Synthesis and Characterization of and Cis−Trans Influence in Cobaloximes with Glyoxime as the Equatorial Ligand[†]

B. D. Gupta,* R. Yamuna, Veena Singh, and Usha Tiwari

Department of Chemistry, IIT Kanpur, UP, India 208016

Received April 25, 2002

The synthesis and characterization of $RCo(gH)_2Py$ (R = methyl through decyl) and $XCo(gH)_2Py$ (X = Cl, Br, NO_2, N_3) is described. Most of these complexes are new and have been synthesized for the first time. The X-ray structure of $N_3Co(gH)_2Py$ is reported. The cis−trans influence has been studied by ^1H and ^{13}C NMR, UV−vis, and X-ray diffraction. For a range of X ligands, a clear trend between the ^1H and ^{13}C chemical shifts of the axial and equatorial ligands as well as with the Co-dioxime CT band has been observed. More than 20 correlations have been found. $\delta(^{13}C)$ values for C=N, Py_α, Py_β, and Py_γ in the alkylcobaloximes always occur upfield by 1−3 ppm compared to those in the inorganic cobaloximes, and $\delta(^{13}C)$ for C=N in gH complexes occur significantly upfield, by 12−13 ppm, compared to the values in the corresponding dmgH, chgH, and dpgH complexes.

Introduction

Organocobaloximes[23] have been extensively studied and reviewed in the last three decades.[1] This is due to their use as catalysts[2] and as templates in organic synthesis.[3] However, the main interest still lies in their role as models of vitamin B_{12}.[4] Since Co−C bond cleavage is the key step involved in B_{12}-dependent enzymatic or cobaloxime-mediated reactions, the strength of the Co−C bond as a function of steric and electronic factors with a wide range of axial ligands in cobaloximes and in related complexes with different chelates has been systematically investigated.[1,5−7] Many different approaches to quantitatively rationalize the trend in structural, NMR, thermodynamic, and kinetic properties as a function of steric and electronic effects of the axial ligands in cobaloximes have been reported.[8] 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.[7]

Therefore, model studies have furnished some insight into the factors affecting homolysis at the Co−C bond and have allowed in-depth analysis of the variation in geometry of the R−Co−B fragment (in terms of the electronic and steric properties of R and B groups):[1] for example, the weakening of the Co−C bond is essentially related to the increase in bulk of R that sterically interacts with the dioxime moiety (steric cis influence). An increase in the bulk of B also lengthens the Co−C bond (steric trans influence). The Co−C bond is, however, stabilized by a more basic trans B group (electronic trans influence). The weakening of the Co−B bond has been attributed to the bulk of R (steric trans influence) and the electron-donating ability of R (electronic trans influence). Also, an increase in the bulk of B determines the lengthening of the Co−B bond (steric cis influence).[1c,9,10]

Knowledge of the electronic structures of cobaloximes and an understanding of the related cis and trans

---

[†] Dedicated to Dr. W. Adcock, The Flinders University of South Australia, Adelaide.

* To whom correspondence should be addressed. E-mail: bdg@iitk.ac.in.

(1) (a) Bresciani-Pahor, N.; Forcolin, M.; Marzilli, L. G.; Randaccio, L.; Summers, M. F.; Toscano, P. J. *Coord. Chem. Rev.* **1985**, *63*, 1 and references therein. (b) Toscano, P. J.; Marzilli, L. G. *Prog. Inorg. Chem.* **1984**, *104*, 105. (c) Randaccio, L. *Comments Inorg. Chem.* **1999**, *21*, 327. (d) Gupta, B. D.; Roy, S. *Inorg. Chim. Acta* **1988**, *146*, 209.

(2) (a) Rockenbaur, A.; Eyor, M.; Kwielinsci, M.; Tyrlik, S. *Inorg. Chim. Acta* **1982**, *58*, 237. (b) Nemeth, S.; Simandi, L. *J. Mol. Catal.* **1982**, *12*, 87.

(3) (a) Giese, B. *Radicals in Organic Synthesis*: *Formation of Carbon−Carbon Bonds*; Pergamon Press: Oxford, U.K., 1986. (b) Scheffold, R.; Rytez, G.; Walder, L. In *Transition Metals in Organic Synthesis*; Scheffold, S., Ed.; Wiley: Chichester, U.K., 1983; Vol. 3. (c) Ghosh, A. K.; Chen, Y. *Tetrahedron Lett.* **1995**, 505. (d) Wright, M. W.; Welker, M. E. *J. Org. Chem.* **1996**, *61*, 133. (e) Gupta, B. D.; Singh, V.; Qanungo, K.; Vijaikanth, V.; Sengar, R. S. *J. Organomet. Chem.* **1999**, *582*, 279. (f) Gupta, B. D.; Dixit, V.; Das, I. *J. Organomet. Chem.* **1999**, *572*, 49. (g) Brown, T.; Dronsfield, A.; Jablonski, A.; Wilkinson, A. S. *Tetrahedron Lett.* **1996**, *37*, 5413. (h) Gill, G. B.; Pattenden, G.; Roan, G. A. *Tetrahedron Lett.* **1996**, *37*, 9369. (i) Gage, J. L.; Branchaud, B. P. *Tetrahedron Lett.* **1997**, *40*, 7007.

(4) (a) Halpern, J. *Science* **1985**, *227*, 869. (b) *B_{12}*; Dolphin, D., Ed.; Wiley-Interscience: New York, 1982; Vols. 1 and 2.

(5) (a) Yohannes, P. G.; Bresciani-Pahor, N.; Randaccio, L.; Zangrando, E.; Marzilli, L. G. *Inorg. Chem.* **1988**, *27*, 4738. (b) Summers, M. F.; Marzilli, L. G.; Bresciani-Pahor, N.; Randaccio, L. *J. Am. Chem. Soc.* **1984**, *106*, 4478.

(6) (a) Marzilli, L. G.; Gerli, A.; Calafat, A. M. *Inorg. Chem.* **1992**, *31*, 4617. (b) Hirota, S.; Polson, S. M.; Puckett, J. M., Jr.; Moore, S. J.; Mitchell, M. B.; Marzilli, L. G. *Inorg. Chem.* **1996**, *35*, 5646. (c) Polson, S. M.; Cini, R.; Pifferi, C.; Marzilli, L. G. *Inorg. Chem.* **1997**, *36*, 314.

(7) (a) Randaccio, L.; Furlan, M.; Geremia, S.; Slouf, M.; Srnova, I.; Toffoli, D. *Inorg. Chem.* **2000**, *39*, 3403. (b) Randaccio, L.; Geremia, S.; Nardin, G.; Slouf, M.; Srnova, I. *Inorg. Chem.* **1999**, *38*, 4087.

