# Organocobaloximes with Mixed Dioxime Equatorial Ligands: A Convenient One-Pot Synthesis. X-ray Structures and Cis−Trans Influence Studies

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A simple and general route to the synthesis of organocobaloxime with mixed dioxime ligands, RCo(L)(dpgH)Py [L = dmgH and chgH] (R = Me-Dec), has been described. The crystal structure of four complexes, ClCo(L)(dpgH)Py and MeCo(L)(dpgH)Py [L = dmgH and chgH], is reported. The structural study reveals that both the nonclassical C−H···O as well as the classical O−H···O intermolecular hydrogen bonding is present and leads to the formation of one-dimensional dimeric or polymeric structures. $^1$H and $^{13}$C NMR coordination shifts in the axial pyridine ligand show clear correlations with the chemical shift of the equatorial ligand. These correlations can be rationalized with the aid of the ring current model.

## Introduction

Organocobaloximes (general formula RCo(L)$_2$B, where R, an organic group $\sigma$ bonded to cobalt; B, axial base trans to the organic group; L, dioxime ligand, e.g., gH, glyoxime, dmgH, dimethylglyoxime; chgH, 1,2-cyclohexanedione dioxime; dpgH, diphenylglyoxime (all monoanions)) have extensively been used to mimic the vitamin B$_{12}$ coenzyme.[1] Apart from the structural similarities, the theoretical calculations have shown a close resemblance between the MO calculations of cobalamin and cobaloximes.[2a] This is reflected in their catalytic abilities for many important chemical transformations.[3−8] Finke et al., however, have suggested that the Costa model is a closer electrochemical mimic of B$_{12}$ than the cobaloxime.[2b]

Many papers have appeared in the recent past that 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 NMR spectral data and molecular structure of these complexes.[1a−c] The driving force behind all 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 successful design of novel derivatives with desired properties. Several studies with this aim have appeared in the literature.[9,10,11] For instance, the reported trends in the $^1$H NMR chemical shifts in RCo(dmgH)$_2$B are related to the mutual cis and trans influence of the ligands.[9,10d,11] The reported studies also include the multilinear correlation of $^1$H NMR chemical shifts of B with the wavelength of the Co-dioxH charge transfer band.[11] These spectral correlations were initially rationalized on the basis of the

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**Table 1. $H^1$ NMR and $\lambda_{max}$ of 1b−10b**

| compd | O−H- -O | pyridine α | pyridine β | pyridine γ | dmgH | dpgH | Co−CH$_2$ | rest of alkyl chain | methyl | $\lambda_{max}$(log $\epsilon$) (methanol) |
|---|---|---|---|---|---|---|---|---|---|---|
| **1b** | 18.49 | 8.78, | 7.39, | 7.79 | 2.18 | 7.06−7.10, 7.18−7.22 | | | 1.14 | 447.7 (3.38) |
| **2b** | 18.43 | 8.77, | 7.38, | 7.78 | 2.19 | 7.05−7.11, 7.17−7.29 | 2.05 | | 0.61 | 459.9 (3.41) |
| **3b** | 18.43 | 8.76, | 7.37, | 7.77 | 2.18 | 7.04−7.10, 7.17−7.26 | 1.92 | 1.20−1.26 | 0.89 | 460.0 (3.23) |
| **4b** | 18.42 | 8.76, | 7.38, | 7.78 | 2.18 | 7.04−7.10 7.18−7.29 | 1.94 | 1.14−1.22 1.25−1.36 | 0.87 | 457.1 (3.39) |
| **5b** | 18.43 | 8.76, | 7.38, | 7.77 | 2.18 | 7.04−7.07, 7.18−7.29 | 1.93 | 1.20−1.31 | 0.83 | 460.5 (3.50) |
| **6b** | 18.43 | 8.76, | 7.38, | 7.77 | 2.17 | 7.04−7.10, 7.18−7.23 | 1.93 | 1.16−1.29 | 0.85 | 460.4 (3.40) |
| **7b** | 18.41 | 8.76, | 7.37, | 7.77 | 2.17 | 7.04−7.11, 7.17−7.29 | 1.93 | 1.19−1.28 | 0.86 | 459.4 (3.32) |
| **8b** | 18.43 | 8.76, | 7.37, | 7.77 | 2.17 | 7.04−7.11, 7.18−7.29 | 1.93 | 1.17−1.27 | 0.86 | 460.9 (3.35) |
| **9b** | 18.43 | 8.76, | 7.37, | 7.77 | 2.17 | 7.01−7.10, 7.18−7.29 | 1.93 | 1.23−1.27 | 0.83 | 458.1 (3.36) |
| **10b** | 18.43 | 8.76, | 7.37, | 7.79 | 2.18 | 7.00−7.10, 7.18−7.30 | 1.93 | 1.23−1.27 | 0.87 | 457.0 (3.37) |

cobalt anisotropy,[9] but more recently the ring current formalism has been preferred.[11] As per this model, a ring current resulting from a 12 $\pi$ delocalized electron system of the cobaloxime would affect the nuclei in different ways, depending on their relative position to the metallabicycle, shielding those on top and deshielding those at the sides of the ring. Most of the above information has, however, come from the study of dmgH complexes only. Studies involving other oximes with varying steric and electronic properties such as gH,[12] chgH,[13] and dpgH[2,14] have been few. Much of the information on the correlation study has been derived from $^{1}$H NMR chemical shifts, as only a few cobaloximes have been characterized by both $^{1}$H and $^{13}$C NMR.[1a,9h,11c,12d,15] The in-depth study with $^{13}$C on equatorial ligands other than dmgH is, therefore, lacking. Efforts to correlate $^{1}$H and $^{13}$C resonance were made, but the results were rather poor.[9h,15b]

