Cobaloximes with Dimesitylglyoxime: Synthesis, Characterization, and Spectral Correlations with the Related Cobaloximes[†]

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Alkyl and non-alkyl cobaloximes with dimesitylglyoxime have been synthesized and characterized with ^{1}H and ^{13}C NMR, UV−vis, and X-ray diffraction. The X-ray structures of MeCo(dmestgH)$_2$Py, ClCo(dmestgH)$_2$Py, and BrCo(dmestgH)$_2$Py are reported. The cis−trans influence has been studied by ^{1}H and ^{13}C NMR, UV−vis, and X-ray diffraction and is correlated with the reported cobaloximes. The spectral correlations are much better understood when both cobalt anisotropy and ring current are considered operating together. The trans influence of R/X has been monitored by the coordination shift of the Py$_\gamma$ proton/carbon, and its chemical shift is a net result of the interplay of cobalt anisotropy and the trans effect of the R/X group. Two factors have been considered to study cis influence: (a) the effect of axial ligands on the equatorial dioxime moiety and (b) the effect of dioxime on the axial ligands. It is found that C═N and Py$_\alpha$ are the most sensitive to any change in the molecule. A change in the axial R/X and dioxime moieties affects the C═N resonance, whereas Py$_\alpha$ is sensitive to the change in R/X (trans effect) and the ring current of the dioxime (cis influence). A good correlation between δ(^{13}C, C═N) and $\Delta\delta$(^{1}H, Py$_\alpha$) suggests the presence of ring current throughout the Co(dioxime) metallabicycle, and the negative slope indicates that they are effected in opposite directions. It is found that dmestgH complexes have the maximum cis influence among all the reported cobaloximes. A cyclic voltammetry study for both alkyl and non-alkyl cobaloximes is reported. The reduction from Co(III) to Co(II) and from Co(II) to Co(I) is found to be more difficult in ClCo(dmestgH)$_2$Py as compared to the other chlorocobaloximes (gH, dmgH, dpgH).

Introduction

The chemistry and molecular structure of bis(dimethylglyoximato)cobalt(III) complexes, trivially known as cobaloximes,[1] have been of great interest to chemists for the past four decades for two reasons. First, the coordination chemistry of these complexes is far-reaching, with almost unlimited possibilities for substituents in the axial position and variation in the equatorial ligands.[2] Second, many organometallic cobaloxime derivatives have been used as model compounds for the study of vitamin B$_{12}$ coenzyme.[2]

Many different approaches to qualitatively rationalize the trends in structure, NMR, and thermodynamic and kinetic properties as a function of steric and electronic effects of the axial ligands in cobaloximes have been reported.[3] The recently available crystallographic data on cobalamins suggests that the structural effects of changes in R are similar to those found in cobaloximes and sometimes can be related to their chemical behavior.[4] The studies on cobaloximes have furnished some insight into the factors that affect homolysis of the Co−C bond and have allowed in-depth analysis of the variation in the geometry of the R−Co−B fragment (in terms of electronic and steric properties of R and B).[2,3f,g,h] Most of the studies in the recent past have described the spectral and structural properties of cobaloximes. Despite this wealth of information a great deal of interest has been devoted to the study of correlations between the NMR spectral data and mo-

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(1) Cobaloximes have the general formula RCo(L)$_2$B, where R is an organic group σ-bonded to cobalt, B is an axial base trans to the organic group, and L is a monoanionic dioxime ligand (e.g. glyoxime (gH), dimethylglyoxime (dmgH), 1,2-cyclohexanedione dioxime (chgH), diphenyl glyoxime (dpgH), and dimesitylglyoxime (dmestgH)).

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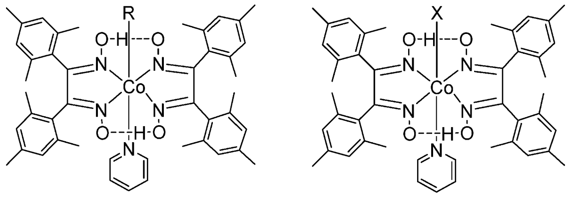
lecular structures of these complexes.[2,5] The driving force behind this work is to obtain a clear relationship between all the properties. This would help to systematize the large amount of chemical information currently available, and it might lead to a successful design of novel cobaloximes with desired properties. Several studies with this aim have appeared in the literature.[3,6,7] For instance, the reported trends in ^{1}H NMR chemical shifts in cobaloximes $(R/X)Co(dmgH)_2B$ have been related to the mutual cis and trans influence of the axial ligands.[3,6] The study also includes the multilinear correlation of ^{1}H NMR chemical shifts of B with the Co−dioxime charge-transfer band.[6] These spectral correlations initially were interpreted by Marzilli et al. on the basis of cobalt anisotropy,[3d,8] but recently López et al. invoked the ring current formalism.[6] As per this model, ring current resulting from the 12-π-delocalized-electron system of cobaloximes (8 electrons from C=N and 4 from Co) would affect the nuclei in different ways, depending upon their relative position to the metallabicycle, shielding those on the top and deshielding those at the sides of the ring. Most of the information has come from the study of cobaloximes with dmgH as the equatorial ligand, and studies involving other dioximes such as gH,[9a,b] chgH,[9c] and dpgH[9d] or mixed dioximes[9e,f] are few. Most of the correlations have been derived from ^{1}H NMR studies, and ^{13}C NMR studies have been done on a few complexes only. Efforts to correlate ^{1}H and ^{13}C NMR resonances were made, but the results were rather poor.[10]

Each of the two models, cobalt anisotropy and ring current, has some shortcomings and do not explain the existing data properly when used in isolation from each other.

We have, therefore, undertaken this study on $(R/X)Co(dmestgH)_2Py$ (see Chart 1). All of the compounds except for **6** are new. The X-ray structures of **1**, **6**, and **7** are reported. The cis−trans influence has been studied by ^{1}H and ^{13}C NMR, UV−vis, and X-ray. The aim of the present study is (a) to rationalize/modify the existing models, (b) to see if ^{13}C gives similar or better information than ^{1}H NMR and if there is any correlation in ^{1}H and ^{13}C resonances, (c) to verify if the trends obtained in dmgH complexes can be extended to other dioxime complexes, and (d) to see if X-ray gives any information on the cis−trans influence.

Chart 1



$RCo(dmestgH)_2Py$ $XCo(dmestgH)_2Py$

R= Me, Et, Pr, Bu, ^{iso}Pr (**1-5**) X = Cl, Br, NO_2, N_3 (**6-9**)

Experimental Section

Glyoxime and alkyl halides were purchased from Aldrich Chemical Co. and were used as received. Silica gel (100−200 mesh) and distilled solvents were used in all chromatographic separations. Dichloroglyoxime, dimesitylglyoxime, chlorocobaloxime[24] were synthesized according to the literature procedure.[11]

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM LAMBDA 400 FT NMR instrument (at 400 MHz for ^{1}H and at 100 MHz for ^{13}C) in $CDCl_3$ solution with TMS as internal standard. NMR data are reported in ppm. UV−vis spectra were recorded on a JASCO V570 spectrophotometer in dry chloroform at 298 K. Elemental analysis was carried out at the Regional Sophisticated Instrumentation Center, Lucknow, and at IIT Kanpur. A Julabo UC-20 low-temperature refrigerated circulator was used to maintain the desired temperature. Cyclic voltammetry measurements were carried out using a BAS Epsilon electrochemical workstation with a platinum working electrode, a Ag/AgCl reference electrode (3 M KCl), and a platinum-wire counter electrode. All the measurements were performed in 0.1 M $^{n}Bu_4NPF_6$ in dichloromethane (dry), at a concentration of 1 mM of each complex. In addition, in a separate series of experiments, an internal reference system (ferrocene/ferrocenium ion) was used. Under the conditions used, the reversible Fc/Fc^{+} potential occurred at 0.51 V vs the Ag/AgCl electrode.