(8) (a) Brown, K. L.; Lyles, D.; Pencovici, M.; Kallen, R. G. *J. Am. Chem. Soc.* **1975**, *97*, 7338. (b) Marzilli, L. G.; Bayo, F.; Summers, M. F.; Thomas, L. B.; Zangrando, E.; Bresciani-Pahor, N.; Mari, M.; Randaccio, L. *J. Am. Chem. Soc.* **1987**, *109*, 6045. (c) Brown, K. L.; Satyanarayana, S. *J. Am. Chem. Soc.* **1992**, *114*, 5674. (d) Datta, D.; Sharma, G. T. *J. Chem. Soc., Dalton Trans.* **1989**, 115. (e) Zangrando, E.; Bresciani-Pahor, N.; Randaccio, L.; Charland, J. P.; Marzilli, L. G. *Organometallics* **1986**, *5*, 1938. (f) Bresciani-Pahor, N.; Geremia, S.; Lopez, C.; Randaccio, L.; Zangrando, E. *Inorg. Chem.* **1990**, *29*, 1043. (g) Randaccio, L.; Geremia, S.; Zangrando, E.; Ebert, C. *Inorg. Chem.* **1994**, *33*, 4641. (h) Drago, R. S. *Inorg. Chem.* **1995**, *34*, 3543. (i) Drago, R. S. *J. Organomet. Chem.* **1996**, *512*, 61. (j) De Ridder, D. J. A.; Zangrando, E.; Burgi, H. B. *J. Mol. Struct.* **1996**, *374*, 63.

(9) Randaccio, L.; Bresciani-Pahor, N.; Zangrando, E.; Marzilli, L. G. *Chem. Soc. Rev.* **1989**, *18*, 225.

(10) Bresciani-Pahor, N.; Randaccio, L.; Toscano, P. G.; Sandercock, A. C.; Marzilli, L. G. *J. Chem. Soc., Dalton Trans.* **1982**, 129.

10.1021/om020331f CCC: $25.00

influences are, therefore, sought as the basis for systematization of the large body of chemical information currently available and for the successful design of novel derivatives with desired properties. ^1H NMR spectra of cobaloximes have been studied in order to establish the cis and trans influence of X and B ligands in $XCo(dioxH)_2B$ complexes.[11] Most of the studies, however, have been confined to the trans effect only and have been carried out on cobaloximes with dmgH as the equatorial ligand. On the other hand, only a few studies on the ^{13}C NMR spectra of cobaloximes have been reported.[8b−d,f,g,12] Studies involving other oximes with varying steric and electronic properties such as gH,[13] chgH,[14] and dpgH[15] have been few. Therefore, there is very little data available on the effect of the equatorial ligand field on the axial groups (cis influence).[5,7,12a,d,13b,14a,d,15a,16]

The overall evidence from the literature strongly establishes that many of the chemical properties related to the axial fragment, such as the geometry, kinetics, and spectroscopic behavior, are significantly affected by a change in the equatorial ligand (cis effect and cis influence). Hence, there has been a sustained interest in the synthesis of new organocobaloximes with new or modified equatorial ligands.

We have, therefore, undertaken the study of cobaloximes, $RCo(gH)_2Py$ and $XCo(gH)_2Py$. Most of the complexes are new and have been synthesized for the first time. The X-ray structure of $N_3Co(gH)_2Py$ is reported. The cis and trans influences have been studied by ^1H and ^{13}C NMR, UV−vis, and X-ray diffraction. These studies will allow us (a) to verify if the trends in ^1H NMR and UV data, reported earlier for inorganic dmgH complexes exclusively, also apply to gH complexes as well as to the organometallic derivatives, (b) to see if a ^{13}C NMR study gives information similar to or better than that in the ^1H NMR study, (c) to see if there is any correlation in the ^1H and ^{13}C NMR and UV data, and (d) to see if X-ray crystallography reveals any information on the cis and trans influence.

Experimental Section

General Methods. ^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. NMR data are reported in ppm. UV−vis spectra (methanol) were recorded on a Shimadzu 160A spectrometer. Elemental analysis was carried out at the Regional Sophisticated Instrumentation Center, Lucknow. A Julabo UC-20 low-temperature refrigerated circulator was used to maintain the desired temperature.

Glyoxime was purchased from Aldrich Chemical Co. and was used as received. Silica gel (100−200 mesh) and distilled solvents were used in all chromatographic separations. The chlorocobaloximes $ClCo(gH)_2B$ (B = Py, 3-picoline, Py-4^tBu) were prepared using literature procedures.[13a,c]

X-ray Structural Determination and Refinement. Red crystals were obtained by slow evaporation of solution of the complex (**14**) in methanol. A small crystal (0.42 × 0.27 × 0.17 mm^3) was selected and mounted on a Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator. The unit cell parameters were determined from 25 reflections (θ range 2.31−22.47°), and the cell parameters were refined by least squares. Intensities were collected with Mo $K\alpha$ radiation, using the multiscan technique. For this compound 945 intensities were measured in the range (22.47°), and 932 were considered as observed by applying the condition $I > 2.0\sigma(I)$.

The structure was isotropically refined by full-matrix least squares on the F^2 method, using the Shelxl-97 computer program. The function minimized was $[\sum[w(|F_o| - |F_c|)^2]^{0.5}$, where $w = [\sigma^2(F_o^2) + (0.05F_o^2)^2]$.[17a] The hydrogen atoms of the OH groups were located on difference maps and were constrained to those difference map positions. The pertinent crystal data and refinement parameters are compiled in Table 3.

$RCo^{III}(gH)_2Py$ (1−10). These complexes were synthesized by a general procedure detailed earlier for the synthesis of $RCo(dmgH)_2Py$[1d] and involved the reaction of cobaloxime I with alkyl halide. The cobaloxime(I) $Co^I(gH)_2Py$ was generated in situ by the sodium borohydride reduction of $ClCo(gH)_2Py$ (**11**) under inert conditions at 0 °C. The workup procedure was similar to that described in many of our earlier papers.

$MeCo^{III}(gH)_2B$ (15−19). The compounds **15** and **16** were prepared from the corresponding species $ClCo(gH)_2B$ (B = 3-picoline, Py-4^tBu) following the above procedure. However, **17**−**19** could not be synthesized by this procedure. Hence, these were prepared from the aquo complex by the following general procedure.

$CH_3Co(gH)_2H_2O$ (0.11 g, 0.41 mmol) and the appropriate base (1.29 mmol) were suspended in a mixture of methanol (25 mL) and dichloromethane (25 mL), and the suspension was stirred for 2.5 h. An orange solution resulted, which was filtered and concentrated to near-dryness on a rotary evaporator. The orange product was collected and washed with dry diethyl ether.