Keeping the above discussion in mind, we report the synthesis and study of a new class of alkyl cobaloximes with two dissimilar dioxime wings, RCo(L)(L′)Py, in the same molecule where L = dmgH or chgH, L′ = dpgH, and R = alkyl group. All these compounds are new and have been reported for the first time. The spectroscopic studies ($^{1}$H, $^{13}$C, UV−vis) on these complexes have been carried out. The aim of the study is (a) to verify if the trends in $^{1}$H NMR and UV data reported earlier for alkyl cobaloximes also apply to alkyl mixed dioxime cobaloximes, (b) to see if $^{13}$C gives similar or better information than $^{1}$H NMR, (c) to see if there is any correlation in $^{1}$H, $^{13}$C, and UV−vis data, (d) to see if one equatorial wing transmits its electronic effect to the other dioxime wing and thus affects the chemical shifts, and (e) to test the validity of the recently proposed ring current model.

We also report the crystal structure of four cobaloximes with mixed dioxime equatorial ligands, MeCo(dmgH)(dpgH)Py, MeCo(chgH)(dpgH)Py, ClCo(dmgH)(dpgH) Py, and ClCo(chgH)(dpgH)Py.

## Experimental Section

$ClCo^{III}(L)_2Py$ [L = dmgH, chgH, dpgH] were synthesized by the literature procedure.[13b,14c,16] The synthesis of $ClCo^{III}$(dmgH)(dpgH)Py and $ClCo^{III}$(chgH)(dpgH)Py has been detailed earlier by us.[15e] The alkyl halides dimethylglyoxime, diphenylglyoxime, and nioxime were purchased from Aldrich and were used as received. Silica gel (100−200 mesh) and distilled solvents were used in all chromatographic separations.

$^{1}$H and $^{13}$C spectra were recorded on a JEOL JNM LA 400 PT NMR spectrometer (at 400 MHz for $^{1}$H and at 100 MHz for $^{13}$C) in $CDCl_3$ solution with TMS as internal standard. UV−vis spectra were recorded on a Shimadzu 160A spectrometer. The degassed solvent was used for recording spectra. The 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.

**Crystal Structure Determination and Refinements.** Orange crystals were obtained by slow evaporation of solutions of the complexes in methanol. A small crystal size (as in Table 5) was selected and mounted on an Enraf-Nonius CAD-4 diffractometer (Nonius Kappa CCD for compound **22b**) equipped with a graphite monochromator. The unit cell parameters were determined from 25 reflections (39 366 reflections for **22b**) ($2\theta$ range 16−18 for **1b** and **21b**, 2−50 for **22b**, 19−20 for **11b**), and the cell parameters were refined by least-squares. Intensities were collected with Mo Kα radiation, using the $\theta-2\theta$, 2 deg phi and omega scan techniques. For compound **21b**, 4562 intensities were measured in the range 4−51 and 4375 were considered as observed applying the condition $I > 0.0\sigma(I)$, while 4837 reflections were measured for compound **11b** in the same range, from which 4681 were considered as observed. For compound **22b** 39 366 intensities were measured in the range 4−50, from which 4353 were considered as observed applying the above condition, while 4348 reflections were measured for compound **1b** in the same range, from which 4167 were considered as observed applying the condition $I > 1.0\sigma(I)$. Absorption corrections based on scan data were applied to the reflection intensities for these four compounds.

The structures were isotropically refined by full-matrix least-squares method, using the NRC386, NRCVAX, and the SHELXL-93 computer programs.[17] The function minimized was $[\sum[w(|F_o| - |F_c|)^2]^{0.5}]$, where $w = [\sigma^2(F_o^2) + (0.05F_o^2)^2]$.

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**Table 2. $H^1$ NMR and $\lambda_{max}$ of 11b−20b**

| compd | O−H⋯O | pyridine α | pyridine β | pyridine γ | chgH $C_2$ ortho | chgH $C_1$ para | dpgH | Co−$CH_2$ | rest of alkyl chain | methyl | $\lambda_{max}$(log$\epsilon$) (methanol) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **11b** | 18.25 | 8.79 | 7.40, | 7.80 | 1.56−1.74 | 2.55−2.67, 2.75−2.87 | 7.02−7.12, 7.16−7.26 | | | 1.15 | 445.0 (3.21) |
| **12b** | 18.18 | 8.77 | 7.39, | 7.79 | 1.59−1.71 | 2.56−2.66, 2.76−2.84 | 7.02−7.11, 7.16−7.26 | 2.05 | | 0.61 | 461.0 (3.37) |
| **13b** | 18.19 | 8.77 | 7.38, | 7.78 | 1.57−1.75 | 2.54−2.67, 2.73−2.86 | 7.02−7.10, 7.16−7.28 | 1.94 | 1.18−1.30 | 0.90 | 461.7 (3.24) |
| **14b** | 18.18 | 8.77 | 7.38, | 7.78 | 1.57−1.75 | 2.56−2.66, 2.75−2.85 | 7.02−7.10, 7.16−7.26 | 1.95 | 1.15−1.39 | 0.87 | 462.0 (3.50) |
| **15b** | 18.19 | 8.77 | 7.38, | 7.77 | 1.61−1.74 | 2.56−2.67, 2.76−2.84 | 7.02−7.12, 7.17−7.26 | 1.94 | 1.19−1.31 | 0.84 | 462.1 (3.43) |
| **16b** | 18.18 | 8.77 | 7.38, | 7.78 | 1.61−1.71 | 2.56−2.63, 2.76−2.84 | 7.02−7.10, 7.17−7.28 | 1.95 | 1.16−1.31 | 0.85 | 461.9 (3.47) |
| **17b** | 18.18 | 8.77 | 7.38, | 7.78 | 1.59−1.75 | 2.56−2.63, 2.76−2.84 | 7.01−7.10, 7.16−7.29 | 1.97 | 1.17−1.33 | 0.85 | 460.1 (3.44) |
| **18b** | 18.18 | 8.77 | 7.38, | 7.78 | 1.57−1.74 | 2.56−2.67, 2.74−2.86 | 7.01−7.12, 7.15−7.28 | 1.95 | 1.17−1.28 | 0.86 | 462.0 (3.49) |
| **19b** | 18.18 | 8.77 | 7.38, | 7.78 | 1.57−1.74 | 2.53−2.67, 2.76−2.86 | 7.01−7.10, 7.14−7.26 | 1.95 | 1.17−1.30 | 0.86 | 459.3 (3.43) |
| **20b** | 18.17 | 8.77 | 7.38 | 7.80 | 1.61−1.69 | 2.56−2.66, 2.76−2.84 | 7.02−7.10, 7.17−7.29 | 1.95 | 1.23−1.27 | 0.87 | 463.6 (3.33) |