X-ray Structural Determination and Refinement. Orange crystals were obtained by slow evaporation of the solutions of **1**, **6**, and **7** in dichloromethane/acetonitrile. Single-crystal X-ray data were collected at room temperature for **1** and **6** and at 100 K for **7** on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from ref 12a. The data integration and reduction were processed with SAINT[13] software. An empirical absorption correction was applied to the collected reflections with SADABS[14] using XPREP.[15] The structure was solved by direct methods using SHELXTL[16] and was refined on F^2 by the full-matrix least-squares technique using the SHELXL-97[12b] program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atom positional and thermal parameters were not refined but were included in the structure factor calculations. The crystal data for the three structures are collected in Table 1.

$RCo(dmestgH)_2Py$ (1−5). These compounds were synthesized by the general procedure detailed earlier for the synthesis

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Table 1. Crystal Data and Structure Refinement Details for 1, 6, and 7

	[MeCo(dmestgH)$_2$Py]·CH$_2$Cl$_2$	[ClCo(dmestgH)$_2$Py]·CH$_3$CN	[BrCo(dmestgH)$_2$Py]·CH$_2$Cl$_2$
empirical formula	$C_{94}H_{112}Cl_4Co_2N_{10}O_8$	$C_{94}H_{108}Cl_2Co_2N_{12}O_8$	$C_{92}H_{106}Br_2Cl_4Co_2N_{10}O_8$
formula wt	1769.60	1722.68	1895.35
temp (K)	293(2)	293(2)	100(2)
radiation, λ (Å)	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73
cryst syst	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
unit cell dimens			
a (Å)	27.939(15)	27.776(8)	27.579(17)
b (Å)	9.226(5)	9.071(2)	9.116(5)
c (Å)	37.232(2)	36.827(10)	36.610(2)
α (deg)	90.000(0)	90.000(0)	90.000(0)
β (deg)	108.006(17)	108.043(6)	108.493(2)
γ (deg)	90.000(0)	90.000(0)	90.000(0)
V (Å^3)	9127(5)	8822(5)	8729(7)
Z	4	4	4
ρ(calcd) (Mg/m^3)	1.288	1.297	1.445
μ (mm^{-1})	0.541	0.500	1.481
F(000)	3728	3632	3936
cryst size (mm^3)	0.22 × 0.15 × 0.13	0.25 × 0.17 × 0.14	0.26 × 0.18 × 0.15
index ranges	$-37 \le h \le 31$ $-12 \le k \le 12$, $-28 \le l \le 49$	$-26 \le h \le 37$ $-12 \le k \le 11$ $-49 \le l \le 46$	$-36 \le h \le 36$ $-12 \le k \le 12$ $-48 \le l \le 26$
no. of rflns collected	29 710	28 547	28 518
no. of indep rflns	11 254	10 846	10 790
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
GOF on F^2	1.017	1.003	1.053
final R indices ($I > 2\sigma(I)$)	R1 = 0.0689 wR2 = 0.1621	R1 = 0.0837 wR2 = 0.1683	R1 = 0.0727 wR2 = 0.2119
R indices (all data)	R1 = 0.1014 wR2 = 0.1806	R1 = 0.1634 wR2 = 0.2004	R1 = 0.0935 wR2 = 0.2268
no. of data/restraints/params	11 254/0/545	10 846/0533	10 790/0/544

of RCo(dioxime)$_2$Py[7] and involved the reaction of cobaloxime(I) with organic halide. In a typical procedure, N_2 gas was bubbled for 10 min with stirring through a solution of ClCo(dmestgH)$_2$Py (0.100 g, 0.120 mmol) in about 50 mL of ethanol at −10 °C. The solution turned blue after the addition of a few drops of aqueous NaOH followed by a solution of sodium borohydride (0.05 g, 1.2 mmol) in water. The solution immediately turned orange on the addition of methyl iodide (0.07 g, 0.50 mmol) in ethanol (1 mL). Stirring was continued at 0 °C for 1 h. The reaction mixture was poured into 20 mL of water containing a few drops of pyridine. The resulting orange precipitate was filtered, washed with water, and dried. The product was purified on a silica gel column using dichloromethane/petroleum ether (5/1) followed by dichloromethane. Yield: 0.087 g, 90%.

XCo(dmestgH)$_2$Py (6−9). These compounds were synthesized by the substitution of the chloride group in ClCo(dmestgH)$_2$Py (**6**) by another inorganic group X$^-$.[9a,17] In a typical experiment, a solution of sodium azide (0.079 g, 1.22 mmol) in 1 mL of water was added to a refluxing suspension of ClCo(dmestgH)$_2$Py (0.200 g, 0.24 mmol) in 30 mL of methanol. The reaction mixture was further refluxed for 4 h. The solution was evaporated to dryness. The solid was dissolved in a minimum volume of CHCl$_3$ and loaded on the silica gel column. The compound N$_3$Co(dmestgH)$_2$Py (**9**) was eluted out with a mixture of 5−10% CHCl$_3$ in ethyl acetate. Yield: (0.145 g, 72%).

Results and Discussion

Synthesis. We have synthesized two series of complexes, RCo(dmestgH)$_2$Py (**1**−**5**) and XCo(dmestgH)$_2$Py (**6**−**9**). All of the complexes except for **6** are new. Elemental analysis data for **1**−**9** are given in Table 2.

ClCo(dmestgH)$_2$Py was synthesized according to the procedure by Busch et al.[11] The preparation requires the addition of Et$_3$N. However, when we tried to prepare it using the conventional procedure[9c,e] reported for ClCo(dioxime)$_2$Py (dioxime = gH, dmgH, dpgH) we could get a maximum yield of 10%. The side product was EPR active and looked like the radical Co−O$_2$•.[11,18] No attempt was made to analyze this.

Table 2. Elemental Analysis Data for 1−9

		% found (calcd)		
no.	formula	C	H	N
1	$C_{46}H_{54}CoN_5O_4$	69.14 (69.07)	6.78 (6.80)	8.79 (8.76)
2	$C_{47}H_{56}CoN_5O_4$	69.35 (69.36)	6.90 (6.93)	8.64 (8.60)
3	$C_{48}H_{58}CoN_5O_4$	69.67 (69.63)	7.02 (7.06)	8.50 (8.46)
4	$C_{49}H_{60}CoN_5O_4$	69.86 (69.90)	7.16 (7.18)	8.29 (8.32)
5	$C_{48}H_{58}CoN_5O_4$	69.60 (69.63)	7.01 (7.06)	8.42 (8.46)
6	$C_{45}H_{51}ClCoN_5O_4$	65.91 (65.89)	6.23 (6.27)	8.50 (8.54)
7	$C_{45}H_{51}BrCoN_5O_4$	62.46 (62.50)	5.90 (5.94)	8.08 (8.10)
8	$C_{45}H_{51}CoN_6O_6$	65.00 (65.05)	6.18 (6.19)	10.08 (10.11)
9	$C_{45}H_{51}CoN_8O_4$	65.33 (65.36)	6.18 (6.22)	13.58 (13.55)

Inorganic cobaloximes, XCo(dioxime)$_2$Py (X = Br, N$_3$, NO$_2$) have been well described in the literature.[9a] In general, two methods have been used for their preparation (a) by aerial oxidation of the stoichiometric mixture of reactants[9b] and (b) by substitution of chloride in chlorocobaloxime by another nucleophile.[9a,17] We have used method b for the synthesis of XCo(dmestgH)$_2$Py.

