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Synthesis and Structure of Chloro(ligand)bis(diphenylglyoximato)cobalt(III) Complexes

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Abstract

The synthesis and characterization of *trans*-chloro(ligand)bis(diphenylglyoximato)cobalt(III) complexes [ligand = pyridine (py), α-, β-, or γ-picoline (α-pic, β-pic, γ-pic), 3,5-lutidine (lut), *p*-toluidine (*p*-tol) and PPh_3] is presented. X-ray crystal structure determination of the pyridine (**1**) and *p*-toluidine (**6**) derivatives has been carried out. Compound **1** crystallizes in the monoclinic system, space group $P2_1/n$, with $Z = 4$ and unit cell parameters $a = 23.124(4)$, $b = 13.009(3)$ and $c = 11.204(3)$ Å, and $\beta = 93.14(2)°$. Compound **6** crystallizes in the monoclinic system, space group $P2_1/n$, with $Z = 4$ and unit cell parameters $a = 18.792(3)$, $b = 12.540(2)$ and $c = 15.346(3)$ Å, and $\beta = 97.54(2)°$.

Introduction

The chemistry, spectral and structural properties of *trans*-bis(ligand)bis(dimethylglyoximato)cobalt(III) complexes, of the type $[Co(dmgH)_2X(L)]$, have been extensively explored in the last years [1] due to their interest as models for important biochemical complexes [2] as well as to their usefulness as templates in many organic syntheses [3] or as catalysts in chemical processes [4]. In particular, *cis*- and *trans*-influences of the axial ligands L or X have been shown to affect both the NMR spectra [5, 6a, 6b] and structure [6] of the other ligands.

Substitution of the equatorial methyl group in dmgH by a hydrogen (gH) [7] or a phenyl group (dpgH) [6d, 8], could also give rise to *cis*-effects detectable in the NMR spectra and/or in the molecular structure. The octahedral derivatives of dpgH, however, have been scarcely studied, in contrast with the dmgH ones, or with the large number of studies on square planar dpgH derivatives [9]: only the synthesis and electronic spectra of a few alkylbis(dpgH)cobalt(III) complexes have been reported [10], and for only one of these compounds was the ^1H NMR spectrum given [10c], while no molecular structures of such compounds have been determined so far. We have recently presented the synthesis, electronic and NMR spectra of several halo(ligand)bis(diphenylglyoximato)cobalt(III) compounds [6d]. In this paper we wish to report further examples of this family of compounds and the first structural determination of octahedral diphenylglyoximato complexes.

Experimental

Diphenylglyoxime (analytical grade) and other ligands were obtained from standard sources and used as received. Elemental analyses were carried out at the Instituto de Química Bio-Orgánica (C.S.I.C., Barcelona). Infrared and ultraviolet (CH_2Cl_2) spectra were recorded with a Beckman IR-20A and a Beckman UV 5230 spectrophotometer, respectively. ^1H NMR spectra were obtained at 20–25 °C on a Bruker WP-80-54 spectrometer using $CDCl_3$ (99.8%) as solvent and operating at 80.13 MHz, with TMS as 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.

Preparation of the Complexes

[Co(dpgH)$_2$Cl(py)] (1)

To a solution containing 1.5 g (2.62 mmol) of $[Co(dpgH)_2Cl(H_2O)]$ [11] in 70 ml of acetone,

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0.20 ml of pyridine were added. The mixture was vigorously stirred at room temperature for 2 h and concentrated until a brown precipitate appeared. The product was filtered and air-dried (melting point (m.p.) 227–230 °C, dec.; yield 71%). *Anal.* Calc. for $CoClC_{34}H_{31}N_5O_5$: C, 59.70; H, 4.57; N, 10.24; Cl, 5.18. Found: C, 60.8; H, 4.3; N, 10.8; Cl, 5.3%.

[Co(dpgH)$_2$Cl(α-pic)]·2H$_2$O (2)

α-Picoline (0.20 ml, 2.04 mmol) was added to a solution of $[Co(dpgH)_2Cl(H_2O)]$ (1.17 g, 2.04 mmol) in acetone (65 ml). The mixture was stirred at room temperature for 4 h and its volume reduced to one third by rotary evaporation. The brown product formed was filtered, washed with cold acetone and air-dried (m.p. 215–218 °C, dec.; yield 64%). *Anal.* Calc. for $CoClC_{34}H_{33}N_5O_6$: C, 58.16; H, 4.70; N, 9.98; Cl, 5.06; weight loss, 5.13. Found: C, 58.9; H, 4.6; N, 9.8; Cl, 5.2; weight loss, 5.13%.