**Table 3. $^{13}C$ NMR of 1b−10b**

| | **1b** | **2b** | **3b** | **4b** | **5b** | **6b** | **7b** | **8b** | **9b** | **10b** |
|---|---|---|---|---|---|---|---|---|---|---|
| dmgH | 12.17 | 12.15 | 12.18 | 12.18 | 12.18 | 12.17 | 12.18 | 12.20 | 12.17 | 12.18 |
| C=N(dpgH) | 150.57 | 150.57 | 150.64 | 150.63 | 150.61 | 150.61 | 150.61 | 150.59 | 150.60 | 150.60 |
| $Py_\alpha$ | 150.05 | 150.05 | 149.99 | 150.02 | 150.03 | 150.03 | 150.03 | 150.00 | 150.01 | 150.02 |
| C=N(dmgH) | 149.36 | 149.33 | 149.40 | 149.37 | 149.36 | 149.35 | 149.35 | 149.34 | 149.35 | 149.34 |
| $Py_\beta$ | 125.39 | 125.32 | 125.32 | 125.31 | 125.31 | 125.30 | 125.31 | 125.31 | 125.31 | 125.31 |
| $Py_\gamma$ | 137.74 | 137.62 | 137.63 | 137.62 | 137.60 | 137.60 | 137.61 | 137.62 | 137.62 | 137.61 |
| C* | 130.25 | 130.31 | 130.30 | 130.35 | 130.34 | 130.36 | 130.35 | 130.34 | 130.34 | 130.35 |
| Cα | 129.56 | 129.50 | 129.50 | 129.48 | 129.45 | 129.49 | 129.49 | 129.48 | 129.48 | 129.49 |
| Cβ | 127.82 | 127.81 | 127.81 | 127.83 | 127.81 | 127.83 | 127.83 | 127.82 | 127.82 | 127.82 |
| Cγ | 128.72 | 128.67 | 128.67 | 128.66 | 128.66 | 128.66 | 128.66 | 128.66 | 128.69 | 128.66 |
| C1 | | | 35.72 | | | | | 33.40 | 33.42 | 33.43 |
| C2 | | 16.00 | 23.94 | 33.11 | 32.93 | 31.72 | 31.91 | 31.87 | 31.93 | 31.92 |
| C3 | | | 15.02 | 23.74 | 30.37 | 30.70 | 30.74 | 30.74 | 30.79 | 30.73 |
| C4 | | | | 14.04 | 22.52 | 30.42 | 29.70 | 30.71 | 30.72 | 29.67 |
| C5 | | | | | 14.10 | 22.68 | 29.17 | 29.45 | 29.61 | 29.62 |
| C6 | | | | | | 14.09 | 22.65 | 29.31 | 29.49 | 29.57 |
| C7 | | | | | | | 14.15 | 22.69 | 29.31 | 29.50 |
| C8 | | | | | | | | 14.13 | 22.68 | 29.38 |
| C9 | | | | | | | | | 14.13 | 22.70 |
| C10 | | | | | | | | | | 14.13 |

