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New organometallic cobaloximes containing an equatorial diphenylglyoximato(-1) ligand. Comparison between their properties and those of other B_{12} model compounds. Crystal structure of *trans*-[Co(dpgH)$_2$(CH$_3$)(pyridine)]

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Abstract

The synthesis and characterization of organometallic and inorganic cobalt(III) compounds of the type *trans*-[Co(dpgH)$_2$(R)(L)] are reported, where dpgH represents diphenylglyoximate monoanion, R = Cl, CH$_3$, CH$_2$CH$_3$, CH$_2$Cl or ^{i}Bu; and L is either an organic N-donor ligand (pyridine, 3,5-lutidine or γ-picoline), or trimethylphosphite. Their structural and spectroscopic properties are studied and compared with those previously reported for analogous compounds containing dimethylglioximato(-1), (dmgH); glyoximato(-1), (gH), or $N^2,N^{2\prime}$-propanediylbis(2,3-butanedione, 2-imine-3-oxime), ((DO)(DOH)pn), as equatorial ligands. The ^{1}H-NMR chemical shifts of the axial R group in the diphenylglyoximato compounds can be accurately estimated from those of the dimethylglyoximato or glyoximato analogues and allow the detection of electronic *cis*-effects. The first X-ray crystal structure of an organometallic bis(diphenylglyoximato)cobalt(III) compound, [Co(dpgH)$_2$(CH$_3$)(py)], is reported. The Co–C bond length in this type of complex seems not to be sensitive to changes in equatorial ligands.

Introduction

Since 1964, when Schrauzer and Kölne [1] initiated the study of octahedral Co^{III} compounds containing two dimethylglyoximato ligands in the equatorial sites as models for vitamin B_{12} [2–5] there have been a number of papers on the spectral and structural properties of Co^{III} systems of general formulae [Co(chelate)X(L)] and [Co(chelate)X(L)]Y [3–9]. The chelate group in these compounds is either a tetradentate ligand such as N$_2$,O$_2$-Schiff base dianion [6–8], a mixed oxime–Schiff base monoanion [9], (known as Costa-type systems), or two bidentate dioximate groups (dimethylglyoximate (dmgH) [3–5] or glyoximate (gH) [10–12] monoanions or methylphenyldioximate [13–14]). The axial ligands X and L are a monoanionic group and a neutral N- or P-donor, respectively, and Y is the counterion.

Although the most extensively studied B_{12} model compounds are those containing dmgH as equatorial ligand, the two analogous series derived by substitution of the equatorial methyl groups of dmgH by either hydrogen atoms (gH-derivatives) or phenyl rings (dpgH-compounds) (Fig. 1) [15–21] have scarcely been studied. Furthermore, only a few examples of organometallic diphenylglyoximato derivatives, $[Co(dpgH)_2(R)(L)]$, have been reported [17], and no molecular structures of such compounds have been determined up to now. We therefore decided to examine the electronic and steric effects of the substituents in the equatorial ligands on the properties of these complexes.

We previously [19,21] reported the syntheses and X-ray crystal structures of some inorganic halo(ligand)bis(diphenylglyoximato)cobalt(III) derivatives. In order to compare the effects of the equatorial ligand on the properties of the organometallic cobaloximes, e.g. the axial Co–C bond length, we have synthesized and studied the $[Co(dpgH)_2(R)(L)]$ compounds where $R = CH_3$, CH_2CH_3, CH_2Cl or ${}^iBu$, and L = pyridine (py), 3,5-lutidine (lut), 4-methylpyridine (γ-pic) or $P(OMe)_3$. The spectral and structural properties of the new compounds are compared with those of the two families of related complexes previously reported, (namely ($[Co(dmgH)_2(R)(L)]$ and $[Co(gH)_2(R)(L)]$).

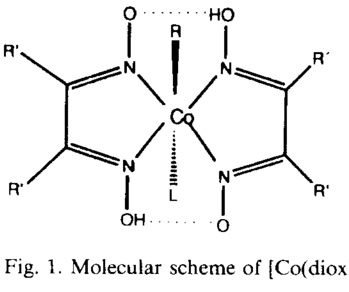
Results and discussion

I. *Diphenylglyoximate derivatives*

Synthesis and reactivity

Addition of cobalt chloride hexahydrate to an acetone suspension of diphenylglyoxime followed by air-oxidation produced brown crystals. Their Cl-analysis, infrared, ultraviolet and ^1H-NMR spectra were identical to those reported for $[Co(dpgH)_2Cl(H_2O)]$ prepared previously [19,21] by Yamazaki's method [22]. The most important feature of our procedure is that the yield is higher (> 90%).

In the light of previous studies [23] on compounds with dimethylglyoximate, we expected the formation of a green compound similar to $H[Co(dmgH)_2Cl_2]$. However, the impossibility of obtaining the analogous compound with the glyoximato ligand, gH, has been pointed out [11], and so $dpgH_2$ and gH_2 groups appear to have show similar chemical behaviour towards Co^{II} in acetone.



R′	dioxH
Me	dmgH
H	gH
Ph	dpgH

Fig. 1. Molecular scheme of $[Co(dioxH)_2(R)(L)]$.

Addition of nitrogen donor ligands (pyridine, γ-picoline or 3,5-lutidine) or trimethylphosphite to methanolic suspensions of $[Co(dpgH)_2Cl(H_2O)]$ results in the substitution of the axial aquo- group by the organic neutral L-ligands (eq. 1):

$$[Co(dpgH)_2Cl(H_2O)] + L \rightarrow [Co(dpgH)_2Cl(L)] + H_2O \qquad (1)$$

The results reported here thus reveal the generality of the preparative method described previously [19,21].

