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Inorganic cobaloximes with mixed dioxime equatorial ligands: a convenient one pot synthesis and *cis* influence studies: X-ray crystal structures of $N_3Co^{III}(dmgH)(dpgH)Py$ and $N_3Co^{III}(chgH)(dpgH)Py$

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Abstract

A simple and general route to the synthesis of cobaloxime with mixed dioxime ligands, XCo(L)(L′)Py, L,L′ = dmgH/dpgH and chgH/dpgH; X = Cl, Br, NO_2, N_3, has been described. These compounds are reported for the first time. The synthesis is confirmed by the X-ray structures of $N_3Co(dmgH)(dpgH)Py$ and $N_3Co(chgH)(dpgH)Py$. The *cis* and *trans* effects on these complexes and on $XCo(L)_2Py$ (L = dmgH, chgH, dpgH; X = Cl, Br, NO_2, N_3) complexes have been studied by ^1H-, ^{13}C-NMR, UV, and X-ray. For a range of X ligands, a clear trend between the ^1H, ^{13}C chemical shifts of the equatorial and axial ligands as well as with the Co–dioxime CT band has been observed. The analysis of the ^{13}C values and X-ray data shows that one dioxime wing effects the other dioxime wing in the mixed dioxime complexes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cobalt; Cobaloxime; Dioxime; *cis–trans* Influence

1. Introduction

The studies on organocobaloximes[1] in the past three decades has provided a considerable amount of structural, spectroscopic, thermodynamic, and kinetic data for a wide variety of R and L ligands [1]. The trends in these properties as a function of the steric and electronic properties of the axial R and L ligands have been qualitatively interpreted [2]. Attempts have also been made to achieve a quantitative rationalization as well [3]. For example, the weakening of the Co–C bond (steric *cis* influence) is essentially related to the increase in the bulkiness of R, which sterically interacts with the dioxime moiety. An increase in the bulkiness of L also lengthens the Co–C bond (steric *trans* influence). The weakening of the Co–L bond (electronic *trans* effect and influence) has been attributed to the electron donating ability of R as well as to the bulkiness of R, which through a bending of the dioxime moiety towards L lengthens the Co–L bond (steric *trans* influence). Also, an increase in the bulkiness of L determines the lengthening of the Co–L bond (steric *cis* influence).

Most of the above information has come from the study of cobaloximes (both organic and inorganic) with dmgH as the equatorial ligand. The studies involving other oximes with varying steric and electronic properties such as gH [4], chgH [5] and dpgH [6] have been few. We have recently shown that the *cis* influence of the dioxime ligand in alkyl cobaloximes varies in the order dpgH > chgH > dmgH [7]. A comparison of the structural parameters of bis(dioxime) vitamin B_{12} models have indicated that lateral compression and the α-bending angle are related to the steric bulkiness of the dioxime substituent [8].

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[1] General formula: $RCo(L)_2B$, where R, an organic group σ bonded to cobalt; B, axial base *trans* to the organic group; L, dioxime ligand (e.g. gH, glyoxime; dmgH, dimethylglyoxime); chgH, 1,2-cyclohexanedione dioxime; dpgH, diphenylglyoxime (all monoanions).

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There have been only a very few studies on the effect of the equatorial ligand field on the axial groups (*cis* influence). This is due to the paucity of complexes with dioximes other than dmgH.

The spectroscopic characteristics of cobaloximes with dmgH as the equatorial ligand show a systematic variation with X [9]. Much of the information on the correlation study has been derived from the ^{1}H-NMR chemical shifts as only a few cobaloximes have been characterized by both ^{1}H- and ^{13}C-NMR [[6b,10]]. Studies with ^{13}C-NMR are, therefore, lacking.

We believe that a more comprehensive spectroscopic and structural study of a large number of cobaloximes with different dioximes and various X ligands (having a range of sigma and pi donor/acceptor properties) would enable a more rigorous treatment of the statistical data with a greater degree of confidence. The present study, therefore, gains importance in this direction.

Table 1
Molar distribution (%) in the reaction of (**1b**) and (**5b**) with X^-

1a–8a	**1c–4c**	**1b–8b**
53.1	2.0	46.9
24.0	27.4	48.4
53.0	0.7	46.3
11.8	52.0	36.2
25.8	5.7	68.5
7.8	7.4	84.8
7.8	30.4	61.7
0.5	17.7	81.7

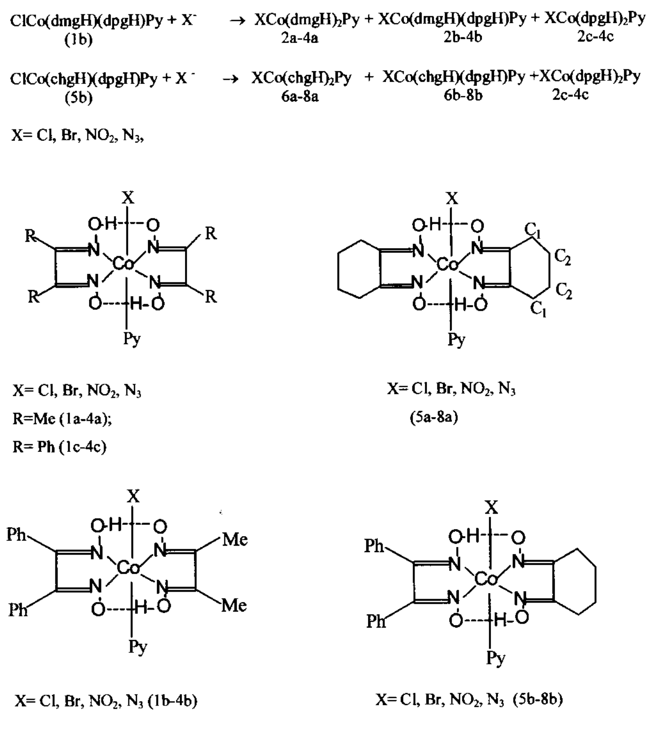

Fig. 1. Structure of cobaloximes.