**Table 4. $^{13}C$ NMR of 11b−20b[a]**

| | **11b** | **12b** | **13b** | **14b** | **15b** | **16b** | **17b** | **18b** | **19b** | **20b** |
|---|---|---|---|---|---|---|---|---|---|---|
| C=N (dpgH) | 150.53 | 150.59 | 150.68 | 150.66 | 150.64 | 150.64 | 150.64 | 150.64 | 150.64 | 150.65 |
| C=N (chgH) | 149.93 | 150.13 | 150.23 | 150.21 | 150.19 | 150.19 | 150.19 | 150.18 | 150.17 | 150.18 |
| $Py_\alpha$ | 150.09 | 150.13 | 150.05 | 150.05 | 150.05 | 150. 05 | 150. 05 | 150. 05 | 150. 05 | 150.12 |
| $Py_\beta$ | 125.36 | 125.32 | 125.32 | 125. 32 | 125. 32 | 125. 32 | 125. 32 | 125. 32 | 125.34 | 125.32 |
| $Py_\gamma$ | 137.70 | 137.62 | 137.62 | 137.62 | 137.61 | 137.61 | 137.61 | 137.61 | 137.60 | 137.60 |
| C* | 130.20 | 130.32 | 130.33 | 130.37 | 130.36 | 130.36 | 130.37 | 130.38 | 130.38 | 130.38 |
| Cα | 129.50 | 129.53 | 129.54 | 129.49 | 129.49 | 129.49 | 129.53 | 129.53 | 129.49 | 129.50 |
| Cβ | 127.71 | 127.82 | 127.84 | 127.83 | 127.83 | 127.83 | 127.77 | 127.82 | 127.81 | 127.82 |
| Cγ | 128.65 | 128.67 | 128.68 | 128.65 | 128.64 | 128.64 | 128.64 | 128.63 | 128.63 | 128.64 |
| $C_1$ (chgH) | 25.23 | 25.27 | 25.32 | 25.31 | 25.31 | 25.31 | 25.31 | 25.27 | 25.31 | 25.31 |
| $C_2$ (chgH) | 21.39 | 21.52 | 21.52 | 21.50 | 21.51 | 21.51 | 21.51 | 21.51 | 21.51 | 21.51 |
| C1 | 12.72 | | 35.81 | | 33.39 | 33.48 | 33.48 | 33.46 | 33.47 | 33.50 |
| C2 | | 16.06 | 23.95 | 33.17 | 32.89 | 31.75 | 31.88 | 31.89 | 31.94 | 31.93 |
| C3 | | | 15.06 | 23.74 | 30.38 | 30.71 | 30.70 | 30.73 | 30.73 | 30.74 |
| C4 | | | | 14.08 | 22.54 | 30.39 | 29.70 | 29.47 | 30.70 | 30.70 |
| C5 | | | | | 14.09 | 22.66 | 29.18 | 29.32 | 29.60 | 29.63 |
| C6 | | | | | | 14.11 | 22.66 | 29.26 | 29.49 | 29.53 |
| C7 | | | | | | | 14.16 | 22.70 | 29.34 | 29.46 |
| C8 | | | | | | | | 14.11 | 22.68 | 29.40 |
| C9 | | | | | | | | | 14.13 | 22.71 |
| C10 | | | | | | | | | | 14.13 |

[a] C*: phenyl carbon attached to −C=N. Cα, Cβ, Cγ: phenyl carbons.

The hydrogen atoms of the OH groups were located on difference maps and constrained to the difference map positions. The orientations of the methyl H atoms were also determined from difference maps and refined with an overall isotropic temperature factor. The cyclohexane group of **11b** and **22b** has disorder with 70−30 occupancies (a and b atoms) and

**Table 5. Crystal Data and Structure Refinement Parameters for 21b, 22b, 1b, and 11b**

| | **21b** | **22b** | **1b** | **11b** |
|---|---|---|---|---|
| formula | $CoClO_4N_5C_{23}H_{23}$ | $CoClO_4N_5C_{25}H_{25}$ | $CoO_4N_5C_{24}H_{26}$ | $CoO_4N_5C_{26}H_{28}$ |
| fw | 527.85 | 553.88 | 507.43 | 533.47 |
| cryst size, mm | 0.16 × 0.36 × 0.40 | 0.25 × 0.35 × 0.55 | 0.36 × 0.38 × 0.40 | 0.24 × 0.36 × 0.56 |
| cryst color | orange | orange | orange | orange |
| $a$, Å | 9.130(2) | 15.334(1) | 9.0192(13) | 15.165(4) |
| $b$, Å | 9.4271(14) | 9.332(1) | 9.6727(15) | 9.481(2) |
| $c$, Å | 14.581(3) | 17.806(1) | 14.589(2) | 17.933(6) |
| $\alpha$, deg | 83.788(14) | | 83.313(13) | |
| $\beta$, deg | 88.899(15) | 103.11(1) | 78.701(12) | 102.75(2) |
| $\gamma$, deg | 71.181(14) | | 72.286(12) | |
| $V$, Å$^3$ | 1180.8(4) | 2481.6(3) | 1186.7(3) | 2514.8(12) |
| cell detn, reflns | 25 | 39,366 | 25 | 25 |
| cell detn, $2\theta$ range, deg | 16−18 | 2−50 | 16−18 | 19−20 |
| $d$(calcd), g cm$^{-3}$ | 1.48 | 1.48 | 1.42 | 1.41 |
| space group | $P\bar{1}$ | $P2_1/n$ | $P\bar{1}$ | $P2_1/n$ |
| $Z$ | 2 | 4 | 2 | 4 |
| $F$000 | 545.1 | 1146.0 | 528.8 | 1111.75 |
| radiation | Mo K$\alpha$, graphite monochromated | | | |
| $\lambda$, Å | 0.7107 | 0.7107 | 0.7107 | 0.7107 |
| temp, K | 293 | 298 | 293 | 293 |
| linear abs coeff, mm$^{-1}$ | 0.88 | 0.84 | 0.76 | 0.72 |
| diffractometer | Enraf-Nonius CAD-4 | Nonius Kappa CCD | Enraf-Nonius CAD-4 | Enraf-Nonius CAD-4 |
| scan technique | $\theta-2\theta$ | 2° phi and omega scans | $\theta-2\theta$ | $\theta-2\theta$ |
| $2\theta$ range, deg | 4−51 | 4−50 | 4−50 | 4−51 |
| $h, k, l$ ranges | −11, 11; −11, 11; −17, 0 | −18, 18; −11, 11; −21, 21 | −10,10;−11,11; −17, 0 | −18, 18; 0, 11; 0, 21 |
| drift of stds, % | 1.4 | 1.0 | 2.2 | 1.6 |
| absorption correction | analytical | none | analytical | analytical |
| absorption range | 0.54−0.87 | | 0.74−0.79 | 0.75−0.86 |
| no. of reflns measd | 4562 | 39 366 | 4348 | 4837 |
| no. of unique reflns | 4375 | 4353 | 4167 | 4681 |
| $R$ for merge | 0.020 | 0.030 | 0.015 | 0.019 |
| no. of reflns in refinement, $I > 0.0\sigma(I)$ | 4375 | 4353 | $I > 1.0\sigma(I)$ 3396 | 4681 |
| no. of params refined | 307 | 327 | 308 | 323 |
| $R(F)$, $R_w(F)$ | 0.059, 0.064 | 0.053, 0.079 | 0.040, 0.053 | 0.069, 0.068 |
| $R$ for $I > 3.0\sigma(I)$ | 0.039 | 0.036 | 0.035 | 0.039 |
| GOF | 0.94 | 1.20 | 1.26 | 0.93 |
| $P$, $w^{-1} = [\sigma^2(I) + pI^2]/4F^2$ | 0.05 | 0.05 | 0.03 | 0.05 |
| largest $\Delta/\sigma$ | 0.00 | 0.00 | 0.00 | 0.00 |
| extinction corr | none | | 0.04(3) | none |
| final diff map, e Å$^{-3}$ | −0.49(10), +0.79(10) | −0.29(8), +1.02(8) | −0.25(5), +0.42(5) | −0.53(9), +0.55(9) |