We also studied replacement of the chloro ligand by CN^- in complexes of the type $[Co(dpgH)_2Cl(L)]$. The method described for the analogous cobaloximes with 2,6-dimethylpyrazine as neutral ligand was used [19], but in all cases the material isolated was a mixture of monocyano- and polynuclear μ-cyanocobaloximes. The difficulties in preparing $[Co(dmgH)_2(CN)(L)]$ have been stressed by Marzilli et al. [24]. With Co/CN^- molar ratio > 1 a yellow compound was formed. The elemental analyses, infrared spectra and the conductivity of its acetone solutions were consistent with the formula $Na[Co(dpgH)_2(CN)_2] \cdot 2H_2O$ [20].

In order to obtain organometallic cobaloximes of the type $[Co(dpgH)_2R(L)]$, we studied reactions similar to those described for the preparation of $[Co(dmgH)_2R(L)]$, which consist in a reductive elimination by $NaBH_4$ followed by the oxidative addition of the alkyl halide(RX) (eq. 2) [25].

$$[Co(dpgH)_2Cl(L)] \xrightarrow[2.\ R\text{-}X]{1.\ NaBH_4} [Co(dpgH)_2R(L)] \qquad (2)$$

Four different chloro(ligand)cobaloximes, with L = lut, γ-pic, py and $P(OMe)_3$ were used as starting materials, and CH_3I, CH_3CH_2I, ^iBuI and CH_2Cl_2 were alkylating agents. In all cases, the reactions gave the corresponding organometallic cobaloximes.

The phosphite derivatives can be readily obtained by axial ligand (L) exchange reactions, using a molar ratio of entering ligand to cobalt complex of 1.5 (eq. 3).

$$[Co(dpgH)_2R(L)] + P(OMe)_3 \rightarrow [Co(dpgH)_2R(P(OMe)_3)] + L \qquad (3)$$

Characterization of the complexes

All the compounds were characterized by elemental analyses (C, H, and N). For compounds **1**, **8** and **11** Cl^- analyses were also performed. The infrared spectra of the compounds showed the characteristic absorption bands [26] of the bis(diphenylglyoximato) complexes, as well as those of the neutral L groups. The conductivities of 10^{-3} *M* acetone solutions of the complexes revealed that the new compounds are non-electrolytes except for the dicyano derivative.

NMR spectra

The ^1H-NMR spectra of the compounds consisted of a multiplet in the range 7.15–7.30 ppm (Table 1), which was assigned to the aromatic protons of the diphenylglyoximato ligand [19,21]. The resonances due to the aromatic protons of the neutral L groups were also observed in the downfield region of the spectra. Other resonances, such as those of the alkyl R group and the methyl- or methoxy-substituents of the L ligand, were also present in the upfield region.

In some cases, an extra singlet at ca. 17–18 ppm was observed. This signal was assigned to the resonance of the protons involved in the two hydrogen bonds of the

Table 1

^{1}H-NMR data for compounds of general formula [Co(dpgH)$_2$(R)(L)]

R	C_6H_5(dpgH) [c]	R	H_α(L)	H_β(L)	H_γ(L)	CH_3(L)	O-H···O
L = lut							
Cl	7.26	–	8.23	–	7.41	2.29	[a]
CH_3	7.20	1.40	8.54	–	7.46	2.33	[a]
CH_2CH_3	7.19	0.80 [d] 2.31 [e]	8.53	–	7.45	2.34	17.53
CH_2Cl	7.18	4.31	8.57	–	[b]	2.32	17.65
^{i}Bu	7.17	1.02 2.20 [f]	8.52	–	[b]	2.32	[a]
L = γ-pic							
Cl	7.25	–	8.41	[b]	–	2.40	[a]
N_3	7.25	–	8.45	[b]	–	2.42	[a]
CH_3	7.19	1.42	8.73	7.61	–	2.38	[a]
CH_2CH_3	7.19	0.81 [d] 2.27 [e]	8.79	[b]	–	2.39	[a]
CH_2Cl	7.21	4.30	8.71	[b]	–	2.42	[a]
L = py							
CH_3	7.18	1.44	8.92	7.47	7.83	–	[a]
CH_2CH_3	7.19	0.81 [d] 2.35 [e]	8.93	7.43	7.84	–	[a]
L = P(OMe)$_3$							
CH_3	7.23	1.77	–	–	–	3.75	17.76
CH_2CH_3	7.22	0.84 [d] 2.43 [e]	–	–	–	3.74	[a]

[a] Not observed. [b] Overlapped with C_6H_5(dpgH). [c] multiplet. [d] Quartet. [e] Triplet. [f] Doublet.

Co(dpgH)$_2$ moiety, and it was shifted upfield from the values reported for cobaloximes with dmgH as equatorial ligand and identical L and R groups (18–19 ppm).

For cobaloximes of general formula [Co(dpgH)$_2$(CH$_3$)(L)] the CH$_3$-axial group resonance moved slightly downfield when the L was changed from lutidine to pyridine, in keeping with an increase in the basicity of the ligand [27]. The same feature was found for the ethyl derivatives, and is consistent with the behaviour of the much-studied dmgH complexes [5].