[Co(dpgH)$_2$Cl(β-pic)] (3)

To a solution containing 1.7 g (2.97 mmol) of $[Co(dpgH)_2Cl(H_2O)]$ in acetone (42 ml), β-picoline (0.30 ml, 3.1 mmol) was added. The mixture was stirred at room temperature for 1 h and the brown precipitate formed during the reaction removed by filtration and air-dried (m.p. 220–223 °C, dec.; yield 66%). *Anal.* Calc. for $CoClC_{34}H_{29}N_5O_4$: C, 61.32; H, 3.46; N, 10.52; Cl, 5.33. Found: C, 61.0; H, 4.33; N, 10.3; Cl, 5.6%.

[Co(dpgH)$_2$Cl(γ-pic)] (4)

This complex was prepared using the same method as described for 3, using the stoichiometric amount of γ-picoline (m.p. 233–236 °C, dec.; yield 72%). *Anal.* Calc. for $CoClC_{34}H_{29}N_5O_4$: C, 61.32; H, 4.36; N, 10.52. Found: C, 61.2; H, 4.4; N, 10.3%.

[Co(dpgH)$_2$Cl(lut)]·H$_2$O (5)

To a solution of $[Co(dpgH)_2Cl(H_2O)]$ (1.9 g, 3.3 mmol) in acetone (50 ml), 3,5-lutidine (0.36 ml, 3.3 mmol) was added. The mixture was vigorously stirred at room temperature for 3 h, and the brown-reddish product formed was removed by filtration and air-dried (m.p. 222–224 °C, dec.; yield 66%). *Anal.* Calc. for $CoClC_{35}H_{33}N_5O_5$: C, 60.26; H, 4.50; N, 10.04; weight loss, 2.58. Found: C, 59.6; H, 4.06; N, 9.82; weight loss, 2.68%.

[Co(dpgH)$_2$Cl(p-tol)]·CH$_3$COCH$_3$ (6)

This product was prepared through the same procedure used for **5**, using the stoichiometric amount of *p*-toluidine (m.p. 226–228 °C, dec.; yield 68%). *Anal.* Calc. for $CoClC_{38}H_{37}N_5O_5$: C, 61.83; H, 5.05; N, 9.49; Cl, 4.80. Found: C, 61.9; H, 4.9; N, 9.5; Cl, 5.1%.

[Co(dpgH)$_2$Cl(PPh$_3$)] (7)

This complex was prepared using the method described for **5**, using the stoichiometric amount of triphenylphosphine (m.p. 217–221 °C, dec.; yield 65%). *Anal.* Calc. for $CoClPC_{46}H_{37}N_4O_4$: C, 66.11; H, 4.43; N, 6.70. Found: C, 66.6; H, 4.5; N, 6.8%.

Crystal Structure Determination and Refinement

Prismatic crystals of compounds **1** and **6** (0.1 × 0.1 × 0.15 mm in both cases) were selected and mounted on a Philips PW-1100 four circle diffractometer. The unit-cell parameters were determined from 25 reflections ($4° \leqslant \theta \leqslant 12°$) and refined by least-squares. Intensities were collected with graphite monochromatized Mo Kα radiation, using the ω-scan technique, scan width 0.8° and scan speed $0.03°\ s^{-1}$. For compound **1**, 4484 intensities were measured in the range $2 \leqslant \theta \leqslant 25°$, and 4296 were considered as observed applying the condition $I \geqslant 2.5\sigma(I)$, while 4921 reflections were measured for compound **6** in the same range, from which 4806 were considered as observed. Three intensities were measured every two hours as orientation and intensity control and significant intensity decay was not observed. Lorentz polarization corrections but no absorption corrections were made.

Both structures were solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares method [12, 13]. For compound **1**, three peaks of the same height were observed in a difference synthesis after three isotropic refinement cycles, which were assigned to a methanol molecule incorporated in the recrystallization process; these sites were refined as N atoms with occupancy factors of 2/3. After anisotropic refinement cycles, hydrogen atoms were located from difference syntheses and refined with an overall isotropic temperature factor.