$CH_3Co(gH)_2H_2O$: Dowex 50w-X8 ion-exchange resin (H^+ form, 50−100 mesh, 2.00 g, 10.2 mequiv) was added to a solution of $CH_3Co(gH)_2Py$ (0.90 g, 2.76 mmol) in a mixture of

---

(11) (a) Trogler, W. C.; Marzilli, L. G. *Inorg. Chem.* **1975**, *14*, 2942. (b) Trogler, W. C.; Stewart, R. C.; Epps, L. A.; Marzilli, L. G. *Inorg. Chem.* **1974**, *13*, 1564. (c) Hill, H. A. O.; Morallee, K. G. *J. Chem. Soc. A* **1969**, 554. (d) Bied-Charreton, C.; Gaudemer, A. *Bull. Soc. Chim. Fr.* **1972**, 861. (e) Gilaberte, J. M.; Lopez, C.; Alvarez, S. *J. Organomet. Chem.* **1988**, *342*, C13. (f) Lopez, C.; Alvarez, S.; Solans, X.; Font-Altaba, M. *Inorg. Chim. Acta* **1986**, *111*, L19. (g) Lopez, C.; Alvarez, S.; Solans, X.; Font-Altaba, M. *Inorg. Chem.* **1986**, *25*, 2962.

(12) (a) Gilaberte, J. M.; Lopez, C.; Alvarez, S.; Font-Bardia, M.; Solans, X. *New J. Chem.* **1993**, *17*, 193. (b) Stewart, R. C.; Marzilli, L. G. *Inorg. Chem.* **1977**, *16*, 424. (c) Bied-Charreton, C.; Septe, B.; Gaudemer, A. *Org. Magn. Reson.* **1975**, *7*, 116. (d) Gupta, B. D.; Tiwari, U.; Barclay, T.; Cordes, W. *J. Organomet. Chem.* **2001**, *629*, 83. (e) Gupta, B. D.; Yamuna, R.; Singh, V.; Tiwari, U.; Barclay, T.; Cordes, W. *J. Organomet. Chem.* **2001**, *627*, 80.

(13) (a) Toscano, P. J.; Swider, T. F.; Marzilli, L. G.; Bresciani-Pahor, N.; Randaccio, L. *Inorg. Chem.* **1983**, *22*, 3416 and references therein. (b) Bresciani-Pahor, N.; Randaccio, L.; Zangrando, E.; Toscano, P. J. *Inorg. Chim. Acta* **1985**, *96*, 193. (c) Lopez, C.; Alvarez, S.; Solans, X.; Font-Altaba, M. *Inorg. Chim. Acta* **1986**, *121*, 71. (d) Megnamisi-Belombe, M.; Endres, H.; Rossato, E. *Acta Crystallogr., Sect. C* **1983**, *C39*, 705.

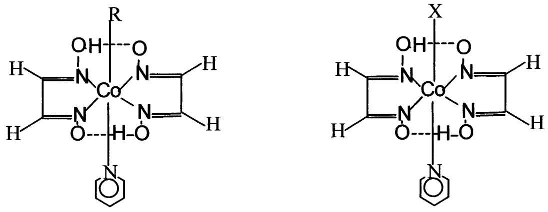
(14) (a) Gupta, B. D.; Qanungo, K.; Barclay, T.; Cordes, W. *J. Organomet. Chem.* **1998**, *560*, 155. (b) Gupta, B. D.; Roy, M.; Das, I. *J. Organomet. Chem.* **1990**, *397*, 219. (c) Dodd, D.; Johnson, M. D.; Lockman, B. L. *J. Am. Chem. Soc.* **1977**, *99*, 3664. (d) Gupta, B. D.; Qanungo, K.; Yamuna, R.; Pandey, A.; Tewari, U.; Singh, V.; Vijaikanth, V.; Barclay, T.; Cordes, W. *J. Organomet. Chem.* **2000**, *608*, 106.

(15) (a) Lopez, C.; Alvarez, S.; Font-Bardia, M.; Solans, X. *J. Organomet. Chem.* **1991**, *414*, 245. (b) Lopez, C.; Alvarez, S.; Solans, X.; Font-Bardia, M. *Polyhedron* **1992**, *11*, 1637. (c) Lopez, C.; Alvarez, S.; Aguilo, M.; Solans, X.; Font-Altaba, M. *Inorg. Chim. Acta* **1987**, *127*, 153. (d) Schrauzer, G. N.; Lee, L. P.; Sibert, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 2997.

(16) (a) Gupta, B. D.; Qanungo, K. *J. Organomet. Chem.* **1997**, *543*, 125. (b) Gupta, B. D.; Qanungo, K. *J. Organomet. Chem.* **1998**, *557*, 243. (c) Gupta, B. D.; Qanungo, K.; Singh, V.; Shobini, *Ind. J. Chem.* **1998**, *37A*, 707.

(17) (a) The structure was solved by using the WINGX 1.61 crystallographic collective package (Farrugia, L. J. WINGX Version 1.61, an Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single-Crystal X-ray Diffraction Data; Department of Chemistry, University of Glasgow). (b) Schrauzer, G. N.; Windgassen, R. J. *J. Am. Chem. Soc.* **1966**, *88*, 3738.

Chart 1



R= Me-Dec (1-10) X= Cl, Br, NO_2, N_3 (11-14)

$MeCo(gH)_2B$ (15-19) B= 3-picoline, Py-4 ${}^{t}Bu$, imidazole, morpholine, piperidine

$XCo(gH)_2Py$-4 ${}^{t}Bu$ X= Cl, Br, NO_2, N_3 (20-23),

$ClCo(gH)_2B$ (B =3-picoline) (24)

methanol (140 mL) and water (20 mL). The mixture was warmed and stirred in a beaker covered with a watch glass for 1 h. The solution was filtered hot, and the filtrate was concentrated to a small volume on the rotary evaporator. The orange product obtained on cooling was washed well with acetone and dichloromethane. Yield: 0.65 g (70%).

$XCo^{III}(gH)_2Py$ (12−14). These compounds were synthesized by the substitution of the Cl group in $ClCo(gH)_2Py$ (**11**) by another inorganic group. General procedure: a solution of sodium azide (0.045 g, 0.692 mmol) in 5 mL of water was added to a refluxing suspension of $ClCo(gH)_2Py$ (0.200 g, 0.575 mmol) in 25 mL of methanol. The reaction mixture was further refluxed for 2 h. The solution was concentrated and was purified by column chromatography using silica gel. The compound, $N_3Co(gH)_2Py$, was eluted with 100% ethyl acetate. Yield: 0.116 g (57%).

$XCo^{III}(gH)_2Py$-4^{t}Bu (21−23). These compounds were prepared from $ClCo^{III}(gH)_2Py$-4^{t}Bu (**20**) using the same procedure as described above for **12**−**14**.