^{13}C-NMR spectra of these compounds showed a signal in the downfield region (154.00–149.50 ppm), which was assigned to the oximinic carbon atoms (C=N) of the equatorial dpgH groups. In the range 135.00–126.00 ppm there was a group of 4 signals which were each assigned to one of the four types of aromatic carbon nuclei on the phenyl rings of the Co(dpgH)$_2$ moiety: $C^\star$, C_α, C_β and C_γ, respectively (Fig. 2). The resonances of the aromatic carbon atoms of the neutral L groups were also present at lower fields than the solvent signal.

The resonances of the methyl- or methoxy-substituents on the L ligand appeared in the upfield region of the spectra. For the organometallic derivatives with R = CH$_2$CH$_3$ and ^{i}Bu the resonances of the methyl carbon atoms were also observed (Table 2).

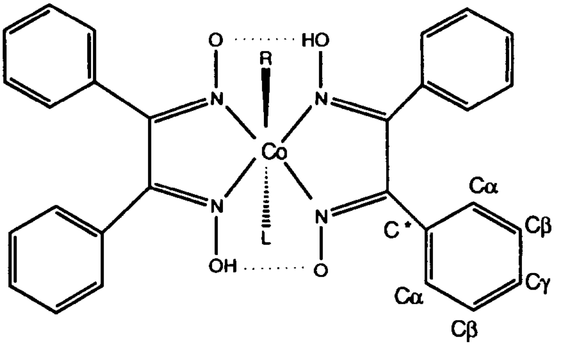


Fig. 2. Labelling of the carbon atoms of the diphenylglyoximato moiety in [Co(dpgH)$_2$(R)(L)].

Ultraviolet–visible spectra

Details of the main absorption bands observed in the ultraviolet–visible spectra of the compounds are available from the authors. The assignments were tentative owing to the existence of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ absorption bands of the aromatic neutral ligands [28] as well as those corresponding to the phenyl rings of the equatorial group. However, the identification of the $d \rightarrow d$ electronic transitions of the cobalt(III) center was quite clear in all cases.

Structure of [Co(dpgH)$_2$(CH$_3$)(py)]

A perspective drawing of the molecular structure of [Co(dpgH)$_2$(CH$_3$)(py)] and the numbering scheme are shown in Fig. 3. Selected bond distances and angles are presented in Tables 3 and 4, respectively. The structure consists of discrete molecules linked by Van der Waals' forces. The cobalt atom is linked to four nitrogen atoms belonging to two diphenylglyoximate groups in an equatorial plane (Fig. 3). The cobalt atom deviates 0.05 Å from the mean equatorial CoN$_4$ plane towards the neutral pyridine ligand. One methyl group and the nitrogen of the pyridine ligand occupy the axial positions, thus completing the octahedral coordination sphere of the cobalt atom.

The Co–N(dpgH) bond distances (Table 3) are slightly shorter than those reported for [Co(dpgH)$_2$(Cl)(L)] (1.940(5) Å and 1.901(6) Å for L = py and p-toluidine, respectively [21]) and [Co(dpgH)$_2$(NO)] [29], and similar to those reported by Uchida et al. [14] for $(+)_{589}$-2-cyanoethylbis(E,E-1-phenyl-1,2-propanedionedioximato-N,N')(pyridine)cobalt(III) (average 1.888(4) Å). Furthermore, the C–C bond of the chelating ligand, C(3)–C(4), is slightly longer than that found by Uchida et al. [14] for the complex containing an asymmetric equatorial group mentioned previously.

On the other hand, the Co–C(7) and Co–N(8) bonds are practically perpendicular to the equatorial plane (Table 4). The pyridine ligand maintains its planarity and the Co–N(8) bond distance, 2.053(4) Å, is intermediate between the values found for [Co(dpgH)$_2$Cl(L)] (1.965(5) Å and 2.003(3) Å for L = py and p-toluidine, respectively) [21] and those reported previously for other B$_{12}$ model compounds of the type [Co(chel)(R)(py)] where chel = 1-phenyl-1,2-propanedionedioximato-N,N' (Co–N(py) = 2.094(4) Å, R = CH$_2$CH$_2$CN [14]), N^2,$N^{2\prime}$-propanediyl-bis(2,3-

Table 2

^{13}C-NMR data (in ppm) for [Co(dpgH)$_2$(R)(L)]

L	R	dpgH[d]				C=N	L			Me or OMe	H(R)
		C*	C_α	C_β	C_γ		$C_{\alpha'}$	$C_{\beta'}$	$C_{\gamma'}$		
lut	Cl	129.80	129.80	127.93	127.93	153.48	148.16	133.89	140.85	18.46	–
	CH_3	130.21	129.66	127.82	128.87	150.63	147.29	134.88	139.42	18.56	–
	Et[a]	130.31	129.64	127.83	128.82	150.62	147.64	134.72	139.19	18.42	15.94
	^{i}Bu	[b]	129.66	127.90	128.87	[b]	[b]	[b]	[b]	[b]	[b]
γ-pic	Cl[c]	129.82	129.82	127.95	127.95	152.51	150.25	127.82	[b]	[b]	–
	CH_3[c]	129.69	129.51	127.65	128.73	150.58	149.28	[b]	[b]	[b]	–
	Et[a]	130.53	129.66	127.83	128.85	150.71	149.53	126.44	[b]	20.74	15.86
	CH_2Cl	[b]	129.70	127.93	129.70	[b]	[b]	[b]	[b]	[b]	[b]
py	Cl	129.81	129.81	127.97	[b]	153.69	151.14	126.10	139.44	–	–
	CH_3	130.09	129.71	127.90	129.01	150.90	150.09	125.66	138.12	–	–
	Et[a]	130.14	129.63	127.84	128.89	150.85	150.12	125.51	137.87	–	16.07
$P(OMe)_3$	CH_3	130.45	129.62	127.96	128.85	149.94	–	–	–	52.83	–
	Et[a]	130.66	129.70	127.99	128.81	149.81	–	–	–	52.42	–

[a] Et = CH_2CH_3. [b] Not observed. [c] Low solubility in chloroform. [d] The carbon assignment is referred to the notation shown in Fig. 2.