The minimized function was $\Sigma w(|F_o| - |F_c|)^2$, where $w = (\sigma^2(F_o) + 0.058|F_o|^2)^{-1}$ and the final R values were 0.062 (R_w = 0.072) for compound **1** and 0.052 (Rw = 0.060) for compound **6**. Final atomic coordinates are listed in Tables I and II, and perspective views of the molecular structures together with the atom numbering schemes are shown in Figs. 1 and 2. See also 'Supplementary Material'.

Crystal data of compound 1

$C_{33}H_{27}N_6O_4ClCo \cdot CH_3OH$: F_w = 684.0, monoclinic, a = 23.124(4), b = 13.009(3), c = 11.204(3) Å, β = 93.15(2)°, V = 3365(2) Å^3, $P2_1/n$, Z = 4, D_x = 1.350 g cm^{-3}, $F(000)$ = 1416, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 6.6 cm^{-1}, 288 K.

Crystal data of compound 6

$C_{34}H_{31}N_5O_4ClCo \cdot CH_3COCH_3$: F_w = 738.13, monoclinic, a = 18.792(3), b = 12.540(2), c = 15.346(3) Å, β = 97.54(2)°, V = 3585(2) Å^3,

TABLE I. Atomic Coordinates (Co and Cl × 10^5; Other Atoms ×10^4) and Equivalent Thermal Parameters for [Co(dpgH)$_2$Cl(py)]·CH$_3$OH (1)

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
Co	15105(3)	13771(6)	14410(7)	2.45(4)
Cl	66795(8)	19666(13)	60622(17)	3.89(8)
N(1)	8618(2)	91(4)	8256(5)	2.87(22)
C(2)	8321(3)	577(6)	7350(7)	3.90(32)
C(3)	8370(4)	1626(6)	7168(9)	4.90(40)
C(4)	8742(3)	2194(6)	7922(8)	4.46(37)
C(5)	9052(3)	1697(5)	8825(8)	4.22(36)
C(6)	8990(3)	652(5)	8953(7)	3.37(29)
O(11)	2620(2)	1299(4)	2707(4)	3.43(20)
N(11)	2327(2)	1153(4)	1651(5)	2.66(22)
C(11)	2589(3)	863(5)	716(5)	2.76(26)
C(12)	2191(3)	806(5)	-370(5)	2.81(25)
N(12)	1665(2)	1071(4)	-172(5)	2.75(21)
O(12)	1244(2)	1077(4)	-1044(4)	3.58(20)
O(21)	413(2)	1552(4)	156(4)	3.51(23)
N(21)	696(2)	1588(4)	1235(5)	2.82(26)
C(21)	425(3)	1791(6)	2184(6)	2.92(31)
C(22)	813(3)	1837(6)	3277(6)	2.97(32)
N(22)	1361(2)	1698(5)	3049(5)	3.05(26)
O(22)	1785(2)	1750(4)	3895(4)	3.87(24)
C(111)	3227(3)	678(5)	768(6)	2.85(27)
C(112)	3592(3)	1236(6)	78(7)	3.94(33)
C(113)	4188(4)	1086(8)	184(8)	5.89(42)
C(114)	4424(3)	357(8)	1026(8)	5.20(45)
C(115)	4054(3)	231(7)	1683(8)	4.65(37)
C(116)	3455(3)	65(6)	1575(7)	3.73(32)
C(121)	2388(3)	465(5)	-1542(6)	2.97(26)
C(122)	2203(3)	1000(7)	2576(6)	4.28(36)
C(123)	7377(5)	4362(10)	1319(8)	6.70(54)
C(124)	2688(4)	-227(9)	-3782(9)	6.88(55)
C(125)	2871(3)	-748(7)	-2759(9)	5.46(45)
C(126)	2722(3)	-402(6)	-1655(8)	3.84(34)
C(211)	-214(3)	1982(6)	2157(6)	3.03(33)
C(212)	602(3)	1180(7)	2152(8)	4.63(45)
C(213)	-1191(4)	1368(9)	2134(10)	5.88(53)
C(214)	-1394(4)	2337(9)	2082(9)	5.81(55)
C(215)	-1022(4)	3145(9)	2067(10)	5.63(53)
C(216)	423(4)	2973(6)	2111(8)	4.46(42)
C(221)	617(3)	1988(5)	4503(6)	3.11(33)
C(222)	166(3)	1397(6)	4897(8)	4.06(39)
C(223)	-3(4)	1504(8)	6077(8)	5.06(49)
C(224)	269(4)	2185(8)	6827(8)	5.13(47)
C(225)	714(4)	2791(8)	6433(8)	5.28(48)
C(226)	892(4)	2691(7)	5287(7)	4.04(39)
N(CH$_3$OH)	-196(3)	4194(6)	9261(7)	5.53(4)
N'(CH$_3$OH)	367(3)	4315(5)	9617(6)	5.10(4)
N''(CH$_3$OH)	-574(4)	4918(7)	9669(8)	6.51(6)