The synthesis of RCo(dmestgH)$_2$Py was accomplished by a slight modification of the well-established procedure for RCo(dioxime)$_2$Py complexes. The cobaloxime(I) anion was generated in situ by NaBH$_4$ reduction of the preformed chlorocobaloxime followed by oxidative alkylation.[2e] We found that ethanol was a better solvent than methanol. A large excess of ethanol and a 10-fold excess of NaBH$_4$ was essential; otherwise, the yield was poor and the starting complex ClCo(dmestgH)$_2$Py was recovered.

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Table 3. ^{1}H NMR Data for 1−9 in $CDCl_3$[a]

	Py				mesityl group				
no.	α (d)	*β* (t)	*γ* (t)	O−H···O	Me (2)	Me (4 and 6)	aromatic(s)	Co−CH_2	rest of alkyl chain
1	8.99	7.41	7.88	18.94	1.51	2.16 2.19	6.61 6.73	1.45	
2	8.95	7.40	7.86	18.75	1.45	2.16 2.22	6.60 6.73	2.42	0.94 (t)
3	8.95	7.40	7.86	18.77	1.45	2.17 2.20	6.60 6.73	2.30	0.95 (t), 1.56
4	8.96	7.40	7.86	18.76	1.45	2.17 2.21	6.61 6.73	2.32	0.91 (t), 1.40 (q), 1.62 (m)
5	8.98	7.36	7.82	18.68	1.45	2.15 2.27	6.59 6.73	2.66	1.02 (d)
6	8.66	7.34	7.87	18.82	1.55	2.19 2.25	6.65 6.78		
7	8.66	7.34	7.87	18.83	1.54	2.19 2.29	6.64 6.78		
8	8.68	7.39	7.91	18.51	1.49	2.14 2.19	6.64 6.78		
9	8.66	7.36	7.88	18.62	1.51	2.20 2.26	6.65 6.80		

[a] ClCo(dmestgH)$_2$(morpholine): mesityl group (Me) 2.30, 2.22, 2.24 ppm, aromatic 6.79, 6.81 ppm; morpholine 3.82 (d, J = 10.8 Hz), 3.31 (t, J = 13.2 Hz), 2.58 ppm (q, J = 10.4 Hz).

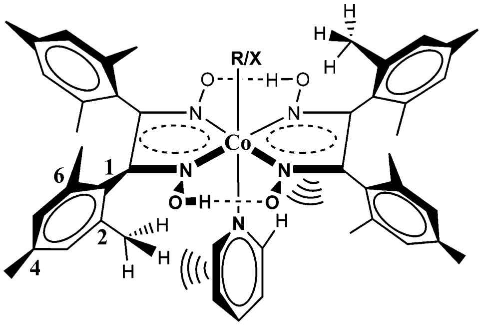
Table 4. ^{13}C NMR Data for 1−9 in $CDCl_3$[a]

		Py						
no.	C=N	α	*β*	*γ*	mesityl (Me)	Co−CH_2	aromatic	others
1	152.33	151.03	124.94	138.33	20.00, 20.43, 21.04	27.72	126.62, 128.28, 128.58, 137.00, 137.83, 138.69	
2	152.46	151.16	125.00	138.27	19.93, 20.34, 21.03	26.50	126.62, 128.32, 128.62, 137.11, 137.82, 138.70	16.64
3	152.45	151.12	124.99	138.25	19.90, 20.21, 21.02	37.91	126.62, 128.31, 128.63, 137.12, 137.77, 138.70	28.45, 22.62
4	152.43	151.13	124.95	138.21	21.00, 20.25, 19.92	33.40	126.63, 128.30, 128.61, 137.12, 137.77, 138.66	32.61, 24.03, 13.95
5	153.02	151.26	124.82	*b*	20.40, 20.89, 20.95	42.25	126.63, 128.40, 128.67, 137.26, 138.12,138.62, 137.84	27.37
6	155.57	152.06	125.26	*b*	19.94, 20.28, 21.10		126.11, 128.10, 128.87, 136.60, 139.60, 139.12, 139.26	
7	156.00	151.74	125.24	*b*	20.03, 20.45, 21.06		126.17, 128.09, 128.90, 139.55, 136.68, 139.23, 139.28	
8	155.75	151.56	125.49	*b*	19.94, 20.27, 21.08		125.83, 128.14, 128.94, 136.54, 138.63, 139.49, 138.90	
9	155.52	152.05	125.39	*b*	19.75, 19.92, 21.07		126.00, 128.16, 128.86, 136.57, 138.61, 139.06, 139.40	

[a] ClCo(dmestgH)$_2$(morpholine): C=N 155.99 ppm; mesityl group (Me) 20.37, 21.08, 21.27 ppm; aromatic 125.89, 128.32, 129.28, 136.20, 139.51, 139.57 ppm; morpholine 49.85, 68.30 ppm. [b] Merge with aromatic carbons.

Spectroscopy: Characterization of the Complexes. The free ligand dmestgH$_2$ has been fully characterized by Busch et al. ^{13}C NMR values (but not ^{1}H) for ClCo(dmestgH)$_2$Py were reported but not assigned.[11] There is a drastic change in ^{1}H NMR when dmestgH$_2$ is coordinated to cobalt in complexes **1**−**9**; for example, both of the *o*-methyl groups in uncoordinated dmestgH$_2$ are equivalent and appear at 2.14 ppm, whereas these are nonequivalent in **1**−**9**. This is due to restricted rotation around the C−C bond between oximinic carbon and phenyl carbon. One of the three methyl groups of mesityl group at 2-position is close to axial pyridine ring (see X-ray details later) and is highly shielded by the ring current and appears at around 1.50 ppm. This is confirmed by ^{1}H NMR spectrum of ClCo(dmestgH)$_2$(morpholine). Here, morpholine lacks ring current and hence no shielding to the methyl at 2-position occurs and thus it appears close to the other methyl at 4- and 6-positions (see footnote in Table 3). The chemical shift of the methyl group at the 6-position is affected by the nature of the axial R/X group. However, the shift is not that large. The methyl at the 4-position is not affected at all and remains constant. Because of the restricted rotation of the mesityl group, two aromatic hydrogens of the mesityl group also are nonequivalent in **1**−**9** and occur downfield compared to the free ligand.

Chart 2. Numbering Scheme and Ring Current Effect of the Metallabicycle and Pyridine Ring



The ^{1}H NMR spectra of the other complexes are easily assigned on the basis of the chemical shifts. The signals are assigned according to their relative intensities and are consistent with the related dioxime compounds previously described.[7] On the other hand, ^{13}C chemical shifts have been assigned for only a few cobaloximes until recently. Further comments are, therefore, warranted on these assignments.