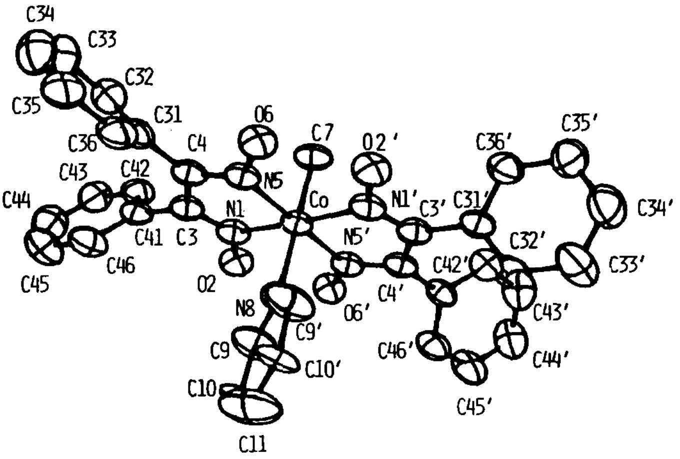


Fig. 3. Molecular structure and atom labelling for compound 12: [Co(dpgH)$_2$(CH$_3$)(py)]. (H-atoms are not shown.)

butanedione, 2-imine-3-oxime) (Co–N(py) = 2.106(3) Å and R = CH$_3$ [30]) or its 2,2″-dimethyl-derivative (Co–N(py) = 2.105(3) Å for R = CH$_3$ [30]).

The plane of the axial pyridine in the diphenylglyoximato compound almost bisects the line between the hydrogen-bonded oxygen atoms of the dioximato groups. The same orientation has been found for the chloropyridine derivative [21], and for most of the planar N-donor ligands, L, in compounds of general formulae [Co(dmgH)$_2$(R)(L)] [3,5,19] and [Co(gH)$_2$(R)(L)] [3,20], and even for the cobalt complex containing the asymmetrical equatorial ligand [14]. Hence, the orientation of the axial pyridine ligand cannot be attributed to the steric influence of the C$_6$H$_5$-rings of the equatorial dpgH groups.

The Co–C(7) bond distance of 1.997(4) Å is similar to that found for organometallic cobaloximes of general formula [Co(dmgH)$_2$(CH$_3$)(L)], where L represents a planar N-donor ligand (1.985–2.009 Å) [3,5] and very close to the Co–C bond

Table 3

Bond lengths (in Å) [a] for [Co(dpgH)$_2$(CH$_3$)(py)]

N(1)–Co	1.884(3)	C(32)–C(31)	1.368(5)
N(5)–Co	1.883(2)	C(36)–C(31)	1.381(5)
C(7)–Co	1.997(4)	C(33)–C(32)	1.397(5)
N(8)–Co	2.053(4)	C(34)–C(33)	1.375(6)
O(2)–N(1)	1.360(3)	C(35)–C(34)	1.354(7)
C(3)–N(1)	1.291(4)	C(36)–C(35)	1.410(6)
C(4)–C(3)	1.464(4)	C(42)–C(41)	1.408(5)
C(31)–C(3)	1.489(4)	C(46)–C(41)	1.389(5)
N(5)–C(4)	1.304(4)	C(43)–C(42)	1.376(5)
C(41)–C(4)	1.482(4)	C(44)–C(43)	1.357(6)
O(6)–N(5)	1.344(3)	C(45)–C(44)	1.354(7)
C(9)–N(8)	1.335(4)	C(46)–C(45)	1.388(6)
C(10)–C(9)	1.352(6)		
C(11)–C(10)	1.356(6)		

[a] Standard deviations are given in parentheses.

Table 4

Bond angles (in deg) [a] for [Co(dpgH)$_2$(CH$_3$)(py)]

N(5)–Co–N(1)	80.8(1)
C(11)–C(10)–C(9)	117.5(5)
C(7)–Co–N(1)	87.5(1)
C(10)–C(11)–C(10)	120.9(6)
C(7)–Co–N(5)	89.6(1)
C(32)–C(31)–C(3)	120.2(3)
N(8)–Co–N(1)	92.5(1)
C(36)–C(31)–C(3)	120.3(3)
N(8)–Co–N(5)	90.4(1)
C(36)–C(31)–C(32)	119.6(3)
N(8)–Co–C(7)	180.0 [b]
C(33)–C(32)–C(31)	120.3(3)
O(2)–N(1)–Co	122.0(2)
C(34)–C(33)–C(32)	120.3(4)
C(4)–C(3)–N(1)	112.5(3)
C(35)–C(34)–C(33)	119.5(4)
C(31)–C(3)–N(1)	122.8(3)
C(36)–C(35)–C(34)	120.8(4)
C(31)–C(3)–C(4)	124.7(3)
C(35)–C(36)–C(31)	119.4(4)
N(5)–C(4)–C(3)	111.7(3)
C(42)–C(41)–C(4)	120.2(3)
C(41)–C(4)–C(3)	124.6(3)
C(46)–C(41)–C(4)	120.9(3)
C(41)–C(4)–N(5)	123.6(3)
C(46)–C(41)–C(42)	118.9(3)
C(4)–N(5)–Co	117.4(2)
C(43)–C(42)–C(41)	119.3(4)
O(6)–N(5)–Co	121.8(2)
C(44)–C(43)–C(42)	120.9(4)
O(6)–N(5)–C(4)	120.7(2)
C(45)–C(44)–C(43)	120.8(4)
C(9)–N(8)–Co	122.2(2)
C(46)–C(45)–C(44)	120.4(4)
C(10)–C(9)–N(8)	124.2(4)
C(45)–C(46)–C(41)	119.7(4)
C(9)–N(8)–C(9)	115.7(4)