$P2_1/n$, $Z = 4$, $D_x = 1.345$ g cm^{-3}, $F(000) = 1512$, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 6.24 cm^{-1}, 288 K.

TABLE II. Atomic Coordinates (×10^4) and Equivalent Thermal Parameters for [Co(dpgH)$_2$Cl(*p*-tol)]·CH$_3$COCH$_3$ (6)

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
Co	2057(0)	1859(0)	1658(0)	2.52
Cl	2018(1)	102(1)	1938(1)	4.02
N(1)	2100(2)	3433(3)	1451(2)	2.82
C(1)	2522(2)	3817(3)	791(2)	2.85
C(2)	2186(2)	3971(4)	-60(3)	3.68
C(3)	2591(3)	4287(4)	722(3)	4.31
C(4)	3329(3)	4461(4)	514(3)	4.37
C(5)	3650(2)	4321(4)	349(3)	4.00
C(6)	3253(2)	3998(3)	1002(3)	3.24
C(7)	3781(4)	4825(5)	1227(4)	7.33
O(11)	669(1)	1883(3)	654(2)	4.25
N(11)	1367(2)	1694(3)	639(2)	3.09
C(11)	1618(2)	1461(3)	93(3)	2.96
C(12)	2407(2)	1327(3)	29(3)	2.69
N(12)	2697(2)	1540(3)	827(2)	2.70
O(12)	3411(1)	1424(2)	1073(2)	3.29
O(21)	3439(1)	1931(2)	2648(2)	3.61
N(21)	2730(2)	2049(3)	2680(2)	2.89
C(21)	2473(2)	2247(3)	3417(3)	2.76
C(22)	1675(2)	2331(3)	3274(2)	2.74
N(22)	1404(2)	2131(3)	2476(2)	2.98
O(22)	689(1)	2191(3)	2230(2)	3.86
C(111)	1155(2)	1428(4)	-953(3)	3.22
C(112)	1345(2)	2009(4)	1666(3)	3.67
C(113)	896(3)	2067(4)	2466(3)	4.72
C(114)	242(3)	1514(5)	-2558(3)	5.57
C(115)	59(3)	891(5)	1865(3)	5.05
C(116)	509(3)	871(4)	-1070(3)	4.21
C(121)	2798(2)	938(3)	-691(3)	3.03
C(122)	2569(2)	-4(4)	1122(3)	3.96
C(123)	2925(3)	-377(4)	1795(3)	4.79
C(124)	3498(3)	180(5)	-2055(3)	5.05
C(125)	3715(3)	1121(5)	-1631(3)	4.91
C(126)	3368(2)	1492(4)	-942(3)	3.71
C(211)	2904(2)	2349(3)	4295(2)	2.93
C(212)	2655(3)	1871(4)	5018(3)	4.07
C(213)	3057(3)	1980(4)	5847(3)	5.07
C(214)	3697(3)	2518(5)	5956(3)	5.20
C(215)	3940(3)	2994(4)	5243(3)	4.82
C(216)	3560(2)	2902(4)	4401(3)	4.03
C(221)	1218(2)	2673(3)	3948(2)	2.84
C(222)	660(2)	2018(4)	4134(3)	3.95
C(223)	213(3)	2362(5)	4728(4)	5.07
C(224)	302(3)	3342(5)	5125(3)	4.75
C(225)	845(3)	3990(5)	4923(3)	4.88
C(226)	1319(2)	3652(4)	4349(3)	3.83
O(31)	5846(2)	324(3)	5996(3)	6.80
C(32)	461(3)	5177(4)	1428(4)	4.83
C(33)	-18(3)	6029(5)	1014(4)	7.10
C(34)	480(3)	4918(5)	2402(4)	6.34

