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A study of *cis* influence in alkyl cobaloximes

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Abstract

Thirty-nine alkylcobaloximes have been synthesized (many of them new) and characterized with three different dioxime ligands, dmgH, dpgH and chgH. The chgH cobaloximes have been synthesized for the first time from $ClCo(chgH)_2Py$ complexes. A rapid purification procedure using column chromatography affording analytically pure products has been established for all the three series of cobaloximes. Methanol has been found to be the best solvent for the study of cobalt–carbon charge transfer (Co–C CT) band as the alkylcobaloximes exhibit a prominent maxima in this solvent. For $MeCo(dpgH)_2Py$ the Co–C CT band is not resolved; a λ_{max} value of 453. 6 nm is proposed for it. The literature value of 473 nm is doubtful. The variation of λ_{max} values with increasing alkyl chain length is surprisingly similar for all the three series of cobaloximes. ^{13}C-Spectroscopy has revealed that the P_α experiences the most *cis* influence and P_β the least. The *cis* influencing ability of the chgH ligands have been found to be negligible (as compared to dpgH) on the alkyl chain as well as on the P_β and P_γ carbons. ^1H-NMR studies indicate that the *cis* influence is felt most by the cobalt bound methylene protons followed by P_α and P_β. Interestingly, the O–H–O resonance for the chgH cobaloximes appear ~0.5 ppm upfield than the analogous dmgH complexes in all the thirteen alkylcobaloximes. The order of *cis* influencing ability has been found to be dpgH > chgH > dmgH by all the three spectroscopic techniques. This sequence is exactly the reverse order of the corresponding Co(I) nucleophilicities. C=N and N–O stretching frequencies in the IR studies for three series of cobaloximes follow the order dmgH > chgH > dpgH. The order can be explained if one invokes the electronic effect of the substituents on the dioximic moiety. © 1997 Elsevier Science S.A.

1. Introduction

Organocobaloximes, $RCo(L)_2B$ (where R is an organic group, L = dmgH and B is a coordinating base) have been extensively studied [1], ever since Schrauzer first highlighted their importance as models of coenzyme B_{12} [2]. Since then it has outgrown its initial relevance and has gained significance of its own, mainly because of its rich chemistry [3]. It was found to be a convenient source of free radicals [4], even in aqueous medium [5], and its ability to serve as catalysts [6] and as templates [7] in organic reactions are well documented in the literature. Applications apart, these are ideal systems, like platinum(II) complexes, to study the *cis* and *trans* effects [8]. The *trans* influence has been extensively studied [9], whereas examples of *cis* influence have been rather few [10]. This is primarily due to (a) the *trans* influence is much more pronounced as compared to *cis* influence and (b) paucity of cobaloximes with equatorial ligand other than dmgH. The literature survey further reveals that most of the study, however, has been confined to dmgH as the equatorial ligand. *Cis–trans* influence studies on cobaloximes with other equatorial ligands like gH [11], dpgH [12], and mpgH [13] are few and scattered.

The importance of organocobaloximes with ligands other than dmgH has recently been perceived in many reactions; for example, it has been demonstrated by Welker et al. [7] that in cobaloxime mediated Diels Alder reactions, the use of sterically demanding dpgH as the equatorial ligand instead of dmgH, results in marked improvement of the exo/endo selectivity. We have observed a faster oxygen insertion in $RCo(chgH)_2B$ complexes as compared to $RCo(dmgH)_2B$ complexes

Abbreviations: dmgH, dimethylglyoxime; gH, glyoxime; dpgH, diphenylgyloxime; mpgH, methyphenylglyoxime; chgH, 1,2-cyclohexanedionedioxime, all mono anions

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[14]. Branchaud and Choi have found that in the cobaloxime mediated alkyl–alkenyl cross coupling reactions, the dpgH complexes suppress premature β-hydrogen elimination [15].

Keeping the above in view, we here report the synthesis of many new cobaloximes with chgH and dpgH as equatorial ligands. We have also initiated a systematic and detailed study of such organocobaloximes with an aim to study how the replacement of the dmgH group by the dpgH/chgH, effects the *cis*, axial R and B groups, as well as the cobalt–carbon charge transfer transition. We therefore report a detailed spectroscopic study using UV-vis, ^{1}H- and ^{13}C-NMR to arrange the equatorial ligands in order of their *cis* influencing ability.

2. Results and discussion

2.1. Synthesis

The reduction of $ClCo(L_2)Py$ and its subsequent reaction with the alkyl halide is essentially similar for all the three equatorial ligands. However, it was observed that the oxidative addition became increasingly more difficult for the long chain alkyl halides, $H-(CH_2)_n-X$ ($n > 8$). In fact decylcobaloxime, **10a**, could be prepared only with some difficulty and we failed to synthesize hexadecylcobaloxime by the above procedure. Tetradecyl and pentadecylcobaloximes, however, have been reported in the literature [16].

2.2. UV-vis spectra

The cobalt–carbon charge transfer (Co–C CT) spectral studies of the alkylcobaloximes were done in various solvents in order to ascertain the best solvent for the study. Most of the earlier studies have reported the λ_{max} values in water, dichloromethane, chloroform or ethanol [17,18]. Water was not used as the alkyl(pyridine)cobaloximes were sparingly soluble in it.

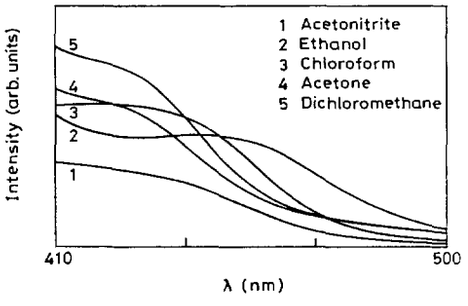


Fig. 1. Appearance of the Co–C CT band of $EtCo(dmgH)_2Py$ (**2a**) in different solvents.