[a] Standard deviations are given in parentheses. [b] Imposed by symmetry.

lengths reported for Costa-type compounds [Co(chel)$_2$(CH$_3$)(py)]X, where (chel)$_2$ = N^2,$N^{2\prime}$-propanediylbis(2,3-butane-dione-2-imine-3-oxime) or its dimethyl-derivative (2.003(3) Å and 2.017(3) Å, respectively [30,31]).

II. Dimethylglyoximate compounds

In order to compare the properties of the new diphenylglyoximate compounds with those of the widely studied dimethylglyoximato analogues we undertook the preparation of γ-picoline derivatives with dmgH as equatorial ligand. The new cobaloximes were characterized by the usual methods, namely, elemental analysis, infrared spectroscopy, conductivities of (10^{-3} M) acetone solutions, and ^{1}H- and

Table 5

^{1}H-NMR signals of the R-group in [Co(dioxH)$_2$(R)(L)]

L	dioxH	CH_3	CH_2CH_3		^{i}Bu		CH_2Cl
lut	dmgH [a]	0.79	1.71 [d]	0.34 [e]	1.57	0.73	3.70
	dpgH	1.40	2.27 [d]	0.80 [e]	2.20	1.02	4.31
γ-pic	dmgH	0.79	1.70 [d]	0.34 [e]	–	–	–
	dpgH	1.42	2.31 [d]	0.80 [e]	–	–	–
py	dmgH [b]	0.82	1.74 [d]	0.35 [e]	–	–	–
	gH [c]	1.02	1.90 [d]	0.53 [e]	–	–	–
	dpgH	1.44	2.35 [d]	0.81 [e]	–	–	–
$P(OMe)_3$	gH [c]	1.27	1.92 [d]	0.69 [e]	–	–	–
	dpgH	1.78	2.43 [d]	0.84 [e]	–	–	–

[a] From refs. 5, 34. [b] From ref. 33. [c] From refs. 10, 11. [d] Quadruplet. [e] triplet.

^{13}C-NMR spectroscopy. The data obtained agree with the proposed formulae for all the compounds.

III. Comparison of the NMR spectra of diphenylglyoximato, dimethylglyoximato and glyoximato complexes

In Table 5 are shown the ^{1}H-NMR chemical shifts of the axial R group in the two series of compounds with dmgH or dpgH; R = CH_3, CH_2CH_3, CH_2Cl or ^{i}Bu, and L = lut, py, γ-pic or $P(OMe)_3$. Previous studies on Costa-type compounds [Co((DO)(DOH)pn)(CH_3)(L)]X have shown that the ^{1}H resonance of the axial methyl group (Co–CH_3) appears at $\delta = 0.74 \pm 0.1$ ppm for 17 different L groups [31]. These values are similar to those reported for cobaloximes containing dmgH [31] as equatorial ligand, $\delta = 0.79 \pm 0.06$ ppm (average value for 15 different axial L groups). For compounds of general formulae [Co(dpgH)$_2$(CH_3)(N-donor ligand)] the signal due to the axial CH_3-protons is shifted downfield and appears at ca. 1.4 ppm. The same trend is found for the protons of the Et and CH_2Cl group in the three series of complexes [Co(dioxH)$_2$(R)(L)] (dioxH = dpgH, dmgH and gH).

Other things being equal, the ^{1}H chemical shifts of the R group appear at lower fields for the dpgH than for the dmgH analogues (Table 5). Figure 4 shows a plot of the ^{1}H-NMR chemical shifts of the axial R groups in compounds of general formulae [Co(dpgH)$_2$(R)(L)] against the corresponding values for their dmgH and gH analogues with identical R and L ligands on the axial sites. The relationship is fairly linear, as shown by eqs. 4 and 5:

$$\delta_R(\text{dpgH}) = 0.484 + 1.051\,\delta_R(\text{dmgH}) \qquad (r^2 = 0.991) \tag{4}$$

$$\delta_R(\text{dpgH}) = 0.158 + 1.187\,\delta_R(\text{gH}) \qquad (r^2 = 0.983) \tag{5}$$

Furthermore, the ^{1}H-NMR resonances of the axial R groups in the three series of compounds with identical L ligand shift upfield in the sequence: dmgH > gH > dpgH.