For RCo(dmestgH)$_2$Py (**1**−**5**), apart from the axial organic group, five sets of ^{13}C resonances for Py$_\alpha$, Py$_\beta$ Py$_\gamma$, C=N, and the mesityl group are observed. These are assigned on the basis of chemical shifts. Py$_\alpha$ and C=N appear close together and are assigned by DEPT.

All of the ^{1}H and ^{13}C NMR values are given in Tables 3 and 4, respectively, and the numbering scheme is given in Chart 2. All of these complexes exist as six-coordinate species in $CDCl_3$ (the solvent used for NMR), as the cobalt-bound CH_3 as well as dmestgH protons do not shift even on the addition of a large excess of pyridine to the NMR sample.

Solubility. The orange solid compounds **1**−**9** are highly soluble in common organic solvents such as dichloromethane, chloroform, and THF and are sparingly soluble/insoluble in methanol, ethanol, acetonitrile, and ether.

Cis and Trans Influence. A cis and trans influence study includes the investigation of all possible steric and electronic changes detectable in the cis and trans ligands. Cobaloximes have become the ideal systems to study these effects in octahedral complexes. In general, either the axial ligand R/X or base B is varied and changes in the cis equatorial dioxime moiety are observed or the axial ligands are kept constant and the equatorial dioxime moiety is varied and changes in the axial ligands are monitored spectroscopically.

We have considered the López model with some modification.[6a] Three factors simultaneously acting on a particular atom to determine the NMR shift of the coordinated ligand from the free ligand are (a) cobalt anisotropy[25] (leads to deshielding of all the ligand atoms through the σ backbone and it decreases with the distance from the metal), (b) the long-range effect of magnetic anisotropy such as ring current arising from the metallabicycle, the axial ligand pyridine, or the phenyl ring of the mesityl group, and (c) metal to ligand back-bonding, which may alter the ring current and/or the cobalt anisotropy.

^{1}H and ^{13}C NMR studies of RCo(dioxime)$_2$Py (dioxime = gH, dmgH, chgH, dpgH) have shown that O−H···O, Py$_\alpha$, and C=N$_{\text{oximinic}}$ are most affected followed by Py$_\gamma$.

The chemical shifts for O−H···O resonances in **1**−**9** are given in Table 3. A comparison of O−H···O values in **1**−**4** with those in RCo(dioxime)$_2$Py shows a high downfield shift in **1**−**4**, nearly 0.5−0.7 ppm as compared to the corresponding dmgH complexes and 1.1−1.2 ppm as compared to gH complexes. However, the values are close to those of the dpgH complexes. The O−H···O resonance follows the order dmestgH > dpgH > dmgH > gH > chgH. This is due to the cis influence of dioxime on O−H···O. A similar order is observed in **6**−**9**. The value, however, remains almost constant within the same series in all the complexes. Surprisingly, the replacement of axial organic R by an inorganic group X does not lead to any significant shift in O−H···O resonance (compare the values for **1**−**4** with those for **6**−**9**).

Trans Influence. (a) ^{1}H Chemical Shift. López and Marzilli have monitored the trans influence of the axial R/X group through the coordination shift of the α-proton of the axial base ligand in (R/X)Co(dmgH)$_2$B (B = 4-^{t}BuPy, 3,5-lutidine, imidazole, 2,6-dimethylpyrazine).[3a,d,6,8,10a] They have mentioned that the variation observed in the remaining protons of the base are small and consequently less affected by the nature of the trans R/X ligand, in agreement with their larger distance to the metallabicycle. Also, a different situation appears for the analogous dpgH complexes, where the axial ligand signals are not very sensitive to coordination. This was explained by taking into account the presence of phenylic rings in the neighborhood of the axial ligand, producing deshielding of its nuclei.[6b] We disagree with their proposal and believe that the trans influence should, in fact, be monitored through the coordination shift ($\Delta\delta = \delta_{\text{complexes}} - \delta_{\text{free base}}$) of the γ-proton only, since the chemical shift of the α-proton includes not only the trans influence of R/X but also the cis influence of the dioxime moiety. In the study by López and Marzilli, either the base did not have a γ-proton or the signal was masked by the solvent peaks and hence was not considered for study. Besides, the phenyl ring in dpgH complexes is more than 5 Å away from the Py$_\alpha$ proton and hence should not affect the chemical shift of Py$_\alpha$. Since ^{1}H NMR operates in a through-bond as well as through-space manner but ^{13}C NMR operates mainly through-bond, any shift in ^{13}C δ(Py$_\alpha$) will be due to cobalt anisotropy only, whereas the change in ^{1}H δ(Py$_\alpha$) is affected both by cobalt anisotropy as well as by ring current of the dioxime. Both operate in opposite directions. López and Marzilli made no attempt to rationalize this by ^{13}C NMR study.

The chemical shift of Py$_\gamma$ proton is a net result of the interplay of cobalt anisotropy and the trans effect of the R/X group. In the present study the Py$_\gamma$ proton resonance on coordination to the cobaloximes moiety in **1**−**5** shifts downfield, and the downfield shift is much larger in the dpgH and dmestgH complexes (about 0.45 ppm) than in the corresponding dmgH and chgH complexes (about 0.25 ppm). The large cobalt anisotropy in dpgH or dmestgH complexes leads to more electron withdrawal from pyridine and causes deshielding of the γ-proton.

(b) ^{13}C Chemical Shift. ^{13}C δ(Py$_\gamma$) shifts downfield on coordination to cobalt, and the downfield shift is much larger in dpgH and dmestgH complexes as compared to dmgH and chgH complexes. This is similar to ^{1}H NMR information.

^{1}H and ^{13}C NMR studies, however, give conflicting information on the inorganic cobaloximes. For example, there is no significant shift in the ^{1}H δ(Py$_\gamma$) resonance whether the axial ligand is R or X (compare **1**−**5** with **6**−**9**). This may mean that the cobalt anisotropy is almost same for both R and X. However, the ^{13}C δ(Py$_\gamma$) resonance occurs more downfield (by about 0.7 ppm) in inorganic cobaloximes as compared to the organocobaloximes (compare **6**−**9** with **1**−**5**) and this difference is much larger (about 1.7 ppm) in dmgH and chgH complexes. This is an expected trend, since the cobalt anisotropy is larger for X than for R.

Cis Influence. To study cis influence, we have considered (a) the effect of axial ligands on the equatorial dioxime moiety and (b) the effect of dioxime on the axial ligands. It is found that C=N and Py$_\alpha$ are most sensitive to any change in the molecule. A change in the axial R/X and dioxime moiety will affect the C=N resonance, whereas Py$_\alpha$ is sensitive to the change in R/X (trans effect) and the ring current of the dioxime (cis influence).

