NMR Spectra

The ^1H NMR spectra of the new compounds (Table II) show three well differentiated groups of signals. The protons of the equatorial glyoximato

TABLE II. ^1H NMR ($CDCl_3$) and UV (CH_2Cl_2) Spectra and Analytical Data of the New Compounds (log ϵ given in parentheses)

Compound	δ (ppm)			λ_{max}(nm)	Analysis		
	Complex	Ligand	Assignment			Found	(Calc.)
$[Co(gH)_2Cl(Me_2pz)]$ (1)	7.61		gH	276 (4.28)	C	31.3	(31.88)
	7.84	8.30	H_α(pz)		H	3.8	(3.72)
	2.51	2.52	Me		N	21.9	(22.31)
$[Co(gH)_2Cl(\beta\text{-pic})]$ (2)	7.31		gH		C	32.5	(33.20)
	7.50	7.45	H_γ(pic)		H	3.5	(3.59)
	7.14	7.13	H_β(pic)		N	18.7	(19.37)
	8.41	8.54	H_α, $H_{\alpha'}$(pic)				
	2.33	2.14	Me				
$[Co(gH)_2Cl(\gamma\text{-pic})] \cdot 0.5H_2O$ (3)	7.61		gH		C	32.4	(32.39)
	7.10	7.04	H_β(pic)	320 (sh)	H	3.8	(3.78)
	8.06	8.55	H_α(pic)	253 (4.63)	N	18.6	(18.89)
	2.37	2.10	Me	236 (4.62)	w.l.[a]	2.51	(2.43)

[a] w.l. = Weight loss at 120 °C.

ligand appear at 7.3–7.6 ppm, in good agreement with previously reported glyoximato cobalt(III) complexes [7–9]. The signals around 2.3 ppm are unambiguously assigned to the methyl groups, and those at 7–8 ppm to the aromatic protons of the axial ligands. The equivalence of the four equatorial protons of the β-picoline derivative indicates that there is no substantial barrier for the rotation of the axial group around the $Co-N_{ax}$ bond.

The α-protons of the axially coordinated ligands are shifted upfield with respect to the free ligands, as can be expected for the shielding produced by the 'ring-current' effect of the equatorial bis(glyoximato)-cobalt(III) group; the effect is less pronounced for the β and γ protons, where the inductive effect may even dominate producing a small downfield shift [10, 11]. Comparison of the upfield shift on the α protons of Me_2pz in the glyoximato complex with that of the dimethylglyoximato analogues indicates that the shielding (ring-current effect) is somewhat larger in the glyoximato case.

Description of the Structure

The structure of compound **1** (Fig. 1) consists of discrete molecules linked by Van der Waals interactions. The CH_2Cl_2 molecules occupy interstitial positions and are linked through Van der Waals interactions. The Co atom displays an approximately octahedral coordination. The bis(glyoximato)cobalt group is practically planar: the largest deviations from the mean plane correspond to two oxygen atoms, 0.05 and 0.08 Å, while the Co atom deviates −0.021(1) Å from that plane. These deviations from planarity are well within the range found in similar dimethylglyoximato complexes [1, 11]. Other structural parameters used to describe deviations from planarity of the equatorial groups are the displacement of the Co atom from the N_4 plane ($d = 0.020$ for **1**) and the angle formed by the two C_2N_2 fragments ($\alpha = 1.0°$).

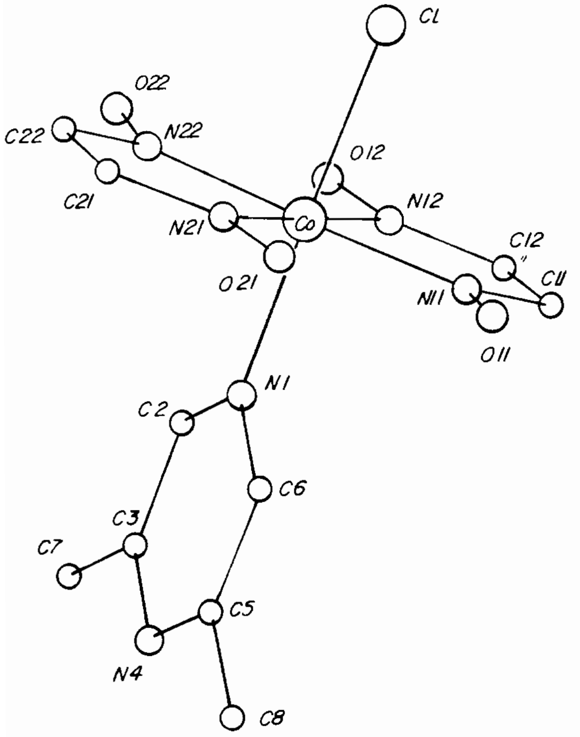

Fig. 1. Molecular structure and numbering scheme of [$Co(gH)_2Cl(Me_2pz)$] (**1**).