The variations on the ^{1}H-NMR chemical shifts of the R group protons for the three series of cobaloximes can be easily seen, by using the term $\Delta\delta_R$, defined as shown in eq. 6:

$$\Delta\delta_R = \delta_R(\text{dpgH}) - \delta_R(\text{dioxH}) \tag{6}$$

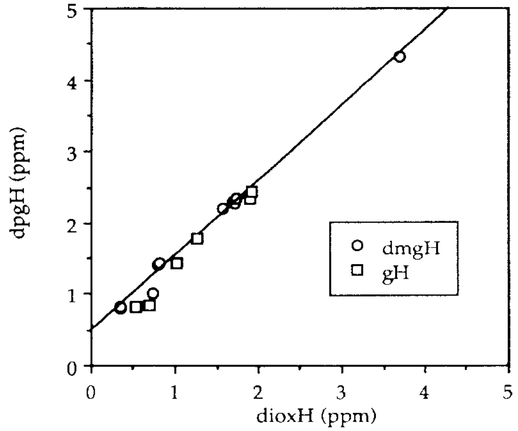


Fig. 4. Graphical representation of the ^{1}H-NMR chemical shifts of the R group in compounds [Co(dpgH)$_2$(RL)(L)], versus the corresponding values for their dmgH and gH analogues. The least squares line for the dpgH/dmgH data sets (eq. 4) is shown. The second fit (dpgH and gH data) is summarized in eq. 5.

where dioxH represents either dmgH or gH. For dioxH = dmgH, the $\Delta\delta_R$ values fall in the range 0.59 ± 0.05 ppm for the H_α-atoms and decrease as the distance between the protons under study and the Co atom increases; thus $\Delta\delta_R = 0.46 \pm 0.02$ ppm for the H_β-atoms in the R group (CH_2- and CH- for the ethyl and ^{i}Bu compounds, respectively) and $\Delta\delta_R = 0.29$ ppm for the methyl protons in the ^{i}Bu derivatives.

A similar trend is found for the H-atoms on the neutral L groups, thus allowing us to establish a sequence for the *cis*-influence of the equatorial dioximato ligands: dpgH > dmgH.

The new compounds with dpgH were also compared with those reported by Marzilli et al. [10,11] with glyoximato in the equatorial plane. In the latter case the corresponding $\Delta\delta_R$ values are also positive, but smaller than those obtained in the study of dmgH and dpgH complexes described above. Thus, we can conclude that the *cis*-influence of the glyoximato group is intermediate between that of the dmgH and dpgH groups, as can be summarized in the sequence $\delta_R(\text{dpgH}) > \delta_R(\text{gH}) > \delta_R(\text{dmgH})$.

The ^{13}C-NMR spectra of the two series of compounds with dmgH and dpgH also show several differences. For example, the oximinic carbon atom resonance shifts upfield when the dmgH ligand is changed for dpgH. Furthermore, the ^{13}C-NMR chemical shifts of the γ-carbon atoms of the axial L group for the dpgH complexes appeared at lower fields than those for analogous compounds containing dmgH as equatorial ligand, but at higher fields than those reported for Costa-type compounds, as shown in Table 6.

Experimental

Diphenylglyoxime and dimethylglyoxime (analytical grade), cobalt(II) chloride hexahydrate and other ligands were obtained from commercial suppliers.

Elemental analyses were carried out at the Instituto de Química Biorgánica (C.S.I.C., Barcelona). Halide analyses were performed by the Schöninger method

Table 6

^{13}C-NMR data for complexes of general formula $[Co(chel)_2(CH_3)(py)]^{m+}$

	C_α	C_β	C_γ
Free pyridine	149.82	123.73	135.89
chel = dmgH [a]	150.06	125.21	137.48
chel = dpgH [b]	150.08	125.51	137.87
$(chel)_2$ = (DO)(DOH)pn [a]	148.77	126.76	138.73

[a] Ref. 31. [b] This work.

[32], and the final determination by the Volhard method. Infrared spectra were recorded on a Perkin–Elmer 1330 infrared spectrophotometer. ^{1}H and ^{13}C-NMR spectra were recorded at 20–25 °C on a Brucker WP-80-50 spectrophotometer with $CDCl_3$ (99.8% and 99.0%, respectively) as solvent and operating at 80.13 MHz and 20.11 MHz. TMS was used as internal standard for ^{1}H-NMR spectra. For the trimethylphosphite derivatives the ^{31}P-NMR spectra were also recorded with $P(OMe)_3$ as internal standard.

Visible and ultraviolet (CH_2Cl_2) spectra were obtained on a Beckman UV-5230 spectrophotometer. Conductivities of 10^{-3} M acetone solutions of the new compounds were measured with a Radiometer CDM3 conductivity bridge. Decomposition points of all the compounds were determined with a Büchi 510 melting point apparatus.

Preparation of the compounds

I. Diphenylglyoximate complexes

A. Inorganic cobaloximes

[Co(dpgH)$_2$Cl(H$_2$O)] (1). To an acetone suspension (200 mL) of diphenylglyoxime ($dpgH_2$) (10.00 g, 41.62 mmol), was added 4.95 g (20.80 mmol) of $CoCl_2 \cdot 6H_2O$. The mixture was stirred at room temperature for 2.5 h, during which it changed gradually from deep blue to green. Slow evaporation of the solvent (ca. 24 h) at room temperature gave brown microcrystals of the desired compound, which were collected by vacuum filtration, washed with 2 (10 mL) portions of H_2O, and air-dried (yield: 93%).

[Co(dpgH)$_2$Cl(L)]. The complexes $[Co(dpgH)_2Cl(lut)]$ (**2**), $[Co(dpgH)_2Cl(\gamma\text{-pic})]$ (**3**) and $[Co(dpgH)_2Cl(py)]$ (**4**) were prepared as previously reported [19,21].