C=N. The extent of electron density (i.e. total effect of cobalt anisotropy and ring current) on Co(dioxime)$_2$ for different dioximes (keeping R/X constant) can be understood by comparing $\Delta\delta$(^{13}C, C=N)[26] in R/XCo(dioximes)$_2$Py. We find that the δ(^{13}C, C=N) resonance in **1**−**9** occurs significantly downfield as compared to the values in other dioximes (about 3−4 ppm compared to dmgH and about 5−6 ppm compared to gH complexes). The order based on the upfield shift value of

$\Delta\delta$(^{13}C, C=N) is gH > dmgH > dpgH > chgH > dmestgH. This means the charge density on C=N in dmestgH complexes is much lower as compared to cobaloximes with other dioximes. This is surprising. This can be rationalized by taking into account the higher anisotropy in the dpgH and dmestgH complexes. The variation in R/X group also affects δ(^{13}C, C=N). For example, it occurs highly upfield (about 2.4 ppm) in **1**−**5** and downfield in **6**−**9** (0.7−1.2 ppm) as compared to the value in uncoordinated demstgH$_2$. This is similar to our earlier findings in other dioxime complexes. However, δ(^{13}C, C=N) always occurs upfield from the signal for the free ligand in the corresponding (R/X)Co(dioximes)$_2$Py (dioxime = gH, dmgH, chgH, dpgH) complexes.[9]

The charge density on C=N should also affect the O−H···O resonance. The higher the charge density on C=N, the stronger the hydrogen bond, and so a more upfield shift of O−H···O would be expected. This is what has been observed (see above).

Py$_\alpha$. A comparison of $\Delta\delta$(^{1}H, Py$_\alpha$) in RCo(dioxime)$_2$Py or XCo(dioxime)$_2$Py (R = Me, Et, Pr, Bu; X = Cl, Br, NO$_2$, N$_3$; dioxime = gH, dpgH, chgH, dpgH, dmestgH) shows that it occurs downfield (by 0.4 ppm) in dpgH and dmestgH complexes as compared to the signals for the other dioximes. This is as expected, on the basis of the higher cobalt anisotropy in the latter, but it cannot be due to the presence of a phenyl ring in dpgH complexes, as suggested by López.

The Py$_\alpha$ proton is close to O−H···O and therefore should be affected by the strength of this bond. The stronger the hydrogen bond, the more upfield the Py$_\alpha$ resonance. This is what is seen here; for example, for MeCo(dmgH)$_2$Py Py$_\alpha$ is at 8.25 ppm and O−H···O at 18.21 ppm and for MeCo(dmestgH)$_2$Py Py$_\alpha$ is at 8.66 ppm and O−H···O at 18.94 ppm.

However, a reverse and unexpected trend is noticed when we compare the coordination shift value, $\Delta\delta$(^{1}H, Py$_\alpha$), of RCo(dioxime)$_2$Py with that of XCo(dioxime)$_2$Py. This consistently occurs upfield (by 0.4 ppm) in the latter. The ring current gives conflicting information; for instance, cobalt d$_{xz}$ and d$_{yz}$ orbitals are involved simultaneously in the Co→axial ligand back-bonding and in the π system of the cobaloxime moiety. An increase in back-bonding would produce a depopulation of these orbitals and consequently decrease the ring current. Since back-bonding is higher in Co→X, it should lead to deshielding of Py$_\alpha$. On the other hand, the Co−N$_{Py}$ bond is shorter in XCo(dioxime)$_2$Py than in RCo(dioxime)$_2$Py, and so Py$_\alpha$ is closer to the metallabicycle and hence should be shifted upfield.

Can this be due to cobalt anisotropy? One would expect Py$_\alpha$ to appear more downfield in XCo(dioxime)$_2$Py than in RCo(dioxime)$_2$Py because of greater cobalt anisotropy in the former.

The recent ^{15}N NMR studies have shown that the cobalt anisotropy works differently in XCo(dmgH)$_2$Py and RCo(dmgH)$_2$Py complexes.[19a] Also, the ab initio calculations in ClCo(dmgH)$_2$Py and MeCo(dmgH)$_2$Py have shown that the charge densities on cobalt and pyridine nitrogens are different in these two compounds (see Supporting Information). For example, MeCo(dmgH)$_2$Py has partial positive charge on cobalt, whereas cobalt in ClCo(dmgH)$_2$Py has a partial negative charge. The pyridine N has partial negative charge and Py$_\alpha$ has positive charge in MeCo(dmgH)$_2$Py, and in contrast, the reverse is true in ClCo(dmgH)$_2$Py (Supporting Information).

Earlier, Brown and LaRossa have correlated the NQR (nuclear quadrupole resonance) and NMR results in cobaloximes based on the electron field gradient (efg) model.[19b] In the simplest possible approach to the NQR studies, they have considered two types of efg: (a) the combined effect of both axial ligands and (b) the effect of the planar equatorial dioxime ligand. They found that, for methylcobaloximes, the average donor strengths of the methyl group and axial base pyridine put together are greater than the donor strength of nitrogen in the planar ligand system, so that the quadruple coupling constant is negative. In the halocobaloximes, on the other hand, the average donor strength of the axial ligands is less than that of the nitrogens in the planar ligand.

In view of the above discussion it is clear that the chemical shifts in Py$_\alpha$ behave differently in organic and inorganic cobaloximes.

Correlations. There is a good correlation between δ(^{13}C, C=N) and $\Delta\delta$(^{1}H, Py$_\alpha$) for all of the nine complexes (**1**−**9**). This suggests the presence of ring current throughout the Co(dioxime) metallabicycle, but the negative slope indicates that they are effected in opposite directions. In contrast, the relatively poor correlation and the positive sign in δ(^{13}C, C=N) with $\Delta\delta$(^{13}C, Py$_\alpha$) indicates that the ring current has little effect.

$$\delta(^{13}\mathrm{C}, \mathrm{C{=}N}) = 156.68(27) - 10.43(72)\,(\Delta\delta(^{1}\mathrm{H}, \mathrm{Py}_\alpha))$$

$$r^2 = 0.97, \text{ esd} = 0.33$$

$$\delta(^{13}\mathrm{C}, \mathrm{C{=}N}) = 147.83(112) + 3.74(67)\,(\Delta\delta(^{13}\mathrm{C}, \mathrm{Py}_\alpha))$$

$$r^2 = 0.82, \text{ esd} = 0.77$$

A good correlation between $\Delta\delta$(^{13}C, C=N dmestgH) and the values for other dioximes is seen, showing that the total field effect of dmestgH complexes is similar to that of the cobaloximes with other dioximes.

$$\Delta\delta(^{13}\mathrm{C}, \mathrm{C{=}N\ dmestgH}) = 2.70(12) + 1.14(3)\,(\Delta\delta(^{13}\mathrm{C}, \mathrm{C{=}N\ dpgH}))$$

$$r^2 = 0.99, \text{ esd} = 0.14$$

$$\Delta\delta(^{13}\mathrm{C}, \mathrm{C{=}N\ dmestgH}) = 6.01(74) + 1.6(17)\,(\Delta\delta(^{13}\mathrm{C}, \mathrm{C{=}N\ dmgH}))$$

$$r^2 = 0.94, \text{ esd} = 0.48$$

$$\Delta\delta(^{13}\mathrm{C}, \mathrm{C{=}N\ dmestgH}) = 6.90(57) + 1.24(9)\,(\Delta\delta(^{13}\mathrm{C}, \mathrm{C{=}N\ gH}))$$

$$r^2 = 0.97, \text{ esd} = 0.34$$

UV−Vis Studies. Solid-state properties were studied from the crystal structure of the dimesitylcobaloxime. The solution behavior of these complexes, though well characterized from NMR, also gets support from the

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Table 5. CV Data for 1, 4, and 6 in DCM with TBAPF$_6$ at 0.2 mV/s at 25 °C