In this paper we report the synthesis and study of complexes of the type *trans* $XCo(L)_2Py$, L = dmgH, chgH, dpgH and XCo(L)(L′)Py, with L = dmgH, L′ = dpgH and L = chgH and L′ = dpgH; X = Cl, Br, NO_2, N_3. The spectroscopic studies (^{1}H, ^{13}C, UV) on these complexes have been carried out. The aim of the study is: (a) to verify if the trends in ^{1}H-NMR and UV data, reported earlier for dmgH complexes, also apply to cobaloximes with other dioxime equatorial ligands; (b) to check if ^{13}C-NMR gives similar or better information than ^{1}H-NMR; (c) to check if there is any correlation in the ^{1}H-, ^{13}C-NMR, and UV data; and (d) to check if one wing of the equatorial dioxime moiety has any effect on the other wing. Besides, we also report for the first time the crystal structures of inorganic cobaloxime with mixed dioxime equatorial ligands, $N_3Co(dmgH)(dpgH)Py$ and $N_3Co(chgH)(dpgH)Py$.

2. Results and discussion

2.1. Synthesis

Inorganic cobaloximes, $XCo(dmgH)_2Py$, have been well described in the literature [1] [9] [10b]. In general, two procedures have been used for the preparation of these complexes: (a) by aerial oxidation of the stoichiometric mixture of the reactants [11] and (b) by substitution of the chloro group in chlorocobaloxime by another nucleophile [10] [12]. However, very little is known on the corresponding dpgH [9] and chgH complexes [5c] and a thorough literature survey shows that inorganic cobaloximes with mixed dioxime ligands, XCo(L)(L′)Py, have never been synthesized before.

We have successfully utilized the substitution method for the synthesis of XCo(dmgH)(dpgH)Py and XCo(chgH)(dpgH)Py. Three products are isolated in each reaction (see Table 1 for molar distribution, see Fig. 1). This may indicate that either the chloro group or the X group has randomized during the reaction. It is very difficult to comment whether the chloro group randomizes before its reaction with X^- or the randomization occurs after the substitution has taken place. Further studies are underway in this direction.

2.2. Spectroscopy

2.2.1. General comments on the ^{1}H- and ^{13}C-NMR assignments

The ^{1}H-NMR spectra of these complexes are easily assigned based on the chemical shifts. The signals are assigned according to their relative intensities and the assignment is consistent with those of the related compounds previously described [9] [10] [12].

Since the ^{13}C values have been assigned for only a few inorganic cobaloximes in the literature [6b] [10], further comments are needed on its assignment.

Table 2
^{1}H-NMR data for compounds **1a–8a**, **1b–8b,** and **1c–4c**

Compound	dmgH (Me)/chgH (C1 and C2)	Pyridine			H–OH	Phenyl
		α	β	λ		
1a	2.40	8.25	7.26	7.73	18.15	–
2a	2.40	8.25	7.26	7.70	18.12	–
3a	2.33	8.32	7.27	7.73	–	–
4a	2.41	8.28	7.23	7.70	–	–
5a	1.65–1.79, 2.78–2.86, 3.04–3.12	8.26	7.27	7.74	17.36	–
6a	1.65–1.77, 2.77–2.85, 3.05–3.14	8.25	7.26	7.73	17.35	–
7a	1.61–1.72, 2.71–2.73, 2.95–2.96	8.30	7.24	7.72	–	–
8a	1.65–1.83, 2.74–2.82, 3.06–3.13	8.32	7.28	7.75	17.55	–
1c	–	8.59	7.36	7.83	18.61	7.21–7.30
2c	–	8.59	7.41	7.84	18.62	7.20–7.30
3c	–	8.63	7.41	7.86	18.45	7.19–7.33
4c	–	8.64	7.39	7.85	18.53	7.23–7.32
1b	2.45	8.44	7.28	7.77	–	7.18–7.25
2b	2.45	8.43	[a]	7.76	–	7.17–7.33
3b	2.39	8.49	7.34	7.80	18.14	7.15–7.30
4b	2.41	8.54	[a]	7.78	18.23	7.23–7.31
5b	1.68–1.82, 2.82–2.90, 3.08–3.16	8.42	7.30	7.78	18.01	7.17–7.27
6b	1.70–1.79, 2.83–2.91, 3.08–3.16	8.41	[a]	7.76	18.01	7.16–7.33
7b	1.69–1.79, 2.77–2.83, 3.01–3.07	8.48	7.36	7.81	17.86	7.14–7.28
8b [b]	1.71–1.83, 2.78–2.88, 3.06–3.14	8.47	7.32	7.79	17.93	7.17–7.28

[a] Merged with dpgH resonance.

[b] It is chiral and gives a optical rotation of +14°.

The ^{13}C resonance of dmgH (Me), chgH (C1 and C2), dpgH[2] (C*, Cα, Cβ, Cγ), Py_{β} and Py_{γ} are easily assigned based on their chemical shifts. The assignment of C=N (dmgH or chgH), C=N (dpgH) and Py_{α} should be done with utmost care as these occur very close to each other. The assigned values match the literature values, though these are few in number. Our previous assignments in $ArCH_2Co(dpgH)(dioxime)Py$ (dioxime = dmgH, chgH) [13] complexes have been quite helpful.

*2.2.1.1. XCo(L$_2$)Py (**1a–8a** and **1c–4c**).* C=N and Py_{α} resonances occur very close to each other. The peak at higher ppm (δ) value is assigned to C=N and the peak with lower δ value is assigned to Py_{α}. In general, C=N has lower intensity as compared to Py_{α} (**1a–4a**, **1c–4c**). However, in case of **5a–8a** C=N has slightly higher intensity than Py_{α}. It is expected that C=N should be of lower intensity as it is a quaternary carbon.

*2.2.1.2. XCo(dmgH)(dpgH)Py (**1b–4b**) and XCo(chgH)-(dpgH)Py (**5b–8b**).* Three peaks are observed in a region that is very close to each other. The highest intensity peak with the lowest δ value is assigned to Py_{α}. Between the other two peaks for C=N (dpgH) and C=N (dmgH or chgH), the peak with higher δ value is assigned to C=N (dpgH) and the other peak to C=N (dmgH or chgH).