The Co–Cl and $Co-N_{ax}$ bonds are practically perpendicular to the equatorial plane as seen in the $N_{eq}-Co-Cl$, $N_{eq}-Co-N_{ax}$ and $Cl-Co-N_{ax}$ bond angles (Table III), while the bidentate nature of the glyoximato ligand introduces sensible deviations from the octahedral angles in the equatorial plane, as in other bis(dioximato) complexes [7–9, 11]. Co-ligand bond distances (Table III) are not significantly different from those in the dimethylglyoximato analogue. No *cis*-influence can be detected in the Co–N1 bond distance: it is practically the same as in the dimethylglyoxime analogue [11], while a *trans*-influence is seen by comparing with a slightly larger Co–N1 bond distance in the alkyl-pyridine glyoximato derivatives [8] (2.064–2.101 Å).

Comparison of structural data of the glyoximato ligands with that of the free glyoxime [14] (Table III) shows some important differences. The NCC bond angles are 118° in the free ligand, in good agreement with an sp^2 hybridization at the carbon atoms, but the formation of a chelate produces a significative deviation from the ideal sp^2 geometry. On the other hand, the opening of CNO bond angles upon coordination (Table III) can be attributed to the formation of the hydrogen bonds between both glyoximato ligands. Another significative variation is the shortening of the N–O bonds from 1.385(1) to 1.337(8) Å, which might be associated with deprotonation of gH_2. All C–C, C–N and N–O bond distances in gH are practically identical to those in previously reported compounds [8, 9] and to those of dmgH in the analogous compound [11], with only small differences in the corresponding bond angles.

The planar Me_2pz group is practically perpendicular to the cobaloxime plane, and parallel to the C–C bonds of the glyoximato groups. The angle τ formed between the N1–C6 bond and the normal to the C11–C12 bond, used to define the conformation of a ring linked to a cobaloxime [10, 11], is 89.4° here. This conformation is the same shown by many dmgH derivatives, indicating that the reason for the conformational preference is not a steric repulsion between the axial ligand and the methyl groups of dmgH.

It is interesting to compare the geometry of the pyrazine ring in compound **1** with that in the di-

TABLE III. Selected Bond Distances and Angles for $[Co(gH)_2Cl(Me_2pz)]$ (**1**), with Estimated Standard Deviations in Parentheses. Values for $[Co(dmgH)_2Cl(Me_2pz)]$ from the Literature [11] are Averages of the Chemically Equivalent Bonds. Values for the Free Ligands gH_2 are also from the Literature [14]

	$[Co(DH)_2Cl(Me_2pz)]$		gH_2
	DH = gH	DH = dmgH	
Bond distances			
Co–Cl	2.230 (1)	2.228 (1)	
Co–N1	1.969 (3)	1.970 (4)	
Co–N11	1.903 (3)	1.891 (4)	
Co–N12	1.912 (3)		
Co–N21	1.898 (3)		
Co–N22	1.890 (3)		
C11–N11	1.286 (5)	1.296 (6)	1.284 (1)
C12–N12	1.287 (5)		
C21–N21	1.291 (5)		
C22–N22	1.298 (5)		
C11–C12	1.442 (6)	1.466 (4)	1.453 (1)
C21–C22	1.455 (6)		
N11–O11	1.345 (4)	1.344 (4)	1.385 (1)
N12–O12	1.343 (4)		
N21–O21	1.330 (4)		
N22–O22	1.330 (4)		
Bond angles			
N11–Co–Cl	89.5 (1)	88.8 (12)	
N12–Co–Cl	89.8 (1)		
N21–Co–Cl	89.3 (1)		
N22–Co–Cl	88.9 (1)		
N11–Co–N1	91.4 (1)	91.2 (19)	
N12–Co–N1	91.3 (1)		
N21–Co–N1	89.6 (1)		
N22–Co–N1	90.1 (1)		
N11–Co–N12	81.5 (1)	81.4 (2)	
N21–Co–N22	83.0 (1)		
Co–N11–C11	115.4 (1)	116.5 (4)	
Co–N12–C12	114.9 (1)		
Co–N21–C21	114.4 (1)		
Co–N22–C22	114.5 (3)		
N11–C11–C12	114.0 (2)	112.7 (3)	118.00 (5)
N12–C12–C11	114.1 (2)		
N21–C21–C22	114.1 (2)		
N22–C22–C21	114.0 (2)		
C11–N11–O11	120.5 (2)	121.8 (6)	112.31 (5)
C12–N12–O12	122.3 (2)		
C21–N21–O21	123.3 (2)		
C22–N22–O22	121.5 (2)		