	Co(III)/Co(II)			Co(II)/Co(I)			Co(IV)/Co(III)					
no.	E_{pc} (V, vs Ag/AgCl)	E_{pc} (V, vs Fc/Fc$^+$)	i_{pc} (μA)	E_{pc} (V, vs Ag/AgCl)	$E_{1/2}$ (V, vs Fc/Fc$^+$)	i_{pc} (μA)	$E_{1/2}$ (V, vs Ag/AgCl)	$E_{1/2}$ (V, vs Fc/Fc$^+$)	ΔE_p (mV)	i_{pc} (μA)	i_{pa} (μA)	i_{pa}/i_{pc}
1	−0.57	−1.08		−1.01	−1.51	15	1.06	0.55	120	148	154	1.04
4	−0.73	−1.24		−1.01	−1.51	23	1.03	0.52	130	121	120	0.99
6	−0.68	−1.19	160	−1.01	−1.51	170	1.33	0.82	110	170	210	1.23

Table 6. CV Data for ClCo(L)$_2$Py in DCM with TBAPF$_6$ at 0.2 mV/s at 25 °C

	Co(III)/Co(II)		Co(II)/Co(I)		Co(IV)/Co(III)	
	E_{pc} (V, vs Ag/AgCl) (ΔE_p (mV))	$E_{1/2}$ (V, vs Fc/Fc$^+$)	$E_{1/2}$ (V, vs Ag/AgCl) (ΔE_p (mV))	$E_{1/2}$ (V, vs Fc/Fc$^+$)	$E_{1/2}$ (V, Ag/AgCl) (ΔE_p (mV))	$E_{1/2}$ (V, vs Fc/Fc$^+$)
ClCo(gH)$_2$Py^a	−0.39 (240)	−0.90	−0.66 (113)	−1.17		
ClCo(dmgH)$_2$Py	−0.66 irrev	−1.17	−1.12 (200)	−1.63	1.20 (190)	0.69
ClCo(dpgH)$_2$Py^a	−0.50 irrev	−1.01	−0.85 (105)	−1.36	1.22 (200)	0.71
ClCo(dmestgH)$_2$Py	−0.68 irrev	−1.19	−1.01 (120)	−1.52	1.33 (120)	0.82

[a] Values are in acetonitrile.

UV−vis studies. In general, the spectra of cobaloximes are recorded in solvents such as chloroform, dichloromethane, ethanol, methanol, and methanol−water mixture and organocobaloximes show a 5-/6-coordination[7,20a] equilibrium in solvents such as methanol and ethanol but exists as 6-coordinated complexes in chloroform and dichloromethane. Here, we have also carried out UV−vis studies in different solvent systems. The solvent has little effect on the Co−C CT band but the Co−dioxime CT band is affected significantly. For example, the Co−C CT band in alkyl complexes **1**−**5** contains two humps at around ~380−390 nm (log ε 3.60) and 420−460 nm (log ε 3.30) and do not show any deviation with change in solvent. On the other hand, the MLCT band in **1**−**9** appears at around 214−220 nm in methanol/dichloromethane (25/1), at 236−240 nm in dichloromethane, and at 234−250 nm in chloroform. This is due to more stabilization of the ground state in the cobalt dioxime moiety in polar solvent.[20b]

Cyclic Voltammetry. In the cyclic voltammogram of cobaloximes, (R/X)Co(dmgH)$_2$B, we expect three types of redox couples: Co(III)/Co(II), Co(II)/Co(I), and Co(IV)/Co(III).[21] Very little work has been reported on the CV studies in cobaloximes, and hence, there is a lack of information on these three redox systems. Also, sufficient data are not available to correlate and generalize the electrochemical behavior of these complexes. It is true that it is difficult to get good CV data in organocobaloximes, but the inorganic cobaloximes give better cyclic voltammograms. No study has reported the values for all three redox systems. In most of the reported work, only the reduction process has been discussed.[9a,21a,b] Part of the difficulty may lie in the decreased solubility of these complexes in the proper solvent system. The other associated problem is the change in coordination number of cobalt during the reduction/oxidation process.[21] The electrochemical parameters reflect even small modifications of the electronic properties of the complexes brought about by the axial and equatorial ligand changes. Only a few reports have appeared on the oxidation process, and these too have been for aquacobaloximes.[21c,d] Most of the reported studies have dealt with the variation in axial ligands only, and very little work has been done on cobaloximes with other dioximes. CV data for **1**, **4**, and **6** are given in Table 5, and CV data for ClCo(L)$_2$Py species are given in Table 6.

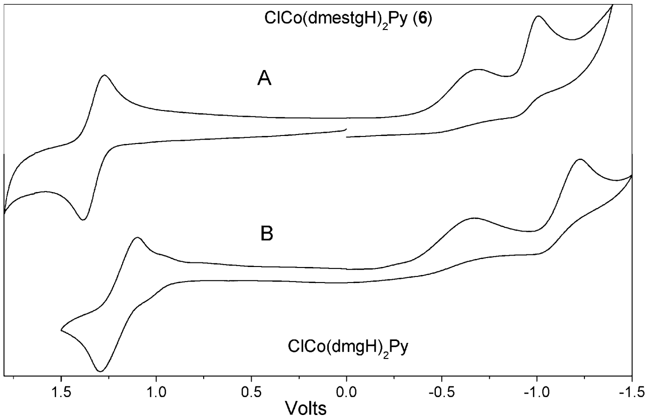

Figure 1. Cyclic voltammograms of **6** (A) and ClCo(dmgH)$_2$Py (B) in CH$_2$Cl$_2$ with 0.1 M (NBu^n$_4$)PF$_6$ as supporting electrolyte at 0.2 V s^{-1} at 25 °C.

The cyclic voltammogram of **6** (Figure 1A) shows two completely irreversible waves in the reductive half, at −0.68 and −0.96 V corresponding to Co(III)/Co(II) and Co(II)/Co(I), respectively. On the oxidation half only one reversible wave corresponding to Co(IV)/Co(III) (+1.33 V) is observed. On comparison of these values with those for the other cobaloximes (gH, dmgH, dpgH), **6** is more difficult to reduce from Co(III) to Co(II) and from Co(II) to Co(I).

(a) Alkyl Cobaloximes. The cyclic voltammograms for **1** and **4** are shown in Figure 2. Due to the large peak height at the oxidation half, the reductive half is very small or is hidden inside the background current. Two sequential one-electron reductions (irreversible), Co(III)/Co(II) and Co(II)/Co(I), and a one-electron oxidation, Co(IV)/Co(III) (quasi-reversible), are observed. **1** is easier to reduce as compared to **4**. This is in line with the higher electron donation ability of the butyl as compared to the methyl group.