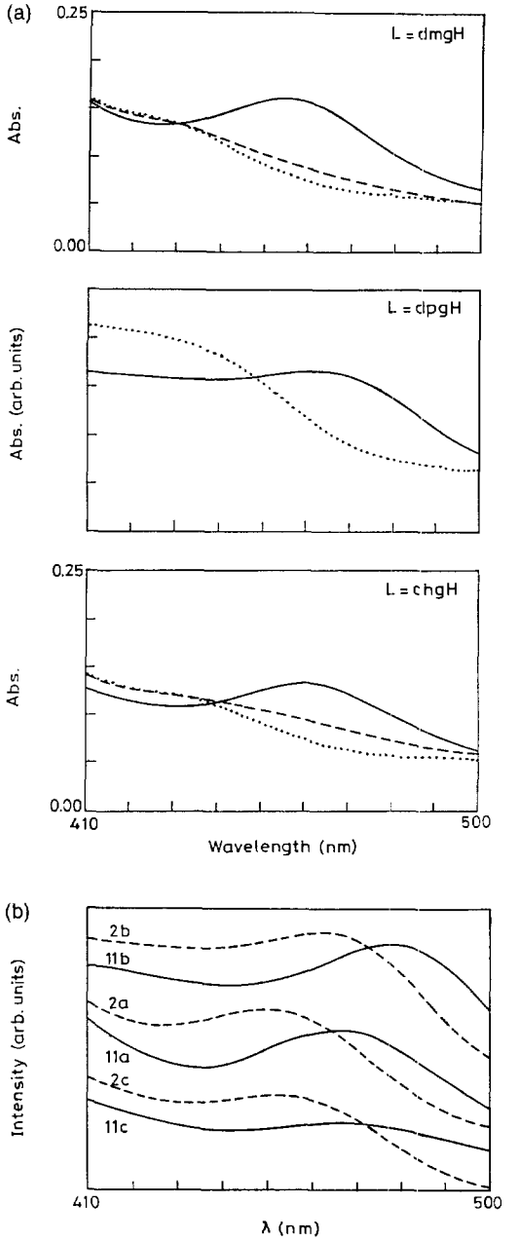


Fig. 2. (a) Effect of the addition of pyridine (———— 0.0 M, --- 10^{-3} M, · · · 10^{-2} M saturation curve) to a 10^{-5} M solution of $^{n}Bu(L_2)Py$ in methanol (L = dmgH, chgH). **4a**, **4b** for L = dpgH; **4c**, the plot is qualitative (see text). (b) Appearance of Co–C CT band of **2** and **11(a,b,c)** in methanol.

We found that using ethanol as solvent, the band assumed a flat hump like shape for all organocobaloximes with L = dmgH and chgH, except methylcobaloximes for which the band appeared as a shoulder. For dpgH complexes the band appearance varied from shoulder to hump. We further found that the band appeared as a broad shoulder (for all the organocobaloximes) on using dichloromethane, acetonitrile, or acetone as the solvent.

Table 1
% Yields of alkylcobaloximes, $RCo(L)_2Py$ (**1–13a,b,c**)

Compound no.	R	L = dmgH (**a**)	L = dpgH (**b**)	L = chgH (**c**)
1	CH_3	70	48	69
2	CH_3CH_2	71	61	73
3	$CH_3(CH_2)_2$	83	19	62
4	$CH_3(CH_2)_3$	71	48	71
5	$CH_3(CH_2)_4$	84	40	89
6	$CH_3(CH_2)_5$	69	58	71
7	$CH_3(CH_2)_6$	67	79	78
8	$CH_3(CH_2)_7$	51	77	52
9	$CH_3(CH_2)_8$	25	62	58
10	$CH_3(CH_2)_9$	34	62	73
11	$(CH_3)_2CH$	69	67	68
12	$CH_3CHCH_2CH_3$	44	62	64
13	$(CH_3)_2CHCH_2CH_2$	79	60	53

All the alklycobaloximes are yellow to orange-red in colour. All are stable to air except isopropyl **11(a,b,c)** and sec-butylcobaloximes **12(a,b,c)** which decompose over a period of several months.

In chloroform it had a flat extended shoulder-like appearance (Fig. 1). In all these cases determination of the λ_{max} with accuracy was not feasible.

We found methanol to be the best and the ideal solvent for this study as the Co–C CT band exhibited a distinct maxima and hence λ_{max} could be determined with accuracy. However with **1b** it appeared as a shoulder in methanol as the 5/6 co-ordinate equilibria (discussed below) in this particular case lies, in all probability, largely towards the six co-ordinate species. Such equilibria are well known for cobaloximes in aqueous media [18].

$$RCo(L)_2Py \Leftrightarrow RCo(L)_2 \{solvated\}$$

Our studies show that similar behaviour is exhibited in methanol also, i.e. alkylcobaloximes exist as an equilibrium mixture of solvated pentacoordinated species and hexacoordinated alkyl(pyridine)cobaloxime, with the equilibrium largely to the right. The evidence for this equilibria is depicted in Fig. 2a [1]. This depicts the changes in the appearance of the CT band on addition of increasing quantities of pyridine to a solution of alkylcobaloxime in methanol. Similar changes were observed by Brown et al. [18] in aqueous solutions. It is obvious that the shape of the CT band (Fig. 2a saturation curve) is similar to the one in chloroform (Fig. 1). Furthermore, the band in chloroform does not change in shape on the addition of a large excess of pyridine. This clearly shows that the species exists as a six coordinate alkyl(pyridine)cobaloxime in chloroform. Similar conclusions were drawn from the ^{1}H-NMR studies (discussed later).