TABLE IV. Bond Distances and Angles for the 2,6-Me_2pz ligand in Complexes $[Co(DH)_2X(Me_2pz)]$, with Estimated Standard Deviations in Parentheses

	DH = gH	DH = dmgH	
	X = Cl	X = Cl [11]	X = Br [11]
Co–N1	1.969 (3)	1.970 (3)	1.954 (2)
N1–C2	1.350 (4)	1.333 (4)	1.343 (4)
N1–C6	1.334 (4)	1.331 (4)	1.338 (4)
N4–C3	1.339 (4)	1.336 (5)	1.373 (4)
N4–C5	1.346 (4)	1.339 (5)	1.378 (4)
C2–C3	1.394 (5)	1.368 (5)	1.379 (4)
C5–C6	1.397 (5)	1.365 (5)	1.413 (4)
C3–C7	1.505 (5)	1.505 (6)	1.477 (5)
C5–C8	1.497 (5)	1.506 (6)	1.525 (5)
C2–N1–C6	117.7 (2)	116.6 (3)	116.4 (2)
C3–N4–C5	117.3 (2)	116.8 (3)	115.7 (2)
N1–C6–C5	121.5 (2)	121.8 (4)	123.4 (3)
N1–C2–C3	120.6 (2)	121.9 (3)	122.1 (3)
N4–C3–C2	121.8 (2)	121.2 (4)	122.6 (3)
N4–C5–C6	121.0 (2)	121.5 (4)	199.6 (3)

methylglyoximato analogue [11] (Table IV). All the bond distances in the ring are larger in the gH than in the dmgH compound, the difference being clearly significant for the carbon–carbon bonds. Similar differences were observed previously between the bromo- and chloro-dmgH derivatives and might be related to small changes in the electronic structure of the cobalt atom, induced by the ligands *cis*- or *trans*- to the Me_2pz.

Acknowledgements

This work was partially sponsored by a grant from the Universitat de Barcelona. We are also grateful for financial support of the computational work from CAICYT (grant number 0657/81).

Supplementary Material

Observed and calculated structure factors, anisotropic thermal parameters, and hydrogen-atom coordinates are available from the authors on request.

References

1 N. Bresciani-Pahor, M. Forcolin, L. G. Marzilli, L. Randaccio, M. F. Summers and P. J. Toscano, *Coord. Chem. Rev., 63,* 1 (1985).
2 R. C. Stewart and L. G. Marzilli, *Inorg. Chem., 16,* 924 (1977).
3 W. C. Trogler and L. G. Marzilli, *Inorg. Chem., 14,* 2942 (1975).
4 W. C. Trogler, R. C. Stewart, L. A. Epps and L. G. Marzilli, *Inorg. Chem., 13,* 1564 (1974).
5 H. A. O. Hill and K. G. Morallee, *J. Chem. Soc. A,* 554 (1969).
6 C. Bied-Charreton, L. Alain and A. Gaudemer, *Bull. Soc. Chim. Fr.,* 861 (1972).
7 P. J. Toscano, T. F. Swider, L. G. Marzilli, N. Bresciani-Pahor and L. Randaccio, *Inorg. Chem., 22,* 3416 (1983).

8 N. Bresciani-Pahor, L. Randaccio, E. Zangrando and P. J. Toscano, *Inorg. Chim. Acta, 96*, 193 (1985).

9 M. Mégnamisi-Bélombé, H. Endres and E. Rossato, *Acta Crystallogr., Sect. C, 39*, 705 (1983).
G. O. Egharevba, M. Mégnamisi-Bélombé, H. Endres, E. Rossato, *Acta Crystallogr., Sect. B, 38*, 2901 (1982).

10 C. López, S. Alvarez, X. Solans and M. Font-Altaba, *Inorg. Chim. Acta, 111*, L19 (1986).

11 C. López, S. Alvarez, X. Solans and M. Font-Altaba, *Inorg. Chem., 25*, 2962 (1986).

12 G. M. Sheldrick, 'SHELX', a program for crystal structure determination, Cambridge University, 1976.

13 International Tables for X-ray Crystallography, Vol. 4, Kynoch Press, Birmingham, 1974, p. 99, 149.

14 G. A. Jeffrey, J. R. Ruble and J. A. Pople, *Acta Crystallogr., Sect. B, 38*, 1975 (1982).