50−50 occupancies, respectively, in the model with all four carbons refined using isotropic displacement parameters. The pertinent crystal data and refinement parameters are compiled in Table 5.

**Synthesis of alkylCo(dmgH)(dpgH)Py (1b−10b).** These were synthesized by two methods. The general procedure is outlined below.

**Method a.** NaOH (1 pellet dissolved in 1.0 mL of water) was added to a suspension of $ClCo^{III}(dmgH)_2Py$ (0.201 g, 0.5 mmol) and $ClCo^{III}(dpgH)_2Py$ (0.326 g, 0.5 mmol) in methanol (10 mL), and the reaction mixture was thoroughly purged with argon for 15 min. The temperature was brought down to 0 °C by a Julabo refrigerator circulator. The reaction mixture turned deep blue after the addition of $NaBH_4$ (0.048 g, 1.27 mmol in 1 mL of water). Methyl iodide (0.213 g, 1.5 mmol) in methanol (5 mL) was added dropwise. The reaction mixture was stirred for 3 h in the dark, during which it was brought to ambient temperature, and the contents were poured into water. The orange-red solid was filtered, dried, and chromatographed on a silica gel column with ethyl acetate/chloroform as eluent, yielding three products: **1a** (0.257 g, 65%), **1b** (0.024 g, 8%), and **1c** (0.065 g, 27%). The products **1a** and **1c** were compared with the authentic samples from our laboratory.

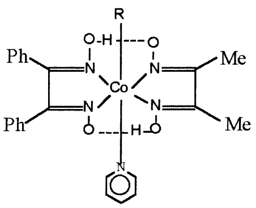
**Method b.** The same procedure as outlined in method a was used except that $ClCo^{III}(dmgH)(dpgH)Py$ (0.529 g, 1 mmol) was used as the starting cobaloxime. Three products were isolated and purified by column chromatography: **1a** (0.037 g, 10%), **1b** (0.241 g, 84%), and **1c** (0.014 g, 6%).

**Synthesis of alkylCo(chgH)(dpgH)Py (11b−20b). Method a.** The same procedure as outlined above for the preparation of **1b** was used. Now a mixture of $ClCo^{III}(chgH)_2$-Py (0.230 g, 0.5 mmol) and $ClCo^{III}(dpgH)_2Py$ (0.326 g, 0.5 mmol) was used. Three products were isolated and purified by column chromatography: **11a** (0.235 g, 59%), **11b** (0.031 g, 9%), and **11c** (0.085 g, 32%). The products **11a** and **11c** were compared with the authentic samples from our laboratory.

**Method b.** The same procedure as outlined above for the preparation of **1b** (method b) was used except that $ClCo^{III}(chgH)(dpgH)Py$ (0.277 g, 0.5 mmol) was used as the starting cobaloxime. Only two products were isolated and purified by column chromatography: **11a** (0.006 g, 4%) and **11b** (0.145 g, 96%).

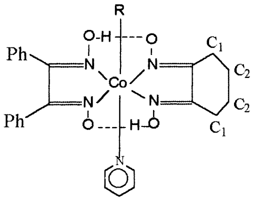
**Separation of Products: Column Details.** The orange-red powder containing the mixture of cobaloximes, dissolved in a minimum amount of chloroform, was loaded on a silica gel (100−200 mesh) column pre-eluted with chloroform. The polarity was increased carefully with ethyl acetate. Three distinct bands were visible with 10% ethyl acetate in chloroform. The first band corresponding to the dpgH complex eluted out completely with 10% ethyl acetate. The mixed ligand complex eluted out with a 10−50% ethyl acetate/chloroform mixture, and the dmgH complex finally came out with a 50−100% ethyl acetate/chloroform mixture. Any deviation in these ratios gave the contaminated products.