In our results, all cobaloximes show the Co–C CT band between 440 and 460 nm (see Table 2). The position of the band maxima Fig. 2b, and the trends in shifts with the increasing alkyl chain length and branching (Table 2), are similar to earlier observations on the analogous dmgH complexes by Schrauzer [19].

A few specific characteristics/observations follow.

(i) The λ_{max} values fall in the order dpgH > chgH > dmgH. The *cis* influence of the equatorial ligands is obvious. The mean difference of λ_{max} values between dpgH and dmgH complexes (12.5 nm) and chgH and dmgH complexes (5.0 nm), shows that the *cis* influence resulting by replacing dmgH by dpgH is substantially more in the former case [2]. Co–C CT band for the secondary cobaloximes **11–13(a,b,c)** occurs at a much higher wavelength than the analogous primary cobaloximes **1–10(a,b,c)**. This difference is much greater (13–16 nm) for isopropyl **11(a,b,c)** than sec-butylcobaloximes **14(a,b,c)** (2–3 nm).

(ii) Branching in the alkyl chain on a carbon not directly attached to the cobalt atom has no significant effect on the λ_{max} of the Co–C CT band (compare **13(a,b,c)** and **5(a,b,c)**).

(iii) The λ_{max} of the Co–C CT band for $MeCo(dpgH)_2Py$ **1b** could not be determined experimentally as discussed above. If its 5/6 equilibrium in methanol had been similar to the rest of the 38 alkyl cobaloximes, then we would expect its λ_{max} value to be 453.6 nm (This is for comparison only, see Fig. 3). The predicted value is arrived at as follows:

$$\lambda_{max}\mathbf{1a} + 1/9\Sigma\Delta\lambda_{max}(dpgH - dmgH)_n = \lambda_{max}\mathbf{1c} + 1/9\Sigma\Delta\lambda_{max}(dpgH - chgH)_n = 453.5\,nm$$

$$\lambda_{max}\mathbf{2b} - 12\,nm = 453.7\,nm \text{ as } \lambda_{max}\mathbf{2a} - \lambda_{max}\mathbf{1a} = \lambda_{max}\mathbf{2c} - \lambda_{max}\mathbf{1c} = 12\,nm$$

[1] Referee's comments acknowledged.

[2] Only λ_{max} values of cobaloximes, **1–10(a,b,c)** are considered for comparisons.

Table 2
λ_{max} (nm) of alkylcobaloximes **1–13(a,b,c)** and their log ϵ values of the Co–C CT band in methanol

Compound no.	L = dmgH (a)		L = dpgH (b)		L = chgH (c)	
	λ_{max} (nm)	log ϵ (nm)	λ_{max} (nm)	log ϵ *	λ_{max}	log ϵ
1	440.8	3.07	453.5 (calc.)	–	445.8	3.13
2	452.8	3.15	465.7	–	457.8	3.22
3	452.0	3.14	463.4	–	458.0	3.17
4	453.5	3.15	467.0	–	458.4	2.98
5	454.2	3.16	467.4	–	458.6	3.25
6	454.0	3.16	467.0	–	459.0	3.24
7	454.2	3.16	466.6	–	459.0	3.23
8	453.9	3.15	466.1	–	458.8	3.23
9	453.8	3.14	465.8	–	458.8	3.18
10	453.4	3.13	465.7	–	458.6	3.24
11	466.6	3.15	479.9	–	471.0	3.20
12	456.7	3.08	469.6	–	462.1	3.13
13	453.0	3.12	467.0	–	451.9	3.24

* ϵ values of dpgH cobaloximes could not be determined because of poor solubility in methanol.

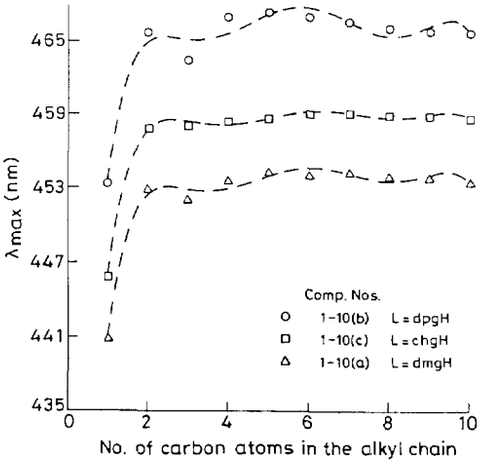


Fig. 3. Variation of the Co–C CT band with increasing alkyl length.

The tabulated value of 453.6 nm is the average of the two nearly identical values extrapolated in four different ways.

Table 3
^{13}C-NMR values of principal ligand resonances (δ ppm)

Compound no.	C=N	P_α	P_γ	P_β
1a	149.89	148.84	137.34	125.03
1b *	150.90	150.09	138.12	125.66
1c	150.04	149.89	137.38	125.09
2a	149.92	148.84	137.22	124.97
2b *	150.85	150.12	137.87	125.51
2c	150.07	149.89	137.25	125.02
3a	149.95	148.99	137.29	125.05
3b#	150.7	149.9	137.8	125.4
3c	150.00	149.92	137.23	124.99
4a	149.89	148.92	137.26	125.01
4b#	150.8	150.0	137.8	125.4
4c	150.03	149.89	137.21	124.98

	C_1	C_2	C_3	C_4	dmgH–Me
1a	11.16				11.79
2a	25.79	15.71			11.76
3a	34.57	23.82	14.76		11.89
4a	32.89	31.86	23.55	13.81	11.86

	C_1	C_2	C_3	C_4	C *	C_α	C_β	C_γ
1b *	–				130.09	129.71	127.90	129.01
2b *	–	16.01			130.14	129.63	127.84	128.89
3b #	36.6	23.9	15.1		130.0	129.5	127.7	128.8
4b #	34.2	33.2	23.7	14.0	130.1	129.5	127.8	128.8

	C_1	C_2	C_3	C_4	C #	C'
1c	11.56				25.05	21.44
2c	26.01	15.82			25.08	21.60
3c	34.60	23.85	14.78		25.08	21.53
4c	33.05	31.77	23.52	13.85	25.22	21.68

* Values from ref. [20].
# On Bruker DRX-300; all the rest on a Bruker WM-400 spectrometer.