2.3. *cis and trans Influence of X*

The *trans* influence of the ligand X can be monitored through the coordination shift ($\Delta\delta = \delta_{\text{complex}} - \delta_{\text{free py}}$) of pyridine (α, β, γ). The *cis* influence of X can be monitored by the ^{13}C resonance of $C{=}N_{(\text{oximinic})}$ and also by Δδ ^{1}H or Δδ ^{13}C of pyridine (α, β, γ) when X is held constant and the equatorial ligand is changed. These are separately discussed below.

2.3.1. *^{1}H chemical shifts*

2.3.1.1. O–H···O *resonance.* ^{1}H-NMR (δ) values for all the compounds are given in Table 2. In certain cases we have not been able to detect the O–H···O peak. We have observed a high upfield shift in chgH complexes, nearly 0.6 ppm as compared to dmgH complexes and 1.25 ppm as compared to dpgH complexes. O–H···O resonance follows the order dpgH (**1c–4c**) > dmgH (**1a–4a**) > chgH (**5a–8a**). This may open up the question as to how the replacement of two methyl groups by the cyclohexane ring residue alters the anisotropy of the cobalt atom or $[Co(chgH)_2]^+$ unit so profoundly so as to merit such a large shift. This is in view of the recent reports on the dmgH complexes with planar nitrogen ligands where the magnetic anisotropy of the entire $[Co(L)_2]^+$ moiety [9] or the anisotropy of cobalt atom [10] have been invoked to explain the ^{1}H-NMR shifts. The large shift in dpgH complexes compared to dmgH or chgH may be due to the high ring currents of the

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[2] See Ref. [9] for numbering in dpgH.

Table 3
^{13}C NMR data of compounds **1a**–**8a**, **1c**–**4c** and **1b**–**8b**

Compound	Ligand	pyridine			dmgH	chgH	dpgH [a]			
	C=N [b]	α	β	γ	(Me)	C1 & C2	C*	Cα	Cγ	Cβ
1a	152.59	150.98	125.73	139.07	13.10	–	–	–	–	–
2a	153.02	150.66	125.68	138.90	13.16	–	–	–	–	–
3a	152.57	150.57	125.74	139.08	12.83	–	–	–	–	–
4a	152.14	151.21	125.71	138.87	12.91	–	–	–	–	–
5a	153.54	151.03	125.70	139.04	–	21.32, 26.13	–	–	–	–
6a	154.04	150.70	125.67	138.89	–	21.36, 26.25	–	–	–	–
7a	153.49	150.67	125.70	139.01	–	21.29, 25.95	–	–	–	–
8a	153.12	151.26	125.73	138.85	–	21.39, 25.99	–	–	–	–
1b	153.10, 153.10	151.04	125.87	139.17	13.20	–	129.90	129.74	129.41	127.90
2b	153.56, 153.45	150.55	125.97	139.30	13.26	–	129.98	129.66	129.36	127.90
3b	153.22, 153.04	150.64	125.88	139.20	12.99	–	129.62	129.55	129.52	127.97
4b	152.74,152.62	151.05	125.86	139.12	12.91	–	129.82	129.54	129.36	127.84
5b	153.95, 153.07	151.04	125.91	139.26		21.18, 26.19	129.92	129.73	129.35	127.88
6b	154.32, 153.61	150.62	125.93	139.22		21.18, 26.26	130.02	129.67	129.33	127.90
7b	154.06, 153.00	150.55	125.95	139.36		21.10, 26.02	129.59	129.55	129.50	127.95
8b	153.44, 152.71	151.06	125.89	139.12		21.11, 25.93	129.79	129.56	129.31	127.83
1c	153.58	151.04	126.10	139.43	–	–	129.80	129.67	129.55	127.93
2c	154.05	150.65	126.12	139.39	–	–	129.75	129.70	129.64	127.95
3c	153.72	150.65	126.08	139.42	–	–	129.82	129.68	129.30	128.01
4c	153.34	151.23	126.11	139.28	–	–	129.92	129.71	129.33	127.96

[a] See Ref.[6] for nomenclature.

[b] **1a**–**4a** refer to dmgH (C=N), **5a**–**8a** refer to chgH (C=N), **1c**–**4c** refer to dpgH (C=N). In **1b**–**8b**, the first value is for dpgH and the second is for dmgH or chgH.

phenyl groups. In the mixed ligand complexes (**1b**–**8b**), O–H···O appears in between the values for the pure complexes **1a**–**8a** and **1c**–**4c**. This may indicate that both wings of the equatorial ligand contribute to the overall effect and thus support the model in which it becomes more appropriate to explain the ^{1}H-NMR shifts based on the magnetic anisotropy of the entire $[Co(L)_2]^+$ unit.

2.3.1.2. *Pyridine resonance.*

1. To observe the *cis* influence of the X group, we find that the magnitude of the coordination shift ($\Delta\delta$ ^{1}H) for pyridine (α, β, γ) is more for dpgH complexes (**1c**–**4c**) as compared to the dmgH or chgH complexes (**1a**–**8a**). The same observation is made in the ^{13}C-NMR chemical shifts (discussed later) and this is similar to our earlier observation [5c]. Also, the coordination shift follows the order $\Delta\delta$ ^{1}H $Py_\gamma > \Delta\delta$ ^{1}H $Py_\beta > \Delta\delta$ ^{1}H Py_α for all complexes (Table 3).
2. The *trans* influence of the X group is monitored through the $\Delta\delta$ ^{1}H Py_α value. The change in the X group leads to a small variation in $\Delta\delta$ ^{1}H Py_α (< 0.05 ppm) and no useful information is anticipated from this small shift. However, recently, Lopez et al. [9] have listed the ligands, based on small upfield shifts (< 0.05 ppm), of $\Delta\delta$ ^{1}H Py_α in dmgH complexes. We obtain an order $Cl \approx Br > NO_2 \approx N_3$ that is similar that obtained by Lopez et al. [9]. This order is independent of the equatorial ligand and applies to all five series of complexes reported here. However, we believe that one should be careful in arriving at such a conclusion that is based on such small variations. The $\Delta\delta$ ^{13}C Py_α values, on the other hand, do show larger variation and lead to a different order of these ligands (see Section 2.3.2.1 (1)).
3. The trans influence of the X group on pyridine is correlated with the *cis* influence on the C=N bond and the methyl protons of the dmgH group in complexes **1a**–**4a** and **1b**–**4b**. Only the α protons show a clear trend and $\Delta\delta$ ^{1}H Py_α has a linear variation with ^{13}C of $C{=}N_{(oximinic)}$ and δ ^{1}H Me (dmgH). The least-squares equations obtained in the correlation are given below.[3] While plotting, we have also included the corresponding $\Delta\delta$ ^{1}H values for $RCo(L)_2Py$ (L = dmgH, chgH and dpgH) [7] and RCo(L)(L′)Py (L = dmgH or chgH; L′ = dpgH and R = Me, Et, Pr and Bu).[4] This is done in order to see if the correlations in inorganic complexes also apply to organometallic complexes.