Results and Discussion

The new compounds have been characterized by means of elemental analyses, infrared and ^{1}H NMR spectra and conductivities of acetonic solutions. The ^{1}H NMR spectra of all the new compounds (Table III) present signals in the zone of 7.18–7.48 ppm, corresponding to the phenylic protons of the equatorial ligand, in good agreement with previously

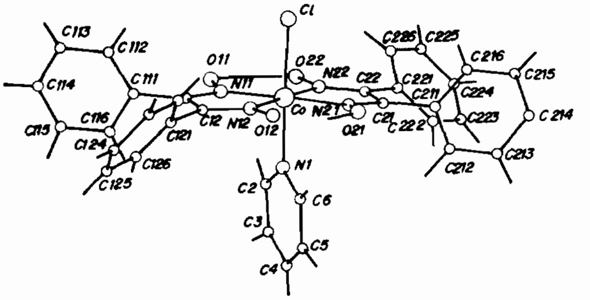


Fig. 1. Perspective view and numeration scheme for the molecular structure of $[Co(dpgH)_2Cl(py)] \cdot CH_3OH$ (1).

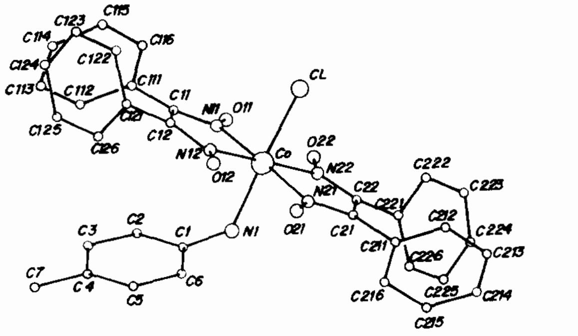
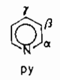
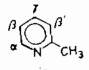
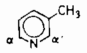
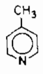
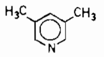
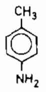


Fig. 2. Perspective view and atom numbering scheme for the molecular structure of $[Co(dpgH)_2Cl(p\text{-tol})] \cdot CH_3COCH_3$ (6).

TABLE III. ^1H NMR and UV Spectra of the New Compounds (log ε in parentheses) of the Type $[Co(dpgH)_2Cl(L)]$. Data for the Free Ligands from the Literature

	L	δ (complex)	Assignment	δ (free L) [18]	λ_{max} (complex)	λ_{max} (free L) [17]	Assignment
1	 py	8.62	H_α(py)	8.57		392	π → π*
		7.12	H_β(py)	7.05	330(sh)	324	n → π*
		7.44	H_γ(py)	7.43	265(4.45)	288	n → π*
		7.32	Ph(dpgH)		235(3.96)	261	π → π*
2	 α-pic	8.56	H_α(pic)	8.51	343(sh)		
		7.37	H_γ(pic)	7.43		288	n → π*
		7.26					
		7.24	Ph(dpgH)		260(4.83)	266	n → π*
		6.90	$H_{\beta'}$(pic)	7.00			
		6.88	H_β(pic)	6.92			
		2.15	CH_3(pic)	2.46			
3	 β-pic	8.45	$H_{\alpha'}$(pic)	8.54	337(sh)		
		8.39	H_α(pic)	8.54		288	n → π*
		7.48	H_γ(pic)	7.45	256(4.72)	268	π → π*
		7.26	Ph(dpgH)		238(4.76)		
		2.15	CH_3(pic)	2.10			
4	 γ-pic	8.36	H_α(pic)	8.55	333(sh)		
		7.28	Ph(dpgH)			284	n → π*
		7.05	H_β(pic)	7.04	256(4.38)	261	π → π*
		2.16	CH_3(pic)	2.10	233(4.41)		
5	 3,5-lut	8.21	H_α(lut)	8.25	331(sh)		
		7.34	H_γ(lut)	7.30	266(4.91)		
		7.25	Ph(dpgH)		240(4.90)		
		2.29	CH_3(lut)	2.30			
6	 p-tol	7.22					
		7.18	Ph(dpgH)		273(4.50)	285	n → π*
		6.99	H_β(tol)	6.81	232(4.37)		
		6.86	H_α(tol)	6.40			
		2.25	CH_3(tol)	2.19			
		2.17	(solvation acetone)				
7	PPh_3	7.48	$Ph(PPh_3)$		336(4.46)		
		7.24	Ph(dpgH)		263(4.97)		