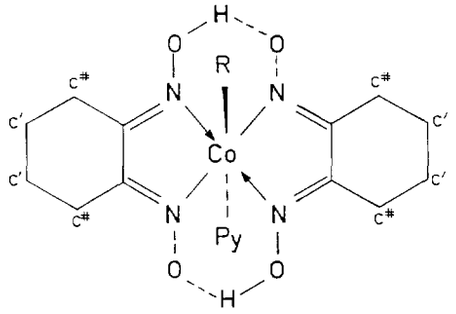


Fig. 4. The assignment of carbon atoms of the cyclohexane ring residue in $RCo(chgH)_2Py$.

(iv) The similarity of the subtle variations of λ_{max} with the alkyl chain length for the three series of cobaloximes stand out clearly from the similar shapes of the best fit lines (polynomials of the order six) (Fig. 3).

2.3. FAB mass spectra

The FAB mass spectra on three samples, one in each series, have the following features in common: (i) the molecular ion peak is always of low intensity, and (ii) the axial base pyridine is lost first, then the fragmentation of the cobaloxime core, $\{Co(L)_2\}$, commences.

$$RCo(L)_2Py \xrightarrow{Py} RCo(L)_2 \xrightarrow{R} \{Co(L)_2\}$$

m/z (relative abundance)

10a M^+ 509 (8), $M^+ + 1$ 510 (4), 430 (46), 298 (87)
10b M^+ 757 (4), $M^+ + 1$ 758 (2), 678 (21), 537 (64)
4c M^+ 477 (21), $M^+ + 1$ 478 (19), 398 (73), 341 (99)

2.4. ^{13}C-NMR

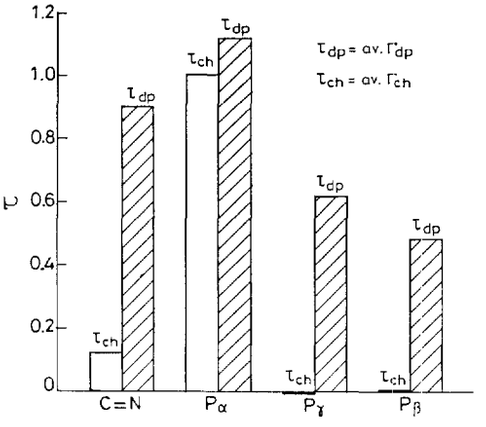
The ^{13}C resonances common to all the three series of compounds, are tabulated for four representative examples **1–4(a,b,c)** (Table 3). The carbon atoms in the phenyl rings of the dpgH complexes, **1–4(b)** were assigned following Lopez et al. [20], and the assignment for the cyclohexane ring residue in the chgH complexes, **1–4(c)** were done as shown in Fig. 4.

The following pertinent points emerge.

(i) If $\Gamma_{dp} = \delta_i^{13}C(dpgH) - \delta_i^{13}C(dmgH)$ [3] and $\Gamma_{ch} = \delta_i^{13}C(chgH) - \delta_i^{13}C(dmgH)$, and $\tau_{dp} = \text{av. } \Gamma_{dp}$ and $\tau_{ch} = \text{av. } \Gamma_{ch}$, where τ_{dp} and τ_{ch} are taken as the extent of *cis* influence due to the replacement of the methyl by the phenyl or by the cyclohexane ring residue, then the order of *cis* influence is

$$dpgH > chgH > dmgH \text{ as } \tau_{dp}P_\alpha, P_\beta, P_\gamma > \tau_{Ch}P_\alpha, P_\beta, P_\gamma$$

(chart1)



This order of *cis* influence is identical to the one obtained by UV-vis study as discussed above.

(ii) It is indeed surprising that $\tau_{oximinic} < \tau P_\alpha$ (for both chgH and dpgH complexes), because any changes in the electron density in the $\{Co(L)_2\}$ moiety (due to changes in L), should in principle, reflect most in the oximinic carbon resonances. It is understandable that the extent of *cis* influence is felt more on the P_α carbon than on P_β or P_γ carbon as it is nearest to the $\{Co(L)_2\}$ moiety. However, it is difficult to explain why, for dpgH complexes at least, P_γ experiences more *cis* influence than P_β [4] (chart 1). Furthermore it is observed that the extent of *cis* influence on the P_α carbon is comparable for both the dpgH and chgH complexes, and the P_β and P_γ carbons in the chgH complexes experience a negligible *cis* influence as compared to dpgH.

(iii) The variation of Γ_{ch} and Γ_{dp} with alkyl chain length show a surprisingly similar behavior for C=N, P_α, P_β and P_γ carbons (Fig. 5). In other words the *cis* influencing ability of the equatorial ligands, as well as the changes in the electron density at the oximinic carbons is effected similarly, if not equally, by the alkyl group at the axial site [21].

[3] For a similar comparison see [21] by Gilaberte et al.