Results and Discussion

Synthesis. The literature survey has shown that only a few complexes of cobalt(III) with glyoxime as the equatorial ligand have previously been synthesized. $MeCo(gH)_2Py$ was the first compound prepared by Schrauzer in 2.5% yield via the sodium borohydride reduction of a basic aqueous methanol mixture of $CoCl_2 \cdot 6H_2O$, glyoxime, and pyridine in the presence of methyl iodide.[17b] Later, Marzilli et al. reported the synthesis and crystal structures of $RCo(gH)_2Py$ ($R = CH_3$, C_2H_5, i-C_3H_7) complexes.[13a,b] These complexes were synthesized in 7−35% yield by the sodium borohydride reduction of $ClCo(gH)_2Py$ in the presence of alkyl halide, a method commonly used for the synthesis of $RCo(dmgH)_2Py$ complexes.

We have synthesized two series of complexes, $RCo(gH)_2Py$ (**1**−**10**) and $XCo(gH)_2Py$ (**11**−**14**), where R is an alkyl group and X is an inorganic group (Chart 1). The complexes **1**−**10** were synthesized by the oxidative alkylation of $Co^{I}(gH)_2Py$ with alkyl halide at 0 °C under an inert atmosphere. The yields vary between 14−35%. The water-soluble $Co^{II}(gH)_2Py$ was the major side product. The inorganic complexes **12**−**14**, synthesized by the substitution of a Cl group in $ClCo(gH)_2Py$ (**11**) by other inorganic groups, were formed in 26−57% yield. $MeCo(gH)_2B$ (**15**−**19**) were prepared either by a base change in the corresponding aquo complex or by the oxidative alkylation of $Co^{I}(gH)_2B$ as described above. The elemental analysis, yield, UV−vis data, and R_f values of the compounds **1**−**24** are given in the Supporting Information. The solubility of the gH complexes **11**−**14** is very poor in chloroform but is significantly improved when the axial base is Py-4^{t}Bu (**20**−**23**). We also observe a small increase in the yield of these compounds as compared to their pyridine analogues.

The lower yield in the gH complexes **1**−**10** is most likely due to the instability of $Co^{I}(gH)_2Py$, to its reduced nucleophilicity, or to a combination of both factors. Schrauzer and Deutsch have reported[18] the relative instability of $Co^{I}(gH)_2L$ ($L = Py$, H_2O, SMe_2, PBu_3), found that $Co^{I}(gH)_2PBu_3$ is approximately 600 times less nucleophilic than $Co^{I}(dmgH)_2PBu_3$, and hypothesized that this result may be due to lower electron donation by the gH ligands relative to that by the dmgH ligands. The nucleophilicity of cobaloxime(I), in general, depends on the nature of the axial base component, and this is expected in view of the effect of axial coordination upon the charge density on the cobalt atom.[18,19]

In an effort to improve the yield of these reactions, we have found that the change of base, temperature, and the solvent has no significant effect on the yield in the reaction of $Co^{I}(gH)_2Py$ with methyl iodide. Since Co^{II} is stable in solution and is in equilibrium with Co^{I} (see CV Studies below), we carried out the reaction of $Co^{II}(gH)_2Py$ with butyl bromide under irradiation at 0 °C. $ButylCo(gH)_2Py$ was obtained in less than 1% yield.

Spectroscopy. General Comments on the ${}^{1}H$ and ${}^{13}C$ NMR Assignments. The ${}^{1}H$ NMR spectra of these 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 literature values on the four compounds of gH complexes[13] and also to those of the related dioxime compounds previously described by us.[12d]

Until recently[12a,b,d,14d] the ${}^{13}C$ chemical shifts have been assigned for only a few inorganic cobaloximes. Although three alkyl gH complexes, $RCo(gH)_2Py$ (R = Me, Et, ${}^{i}Pr$), have been reported,[13] no ${}^{13}C$ NMR measurements were carried out. Further comments are, therefore, warranted on these assignments.

For $RCo(gH)_2Py$ (**1**−**10**), in addition to the alkyl carbons, four sets of ${}^{13}C$ resonances, Py_α, Py_β, Py_γ, and C═N, are observed. Py_α and Py_β are well separated and are assigned on the basis of their typical chemical shifts in other alkylcobaloximes with dmgH, chgH, and dpgH ligands.[12d,16] Py_γ and C═N occur very close together and merge in many cases. The assignment has been confirmed by ${}^{1}H$−${}^{13}C$ correlation experiments. For $MeCo(gH)_2B$ (**15-19**), the assignments are made as for **1**.

The complexes $XCo(gH)_2Py$ (**11**−**14**) are not very soluble in chloroform. The quality of spectra is not as good as for **1**−**10**. More than 12 000 accumulations were required, compared to just 300 in case of **1**−**10**. The assignment is similar to that for the complexes **1**−**10**. The quality of the spectra is, however, much better in the case of $XCo(gH)_2Py$-4^{t}Bu (**20**−**24**), owing to their better solubility in chloroform.

${}^{1}H$ and ${}^{13}C$ values for all the compounds are given in Tables 1 and 2. All these cobaloximes exist as six-coordinated species in $CDCl_3$ (the solvent used for

---

(18) Schrauzer, G. N.; Deutsch, E. *J. Am. Chem. Soc.* **1969**, *91*, 3341.

(19) Schrauzer, G. N.; Deutsch, E.; Windgassen, R. J. *J. Am. Chem. Soc.* **1968**, *90*, 2441.

Table 1. ^{1}H NMR Data for 1−23[a]

	B								
compd	α	β	γ	gH	CH_2Co	rest of alkyl chain	Me	O−H- -O	others
1	8.61	7.39	7.80	7.42			1.02	17.74	
2	8.60	7.38	7.79	7.44	1.88		0.52	17.70	
3	8.60	7.38	7.79	7.43	1.76	1.09−1.19	0.82	17.70	
4	8.61	7.38	7.78	7.43	1.79	1.07−1.29	0.84		
5	8.60	7.37	7.78	7.42	1.78	1.09−1.27	0.82	17.82	
6	8.60	7.37	7.78	7.42	1.78	1.11−1.22	0.84	17.66	
7	8.60	7.37	7.78	7.42	1.78	1.10−1.28	0.85	17.70	
8	8.60	7.37	7.78	7.42	1.78	1.11−1.27	0.86	17.70	
9	8.59	7.37	7.78	7.42	1.78	1.10−1.22	0.87	17.68	
10	8.60	7.37	7.77	7.43	1.78	1.10−1.25	0.88		
11	8.25	7.31	7.78	7.63					
12	8.23	7.32	7.79	7.63					
13	8.29	7.34	7.81	7.61					
14	8.31	7.34	7.80	7.65					
15	8.42	7.27	7.59	7.40			0.99	17.86	2.35
16	8.42	7.31		7.38			0.95	17.81	1.25
17				7.41			1.25	17.83	7.84, 7.15
18				7.56			0.90	17.56	3.47, 2.57, 1.43
19				7.54			0.84	17.57	2.18, 1.74
20	8.06	7.27		7.64				17.46	1.25
21	8.02	7.24		7.60					1.22
22	8.09	7.25		7.58					1.22
23	8.13	7.27		7.64				17.45	1.26