B. Organometallic cobaloximes

[Co(dpgH)$_2$(CH$_3$)(lut)] (5). To a suspension of 1.00 g (1.47 mmol) of $[Co(dpgH)_2Cl(lut)]$ (**2**) in 100 mL of methanol and the resulting mixture under nitrogen was added an aqueous solution (3 mL) of NaOH (1 pellet). When the starting material had dissolved completely a solution of 0.12 g (3.16 mmol) of $NaBH_4$ in 5 ml H_2O was added dropwise, followed by 0.5 mL of CH_3I (8.03 mmol). The mixture was stirred at room temperature for 15 min, and then 20 mL of acetone was added to destroy the excess $NaBH_4$ and the N_2 bubbling was stopped. The orange-red solution was stirred for 10 more minutes and unchanged materials were removed by

filtration and the filtrate was concentrated to ca. 20 ml in a rotary evaporator. The orange microcrystals formed were collected by vacuum filtration and washed with 2 (10 mL) portions of H_2O (yield: 57%) (dec. 228–231° C).

For recrystallization of the compound (0.2 g) was dissolved in a minimum amount of acetone. The solution was filtered and water was added until it became cloudy. Slow evaporation of the solvent at room temperature gave orange crystals.

[Co(dpgH)$_2$(CH$_2$CH$_3$)(lut)] (6). This compound was prepared by the method described for the methyl derivative (**5**) but using the stoichiometric amount of CH_3CH_2I as alkylating agent (yield: 52%) (dec. 224–227° C).

[Co(dpgH)$_2$(CH$_2$Cl)(lut)] (7). The procedure was similar to that described above for the methyllutidine derivative (**5**), but the brown-orange solid isolated was impure and was recrystallized by dissolving the crude material (0.48 g) in 20 mL of acetone, filtering the orange solution, and adding water (8 mL) to give orange crystals of **7** (yield: 38%) (dec. 233–236° C).

[Co(dpgH)$_2$(^{i}Bu)(lut)] (8). This was prepared by the procedure described for the methyllutidine derivative but using the stoichiometric amount of isobutyliodide (0.96 mL) (yield: 43%) (dec. 198–204° C).

[Co(dpgH)$_2$(CH$_3$)(γ-pic)] (9) and [Co(dpgH)$_2$(CH$_2$CH$_3$)(γ-pic)] (10). These were prepared by the methods described above for the lutidine analogues [Co(dpgH)$_2$(CH$_3$)(lut)] (**5**) and [Co(dpgH)$_2$(CH$_2$CH$_3$)(lut)] (**6**) but from [Co (dpgH)$_2$Cl(γ-pic)] (**3**) as starting material and stoichiometric amounts of CH_3I and CH_3CH_2I, respectively. (yields: 56% for **9** and 49% for **10**) (dec. 218–221° C for **9** and 209–212° C for **10**)

[Co(dpgH)$_2$(CH$_2$Cl)(γ-pic)] (11). To a suspension of [Co(dpgH)$_2$Cl(γ-pic)] (**3**) (2.00 g, 3.00 mmol) in 100 mL of methanol under nitrogen was added aqueous NaOH solution (1 pellet in 5 mL of H_2O), which brought about dissolution of the starting material. A solution of 0.29 g (7.63 mmol) of $NaBH_4$ in 3 mL of H_2O, was added dropwise to the reddish cobalt(III) solution and when effervescence had ceased 1.0 mL (15.6 mmol) of CH_2Cl_2 was added. The resulting solution was stirred at room temperature for 15 minutes, 20 mL of acetone was added and the N_2 bubbling stopped. The mixture was stirred for a further 10 minutes, the unchanged materials were removed by filtration, and the volume of the orange filtrate was reduced to ca. 30 mL. Addition of H_2O (ca. 20 mL) gave an orange-brown solid, which was filtered off and air dried. Recrystallization was carried out by dissolving 0.8 g of the crude material in 25 mL of acetone, filtering the solution and adding H_2O (ca. 15 mL) to the filtrate. This gave a precipitate of the desired compound (yield: 39%) (dec. 193–196° C)

[Co(dpgH)$_2$(CH$_3$)(py)] (12). Nitrogen was bubbled through a suspension of 0.50 g (0.77 mmol) of [Co(dpgH)$_2$Cl(py)] (**4**) in 100 mL of methanol at room temperature and dissolution of the compound brought about by adding 1 mL of aqueous NaOH (1 pellet in 2 mL). The cobalt(III) species were reduced by adding an aqueous solution (2 mL) of $NaBH_4$ (0.06 g, 1.52 mmol). When the effervescence had ceased, 0.2 mL (3.21 mmol) of CH_3I was added and the mixture was stirred vigorously for 20 minutes, during which the deep green solution gradually turned reddish. Acetone (70 ml) was then added to destroy the excess of $NaBH_4$ and the N_2 bubbling was stopped. The solution was filtered and its volume reduced to ca. 20 mL on a rotary evaporator. The orange, solid formed was filtered off and washed with 2 × 10 mL of water. Good quality crystals for X-ray study were obtained by dissolving the solid in

a 3 : 1 acetone : water mixture and allowing the solvent to evaporate slowly at ca. 4° C during 3 days (yield: 56%) (dec. 230–233° C).

[Co(dpgH)$_2$(CH$_2$CH$_3$)(py)] (13). This compound was prepared by the procedure described above for the methyl pyridine analogue (**12**) but from the stoichiometric amount of CH_3CH_2I (0.25 mL) (yield: 54%) (dec. 219–222° C).

[Co(dpgH)$_2$(CH$_3$)(P(OMe)$_3$] (14). P(OMe$_3$) (0.1 mL, 0.85 mmol) was added to an acetone solution (50 mL) of [Co(dpgH)$_2$(CH$_3$)(lut)] (**5**) (0.55 g, 0.85 mmol); the orange solution gradually turned bright yellow. The mixture was stirred at room temperature for 1 hour and the addition of 20 mL of H_2O produced a pale yellow precipitate, which was collected by vacuum filtration and air-dried (yield: 58%) (dec. 227–230° C).