Compounds (**1a**–**4a** and X = Me, Et, Pr, Bu)

$\delta^{13}C\ (C{=}N) = 150.02\ (13) - 8.63\ (63)\ \Delta\delta\ ^1H\ Py_\alpha$ ($r^2 = 0.96$, estimated S.D. = 0.27 ppm)

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[3] The program ORIGIN and eight data points have been used for each correlation.

[4] B.D. Gupta, Usha Tiwari, and R. Yamuna, unpublished data.

Table 4
^{13}C-NMR data (C=N) of $XCo(L_2)Py$ and $XCo(L)(L')Py$

X	dmgH	ChgH	dpgH	dpgH [a]	dmgH [a]	dpgH [a]	dhgH [a]
Cl	152.59	153.54	153.58	153.10	153.10	153.95	153.07
Br	153.02	154.04	154.05	153.56	153.45	154.32	153.61
NO_2	152.57	153.49	153.72	153.22	153.04	154.06	153.00
N_3	152.14	153.12	153.34	152.74	152.62	153.44	152.71
Me	149.89	150.04	150.90	*150.57*	*150.05*	*150.59*	*150.18*
Et	149.92	150.07	150.85	*150.57*	*150.05*	*150.59*	*150.13*
Pr	149.95	150.00	150.70	*150.64*	*149.99*	*150.68*	*150.23*
Bu	149.89	150.03	150.80	*150.63*	*150.02*	*150.66*	*150.21*

[a] Unpublished work (the values in italics) from our laboratory.

Compounds (**5a**–**8a** and X = Me, Et, Pr, Bu)
$\delta\,^{13}C\ (C{=}N) = 149.79\ (13) - 12.95\ (62)\ \Delta\delta\ ^{1}H\ Py_{\alpha}$ ($r^2 = 0.99$, estimated S.D. = 0.24 ppm)
Compounds (**1c**–**4c** and X = Me, Et, Pr, Bu)
$\delta\,^{13}C\ (C{=}N) = 153.97\ (24) - 8.86\ (98)\ \Delta\delta\ ^{1}H\ Py_{\alpha}$ ($r^2 = 0.92$, estimated S.D. = 0.44 ppm)
Compounds (**1b**–**4b** and X = Me, Et, Pr, Bu)
$\delta\,^{13}C\ (C{=}N) = 152.33\ (7) - 8.65\ (44)\ \Delta\delta\ ^{1}H\ Py_{\alpha}$ ($r^2 = 0.99$, estimated S.D. = 0.18 ppm)
Compounds (**5b**–**8b** and X = Me, Et, Pr, Bu)
$\delta\,^{13}C\ (C{=}N) = 152.68\ (9) - 9.94\ (52)\ \Delta\delta\ ^{1}H\ Py_{\alpha}$ ($r^2 = 0.99$, estimated S.D. = 0.24 ppm)
Compounds (**1a**–**4a** and X = Me, Et, Pr, Bu)
$\delta\,^{1}H\ (Me) = 2.11(1) - 0.90\ (6)\ \Delta\delta\ ^{1}H\ Py_{\alpha}$ ($r^2 = 0.99$, estimated S.D. = 0.03 ppm)
Compounds (**1b**–**4b** and X = Me, Et, Pr, Bu)
$\delta\,^{1}H\ (Me) = 2.34(8) + 0.81(5)\ \Delta\delta\ ^{1}H\ Py_{\alpha}$ ($r^2 = 0.99$, estimated S.D. = 0.02 ppm)

2.3.2. ^{13}C-NMR chemical shifts

2.3.2.1. Pyridine resonance.

1. The ^{13}C resonance of pyridine on coordination to the cobaloxime moiety shifts downfield and this coordination shift ($\Delta\delta = \delta_{complex} - \delta_{free\ py}$) follows the order $\Delta^{13}C\ Py_{\gamma} > \Delta^{13}C\ Py_{\beta} > \Delta^{13}C\ Py_{\alpha}$ for all complexes (Table 3). This order is similar to the one observed above in ^{1}H-NMR studies. This coordination shift can be taken as a measure of the *trans* influence of the axial ligand X.
2. The change in X group, within the same series seems to effect the ^{13}C values for Py_{α} but not Py_{β} and Py_{γ}. For example, $\Delta\delta\ ^{13}C\ Py_{\alpha}$ in **1a**–**8a** and **1c**–**4c** follows the order $N_3 > Cl > Br \geq NO_2$ and in **1b**–**8b** it follows $N_3 \approx Cl > Br \approx NO_2$. Notice that this order is different to what we observed based on $\Delta\delta\ ^{1}H\ Py_{\alpha}$ (see Section 2.3.1.2 (2)). However, $\Delta^{13}C\ Py_{\beta}$ and $\Delta\delta\ ^{13}C\ Py_{\gamma}$ remain similar.
3. To check the *cis* influence of the X group, we keep the same X but change the equatorial ligand (L). It is observed that the $\delta\ ^{13}C$ (Py_{β} and Py_{γ}) in dpgH complexes **1c**–**4c** move downfield by ≈ 0.4 ppm as compared to the corresponding values in dmgH or chgH complexes (**1a**–**8a**). However, there is no change in the Py_{α} value. A similar observation is made in the mixed ligand complexes where $\delta\ ^{13}C\ Py_{\beta}$ and $\delta\ ^{13}C\ Py_{\gamma}$ occur downfield compared to the pure complexes (i.e. **1b**–**4b** > **1a**–**4a** and **5b**–**8b** > **5a**–**8a**).