[a] ^{1}H (Py-4^{t}Bu): α = 8.50 ppm, β = 7.25 ppm; free Py.[12e]

Table 2. ^{13}C NMR Data for 1−23[a]

		pyridine					
compd	C=N	α	β	γ	CH_2-Co	rest of alkyl chain	others
1	137.94	149.73	125.62	138.10			
2	137.95	149.72	125.56	137.95	29.18	15.70	
3	138.03	149.66	125.56	138.03	37.53	23.65, 14.68	
4	137.97	149.70	125.56	138.03	32.66	23.65, 13.85	
5	137.96	149.70	125.56	138.01	32.88	30.07, 22.42, 14.16	
6	138.01	149.70	125.56	138.01	31.64	30.41, 22.74, 14.07	
7	138.02	149.70	125.56	138.02	31.99	30.71, 30.50, 29.12, 22.63, 14.10	
8	137.95	149.71	125.58	138.03	31.85	30.74, 30.47, 29.38, 22.64, 14.11	
9	138.02	149.69	125.56	138.02	31.88	30.74, 30.48, 29.70, 29.44, 29.29, 22.68, 14.12	
10	138.04	149.71	125.56	138.04	31.92	30.75, 30.50, 29.76, 29.59, 29.45, 29.32, 22.70, 14.13	
11	140.56	150.84	126.13	139.52			
12	141.10	150.68	126.18	140.55			
13	140.48	150.31	126.10	139.53			
14	139.85	150.90	126.11	139.40			
15	137.90	149.60	124.94	138.71			18.65
16	137.78	149.06	122.73	162.65	30.45		30.18, 34.89
17	137.49				29.72		146.68, 134.77, 121.53
18	137.95						68.28, 46.61
19	137.71				29.68		47.91, 28.02, 23.55
20	140.62	149.92	123.46	164.72			30.01
21	140.95	149.58	123.46	164.67			30.06
22	140.42	149.61	123.35	164.69			30.06
23	139.76	150.21	123.43	164.62			30.08

[a] Free Py-4^{t}Bu ^{13}C: α 149.51 ppm, β 120.51 ppm, γ 159.66 ppm; free Py.[12e]

NMR), as the cobalt-bound CH_2 as well as gH proton did not shift even on the addition of a large excess of pyridine to the NMR sample. This is similar to our observation in the UV−vis study described later.

Cis and Trans Influence. A cis and trans influence study includes investigations of all possible steric and electronic changes detectable in the cis and trans ligands. Cobaloximes have been the preferred systems for such studies in octahedral systems. Usually either the axial ligand R/X or the basal ligand B is varied, and changes in the cis equatorial dioxime ligand or trans axial ligand are monitored spectroscopically. We have, for convenience, discussed the ^{1}H and ^{13}C results under separate headings.

The chemical shifts for the O−H- - -O resonance of **1**−**14** are given in Table 1. We have not been able to detect the O−H- - -O peak in complexes **4** and **10**−**14**. A comparison of O−H- - -O values in **1**−**10** with those of $RCo(L)_2Py$ (R = alkyl, L = dmgH, chgH, dpgH)[16a] shows a high upfield shift in **1**−**10**, nearly 0.6 ppm as compared to the corresponding dmgH complexes and 0.9−1.2 ppm as compared to dpgH complexes. However, it is slightly downfield (0.1−0.2 ppm) on comparison with the chgH complexes. Overall, the O−H- - -O resonance follows the order dpgH > dmgH > gH > chgH. The value, however, remains almost the same within the same series in all the complexes. This may open up the question as to how the replacement of two methyl groups in dmgH complexes by two hydrogens (gH complexes) alters the anisotropy of the cobalt atom or $[Co(gH)_2]^+$ unit so profoundly as to merit such a large shift. This is in view of the reports on the dmgH complexes with planar nitrogen ligands, where the magnetic anisotropy of the entire $[Co(L)_2]^+$ moiety[12a] or the anisotropy of cobalt atom alone[11b] has been invoked to explain the ^{1}H NMR shifts.

Table 3. Crystal Data and Structure Refinement Details for 14

empirical formula	$C_9H_{11}CoN_8O_4$
fw	354.19
temp	293(2) K
wavelength	0.710 69 Å
cryst syst	orthorhombic
space group	$P2_1cn$
unit cell dimens	
a	8.593(5) Å
b	12.414(5) Å
c	12.479(5) Å
α	90.000(5)°
β	90.000(5)°
γ	90.000(5)°
V	1331.2(11) Å^3
Z	4
density (calcd)	1.767 Mg/m^3
abs coeff	1.324 mm^{-1}
F(000)	720
cryst size	$0.42 \times 0.27 \times 0.17$ mm^3
θ range for data collection	2.31−22.47°
index ranges	$-2 \leq h \leq 9, -3 \leq k \leq 13, -4 \leq l \leq 13$
no. of rflns collected	945
no. of indep rflns	932 (R(int) = 0.5651)
completeness to $\theta = 22.47°$	99.3%
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	932/1/199
goodness of fit on F^2	1.212
final R indices ($I > 2\sigma(I)$)	R1 = 0.0550, wR2 = 0.1777
R indices (all data)	R1 = 0.1117, wR2 = 0.1980
abs structure param	−0.05(11)
largest diff peak and hole	0.602 and −0.664 e Å^{-3}

Trans Influence. (a) ^{1}H Chemical Shift. The trans influence of the axial R/X group can be monitored through the coordination shift ($\Delta\delta = \delta_{\text{complex}} - \delta_{\text{free py}}$) of the α-, β-, and γ-protons in pyridine. The ^{1}H resonance of pyridine in **1**−**10** on coordination to the cobaloxime moiety shifts downfield, and this coordination shift follows the order $\Delta\delta(^1\text{H,Py}_\gamma) > \Delta\delta(^1\text{H,Py}_\beta) \gg \Delta\delta(^1\text{H,Py}_\alpha)$. There is hardly any shift in the ^{1}H Py$_\alpha$ value on coordination to cobalt as compared to the unligated pyridine in **1**−**10**. This is similar to the earlier findings in alkyl dmgH and chgH complexes[12a,16a] and suggests that the alkyl groups are least capable of inducing some shift in Py$_\alpha$. On the other hand, $\delta(^1\text{H,Py}_\alpha)$ signals occur upfield by ∼0.3 ppm in **11**−**14** as compared to the values in **1**−**10**. A similar observation is made in R/XCo(gH)$_2$Py4-^{t}Bu (compare **16** with **20**−**23**). The upfield shift in Py$_\alpha$ is anticipated, in view of the shielding caused by the ring current effect of the equatorial glyoximato ligand field. A comparison of the upfield shift in Py$_\alpha$ in **11**−**14** with the corresponding values in other dioxime analogues indicates that this shielding is least pronounced in the dpgH complexes.[12d]

Py$_\beta$ and Py$_\gamma$ are farther away from the ring current and hence are not effected by any change in R/X (compare the values in **1**−**10** with those in **11**−**14**).