[Co(dpgH)$_2$(CH$_2$CH$_3$)(P(OMe)$_3$] (15). This compound was prepared by the procedure described for complex **14** but from [Co(dpgH)$_2$(CH$_2$CH$_3$)(lut)] (**6**) and the stoichiometric amount of P(OMe)$_3$ as starting materials (yield: 61%) (dec. 202–205° C).

II. Dimethylglyoximate complexes

A. Inorganic cobaloximes

[Co(dmgH)$_2$Cl(py)] (16), [Co(dmgH)$_2$Cl(lut)] (17) and [Co(dmgH)$_2$Cl(P(OMe)$_3$)] (18). These compounds were prepared, by the methods previously described [19,33], from H[Co(dmgH)$_2$Cl$_2$] as starting material [23].

[Co(dmgH)$_2$Cl(γ-pic)] (19). γ-Picoline (0.9 mL, 8.76 mmol) was added to a methanol–water solution (80 : 20) of H[Co(dmgH)$_2$Cl$_2$] [23] (3.10 g, 8.6 mmol). The mixture was stirred for 2 hours at room temperature and the brown crystals formed were collected by vacuum filtration, washed with 2 × 10 mL H_2O, and air-dried (yield: 80%) (dec. 229–233° C).

B. Organometallic cobaloximes

[Co(dmgH)$_2$(R)py] (R = CH$_3$ (20) and R = CH$_2$CH$_3$ (21)). These compounds were made by Hill and Morallee's method [34].

[Co(dmgH)$_2$(R)(lut)] (R = CH$_3$ (22), R = CH$_2$CH$_3$ (23), R = CH$_2$Cl (24) and R = ^{i}Bu (25). These complexes were prepared as previously described [33].

[Co(dmgH)$_2$(R)(P(OMe)$_3$)] (R = CH$_3$ (26) and R = CH$_2$CH$_3$ (27)). These compounds were obtained using the standard procedures [3,5,19,34].

[Co(dmgH)$_2$R(γ-pic)] (R = CH$_3$ (28) and R = CH$_2$CH$_3$ (29)). The preparation of these compounds was carried out as described for the lutidine analogues [23,24], but using [Co(dmgH)$_2$Cl(γ-pic)] (**19**) as starting material (yields: 42% and 39%, respectively).

Crystal data for compounds 5 and 12

$C_{36}H_{28}N_5O_4Co$ (**5**), F.W. = 653.59, triclinic, $a = 17.569(4)$, $b = 15.775(4)$, $c = 13.889(3)$ Å, $\alpha = 112.59(3)$, $\beta = 105.84(3)$, $\gamma = 91.33(3)°$, $V = 3383(2)$ Å^3, space group $P\bar{1}$, $D_x = 1.282$ g cm^{-3}, $Z = 4$, $F(000) = 1352.0$, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 5.76$ cm^{-1}, 298 K.

$C_{34}H_{30}N_5O_4Co$ (**12**), F.W. = 631.58, monoclinic, $a = 22.558(2)$, $b = 10.387(1)$, $c = 13.913(1)$ Å, $\beta = 103.12(1)°$; $V = 3174.9(8)$ Å^3, space group $C2/c$, $D_x = 1.321$ g cm^{-3}, $Z = 4$, $F(000) = 1312.0$, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 6.11$ cm^{-1}, 298 K.

Crystal structure determination and refinement

A prismatic crystal ($0.1 \times 0.1 \times 0.2$ mm) of compound **12** was selected and mounted on an Enraf–Nonius CAD4 diffractometer. Unit-cell parameters were determined from automatic centering of 25 reflections ($12 \leqslant \theta \leqslant 16°$) and refined by a least-squares method. Intensities were collected with graphite-monochromatized Mo-K_α radiation, using the ω–2θ scan technique. 2644 reflections were measured in the range $2 < \theta < 25°$ and 2176 were assumed as observed applying the condition $I \geqslant 2.5\sigma(I)$. R_{int} on F was 0.014. Three reflections were measured every two hours as orientation and intensity control; significant intensity decay was not observed. Lorentz and polarization, but no absorption corrections were made.

The structure was solved by direct methods, using the SHELX86 computer program [35], and refined by full-matrix least-squares method, with the SHELX76 computer program [36]. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = \{\sigma^2(F_o) + 0.0025|F_o|^2\}^{-1}$, f, f' and f'' were taken from the International Tables for X-Ray Crystallography [37]. The positions of 28 H atoms were computed and refined with an overall isotropic temperature factor using a riding model. The final R factor was 0.046 ($wR = 0.055$) for all observed reflections. The number of refined parameters was 202. Max. shift/esd = 0.1; Maximum and minimum peaks in final difference synthesis were 0.4 and -0.4 e Å^{-3}, respectively.

The poor quality of the crystals obtained of compound **5** did not allow us to achieve an accurate resolution or refinement of its crystal structure.

Supplementary material

Tables containing elemental analyses, visible-ultraviolet spectral data for [Co(dpgH)$_2$(R)(L)], ^{1}H and ^{13}C-NMR data for [Co(dmgH)$_2$(R)(γ-pic)], and final atomic coordinates, thermal parameters, observed and calculated structure factors for [Co(dpgH)$_2$(CH$_3$)(py)] are available from the authors upon request.

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