The Co(II)/Co(I) potential should be affected only by the dioxime moiety, since there is no axial ligation in

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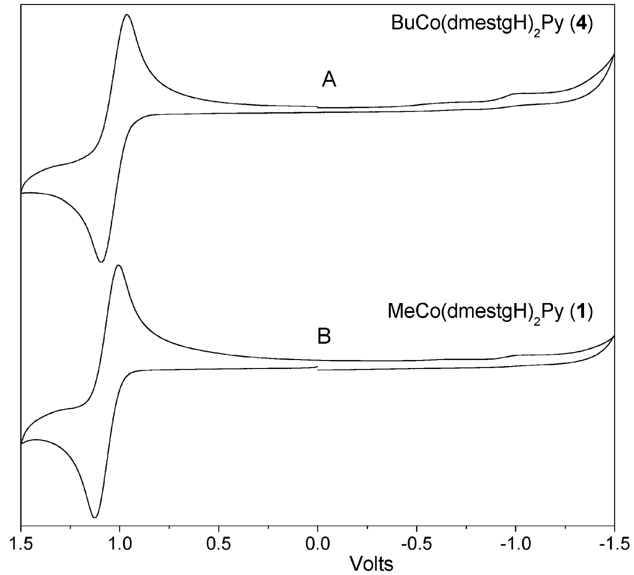

Figure 2. Cyclic voltammograms of **1** (A) and **4** (B) in CH_2Cl_2 with 0.1 M $TBAPF_6$ as supporting electrolyte at 0.2 V s^{-1} at 25 °C.

Co(I). This is what we observe. The gH complex is the easiest to reduce and dmestgH complex is the most difficult to reduce from Co(II) to Co(I).

The irreversibility can be attributed to two reasons: (a) the slow rate of the Co(III)/Co(II) electrode reaction so that the initial Co(III) complex and the reduced Co(II) complex are not in equilibrium with each other at the electrode surface and/or (b) the electrochemically generated Co(II) complex does not get recycled electrochemically to give the original Co(III) complex.

(b) Co(IV)/Co(III). Though the ratio i_{pa}/i_{pc} and ΔE_p are slightly higher than that of a quasi-reversible one-electron process in **1**, **4**, and **6**, there is an increase in ΔE_p with increasing scan rate, indicating that the electron transfer is quasi-reversible and consequently no bond breaking is presumed to be occurring during the course of oxidation. This is further substantiated by the dependence of the Co(IV)/Co(III) $E_{1/2}$ values on the axial alkyl group or halide. As indicated by $i_{pa}/i_{pc} = 1$ for all of the complexes, the oxidized products ((R/X)Co^{IV}(dmestgH)$_2$Py are stable. Complexes with other dioximes such as dmgH, dpgH, and gH also undergo oxidation to Co(IV) and are found to be stable, except for the gH complex.

X-ray Crystallographic Studies. Description of the Structures of 1, 6, and 7. A slow evaporation of solvent from the solution of complexes **1**, **6**, and **7** (CH_2Cl_2/acetonitrile) in the refrigerator resulted in the formation of orange crystals. The X-ray analysis of these crystals showed the compositions as [MeCo(dmestgH)$_2$Py]·CH_2Cl_2, [ClCo(dmestgH)$_2$Py]·CH_3CN, and [BrCo(dmestgH)$_2$Py]·CH_2Cl_2, respectively. The "Diamond" diagrams of the molecular structures of **1**, **6**, and **7** along with selected numbering schemes are shown in Figures 3−5**,** respectively. Selected bond lengths, bond angles, and structural parameters are given in Table 7 and are compared with those of related cobaloximes (Supporting Information).

The geometry around the central cobalt atom is distorted octahedral with four nitrogen atoms of the dioxime in the equatorial plane and pyridine and methyl (or Cl or Br) axially coordinated. The deviations of the cobalt atoms from the mean equatorial N4 plane are −0.0177(4), −0.0095(3), and −0.0130(3) Å. The deviation is toward the axial R/X group. In contrast, the deviation is always toward pyridine in cobaloximes with other dioximes (gH, dmgH, dpgH) and also in Costa type complexes.

The structural studies on cobaloximes have focused mainly on five points:[2c] (a) the axial Co−N bond length, (b) the Co−C bond length, (c) the puckering of the equatorial dioxime ligand, i.e., the butterfly bending angle (α), (d) the torsion angle between the axial base pyridine and equatorial ligand, and (e) the deviation of the cobalt atom from the mean equatorial N_4 plane. The methyl at the 2-position in the mesityl group is close to the pyridine ring, which causes pyridine to bend in the solid state.

The Co−C/Cl/Br bond distances (2.002(3), 2.2243(15), 2.3396(12) Å) and Co−N5 bond distances (2.086(3), 1.978(3), 1.986(4) Å) in **1**, **6**, and **7** do not differ significantly from the reported values for the corresponding Me/XCo(dioxime)$_2$Py cobaloximes.[22,23]

The butterfly bending angle in **1** is 7.25° and is much larger than the reported value for MeCo(dioxime)$_2$Py complexes (dpgH, 4.7°; dmgH, 3.2°; gH, 2.0°). The corresponding values in **6** and **7** are also large (6.64 and

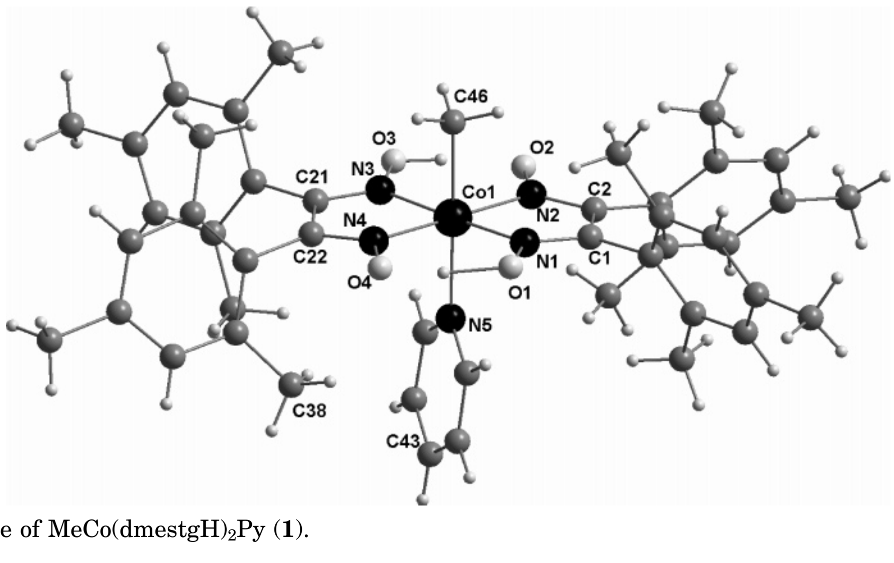

Figure 3. Structure of MeCo(dmestgH)$_2$Py (**1**).

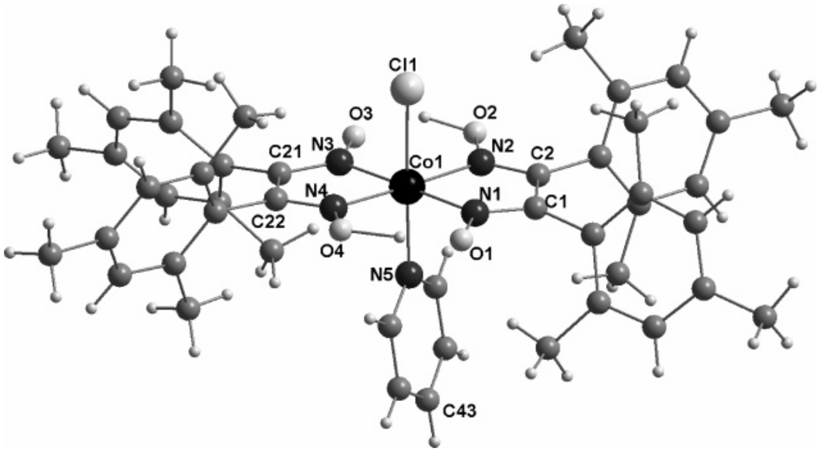

Figure 4. Structure of ClCo(dmestgH)$_2$Py (**6**).