The order of ligands, based on the decreasing order of upfield shift induced in Py$_\alpha$ in **1**−**14**, is Cl ≈ Br > NO$_2$ ≈ N$_3$ > Me ≈ Et ≈ other alkyls. This order seems to suggest that the coordination shift $\Delta\delta(^1\text{H,Py}_\alpha)$ is related to the covalence of the trans metal bond. This order is similar to the earlier findings by Lopez et al.,[12a] who have listed the ligands on the basis of small upfield shifts (<0.05 ppm) of $\Delta\delta(^1\text{H,Py}_\alpha)$ in R/XCo(dmgH)$_2$Py complexes. We believe that one should be careful in arriving at such a conclusion that is based on such small variations. $\Delta\delta(^{13}\text{C,Py}_\alpha)$ values do show a larger variation and should, therefore, give a more reliable order (see below).

(b) ^{13}C Chemical Shift. Most of the conclusions based on the ^{13}C chemical shift in **1**−**14** are similar to those based on the ^{1}H chemical shift. The ^{13}C Py$_\alpha$ resonance seems to be the most sensitive to the variation in R/X (compare the value in **1**−**10** vs **11**−**14** in Table 2). However, the order of the ligands based on $\Delta\delta(^{13}\text{C,Py}_\alpha)$ follows Cl ≈ N$_3$ >Br > NO$_2$ > >Me ≈ Et ≈ other alkyls. This is different from what we observed on the basis of the ^{1}H NMR chemical shifts.

The effect of base on the trans methyl group is observed, and on the basis of the ^{1}H values the order observed is imidazole > py > 3-picoline > Py-4^{t}Bu > morpholine > piperidine. This order correlates with the pK_b value of the free base, except for the value in imidazole. The methyl signal in the ^{13}C NMR is observed in only two cases, and hence, no comment can be made.

Cis Influence. With regard to the cis influence, we have considered (a) the effect of axial ligands on the equatorial dioxime ligand (b) the effect of the dioxime moiety on the axial ligands.

(a) The variation in R/X affects the gH resonance: for example, the gH resonance shifts downfield by 0.2 ppm in **11**−**14** as compared to the values in **1**−**10** (Table 1). This effect is opposite to the trans influence observed on the Py$_\alpha$ group, where an upfield shift was observed. The ring current model[11f,g,20] accounts for this observation. Similarly, the effect of the X group on $\delta(^{13}\text{C,C{=}N})$ in **11**−**14** is observed and it follows the order Br > Cl ≈ NO$_2$ > N$_3$. However, $\delta(^{13}\text{C,C{=}N})$ remains almost same in **1**−**10** (Table 2). This is similar to our earlier findings in cobaloximes with other dioximes.[12d] This means that the above order of the effect of X on the C=N chemical shifts is maintained for all four sets of dioximes (gH, dmgH, chgH, and dpgH).

The effect of B on $\delta(^1\text{H})$ for the gH proton gives the order piperidine ≈ morpholine > py > 3-picoline ≈ Py-4^{t}Bu ≈ imidazole. However, no significant effect of B on the $\delta(^{13}\text{C,C{=}N})$ value is observed (Tables 1 and 2).

(b) The cis influence of the dioxime ligand on pyridine is observed by comparing the coordination shift of pyridine ($\Delta\delta(^1\text{H})$) and $\Delta\delta(^{13}\text{C,Py}_\alpha\text{,Py}_\beta\text{,Py}_\gamma)$, keeping the same R/X but changing the equatorial ligand. A comparison of the $\Delta\delta(^1\text{H,Py}_\alpha\text{,Py}_\beta\text{,Py}_\gamma)$ values in **1**−**14** with the values in other cobaloximes, R/XCo(dioxime)$_2$Py, gives the order as dpgH ≥ gH > dmgH ≈ chgH. A similar order is observed on the basis of the comparison of the $\Delta\delta(^{13}\text{C,Py}_\beta\text{,Py}_\gamma)$ values in **1**−**4** and **11**−**14** with those of the other dioxime complexes. $\Delta\delta(^{13}\text{C,Py}_\alpha)$, however, does not shift much.

The effect of the dioxime moiety on the ^{1}H chemical shift of C$_\alpha$ in MeCo(dioxH)$_2$Py complexes follows the order dpgH > gH > chgH > dmgH.[16a] The order cannot be reached on the basis of the ^{13}C values, since C$_\alpha$ is not observed in some cases.

The extent of the electron density on the Co(dioxime)$_2$ chelate ring for different dioximes (keeping R/X and Py constant) can be understood by comparing the $\delta(^{13}\text{C,C{=}N})$ values of the equatorial dioximes in R/XCo(dioximes)$_2$Py. We find that the $\delta(^{13}\text{C,C{=}N})$

---

[20] Alvarez, S.; Vicente, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 6253.

values in gH complexes **1**−**4** and **11**−**14** occur significantly upfield by 12−13 ppm as compared to the values in R/XCo(L)$_2$Py (L = dmgH, chgH, dpgH).[16a] This is the largest shift ever observed in such dioxime complexes. The order based on the upfield shift of $\delta(^{13}\mathrm{C,C{=}N})$ values is gH ≫ dmgH > dpgH ≈ chgH. This would mean that there is much higher charge density on the C=N group in the gH complexes as compared to that in the cobaloximes with other dioximes. These variations can be related to the changes in the electron-donating ability of the dioxime ligand, and any increase in the electron density in the equatorial Co(dioxime)$_2$ moiety will be reflected in the shift of the oximinic carbon atom (C=N). However, this increased charge density may not be entirely due to the cis influence of the dioxime ligand alone but may arise partly due to the substituent effect of the group on the C=N. For example, the ^{13}C chemical shift (C=N) in free gH (unligated) occurs 5−9 ppm upfield as compared to the values in dmgH, chgH, and dpgH.[24]