2.3.2.2. C=N resonance. The *cis* influence of X can be followed through the ^{13}C resonance of $C{=}N_{(oximinic)}$. This is done in two ways (Table 4):

1. On keeping the same X but changing the equatorial ligand, we observe that the $\delta\ ^{13}C$ (C=N) values in dpgH (**1c**–**4c**) and chgH (**5a**–**8a**) complexes occur downfield by ≈ 1.0 ppm as compared to the values in dmgH complexes (**1a**–**4a**).
2. The change in X group within the same series effects $\delta\ ^{13}C$ (C=N) and it follows the order $Br > Cl \approx NO_2 > N_3$ for all complexes.

2.3.2.3. Inorganic cobaloximes versus organocobaloximes. The change in X group (from Cl, Br, NO_2, N_3 to alkyl groups Me, Et, Pr, Bu), within the same series, effects $\delta\ ^{13}C$ for C=N, Py_{α}, Py_{β}, Py_{γ}. All these values occur downfield by 2–3 ppm in inorganic cobaloximes (Table 4).

Correlations: The coordination shift of pyridine ($\Delta\delta\ ^{13}C\ Py_{\alpha}$, $\Delta\delta\ ^{13}C\ Py_{\beta}$ and $\Delta\delta\ ^{13}C\ Py_{\gamma}$) with the variation in X correlate well with the $\delta\ ^{13}C$ of the $C{=}N_{oximinic}$. Also, $\Delta\delta\ ^{13}C\ Py_{\alpha}$ correlates well with the $\delta\ ^{13}C$ Me (dmgH). For all the correlations, the ^{13}C values for alkyl cobaloximes, $RCo(L_2)Py$ (L = dmgH, chgH and dpgH) [7] and $RCo(L)(L')Py$ (L = dmgH or chgH and L′ = dpgH) and R = Me, Et, Pr and Bu have also been included while plotting the values.[5]

Compounds (**1a**–**4a** and X = Me, Et, Pr, Bu)
$\delta\ ^{13}C\ (C{=}N) = 1.28\ (18)\ \Delta\delta\ ^{13}C\ Py_{\alpha} + 151.17\ (18)$ ($r^2 = 0.90$, estimated S.D. = 0.50 ppm)

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[5] B.D. Gupta, Veena Singh, R. Yamuna, and Usha Tiwari, unpublished data.

δ ^{13}C (C=N) = 3.77 (31) $\Delta\delta$ ^{13}C Py$_\beta$ + 145.07 (52) ($r^2 = 0.96$, estimated S.D. = 0.31 ppm)

δ ^{13}C (C=N) = 1.56 (11) $\Delta\delta$ ^{13}C Py$_\gamma$ + 147.76(11) ($r^2 = 0.96$, estimated S.D. = 0.28 ppm)

Compounds (**5a**–**8a** and X = Me, Et, Pr, Bu)

δ ^{13}C (C=N) = 3.00 (57) $\Delta\delta$ ^{13}C Py$_\alpha$ + 150.04 (45) ($r^2 = 0.83$, estimated S.D. = 0.86 ppm)

δ ^{13}C (C=N) = 5.01 (41) $\Delta\delta$ ^{13}C Py$_\beta$ + 143.65 ($r^2 = 0.96$, estimated S.D. = 0.40 ppm)

δ ^{13}C (C=N) = 2.08 (13) $\Delta\delta$ ^{13}C Py$_\gamma$ + 147.16 ($r^2 = 0.99$, estimated S.D. = 0.31 ppm)

Compounds (**1c**–**4c** and X = Me, Et, Pr, Bu)

δ ^{13}C (C=N) = 2.67 (60) $\Delta\delta$ ^{13}C Py$_\alpha$ + 150.53 (48) ($r^2 = 0.76$, estimated S.D. = 0.81 ppm)

δ ^{13}C (C=N) = 4.46 (46) $\Delta\delta$ ^{13}C Py$_\beta$ + 143.03(95) ($r^2 = 0.94$, estimated S.D. = 0.40 ppm)

δ ^{13}C (C=N) = 1.90 (11) $\Delta\delta$ ^{13}C Py$_\gamma$ + 146.99 (32) ($r^2 = 0.99$, estimated S.D. = 0.24 ppm)

Compounds (**1b**–**4b** and X = Me, Et, Pr, Bu)

δ ^{13}C (C=N) = 1.64 (26) $\Delta\delta$ ^{13}C Py$_\alpha$ + 151.45 (21) ($r^2 = 0.88$, estimated S.D. = 0.55 ppm)

δ ^{13}C (C=N) = 4.58 (24) $\Delta\delta$ ^{13}C Py$_\beta$ + 143.25 (45) ($r^2 = 0.99$, estimated S.D. = 0.19 ppm)

δ ^{13}C (C=N) = 1.67 (9) $\Delta\delta$ ^{13}C Py$_\gamma$ + 147.65 (23) ($r^2 = 0.99$, estimated S.D. = 0.19 ppm)

Compounds (**5b**–**8b** and X = Me, Et, Pr, Bu)

δ ^{13}C (C=N) = 3.33 (92) $\Delta\delta$ ^{13}C Py$_\alpha$ + 150.30 (72) ($r^2 = 0.74$, estimated S.D. = 0.97 ppm)

δ ^{13}C (C=N) = 5.68 (33) $\Delta\delta$ ^{13}C Py$_\beta$ + 141.47 (64) ($r^2 = 0.99$, estimated S.D. = 0.27 ppm)

δ ^{13}C (C=N) = 2.07 (10) $\Delta\delta$ ^{13}C Py$_\gamma$ + 146.98 (27) ($r^2 = 0.99$, estimated S.D. = 0.23 ppm)

Compounds (**1a**–**4a** and X = Me, Et, Pr, Bu)

δ ^{13}C Me(dmgH) = 12.37(6) + 0.579 (6) $\Delta\delta$ ^{13}C Py$_\alpha$ ($r^2 = 0.94$, estimated S.D. = 0.17 ppm)

2.3.2.4. *cis Influence of the equatorial dioxime ligand.*

In view of our recent study on the *cis* influence in organocobaloximes [5c] [7] [8] , the present results allow us to extend our earlier conclusions further. The extent of electron density on the Co(dioxime)$_2$ chelate ring for different dioximes (X and B held constant) can be understood by comparing ^{13}C chemical shifts of (C=N) of the equatorial dioxime ligand, for example for X = Cl, Br, NO$_2$, N$_3$, Me, Et, Pr, Bu and B = Py, this follows the order dpgH ≥ chgH > dmgH > gH. In this order only three values of the gH complex (X = Cl, Me, Et) are used [5c].