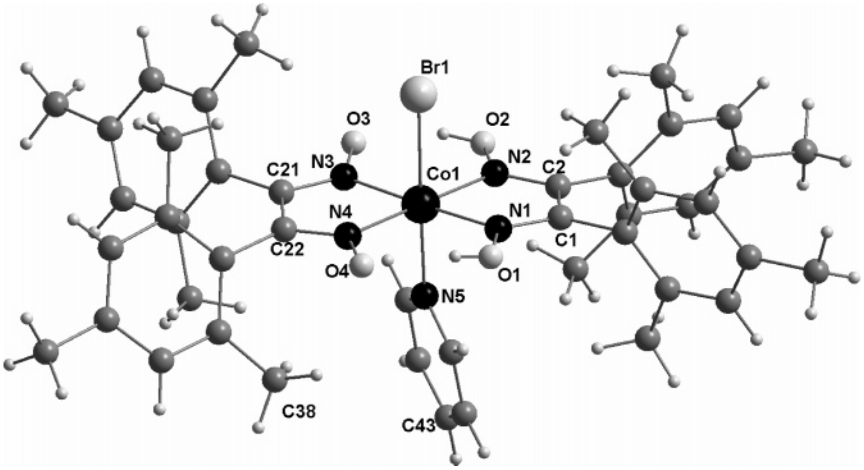

Figure 5. Structure of BrCo(dmestgH)$_2$Py (**7**).

Table 7. Selected Bond Lengths and Angles and Structural Data for 1, 6, and 7

	1	**6**	**7**
Co−C46 (Å)	2.002(3)		
Co−Cl/Br (Å)		2.2243(15)	2.3396(12)
Co−N5 (Å)	2.085(3)	1.978(3)	1.986(4)
C−Co−N(ax) (deg)	178.33(11)	177.99(12)	177.67(10)
O1−O4 (Å)	2.493(1)	2.480(4)	2.478(4)
O2−O3 (Å)	2.484(1)	2.478(4)	2.478(4)
d (Å)	−0.0177(4)	−0.009(6)	−0.014(1)
α (deg)	7.25	6.57	6.18
τ (twist) (deg)	67.09	69.50	70.37

6.18°) compared to the reported values for XCo(dioxime)$_2$Py. The positive value of α indicates the bending toward the axial R/X group.

Pyridine, attached to cobalt, has twist angles of 69.50, 70.37, and 67.09° in **1**, **6,** and **7**, respectively, and these angles are much smaller than in the corresponding cobaloximes with other dioximes. Pyridine is inclined toward one dioxime wing (C43−N5−Co1) by 172.35, 172.59, and 172.08°, and this bending of the pyridine ring is unusual and unique. The large bending angle and very low twist angle must be playing key roles in making pyridine inclined. Also, the plane of the pyridine ring lies below one of the N−O bonds of the dioxime in all three of the complexes. Its greater interaction with one side of the dioxime wing as compared to that with the other dioxime wing has resulted in a larger value of α. The Co−N5 bond distance is longer in **1** as compared to those in **6** and **7**, indicating a greater trans influence of the methyl group.

The dihedral angles[27] increase in the order (deg) 4.7 > 3.2 ≈ 3.2 > 2.0. Can this be taken as a measure of the cis influence of the dioxime? If so, then the cis influence order becomes dmestgH > dpgH > chgH ≥ dmgH ≥ gH and this matches the order observed in the ^{1}H and ^{13}C studies.

To summarize, dmestgH complexes behave differently from the reported cobaloximes; for example, the pyridine twist angle is small and the displacement of the cobalt atom from N$_4$ plane is negligible and is toward the axial methyl group, unlike in other cobaloximes, where it is toward pyridine. The higher steric cis effect

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(22) (a) Bresciani-Pahor, N.; Randaccio, L.; Zangrando, E.; Toscano, P. J. *Inorg. Chim. Acta* **1985**, *96*, 193. (b) Parker, W. O.; Zangrando, E.; Bresciani-Pahor, N.; Randaccio, L.; Marzilli, L. G. *Inorg. Chem.* **1985**, *24*, 3908.

(23) (a) López, C.; Alvarez, S.; Aguilo, M.; Solans, X.; Font-Altaba, M. *Inorg. Chim. Acta* **1987**, *127*, 153. (b) Geremia, S.; Dreos, R.; Randaccio, L.; Tauzher, G.; Antolini, L. *Inorg. Chim. Acta* **1994**, *216*, 125.

(24) Chloro(pyridine)bis(2,3-dimesitylglyoxal dioximato-$\kappa^4 N$)cobalt(III).

(25) Cobalt anisotropy is the total field effect of the CoC$_4$N$_4$ system. The field effect is the combination of the inductive effect of cobalt and the effect of donation through Co→dioxime and Co→axial ligand and back-donation.

(26) Instead of δ(^{13}C, C=N), the $\Delta\delta$(^{13}C, C=N) value has been taken. This is to avoid the direct effect of substituent on δ(C=N) value. $\Delta\delta$(^{13}C, C=N) represents the field effect.

(27) The dihedral angle (butterfly bending angle) is the angle between two dioxime planes: i.e., the O1N1C1C2N2O2 plane and the O3N3C21C22N4O4 plane.

of dioxime with pyridine as compared to that with the methyl group in MeCo(dioxime)$_2$Py complexes leads to the deviation of cobalt toward pyridine. However, in dmestgH complexes, the C−H π interaction between the pyridine ring and the methyl group of dimesityl ligand forces the cobalt to deviate toward the axial methyl group.

All three of the crystal structures show that the cobaloxime units propagate as two-dimensional layers through very weak intermolecular C−H···O hydrogen bonding and C−H···π (Supporting Information).

Conclusion

The spectral correlations are understood much better when both cobalt anisotropy and ring current are considered to operate together. Dimesitylglyoxime complexes are found to have the maximum cis influence among all the reported cobaloximes. ^{13}C NMR gives better information than ^{1}H NMR. The cis influence order, on the basis of ^{1}H and ^{13}C studies, is dmestgH > dpgH > chgH ≥ dmgH ≥ gH. The dihedral angle also gives the same order. However, a change in the equatorial ligand field does not lead to any significant change in the Co−C bond length. A good correlation between $\delta(^{13}\mathrm{C}, \mathrm{C{=}N})$ and $\Delta\delta(^{1}\mathrm{H}, \mathrm{Py}_{\alpha})$ suggests the presence of ring current throughout the Co(dioxime) metallabicycle, and the negative slope indicates that they are effected in opposite directions. Among all the reported cobaloximes, the dimesitylglyoxime complex is the most difficult to reduce from Co(II) to Co(I).

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Supporting Information Available: Tables and figures containing coordination shift values for pyridine in **1**−**9** and other dioximes (^{1}H and ^{13}C NMR) and two-dimensional layer C−H−π and π−π interactions and CIF files for the crystal structures of **1**, **6** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org. The CIF files have also been deposited with the Cambridge Crystallographic Data Centre; CCDC number for **1**, **6**, and **7** are 251396, 251397, and 251398, respectively. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EX, U.K. (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk/).

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