reported diphenylglyoximato cobalt(III) complexes [6d]. The signals appearing at $\delta \simeq 2.3$ ppm are unambiguously assigned to the methyl groups of the axial ligand, and the remaining signals at 7–8 ppm to the aromatic protons of the axial ligands. The fact that the chemical shifts of the aromatic protons of the axial ligands are little sensitive to coordination has been explained as due to the opposite effects of the magnetic anisotropy of the cobaloxime moiety and the ring-current effect from the equatorial phenyls [6d].

The equivalence of the four equatorial phenyl groups in compounds **1**, **3**, **4** and **7** indicates that there is no substantial barrier for the rotation of the axial group around the Co–N_{ax} bond. In the α-picoline and *p*-toluidine derivatives (**2** and **6**) the existence of two signals for those phenyl groups suggests that rotation of the axial ligand around the Co–N_{ax} bond is slow in the NMR time scale, but when a spectrum was recorded in CD_2Cl_2, where no solvent band appears in the same zone, integration and comparison with simulated spectra for AA′BB′C systems indicate that the component at higher fields corresponds to the α-protons and the component at lower fields to the β- and γ-protons. The methyl group of the α-picoline ligand in compound **2** presents an important upfield coordination shift (Table III), as should be expected since it is placed close to the CoN_4C_4 metallabicycle, where the effect of the cobaloxime ring-current is stronger [6d, 8].

The UV spectra of these compounds are not easy to interpret, since the crystal field transitions in these compounds are usually hidden under the intense metal-to-ligand charge transfer bands [14–16]. These bands, in turn, appear close to the aromatic ligand's $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The band appearing in the complexes at *ca.* 335 nm, however, can be tentatively assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition [14d], since it varies little through the series of compounds and in most cases its assignment to the aromatic ligand [17] can be ruled out.

In [Co(dpgH)$_2$Cl(py)] (**1**) (Fig. 1) the geometry of the coordination sphere around the cobalt atom is similar to that in the dmgH complexes (Table IV). The CoN_4 equatorial group defines a plane (largest) deviation is 0.010(6) Å for N12); deviations of other atoms in the glyoximato groups from this plane are smaller than 0.08 Å, while two of the C–C (phenylglyoximato) bonds present a larger deviation (0.186 Å for C121 and 0.219 Å for C221). The C1 and N1 axial donor atoms stand at 90.0(2)° of the equatorial plane. The C11–C12 and C21–C22 bonds (1.482(4) Å) are somewhat larger than the average in analogous dmgH compounds (1.466(3) Å) [1a], although the difference might be not significative. The pyridine ring is practically planar and parallel to the glyoxime C–C bonds, its conformation being defined [6d] by a torsion angle τ = 85.9(9)°. One pair of equatorial phenyl groups forms angles of 48.3° and 56.3° with the $CoN_4C_4O_4$ plane, and the corresponding angles for the other pair of phenyls are 81.3° and 51.2°.

TABLE IV. Selected Bond Distances and Angles of [Co(dpgH)$_2$Cl(py)]·CH_3OH (**1**) and Co(dpgH)$_2$Cl(*p*-tol)·CH_3COCH_3 (**6**), with Estimated Standard Deviations in Parentheses. Values for [Co(dmgH)$_2$X(L)] are the Averages of Chemically Equivalent Bonds for Non-organometallic Compounds, as Given in Ref. 1a