Inorganic Cobaloximes vs Organocobaloximes. A comparison of the $\delta(^{13}\mathrm{C})$ values for C=N, Py$_\alpha$, Py$_\beta$, and Py$_\gamma$ in **11**−**14** with the values in **1**−**10** shows that the latter occur upfield by 1−3 ppm. We have made similar observations earlier.[12d]

Correlations.[25] The trans influence is correlated with the cis influence experienced by the gH protons of the equatorial ligand:

$$\delta(^{1}\mathrm{H,gH}) = 7.45(0) - 0.58(5)[\Delta\delta(^{1}\mathrm{H,Py}_\alpha)]$$

$$r^2 = 0.97,\ \mathrm{esd} = 0.02\ \mathrm{ppm}$$

The chemical shifts of Py$_\alpha$, affected by the cobalt electrons, correlate well with the equatorial gH protons, affected by the C=N bonds. This indicates electron delocalization throughout the CoC$_4$N$_4$ system. It thus seems appropriate to explain the chemical shifts in terms of the magnetic anisotropy of the whole Co(dioxime)$_2^+$ metallabicycle rather than consider separate effects for cobalt and the C=N bonds.

The ^{13}C chemical shift of the C=N group of the dioxime moiety in **1**−**4** and **11**−**14** occurs at higher field than in their analogues with other dioximes (dmgH, chgH, dpgH) having identical R/X and B groups. Fairly good correlations are found:

$$\delta(^{13}\mathrm{C,C{=}N\ gH}) = -5.84(485) + 0.96(03)[\delta(^{13}\mathrm{C,C{=}N\ dmgH})]$$

$$r^2 = 0.99,\ \mathrm{esd} = 0.12\ \mathrm{ppm}$$

$$\delta(^{13}\mathrm{C,C{=}N\ gH}) = 3.24(777) + 0.89(05)[\delta(^{13}\mathrm{C,C{=}N\ dpgH})]$$

$$r^2 = 0.98,\ \mathrm{esd} = 0.21\ \mathrm{ppm}$$

$$\delta(^{13}\mathrm{C,C{=}N\ gH}) = 28.54(540) + 0.73(04)[\delta(^{13}\mathrm{C,C{=}N\ chgH})]$$

$$r^2 = 0.99,\ \mathrm{esd} = 0.18\ \mathrm{ppm}$$

These variations can be related to the changes in the electron-donating ability of the equatorial group. An increase in the electronic density of the equatorial Co(dioxime)$_2$ moiety will be reflected in a shift of the oximinic carbon atom. We may conclude that the upfield shift of the C=N resonance follows the order gH ≫ dmgH > chgH ≥ dpgH.

A good correlation between the $\delta(^{1}\mathrm{H,gH})$ value and the $\Delta\delta(^{13}\mathrm{C,Py}_\alpha)$ value is observed. This relationship is analogous to that in the previously described cobaloximes RCo(dioxime)$_2$B (dioxime = dmgH, chgH, dpgH; B = nitrogen bases).[12d,14d]

$$\delta(^{1}\mathrm{H,gH}) = 7.46(1) + 0.20(2)[\Delta\delta(^{13}\mathrm{C,Py}_\alpha)]$$

$$r^2 = 0.93,\ \mathrm{esd} = 0.03\ \mathrm{ppm}$$

This means one can get the same information using either ^{1}H or ^{13}C chemical shifts.

The chemical shift $\delta(^{13}\mathrm{C,C{=}N})$ correlates well with the coordination shift of pyridine ($\Delta\delta(^{13}\mathrm{C,Py}_\alpha)$, $\Delta\delta(^{13}\mathrm{C,Py}_\beta)$, and $\Delta\delta(^{13}\mathrm{C,Py}_\gamma)$) and also with the $\Delta\delta(^{1}\mathrm{H,Py}_\alpha)$ and $\Delta\delta(^{1}\mathrm{H,Py}_\beta)$ values (Supporting Information).

UV−Vis Spectra. The alkyl complexes **1**−**10** show a Co−C CT band between 456 and 459 nm with an intensity (log ϵ) in the range 3.64−4.54 and a MLCT band around 234 nm with log ϵ in the range 4.23−4.54. However, we are unable to see the Co−C CT band in **1**, though Schrauzer[15d] has reported this value at 405 nm in an alcohol−water mixture. In some cases, a shoulder near 305 nm is also seen and it is assigned to a d−d transition. The complexes **11**−**14**, however, show only the MLCT band around 255 nm (log ϵ 3.22−3.59). The assignments are made on the basis of previous work in organocobaloximes with similar dioximes.[12a,d,14d] The position of the Co−C CT band depends on the dioxH ligand on the equatorial site: for example, the $\lambda_{\mathrm{Co-C}}$ band in MeCo(dioxH)$_2$Py has been found to be at 405, 440.8, 445.8, and 473 nm for dioxH = gH, dmgH, chgH, dpgH.[15d,16a] This can be explained in terms of the variations observed in the electron-donating ability of the dioxH ligand.

Most of the earlier studies in RCo(dmgH)$_2$Py have reported the $\lambda_{\max}$ values in solvents such as chloroform, dichloromethane, ethanol, and water. Organocobaloximes show a 5-/6-coordinate equilibrium, depending upon the solvent used.[8a] Since nothing is known about the solution behavior of the gH complexes, we have carried out the UV−vis studies in various solvents in order to ascertain the best solvent for such a study. Our studies show that the behavior of gH complexes **1**−**10** in solution is similar to that of the organocobaloximes RCo(dioxH)$_2$Py (dioxH = dmgH, chgH, dpgH) described before[16a] (Supporting Information).

A good correlation is found between the $\lambda_{\max}$(MLCT) values of gH complexes **1**−**14** with the $\Delta\delta(^{1}\mathrm{H,Py}_\alpha)$ and $\Delta\delta(^{13}\mathrm{C,Py}_\alpha)$ values:

$$\lambda_{\max}(\mathrm{gH}) = 237.45(101) - 59.22(471)[\Delta\delta(^{1}\mathrm{H,Py}_\alpha)]$$

$$r^2 = 0.96,\ \mathrm{esd} = 2.25\ \mathrm{nm}$$

$$\lambda_{\max}(\mathrm{gH}) = 238.35(167) + 18.66(263)[\Delta\delta(^{13}\mathrm{C,Py}_\alpha)]$$

$$r^2 = 0.89,\ \mathrm{esd} = 3.84\ \mathrm{nm}$$

Also we observe good correlations between the $\lambda_{\max}$(MLCT) values of gH complexes **1**−**4** and **11**−**14** with

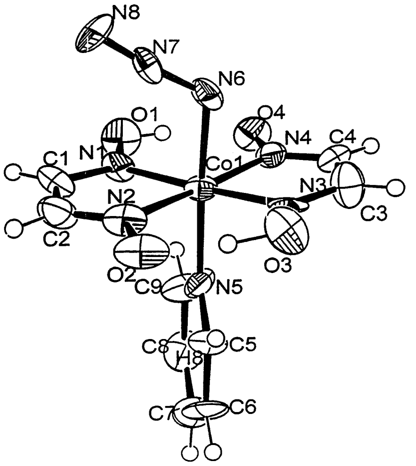


Figure 1. ORTEP plot of the structure of $N_3Co(gH)_2Py$ (**14**).

the λ_{max}(MLCT) values of the corresponding dioxime complexes (dmgH and chgH) (Supporting Information). This is similar to what we have observed in the ^{13}C NMR chemical shifts. Many other correlations of the λ_{max}(MLCT) values of gH complexes **1**−**14** with the $\Delta\delta$(^{1}H,Py$_{\beta}$), $\Delta\delta$(^{13}C,Py$_{\beta,\gamma}$), and δ(^{13}C,C=N) values have also been observed (Supporting Information).