The *cis* influence of the dioximes, based on the coordination shift of the pyridine ring protons or carbon, has already been discussed (see Sections 2.3.1.2 and 2.3.2.1).

2.3.2.5. *Effect of one equatorial dioxime wing on the other dioxime wing.*

We have considered whether one equatorial dioxime wing has any effect on the other dioxime wing, i.e. the effect of dmgH or chgH wing on the dpgH wing. ^{1}H-NMR data show that the methyl (dmgH) resonance in **1a**–**4a** appears at 0.05 ppm upfield as compared to the value in **1b**–**4b**. Similarly, the cyclohexyl protons in **5b**–**8b** appear at 0.05 ppm downfield than in **5a**–**8a** (Table 2). A similar observation is made in ^{13}C-NMR values (Table 5). For example, the methyl (dmgH) resonance in **1b**–**4b** appears at 0.1 ppm downfield than in **1a**–**4a**. There is no change in the chemical shift of the C1 carbon in **5b**–**8b** compared to **5a**–**8a**, but the C2 carbon appears at 0.15 ppm upfield in the former as compared to the latter. The comparison of the ^{13}C values of the phenyl carbons in **1b**–**14b** with **1c**–**4c** also does not give any information since these are very close to each other.

Table 5
Coordination shift

X	**1a–4a**	**5a–8a**	**1c–4c**	**1b–4b**	**5b–8b**	**1a–4a**	**5a–8a**	**1c–4c**	**1b–4b**	**5b–8b**
	Δ ^{13}C Py$_\alpha$					*Δ ^{1}H Py$_\alpha$*				
Cl	1.17	1.21	1.22	1.20	1.22	−0.32	−0.31	0.02	−0.13	−0.15
Br	0.84	0.88	0.83	0.73	0.80	−0.32	−0.32	0.02	−0.14	−0.16
NO$_2$	0.75	0.85	0.85	0.82	0.73	−0.25	−0.27	0.06	−0.08	−0.07
N$_3$	1.39	1.44	1.41	1.23	1.24	−0.29	−0.25	0.07	−0.03	−0.10
	Δ ^{13}C Py$_\beta$					*Δ ^{1}H Py$_\beta$*				
Cl	2.00	1.97	2.37	2.14	2.18	0.21	0.22	0.31	0.23	0.25
Br	1.95	1.94	2.39	2.24	2.20	0.21	0.21	0.36	–	–
NO$_2$	2.01	1.97	2.35	2.15	2.22	0.22	0.19	0.36	0.29	0.29
N$_3$	1.98	2.00	2.38	2.13	2.16	0.18	0.23	0.34	–	0.27
	Δ ^{13}C Py$_\gamma$					*Δ ^{1}H Py$_\gamma$*				
Cl	3.18	3.15	3.54	3.28	3.37	0.30	0.31	0.40	0.34	0.35
Br	3.01	3.00	3.50	3.41	3.33	0.27	0.30	0.41	0.33	0.33
NO$_2$	3.19	3.12	3.53	3.31	3.47	0.30	0.29	0.43	0.37	0.38
N$_3$	2.98	2.96	3.39	3.23	3.23	0.27	0.32	0.42	0.35	0.36

Free pyridine [5].

Table 6
λ_{max} ($CHCl_3$) (log ε) for $XCo(L_2)Py$ and $XCo(L)(L')Py$

X	dmgH (**1a**–**4a**)	chgH (**5a**–**8a**)	dpgH (**1c**–**4c**)	dmgH/dpgH (**1b**–**4b**)	chgH/dpgH (**5b**–**8b**)
Cl	255.2 (3.70)	257.0 (4.30)	245.2 (3.75)	259.0 (4.62)	244.8 (3.78)
Br	260.4 (3.57)	260.2 (3.57)	260.0 (3.73)	263.8 (3.52)	258.2 (3.52)
NO_2	253.4 (3.51)	253.8 (4.56)	260.4 (3.77)	259.6 (3.45)	259.2 (3.63)
N_3	250.4 (3.38)	253.0 (4.20)	255.5 (3.70)	254.4 (3.50)	255.6 (3.36)

The δ ^{13}C (C=N) seems to be more sensitive to changes in the equatorial plane. The comparison of δ ^{13}C (C=N) in **1c**–**4c** with the δ ^{13}C (C=N) (dpgH) in **1b**–**4b** shows that the latter moves upfield by about 0.5 ppm whereas the δ ^{13}C (C=N) (dpgH) value moves downfield by about 0.4 ppm in case of **5b**–**8b**. This further means that there is a higher charge density on C=N (dpgH) in **1b**–**4b** and lower in **5b**–**8b** as compared to the pure complexes **1c**–**4c**. We believe that this is due to the effect of one dioxime wing on the other dioxime wing. Recently, we have made similar observation in the BnCo(dmgH)(dpgH)Py and BnCo(chgH)(dpgH)Py complexes [13]. However, we cannot comment on the origin of this effect at this stage but it might be due to the electronic effect of one wing on the other. Studies are underway to see if it is a general phenomenon and applies to other mixed dioximes complexes also.

2.3.3. UV–vis spectra

All the cobaloximes exhibit an intense Co–dioxH CT band between 245 and 260 nm in chloroform (Table 6). The λ_{max} values for any X group is independent of the equatorial ligand, i.e. for any particular X the λ_{max} value is almost same for all the equatorial ligands. We have not been able to achieve any good correlation of λ_{max} with $\Delta\delta$ ^1H Py or $\Delta\delta$ ^{13}C Py values (in all, 30 correlations were tried).