[4] Interestingly, it has been observed that the ^{13}C chemical shift of the γ carbon of 4 ^{t}buby in cobaloximes is most sensitive to the changes in the *trans* ligand, X [22]. Drago [23,24] has even pointed out the possibility of using the P_γ carbon as a spectral probe for studying the chemical shifts as a function of ligand, X. The shifts calculated by considering the changes in magnetic anisotropy of cobalt alone, indicate that the P_α should be most effected and P_γ the least [22].

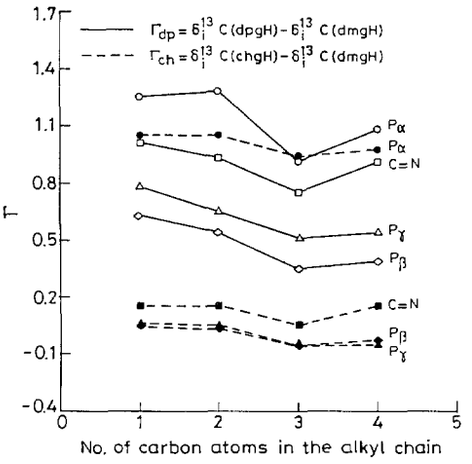
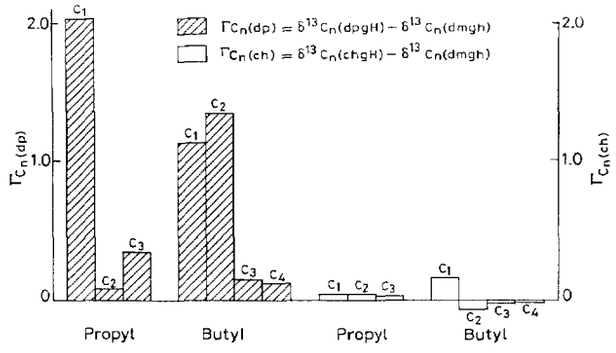


Fig. 5. Variation of Cis influence (Γ) on the carbon atoms of the $\{Co(L)_2Py\}$ moiety with increasing alkyl chain length.

(iv) The *trans* influencing ability is negligible as compared to the *cis* influence, as C=N, P_α, P_β, P_γ resonances vary slightly with increasing alkyl chain length.

(v) The *cis* influence of the chgH ligand is negligible on the carbon atoms of the alkyl chain as compared to dpgH ligands (chart 2). Though it appears that the *cis* influencing ability falls off with distance from the $\{Co(L)_2\}$moiety, it again becomes difficult to rationalize the anomalous behavior of Γ_{C3dp} and Γ_{C2dp} of propyl and butyl cobaloximes respectively (chart 2).



2.5. ^{1}H-NMR

The ^{1}H-NMR (δ) values for the compounds **1–13(a,b,c)** are given in Table 5. The species exists as six coordinated alkyl(pyridine)cobaloximes in $CDCl_3$ (the solvent used for NMR studies), as the cobalt bound methylene as well as the dmgH–Me proton resonances did not shift even on addition of a large excess of pyridine directly to the NMR sample.

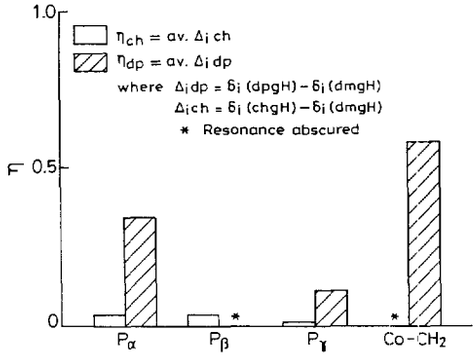
The P_β resonances in the dpgH cobaloximes **1–13(b)** are merged with the dpgH–phenyl resonance and so is the case with the Co–CH_2 resonance in chgH cobaloximes **1–13(c)** which merge with cyclohexane ring proton resonance.

The comparison [5] of the extent of *cis* influence on the four sets of resonances P_α, P_β, P_γ and Co–CH_2 is made as follows.

$\Delta_i dp = \delta_i dpgH - \delta_i dmgH$; $\Delta_i ch = \delta_i chgH - \delta_i dmgH$

and $\eta_{dp} = av.\Delta_i dp$; $\eta_{ch} = av.\Delta_i ch$

The conclusions are quite general and hold true for all alkylcobaloximes. If η is taken to be the extent of *cis* influence (except of course for O–H–O) then it is apparent from chart 3 that the order of *cis* influence is dpgH > chgH > dmgH. An exactly similar order was observed in UV-vis and ^{13}C-NMR studies as discussed above. The extent of *cis* influence is felt most on the Co–CH_2 followed by P_α and P_γ protons.



The downfield shift of the P_α and Co–CH_2 resonances in dpgH as compared to dmgH/chgH complexes can be ascribed to long range interaction with the phenyl rings [25], and for the O–H–O resonance, this may be due to increased O–O distance as mentioned by Lopez et al. [10].

We have observed a high upfield shift for the O–H–O resonance, nearly 0.5 ppm in chgH cobaloximes. This opens up the question as to how the replacement of the methyl group by the cyclohexane ring residue alters the anisotropy of the cobalt atom and/or the ring current in the metallabicycle so profoundly as to merit such a large shift. This is in view of the earlier reports on the dmgH complexes where electronic delocalisation on the entire $Co(dioxoH)_2$ moiety [21] as well as the anisotropy of the cobalt atom [8] has been invoked to explain the ^{1}H-NMR shifts. .

[5] Based on the P_α and P_γ resonance only, other resonances being obscured (stated above); only **2–10(a,b,c)** are considered for comparison as the others do not have a direct cobalt bound methylene.