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 (**1b**, **11b**, **21b**, and **22b**) as 145905, 145906, 145907, and 145908, respectively. Copies of the data can be obtained free of charge from the



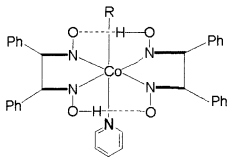
RCo(dmgH)(dpgH)Py

R= Me-Dec (1b-10b)



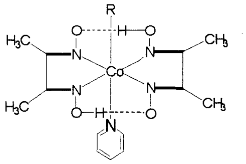
RCo(chgH)(dpgH)Py

R= Me-Dec (11b-20b)



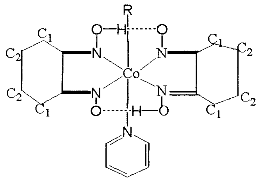
RCo(dpgH)₂Py

(1a-10a)



RCo(dmgH)₂Py

(1c-10c)



RCo(chgH)₂Py

(11c-20c)

Director, CCDC, 12 Union Rd., Cambridge CB2 1EX, UK (fax +44-1223-336033; e-mail: deposit@ccdc.com.ac.uk or www: http:/www.ccdc.cam.ac.uk).

## Results and Discussion

**Synthesis.** Organocobaloximes, RCo(L$_2$)B, have been synthesized by a number of methods; however organocobaloximes with mixed dioxime ligands, RCo(L)(L′)B, have virtually been unknown until recently.[15e]

Schrauzer et al. have reported the following reaction and proposed that the reaction undoubtedly proceeds by stepwise displacement of the dmgH$_2$ ligand and the reaction does not involve an ionic intermediate like CH$_3$−Co$^{2+}$. However, they could not isolate the intermediate mixed ligand complex, MeCo(dmgH)(chgH)B (B = Py or H$_2$O).[18]

$$\mathrm{MeCo(dmgH)_2H_2O} + \mathrm{chgH_2} \xrightarrow[\text{toluene, Py}]{140\ {}^\circ\mathrm{C}} \mathrm{MeCo(chgH)_2Py}$$

Later, Johnson et al. reported the kinetics and mechanistic study of the apparent alkyl transfer from alkylcobaloximes to cobaloxime(I), cobaloxime(II), and cobaloxime(III) reagents.[13c] They have proposed the formation of mixed ligand species, RCo(dmgH)(chgH)B, in solution. However, they did not isolate the species. Only solution NMR values of the mixtures are reported.

We have recently published the synthesis of benzyl cobaloximes with mixed dioxime ligands.[15e] In view of these findings and the fact that oxidative alkylation of cobaloxime(I) by alkyl halides finds a much wider use in the synthesis, we have, first, carried out the reaction of alkyl halide with a 1:1 mixture of Co$^{I}$ (dmgH)$_2$Py and Co$^{I}$ (dpgH)$_2$Py under strict inert conditions. Three products were formed, but the yield of the desired alkyl mixed ligand complexes **1b**−**10b** was very poor (as given in the Supporting Information). Similar results were obtained in the reaction of a 1:1 mixture of Co$^{I}$(chgH)$_2$Py and Co$^{I}$(dpgH)$_2$Py with alkyl halides. RCo(dpgH)$_2$Py (**1a**−**10a**) was found to be the major product in all these reactions. We have made no attempt to study the details of the extent of formation of each product with time. The basic aim was to improve the yield of the mixed ligand complex, and we were able to achieve this by the reaction of alkyl halide with Co$^{I}$(L)(dpgH)Py [ L = dmgH, chgH], generated in situ by the sodium borohydride reduction of ClCo(L)(dpgH)Py [L = dmgH or chgH]. The desired complexes were formed in high yield (67−84%). In all, 20 new alkyl mixed ligand complexes (**1b**−**20b**) were synthesized. In all these reactions the side products, **1a**−**10a** and **1c**−**20c**, were formed in less than 10% yield. The spectral characteristics of the compounds **1b**−**20b** are given in Tables 1−4. The elemental analysis and the $R_f$ values of compounds **1b**−**20b** are given in the Supporting Information. The spectral characteristics of complexes **1a**−**10a** and **1c**−**20c** have been described before.[19] The synthesis of compounds was confirmed by X-ray structures on MeCo(dmgH)(dpgH)Py and MeCo(chgH)(dpgH)Py.

We have made no attempt to study its mechanism in detail. However our results support the earlier observation by Johnson et al. that the randomization of the dioxime ligand along with the alkyl transfer in the presence of cobaloxime(I) is taking place.[13c]

$^1$H, $^{13}$C, and $\lambda_{\max}$ of alkyl cobaloximes **1a**−**10a** and **1c**−**20c** have previously been reported by us.[19] These have been helpful in the assignment of $^1$H NMR values in **1b**−**20b**. $^{13}$C values have been assigned for only a few organocobaloximes in the literature.[1a,9h,11c,14a] The following information might be useful in the assignment of $^{13}$C shifts in **1b**−**20b**.

The $^{13}$C resonances of dmgH (Me), chgH (C1 and C2), dpgH (C*, C$_\alpha$, C$_\beta$, C$_\gamma$), Co−CH$_2$, and Py$_\beta$ and Py$_\gamma$ are easily assigned on the basis of their chemical shifts. The assignment is consistent with those of the related and previously described alkylcobaloximes.[19] However, the assignment of C=N (dmgH or chgH), C=N (dpgH), and Py$_\alpha$ has been difficult since these occur very close to each other. The assignment has been confirmed by $^1$H−$^{13}$C correlation experiments.