2.4. X-ray crystal structures

2.4.1. Crystal structure determination and refinements

Orange crystals were obtained by slow evaporation of the solutions of the complexes in methanol. A crystal of small size (as in Table 7) was selected and mounted on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator. The unit cell parameters were determined for 25 reflections and the cell parameters were refined by full-matrix least-squares on F^2. Intensities were collected with Mo–K_α radiation, using the multiscan technique. For compound **4b**, 4663 intensities were measured in the range of 3.21–26.00° and 4663 were considered as observed applying the condition $[I > 2\sigma(I)]$, while 6930 reflections were measured for compound **8b** in the range of 2.65–26.00°, from which 4815 were considered as observed. Empirical absorption corrections based on ψ-scan data were applied to the reflection intensities for these two compounds.

The structures were isotropically refined by full-matrix least-squares method, using the NRC 386 and the SHELXL-97 computer programs. The function minimized was $[\Sigma W(IF_oI - IF_cI)^2]^{0.5}$, where $W = [\sigma^2(F_o^2) + (0.05F_o^2)^2]$. The hydrogen atoms of the OH groups were located on difference map positions (see Table 8 for O–H–O distances). The orientations of the methyl H-atoms were also determined from difference maps and refined with an overall isotropic temperature factor. The most outstanding structural parameters of these two compounds are summarized in Table 8 and the perspective views of the molecular structures together with the atom numbering schemes are shown in Figs. 2 and 3.

2.4.2. Description of the structures

The cobalt atom is linked to four nitrogen atoms belonging to the equatorial plane. Out of this, two nitrogen atoms belong to dpgH and the other two belong to dmgH or chgh ligand. The Co-atom displays an approximately octahedral coordination. The Co-atom in compound **4b** is 0.037 (2) Å out of the mean plane of the four nitrogen atoms, while it is 0.028(2) Å in compound **8b**. The displacement is towards pyridine in both cases. Pyridine ring is practically planar and parallel to the glyoxime C–C bonds, its conformation being defined by a twist of 78.79 and 84.2° for the compounds **4b** and **8b**, respectively. The $Co–N_{6(ax)}$ and $Co–N_{5(ax)}$ bonds are approximately perpendicular (90°) to the equatorial plane as seen in the $N_{(eq)}–Co–N_{(ax)(N3)}$, $N_{(eq)}–Co–N_{(ax)(py)}$ and $N_{(ax)(N3)}–Co–N_{(ax)(py)}$ bond angles. $N_1–N_2$ and $N_3–N_4$ equatorial bond distances are shorter than $N_2–N_3$ and $N_1–N_4$ bonds. This allows the location of the oxime bridge hydrogen. The butterfly bending angle [α] for **4b** is higher (3.1°) than in **8b** (1.2°).

trans Effect: The *trans* effect is seen if we compare the $Co–N_5$ bond distance in **4b** vs **1b**, **8b** vs **5b** and also **4a** vs **1a** [14,16]. The bond is longer in N_3 complexes (**4b**, **8b** and **4a**) as compared to their chloro analogs (**1b**, **5b** and **1a**) (Table 8).

cis Effect: The *cis* effect is seen if we hold X and B and change the equatorial plane. A comparison of $Co–N_5$ in **1a** vs **1b**, **1c** and **5b**, shows that the bond is

Table 7
Crystal data and structure refinement for **4b** and **8b**

	4b	**8b**
Empirical formula	$C_{23}H_{23}CoN_8O_4$	$C_{25}H_{25}CoN_8O_4$
Formula weight	534.42	560.46
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.7107	0.7107
Crystal system	Monoclinic	Orthorhombic
Space group	*C*2/*c*	*Pna*21
Unit cell dimensions		
a (Å)	14.5786(9)	18.5677(7)
b (Å)	9.2287(10)	10.1602(11)
c (Å)	18.2450(5)	13.7534(7)
α (°)	90	90
β (°)	104.5505(6)	90
γ (°)	90	90
V (Å^3)	2376.0(3)	2594.6(3)
Z	4	4
D_{calc} (Mg m^{-3})	1.494	1.435
Absorption coefficient (mm^{-1})	0.770	0.709
F(000)	1104	1160
Crystal size (mm)	0.36 × 0.24 × 0.20	0.26 × 0.20 × 0.06
Index ranges	$-17 \le h \le 17$, $-11 \le k \le 11$, $-22 \le l \le 21$	$-22 \le h \le 22$, $-12 \le k \le 12$, $-16 \le l \le 16$
Completeness to theta = 26.00° (%)	99.6	99.9
Absorption correction (1998)	Empirical, R.A. Jacobson, Molecular Structure Corp.	Empirical, R.A. Jacobson, Molecular Structure Corp.
Max/min transmission	1.00, 0.89	1.00, 0.63
Data/restraints/parameters	4663/0/335	4815/1/345
Goodness-of-fit on F^2	1.183	1.153
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0526$, $wR_2 = 0.1210$	$R_1 = 0.0713$, $wR_2 = 0.1741$
R indices (all data)	$R_1 = 0.0775$, $wR_2 = 0.1350$	$R_1 = 0.0844$, $wR_2 = 0.1834$

longer in **1b**, **1c** and **5b**. Similarly, the Co–N_5 bond is longer in **4b** and **8b** as compared to **4a**.

Effect of one dioxime wing on the other wing: N_1–C_1/N_2-C_2 in **1b** and **5b** is shorter than in **1c**. Similarly, it is shorter in **4a** and **4b** as compared to the distance in **8b**. The N_3–C_{20}/N_4–C_{21} distance is shorter in **1a** as compared to **1b**. These changes are attributed to the effect of one dioxime wing on the other wing. These results support the ^{13}C-NMR (C=N) values as discussed above.

3. Conclusions

The results described in this paper confirm the previous findings on the dmgH complexes [9] and allow us to conclude further that the influence of the group X in *trans*-XCo(L_2)Py on the spectroscopic properties of these derivatives can be easily understood as derived from the changes on the electronic density of the Co(L_2)py$^+$ moiety. A new series of cobaloximes with mixed dioximes along with two crystals structures have been described. The spectroscopic data show that one wing of the dioxime ligand affects the other wing of the dioxime ligand. Many new correlations have been obtained.