Table 4
Elemental analysis for compound nos. **1–13(a,b,c)**

Compound no.	Anal. cald. for	Found (cal)%		
		C	H	N
1a	$CoC_{14}H_{22}N_5O_4$	44.01 (43.84)	5.75 (5.78)	18.29 (18.27)
1b	$CoC_{34}H_{30}N_5O_4$	64.62 (64.63)	4.82 (4.79)	11.05 (11.09)
1c	$CoC_{18}H_{26}N_5O_4$	49.68 (49.63)	6.09 (6.02)	15.99 (16.09)
2a	$CoC_{15}H_{24}N_5O_4$	45.37 (45.32)	6.15 (6.09)	17.61 (17.63)
2b	$CoC_{35}H_{32}N_5O_4$	65.04 (65.09)	5.02 (4.99)	10.81 (10.85)
2c	$CoC_{19}H_{28}N_5O_4$	50.68 (50.75)	6.32 (6.28)	16.01 (15.59)
3a	$CoC_{16}H_{26}N_5O_4$	46.65 (46.69)	6.41 (6.37)	17.09 (17.03)
3b	$CoC_{36}H_{34}N_5O$	65.57 (65.53)	5.21 (5.19)	10.66 (10.62)
3c	$CoC_{20}H_{30}N_5O_4$	52.01 (51.81)	6.55 (6.52)	15.20 (15.11)
4a	$CoC_{17}H_{28}N_5O_4$	47.93 (47.97)	6.69 (6.63)	16.52 (6.47)
4b	$CoC_{37}H_{36}N_5O_4$	65.97 (65.94)	5.33 (5.38)	10.37 (10.40)
4c	$CoC_{21}H_{32}N_5O_4$	53.01 (52.80)	6.71 (6.75)	14.73 (14.67)
5a	$CoC_{18}H_{30}N_5O_4$	49.21 (49.18)	6.84 (6.88)	15.97 (15.94)
5b	$CoC_{38}H_{38}N_5O_4$	66.38 (66.34)	5.62 (5.57)	10.15 (10.19)
5c	$CoC_{22}H_{34}N_5O_4$	53.79 (53.74)	7.09 (6.97)	14.29 (14.25)
6a	$CoC_{19}H_{32}N_5O_4$	50.25 50.30)	7.17 (7.11)	15.41 (15.45)
6b	$CoC_{39}H_{40}N_5O_4$	66.75 (66.73)	5.67 (5.70)	10.03 (9.98)
6c	$CoC_{23}H_{36}N_5O_4$	54.29 (54.26)	7.23 (7.18)	14.02 (13.86)
7a	$CoC_{20}H_{34}N_5O_4$	51.37 (51.36)	7.39 (7.33)	14.91 (14.98)
7b	$CoC_{40}H_{42}N_5O_4$	67.09 (67.10)	5.93 (5.91)	9.84 (9.79)
7c	$CoC_{24}H_{38}N_5O_4$	55.51 (55.46)	7.39 (7.30)	13.59 (13.48)
8a	$CoC_{21}H_{36}N_5O_4$	52.38 (52.36)	7.49 (7.54)	14.58 (14.55)
8b	$CoC_{41}H_{44}N_5O_4$	67.42 (67.46)	6.02 (6.09)	9.65 (9.60)
8c	$CoC_{25}H_{40}N_5O_4$	56.27 (56.25)	7.63 (7.56)	12.91 (13.12)
9a	$CoC_{22}H_{38}N_5O_4$	53.26 (53.30)	7.79 (7.73)	14.16 (14.14)
9b	$CoC_{42}H_{46}N_5O_4$	67.72 (67.80)	6.28 (6.23)	9.38 (9.42)
9c	$CoC_{26}H_{42}N_5O_4$	56.82 (57.00)	7.79 (7.73)	12.88 (12.79)
10a	$CoC_{23}H_{40}N_5O_4$	54.23 (54.19)	7.93 (7.91)	13.79 (13.75)
10b	$CoC_{43}H_{48}N_5O_4$	68.08 (68.13)	6.41 (6.38)	9.25 (9.24)
10c	$CoC_{27}H_{44}N_5O_4$	57.71 (57.72)	8.02 (7.90)	12.58 (12.47)
11a	$CoC_{16}H_{26}N_5O_4$	46.72 (46.69)	7.35 (6.37)	17.05 (17.03)
11b	$CoC_{36}H_{34}N_5O_4$	65.49 (65.53)	5.26 (5.19)	10.64 (10.62)
11c	$CoC_{20}H_{30}N_5O_4$	51.79 (51.81)	6.56 (6.52)	15.18 (15.11)
12a	$CoC_{17}H_{28}N_5O_4$	48.02 (47.97)	6.65 (6.63)	16.48 (16.47)
12b	$CoC_{37}H_{36}N_5O_4$	66.03 (65.94)	5.40 (5.38)	10.39 (10.40)
12c	$CoC_{21}H_{32}N_5O_4$	53.02 (52.80)	6.77 (6.75)	14.65 (14.67)
13a	$CoC_{18}H_{30}N_5O$	49.20 (49.18)	6.85 (6.88)	15.96 (15.94)
13b	$CoC_{38}H_{38}N_5O_4$	66.39 (66.34)	65.62 (5.57)	10.13 (10.19)
13c	$CoC_{22}H_{34}N_5O_4$	53.72 (53.74)	6.91 (6.74)	14.32 (14.25)

Further, if one considers the bond length arguments by Lopez et al. [10], the upfield shift may point to a decreased O–O distances in the chgH complexes.