$^1$H and $^{13}$C NMR spectra of complexes **1b**−**20b** (Tables 1−4) show some general trends that are described below. We have recently shown that six-coordinate octahedral organocobaloximes are the ideal systems for the study of cis and trans influence.[12d,13b,d,19] It was observed, on the basis of the spectral studies, that the cis influencing ability in alkyl cobaloximes followed the order dpgH > chgH >dmgH. $^1$H and $^{13}$C NMR studies showed that O−H- - -O and Py$_\alpha$ were the most affected, followed by Py$_\gamma$. The present study on alkyl mixed dioxime complexes throws further light on this phenomenon.

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(18) Schrauzer, G. N.; Windgassen, R. J. *J. Am. Chem. Soc.* **1966**, *88*, 3738.

(19) Gupta, B. D.; Kushal, Q. *J. Organomet. Chem.* **1997**, *543*, 125.

The chemical shift values of O−H- - -O in **1b**−**10b** and **11b**−**20b** lie between their parent cobaloximes, $RCo(L)_2Py$ [L = dmgH, chgH, dpgH],[19] and the chemical shifts in **11b**−**20b** are consistently upfield as compared to the value in **1b**−**10b**. Overall, O−H- - -O resonance follows the order dpgH > dmgH-dpgH > chgH-dpgH ≈ dmgH > gH[12d] > chgH. The value, however, remains almost the same within the same series in all the complexes. We have observed a high downfield shift for the O−H- - -O resonance, nearly 0.6 ppm in chgH/dpgH cobaloximes compared to the value in the parent chgH cobaloxime. This difference can be explained by taking into account the presence of a phenylic ring in the neighborhood of the axial ligands and thus producing deshielding of its nuclei.

We have observed that $\delta^1$H Py$_\alpha$ in **1b**−**20b** consistently shifts downfield by about 0.2 ppm compared to free Py$_\alpha$. This may appear to be at variance to the reported work in $XCo(dmgH)_2Py$, where $\delta^1$H Py$_\alpha$ either shifts upfield on coordination to the cobaloxime moiety (X = inorganic group) or remains constant (when X is an alkyl group).[11a,15d,19] An opposite situation occurs in the analogous dpgH compounds, where $\delta^1$H Py$_\alpha$ either occurs downfield by 0.3−0.4 ppm (X = alkyl) or remains almost constant (X = inorganic group).[15d,19] Does it mean that the ring current operates differently in dmgH and dpgH complexes? This may be understood keeping the following information in mind. Cobaloxime is a bicyclic system with 12 $\pi$ electrons, eight from the C═N bonds and four from the metal d$_{xz}$ and d$_{yz}$ orbitals. MO calculations of the EH type show that these electrons occupy six $\pi$ type orbitals delocalized throughout the planar cobaloxime moiety, with topologies analogous to those reported previously for $L_2MC_4H_4$ metallacycles. A ring current resulting from the delocalized electron system of the cobaloxime would affect nuclei in different ways, and many of the spectral correlations in $XCo(dmgH)_2B$ have now been rationalized with the aid of this ring current formalism.[11] Apparently, the situation appears quite opposite in the analogous compounds with dpgH, where the axial ligand signals are not very sensitive to coordination. This difference has been explained by taking into account the presence of a phenylic ring in the neighborhood of the axial ligands and thus producing deshielding of its nuclei. In effect, the values of the shielding constants, as determined by Johnson and Bovey,[20] indicate that the presence of a phenylic group should produce a shift of ≅+0.2 ppm on the signals of the α proton of the axial ligands. It is concluded, therefore, that the same effect operates on both dmgH and dpgH, producing an upfield shift on the axial ligand signal, and this effect is compensated in the case of dpgH by a long-range effect of the phenyl substituent on the equatorial ligand. Since organocobaloximes **1b**−**20b** have two dissimilar equatorial wings, the downfield shift of 0.2 ppm observed in Py$_\alpha$ is justified and supports the ring current model.

It has been observed earlier that the $^1$H chemical shift of Co−C$_\alpha$ in **1c**−**10c** complexes appears upfield by about 0.6 ppm when compared with **1a**−**10a**.[19] The $^1$H chemical shift of Co−C$_\alpha$ in **1b**−**10b** lies between the corresponding value in **1a**−**10a** and **1c**−**10c**. Similar is the case in **11b**−**20b**, and the value lies between **11a**−**20a** and **1c**−**10c**. This is an expected observation since the present systems have dmgH and dpgH wings and their shielding/deshielding effect operates in the opposite direction. Since the overall effect shows deshielding, it may mean that the effect of the dpgH wing is more predominant than the dmgH wing. The same observation was noticed in the Py$_\alpha$ shift. This, once again, supports the ring current model.

The $^1$H and $^{13}$C resonances of pyridine in **1b**−**20b** on coordination to the cobaloxime moiety shift downfield, and this coordination shift ($\Delta\delta = \delta$ complex $- \delta$ free py[15e]) follows the order $\Delta\delta^{13}$C Py$_\gamma$ ≥ $\Delta\delta^{13}$C Py$_\beta$ > $\Delta\delta^{13}$C Py$_\alpha$ (given in the Supporting Information). The same order follows based on the $^1$H NMR values.

A change in alkyl group from Me→Dec within the same series causes no effect on $^1$H and $^{13}$C values for Py$_{\alpha,\beta,\gamma}$, C═N, and dmgH (Me) (see Tables 1−4). Also, there is hardly any change in Py$_{\alpha,\beta,\gamma}$ and C═N values in **1b**−**10b** and **11b**−**20b**.