4. Experimental

XCo(dmgH)$_2$Py (**1a**–**4a**) (X = Cl, Br, NO_2, N_3), XCo(chgH)$_2$Py (**5a** and **8a**) (X = Cl, N_3), ClCo(dpgH)$_2$-Py (**1c**), ClCo(dmgH)(dpgH)Py (**1b**) and ClCo(chgH)-

Table 8
Selected bond lengths (Å)

	4b [a]	**8b** [a]	**1b** [b]	**5b** [b]
$O_1 \cdots HO_4$	1.410(5)	1.355(4)		
O_4–HO_4	1.100(5)	1.140(5)		
O_2–HO_2	1.170(6)	1.102(4)		
$O_3 \cdots HO_2$	1.330(5)	1.400(5)		
Co–N_1	1.887(2)	1.873(5)		
Co–N_2	1.890(2)	1.893(5)		
Co–N_3	1.912(2)	1.920(5)		
Co–N_4	1.903(2)	1.919(5)		
Co–N_5	1.991(5)	1.982(4)	1.9655(23)	1.9765(23)
Co–N_6	1.963(3)	2.017(4)		
N_1–C_1	1.302(4)	1.284(8)	1.283(4)	1.290(4)
N_2–C_8	1.295(4)	1.316(8)	1.290(4)	1.295(4)
N_3–C_{20}	1.288(4)	1.302(8)	1.301(3)	1.303(4)
N_4–C_{21}	1.290(4)	1.272(9)	1.312(3)	1.299(4)

[a] Present study.

[b] From Ref. [15].

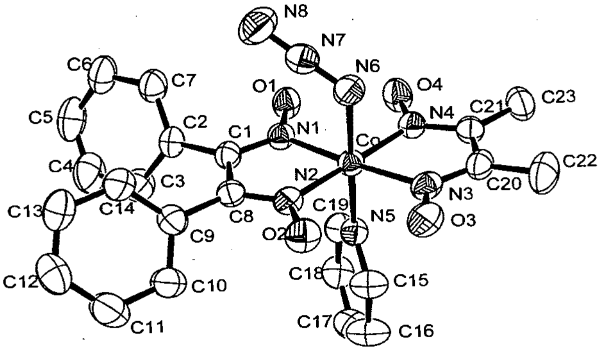

Fig. 2. ORTEP plot of structure $N_3Co(dmgH)(dpgH)Py$ (**4b**).

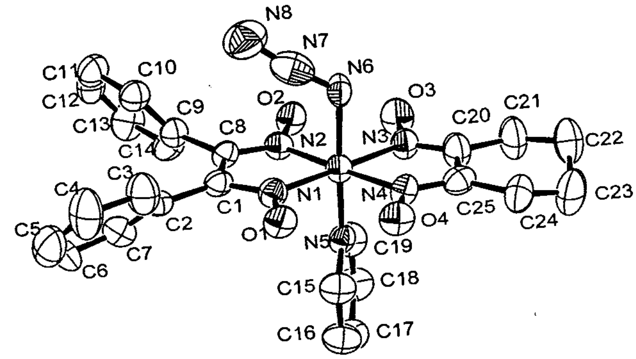

Fig. 3. ORTEP plot of structure $N_3Co(chgH)(dpgH)Py$ (**8b**).

(dpgH)Py (**5b**) are known compounds and were synthesized either by the literature procedures or by the methods detailed earlier by us [5c] [9] [10] [12] [13]. The yields vary between 55 and 83%. All other mixed dioxime complexes (**2b**–**4b** and **6b**–**8b**) were synthesized by the substitution of Cl by the other inorganic groups. Three products were formed in each reaction (Table 1). The other complexes $XCo(chgH)_2Py$ (**6a** and **7a**) ($X=$ Br, NO_2) and $XCo(dpgH)_2Py$ (**2c**–**4c**) ($X=$ Br, NO_2, N_3) were synthesized by the substitution reaction. The complexes $XCo(L)_2Py$ (**2a**–**4a**, **6a**–**8a** and **2c**–**4c**) were also obtained as side products during the preparation of mixed dioxime complexes.

^1H- and ^{13}C-NMR spectra were recorded on a JEOL JNM LA 400 PT NMR Spectrometer (at 400 MHz for ^1H and at 100 MHz for ^{13}C) in $CDCl_3$ solution with TMS as internal standard. UV–vis spectra were recorded on a Shimadzu 160A spectrometer. The elemental analysis was carried out at the Regional Sophisticated Instrumentation Center, Lucknow. The crystal structures were analyzed using an Enraf–Nonius CAD-4 diffractometer.

4.1. General procedure

A suspension of ClCo(chgH)(dpgH)Py (0.700 g, 1.261 mmol) in methanol (80 ml) was heated to reflux. To this, an aqueous solution of NaN_3 (0.098 g, 1.514 mmol in 5 ml of water) was added and the solution was further refluxed for 2 h. At this stage, the solution became clear. The solvent was evaporated to dryness. The residue was dissolved in a minimum volume of $CHCl_3$ and the products were separated by column chromatography. Three products were isolated [**4c** (0.089 g), **8a** (0.002 g), **8b** (0.340 g)] (Table 1).

4.2. Separation of products: column details

The orange-red powder containing the mixture of cobaloximes, dissolved in minimum amount of $CHCl_3$, was loaded on a silica gel (100–200 mesh) column pre-eluted with $CHCl_3$. The polarity was increased carefully with EtOAc. Three distinct bands were visible with 20% EtOAc. The first band corresponding to the dpgH complex came out completely with 20% EtOAc. The mixed ligand complex came out with 40% EtOAc mixture and the dmgH complex finally came out with 60% EtOAc mixture. Any deviation in these ratios may give contaminated products.

Note: The R_f value for certain products is same as that of chlorocobaloxime and therefore one should be careful in the column separation. Any impurity of chlorocobaloxime in the product can be detected only in the ^{13}C-NMR spectra.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 152943 and 152944 for compounds **4b** and **8b**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.com.ac.uk or www: http://www.ccdc.cam.ac.uk).

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