We believe that the subtle interplay of various factors like (i) changes in the anisotropy of cobalt atom [8], (ii) changes in anisotropy of the C=N bond [21], and (iii) alteration of the ring current in the entire 'aromatic like' metallabicycle, brought about by the changes in the electron donating ability of the equatorial ligands together with the long range interactions with the phenyl rings (dpgH complexes), are responsible for the above order of *cis* influence in the ^{1}H-NMR. A rigorous theoretical rationalization would warrant an extensive comparative study of the less explored dpgH and even less understood chgH complexes.

It is also interesting to note some additional features of the present study.

(a) In contrast to the reported work on the organocobaloximes [9a], we find that there is hardly any upfield shift of the P_α protons upon coordination as compared to unligated pyridine. Our observations match with Lopez et al. [21], who have pointed out that the alkyl groups are least capable of inducing any upfield shift of the P_α protons.

(b) Interestingly, if one considers the nucleophilicities of various Co(I) species, dmgH (14.3) > chgH (13.7) > dpgH (13.5) [26], the order is exactly the reverse of the *cis* influencing ability.

2.6. IR spectra

The ν C=N, ν N–O, ν N–O′ of the three series of cobaloximes **1–13(a,b,c)** are listed in Table 6. The

assignments for the dmgH complexes match with the assignments by Blinc et al. [27], Yamazaki et al. [28], and later confirmed by Rutherford et al. [29] using isotopic labeling studies. The assignments for the chgH, **1–13(c)** and dpgh cobaloximes **1–13(b)** are, however, tentative. The spectrums of uncoordinated oximino lig-

Table 5
^{1}H-NMR of organocobaloximes **1–13(a,b,c)** (δ ppm)

Compound no.	H–O–H ∉	P_α (d), J = 6.25 Hz	P_β (m)	P_γ (m)	L Ξ	Co–(CH_n) ∈	Rest alkyl chain
1a	18.21	8.59	7.31	7.65	2.12	0.81	–
1b	18.90	9.00	[b]	7.87	7.19	1.43	–
1c	17.59	8.56	7.24	7.65	3.00–2.06 2.06–1.12	0.87	–
2a	18.15	8.56	7.25	7.64	2.12	1.68	0.34 *
2b	18.68	8.87	[b]	7.75	7.18	2.37	0.81 *
2c	17.53	8.56	7.27	7.65	3.03–2.09 2.09–1.06	[b]	0.37 *
3a	18.28	8.57	7.29	7.71	2.08	1.65	0.68–1.00
3b	18.65	8.90	[b]	7.78	7.24	2.18	0.62–1.25
3c	17.56	8.56	7.31	7.75	3.50–2.06 2.06–1.25	[b]	0.62–1.25
4a	18.22	8.60	7.31	7.72	2.12	1.64	0.35–1.40
4b	18.65	8.90	[b]	7.78	7.19	2.18	0.62–1.40
4c	17.62	8.62	7.28	7.65	3.25–2.06 2.06–1.21	[b]	0.31–1.31
5a	18.18	8.59	7.26	7.65	2.12	1.64	0.31–1.37
5b	18.65	8.87	[b]	7.75	7.24	2.18	0.62–1.50
5c	17.65	8.59	[b]	[b]	3.62–2.21 2.21–0.37	[b]	[b]
6a	18.03	8.54	7.24	7.60	2.12	1.62	0.37–1.40
6b	18.65	8.87	[b]	7.75	7.18	2.18	0.62–1.37
6c	17.59	8.59	7.31	7.68	3.62–2.12 2.12–1.34	[b]	0.67–1.34
7a	18.04	8.53	7.23	7.60	2.12	1.62	0.46–1.37
7b	18.65	8.87	[b]	7.75	7.23	2.18	0.62–1.75
7c	17.65	8.56	7.23	7.65	3.00–2.06 2.06–1.34	[b]	0.46–1.34
8a	18.00	8.53	7.25	7.62	2.11	1.62	0.46–1.34
8b	18.65	8.90	[b]	7.71	7.25	2.18	0.62–1.75
8c	17.53	8.62	7.26	7.68	3.00–2.06 2.06–1.37	[b]	1.06–1.37
9a	18.01	8.54	7.25	7.60	2.12	1.62	0.62–1.40
9b	18.65	8.90	[b]	7.75	7.25	2.18	0.34–1.56
9c	17.37	8.53	7.31	7.62	3.25–2.12 2.12–1.37	[b]	0.43–1.37
10a	18.01	8.53	7.23	7.62	2.10	1.60	0.56–1.43
10b	18.71	8.93	[b]	7.78	7.15	2.21	0.62–1.87
10c	17.62	8.56	7.31	7.59	3.00–2.12 2.12–1.37	[b]	0.50–1.37
11a	18.04	8.54	7.24	7.59	2.14	[b]	0.46 #
11b	18.53	8.87	[b]	7.25	7.15	2.65 ∉	0.87 #
11c	17.37	8.59	7.25	7.65	3.65–2.18 2.18–1.25	[b]	0.46 #
12a	18.22	8.60	7.28	7.65	2.12	1.67–1.56 ⊗	0.56–1.09
12b	18.65	8.87	[b]	7.75	7.25	2.43–2.00 ⊗	0.62–1.25
12c	[a]	8.62	7.34	7.71	3.75–2.09 2.09–1.18	[b]	0.34–1.18
13a	18.18	8.48	7.32	7.65	2.12	1.64 ⊗	0.56–1.37
13b	18.65	8.87	[b]	7.71	7.24	2.21 ⊗	0.50–1.68
13c	[a]	8.50	7.37	7.59	3.00–1.87 1.87–1.06	[b]	0.37–1.06

[a] Resonance not observed; [b] resonances overlap and/or integrate together.
Doublet (J = 7.81 Hz); * triplet (J = 9.40 Hz); ∉, broad singlet **1–13(a,c)**, sharp singlet **1–13(b)**; Ξ, singlet **1–13(a)** and multiplet **1–13(b,c)**; ∈, singlet **1(a,b,c)**, **2–10(a,b,c)** triplet/merged with rest alkyl chain; ⊗ multiplet.