X-ray Crystallographic Studies: Description of the Structure of 14. The ORTEP diagram of $N_3Co(gH)_2Py$ (**14**) is shown in Figure 1. Though the crystal data is of low resolution, it still allows us to make a few general comments on the structure and its comparison with other known structures.

The Co atom is linked to four nitrogen atoms of the glyoximato ligand in the equatorial plane. The cobalt atom displays an approximately octahedral coordination and is −0.069 Å out of the mean plane of the four nitrogen atoms, the displacement being toward the N_3 group. This deviation from planarity (*d*) is slightly more than in **1** (0.050 Å),[13b] and also the displacement in the latter is in the opposite direction: i.e., toward pyridine. A similar deviation toward pyridine (0.069 Å) is found in $N_3Co(dmgH)_2Py$.[21a] The deviation is found to be very small in the $ClCo(gH)_2PzMe_2$ complex (0.020 Å).[13c]

The Co−N_5 and Co−N_6 bonds are perpendicular (90°) to the equatorial plane, as seen in the N_{eq}−Co−N_5, N_{eq}−Co−N_6 and N_5−Co−N_6 bond angles. Co−N_{eq} and Co−N_{axial} (Co−N_5 and Co−N_6) bond distances in **14** are not significantly different from those in $N_3Co(dmgH)_2Py$.[21a] This means that the equatorial dioxH moiety does not have any cis influence. The Co−N_5 bond distance in **1** is longer (2.064 Å) as compared to the value in **14** (1.96 Å), indicating trans influence. A similar effect was observed in $RCo(dmgH)_2Py$ (R = Me, N_3).[21] This may be one of the reasons for the observed difference in ^{1}H and ^{13}C values of pyridine in **1** and **14**.

Table 4. CV Data for $ClCo(L)_2Py$ in CH_3CN and $TBAPF_6$ at 0.1 V s^{-1} at 25 °C

	Co^{III}−Co^{II}	Co^{II}−Co^{I}		
L	E_{pc}, V	$E_{1/2}$, V	ΔE_p, mV	E_{pa}, V[a]
dmgH	−0.53 (irrev)	−1.05	99	
dpgH	−0.45 (irrev)	−0.72	105	1.45 (irrev)
gH	−0.38 (irrev)	−0.69	113	1.50 (irrev)

[a] Ligand oxidation.

The pyridine ring is practically perpendicular to the cobaloxime equatorial plane and is parallel to the glyoxime C−C bonds. Its conformation is defined by a twist of 79.9°. The butterfly bending angle (α), formed by the two C_2N_2 fragments, is 4.3° in **14**. The changes in geometry of gH_2 on deprotonation and coordination are in agreement with those already observed in several analogous cobalt glyoximate complexes.[13b,c]

CV Studies. Cyclic voltammetric studies on cobaloximes that describe entire redox processes are very few.[22] As the yields of the alkyl gH complexes are poor in comparison to those of the corresponding dmgH or dpgH complexes, we have carried out CV studies on three $ClCo(L)_2Py$ compounds (L = dmgH, dpgH, gH) to see if the equatorial ligand plays any role in the stability of cobaloxime(I) or cobaloxime(II). The CV data are given in Table 4. All three cobaloximes exhibit one irreversible reduction (less negative potential) and one reversible reduction (more negative potential) corresponding to one-electron reductions of Co^{III}−Co^{II} and Co^{II}−Co^{I}, respectively. The $E_{p,c}$(Co^{III}−Co^{II}) and $E_{1/2}$(Co^{II}−Co^{I}) values for the gH complex are found to be more anodic than the corresponding values for $ClCo(L)_2Py$ (L = dmgH, dpgH), indicating a greater tendency to undergo reduction. The data also suggest that the Co(I) species is more stable in the gH complex as compared to the dmgH and dpgH cases.

There are only a few papers that describe the oxidation of cobaloximes. There is no peak or couple on the oxidation side of the dmgH complex, whereas one irreversible oxidation peak appears for the dpgH complex and one irreversible peak appears for the gH complex. This may be due to the oxidation of oximes. We have not studied this in detail.

Acknowledgment. We thank the Department of Science and Technology (DST), New Delhi, India, for funding this project (Project No. SP/S1/F20/99).

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for the structural analysis (torsion angle, $\mu(i,j)$ values, atomic parameters, bond lengths and bond angles) have been deposited with the Cambridge Crystallographic Data Centre, CCDC number for (*14*) is 171233. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Rd., Cambridge CB2 1EX, UK (fax +44-1223-336033; email: deposit@ccdc.com.ac.uk or www:http:/www.ccdc.cam.ac.uk).

OM020331F

---

(21) (a) Clearfield, A.; Gopal, R.; Kline, R. J.; Sipski, M. L.; Urban, L. O. *J. Coord. Chem* **1978**, *8*, 5. (b) Bigotto, A.; Zangrando, E.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1976**, 96.

(22) (a) Asaro, F.; Dreos, R.; Nardin, G.; Pellizer, G.; Peressini, S.; Randaccio, L.; Siega, P.; Tauzher, G.; Tavagnacco, C. *J. Organomet. Chem.* **2000**, *601*, 114. (b) Ngameni, E.; Ngoune, J.; Nassi, A.; Belombe, M.; Roux, R. *Electrochim. Acta* **1996**, *41*, 2571.

(23) Cobaloximes have the general formula $RCo(L)_2B$, 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), and diphenylglyoxime (dpgH)).

(24) δ(^{13}C,C=N) (DMSO + $CDCl_3$): $chgH_2$, 152.95; $dmgH_2$, 154.08; $dpgH_2$, 155.25; gH_2, 145.37.

(25) Eight values are taken for each correlation (X = Me, Et, Pr, Bu, Cl, Br, NO_2, N_3).