	Compound 1	Compound 6	[Co(dmgH)$_2$X(L)]
Bond distances			
Co–C1	2.235(2)	2.247(1)	2.25(2)
Co–N1	1.965(3)	2.003(3)	1.966(10)
Co–N11	1.911(5)	1.907(3)	1.897(2)
Co–N12	1.903(5)	1.906(3)	
Co–N21	1.904(5)	1.896(3)	
Co–N22	1.900(6)	1.897(3)	
C11–N11	1.295(8)	1.308(5)	1.296(2)
C12–N12	1.296(8)	1.301(5)	
C21–N21	1.291(9)	1.311(5)	
C22–N22	1.319(9)	1.288(5)	
C11–C12	1.486(8)	1.479(5)	1.466(3)
C21–C22	1.478(9)	1.491(5)	
N11–O11	1.345(7)	1.336(4)	1.345(2)
N12–O12	1.340(6)	1.354(4)	
N21–O21	1.344(7)	1.349(4)	
N22–O22	1.327(7)	1.350(4)	
C11–C111	1.493(8)	1.483(5)	
C12–C121	1.482(9)	1.488(6)	
C21–C211	1.498(9)	1.484(5)	
C22–C221	1.483(10)	1.491(6)	
Bond angles			
N1–Co–C1	178.2(1)	178.1(1)	
N11–Co–C1	89.4(1)	90.9(1)	
N12–Co–C1	88.7(1)	87.8(1)	
N21–Co–C1	91.1(1)	90.0(1)	
N22–Co–C1	90.6(1)	90.6(1)	
N11–Co–N1	89.3(2)	90.8(1)	
N12–Co–N1	89.9(2)	93.4(1)	
N21–Co–N1	90.2(2)	88.3(1)	
N22–Co–N1	90.7(2)	88.3(1)	
N11–Co–N12	81.4(2)	81.4(1)	81.4(1)
N21–Co–N22	81.6(2)	81.3(1)	
Co–N11–C11	116.6(4)	116.4(1)	116.4(1)
Co–N12–C12	116.4(4)	116.7(1)	
Co–N21–C21	116.8(4)	117.2(1)	
Co–N22–C22	116.1(4)	117.1(1)	
N11–C11–C12	112.4(5)	112.7(3)	112.8(1)
N12–C12–C11	113.0(5)	112.6(3)	
N21–C21–C22	113.0(6)	111.3(3)	
N22–C22–C21	112.3(6)	113.0(3)	
Co–N11–O11	122.3(4)	122.1(1)	122.6(1)
Co–N12–O12	121.6(4)	121.7(1)	
Co–N21–O21	122.3(4)	120.7(1)	
Co–N22–O22	121.5(4)	122.1(1)	

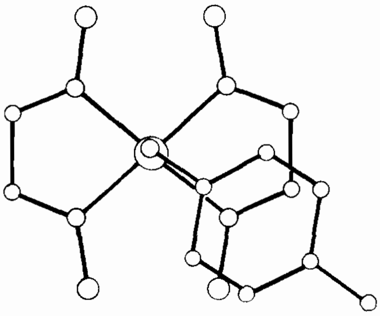


Fig. 3. Projection of the *p*-tol ligand in compound **6** on the plane of the equatorial $CoN_4C_4O_4$ fragment, showing the nearly eclipsed conformation of the $C-N_{ax}$ and one $Co-N_{eq}$ bonds.

The molecular structure of $[Co(dpgH)_2Cl(p\text{-}tol)]\cdot CH_3COCH_3$ (**6**) is formed by discrete molecules of the pseudooctahedral complex presented in Fig. 2 together with the numbering scheme; the acetone molecule is linked through a hydrogen bond to the nitrogen atom of the toluidine (N1–O31 = 2.08(4) Å). The equatorial $Co(dpgH)_2$ group presents the same structural features discussed above for **1** (Table IV). The Co–N1 bond distance is similar to that in $[Co(dmgH)_2X(L)]$ when L is aniline (2.001(5) Å) [19b], chloroaniline (1.999(6) Å) [19a], or sulfanilamide (2.023(8) Å) [19a]. These distances are clearly larger than the corresponding ones in pyridine and related derivatives (Table IV).

The bond distances and angles within the *p*-tol ligand are in good agreement with those in some copper(I) complexes [20]. The *p*-toluidine ligand is oriented in a similar way to that found for 4-chloroaniline in $[Co(dmgH)_2Cl(Cl\text{-aniline})]$ [19a], with its N–C bond practically eclipsed with the Co–N12 equatorial bond (C1–N1–Co–N12 = 2.4°, Fig. 3), but clearly different from the orientation of sulfanilamide in $[Co(dmgH)_2Cl(sulfa)]$. One pair of phenyl groups form angles of 48.3° and 54.1° with the equatorial plane, while for the other pair of phenyls these angles are 42.1° and 59.8°.

Supplementary Material

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

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