Table 6
Selected IR frquencies of organocobaloximes **1–13(a,b,c)** (ν cm^{-1})

Compound no.	ν C = N	ν N–O	ν N–O′
1a	1555	1100	975
1b	1530	1077	925
1c	1545	1075	970
2a	1555	1100	975
2b	1528	1077	927
2c	1530	1068	960
3a	1565	1095	970
3b	1529	1078	929
3c	1553	1080	965
4a	1560	1098	975
4b	1528	1078	927
4c	1540	1073	960
5a	1545	1093	968
5b	1524	1078	927
5c	1545	1078	965
6a	1553	1095	970
6b	1528	1079	927
6c	1530	1080	967
7a	1560	1098	973
7b	1527	1078	927
7c	1540	1070	963
8a	1560	1093	970
8b	1532	1079	922
8c	1545	1068	963
9a	1553	1093	970
9b	1532	1079	922
9c	1528	1065	955
10a	1553	1095	970
10b	1531	1079	927
10c	1545	1063	963
11a	1553	1095	973
11b	1527	1073	924
11c	1543	1073	965
12a	1555	1095	975
12b	1527	1077	924
12c	1548	1080	965
13a	1553	1095	970
13b	1529	1079	929
13c	1548	1078	965

ands are not helpful in the assignments as they exist in a very different environment than the coordinated ones [29].

If the complexes are arranged in the increasing order of frequencies (for C=N and N–O′) then the dpgH < chgH < dmgH is observed and if νN–O is also taken into consideration then the order is dpgH ≅ chgH < dmgH. This is, once again, the reverse order of *cis* influencing ability but in the same order of increasing nucleophilicities. The order can be explained if one invokes the electronic effect of the substituents on the dioximic moiety.

3. Experimental

Cobalt chloride hexahydrate, dimethylglyoxime (Merck India), diphenylglyoxime, 1,2-cyclohexanedionedioxime and all the alkyl halides (Fluka) were used as such without further purification. All solvents were distilled prior to use.

UV-vis spectra were recorded on a Shimadzu 160-A Spectrophotometer. ^{1}H-NMR were recorded on a Bruker WP-80 FT NMR spectrometer in $CDCl_3$. ^{13}C-NMR spectra were recorded on a Bruker WM-400 and Bruker DRX-300 spectrometers in $CDCl_3$. FAB Mass spectra were recorded on a Jeol SX 102/DA-6000 data system using Xenon as FAB gas at room temperature and mNBA as matrix. IR was recorded on a Perkin Elmer 1320 IR spectrometer as nujol mulls. Elemental analysis were carried out at the Regional Sophisticated Instrumentation Centre (RSIC), Lucknow. The purity of all the cobaloximes was checked using TLC.

Chlorocobaloximes, $ClCo(L)_2Py$ (L = dmgH; dpgH) were prepared according to published procedures [20,30]. $ClCo(chgH)_2Py$ was obtained from a separate study in our laboratory [31].

The alkyl cobaloximes $RCo(L)_2Py$ (L = dmgH; dpgH; chgH), **1–13(a,b,c)** have been synthesized by the reaction of $Co^{I}(L)_2Py$, prepared in situ by the borohydride reduction of chlorocobaloxime, $ClCo(L)_2Py$, with appropriate alkyl halide under strict inert atmosphere at 0°C. The work-up procedure was similar to the ones detailed earlier [20,32]. It was observed that for certain long chain alkylcobaloximes the precipitation of the cobaloximes did not occur on pouring the reaction mixture into water. In those cases the cobaloxime was extracted with chloroform or dichloromethane, the organic layer washed with brine, dried over anhydrous magnesium sulphate, and concentrated to few milliliters by a rotavapor. Precipitation was then achieved by pouring it dropwise into light petroleum with constant stirring. The crude product (orange-red for dmgH/chgH and orange-brown for dpgH cobaloximes) was filtered, vacuum dried and was purified by column chromatography as discussed below.

*dmgH/chgH cobaloximes (nos. **1–13(a,c)**).* The crude cobaloxime was dissolved in minimum volume of chloroform/dichloromethane and loaded on to a Silica-Gel (100–200 mesh) column, pre-eluted with the same solvent. The polarity of the eluent was carefully increased by ethylacetate:chloroform/dichloromethane (10–40%) till an orange-red band corresponding to the alkylcobaloxime was distinctly visible. The band was eluted out completely with ethyl acetate: chloroform/dichloromethane (80:20 mixture).

*dpgH cobaloximes (nos. **1–13(b)**).* The orange-brown crude cobaloxime was dissolved in minimum volume of chloroform and loaded on to a Silica Gel (100–200 mesh) column pre-eluted with the same solvent. The polarity of the eluent was very carefully increased with ethyl acetate (2–4%) when an orange-red band corresponding to the alkylcobaloxime eluted out followed by a pale-yellow band corresponding to the

unreacted chlorocobaloxime. Any deviation in polarity from 2–4% ethylacetate may contaminate the organocobaloxime with the unreacted chlorocobaloxime impurity.

The characteristics of all the organocobaloximes, **1–13(a,b,c)**, along with their elemental analysis data, are given in Tables 1–6.

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