If the downfield shift, relative to the free ligand, of the signals corresponding to the H$_\alpha$ or C$_\alpha$ atoms of the axial ligand (Co−CH$_2$) is used as a measure of the cobaloxime ring current intensity, the following series can be established:

dpgH > dmgH-dpgH ≈ chgH-dpgH > dmgH ≈ chgH

A comparison of $\delta^{13}$C in inorganic cobaloximes versus organocobaloximes is made. The change in axial R group from an organic (Me, Et, Pr, Bu) to an inorganic group (Cl, Br, $NO_2$, $N_3$)[15d] within the same series affects $\delta^{13}$C for C═N, Py$_\alpha$, Py$_\beta$, and Py$_\gamma$. However, C═N is the most effected and occurs upfield by 2−3 ppm in organocobaloximes (Tables 3 and 4).

It is likely that the electronic effect of one wing may transmit to the other wing. This, in turn, will effect the ring current in the metallabicycle as a whole unit and affect the chemical shifts. We have, therefore, made an attempt to study the effect of the dpgH wing on the dmgH/chgH wing and vice versa. It is difficult to comment whether this effect operates through bond or through space. A careful study of $^1$H and $^{13}$C NMR spectra gives the following information.

**$^1$H NMR.** The $\delta$ dmgH (Me) resonance in **1b**−**10b** appears consistently downfield by 0.06−0.1 ppm as compared to the corresponding value in **1c**−**10c**. This shift may appear to be small, but Lopez et al. have arranged the ligand X in $XCo(dmgH)_2Py$ complexes based on such small upfield shifts (<0.05 ppm) in Py$_\alpha$.[11c]

We, however, cannot obtain similar information in **11b**−**20b** since $\delta^1$H chgH appears as a multiplet. Similarly, we cannot study the effect of dmgH or chgH on the dpgH wing since the phenyl group appears as a multiplet.

**$^{13}$C NMR.** The $\delta^{13}$C dmgH (Me) in **1b**−**4b** appears downfield by about 0.3−0.4 ppm as compared to the corresponding value in **1c**−**4c**. This supports the finding in the $^1$H NMR study. Similarly C$_1$ (chgH carbon) in **11b**−**14b** appears downfield by 0.2 ppm than the value in **11c**−**14c**. A comparison of the $^{13}$C value in the phenyl ring in **1b**−**4b** versus **1a**−**4a** shows that the C* carbon in the former occurs about 0.2−0.3 ppm downfield as compared to the corresponding value in the latter. $^{13}$C NMR information supports the finding in $^1$H NMR.

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(20) Johnson, C. E.; JR.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1012.

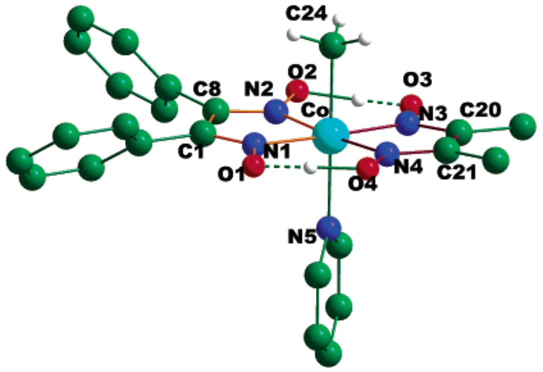


**Figure 1.** Diamond picture of structure MeCo(dmgH)(dpgH)Py (**1b**) (for clarity, most of the hydrogen atoms are omitted).

**Table 6. Selected Bond Lengths (Å) and Bond Angles (deg)**

| | 21b | 22b | 1b | 11b |
|---|---|---|---|---|
| Co–Cl | 2.2215(9) | 2.2322(9) | | |
| Co–Me | | | 1.997(3) | 1.992(3) |
| Co–N$_5$ | 1.9655(23) | 1.9765(23) | 2.060 (2) | 2.0624(24) |
| Co–N$_1$ | 1.8930(22) | 1.8869(24) | 1.878(2) | 1.8759(24) |
| Co–N$_2$ | 1.8792(22) | 1.8922(22) | 1.871(2) | 1.8749(24) |
| Co–N$_3$ | 1.9029(23) | 1.9028(24) | 1.884(2) | 1.8824(24) |
| Co–N$_4$ | 1.9118(23) | 1.9148(22) | 1.891(2) | 1.8886(25) |
| C$_1$–C$_8$ | 1.474(4) | 1.475(4) | 1.477(4) | 1.478(4) |
| C$_{21}$–C$_{20}$ | 1.468(4) | 1.445(4) | 1.465(4) | 1.451(4) |
| N$_1$–O$_1$ | 1.330(3) | 1.345(3) | 1.342(3) | 1.351(3) |
| N$_5$–Co–Cl | 179.25(7) | 178.16(7) | 179.19(12) | 179.33(11) |
| N$_1$–Co–N$_5$ | 90.35(10) | 90.04(9) | 91.77(10) | 90.92(10) |
| N$_2$–Co–Cl | 89.26(8) | 87.68(7) | 87.54(12) | 88.22(12) |
| N$_1$–Co–N$_2$ | 81.75(9) | 81.89(10) | 81.72(10) | 81.67(10) |
| O$_1$–O$_4$ | 2.503(3) | 2.491(3) | 2.472(3) | 2.491(3) |
| O$_2$–O$_3$ | 2.483(3) | 2.492(3) | 2.475(3) | 2.489(3) |
| N$_1$–N$_2$ | 2.469(3) | 2.477(3) | 2.452(3) | 2.453(3) |
| N$_1$–N$_4$ | 2.902(3) | 2.878(3) | 2.867(3) | 2.848(3) |
| N$_3$–N$_4$ | 2.451(3) | 2.478(3) | 2.434(3) | 2.453(3) |
| N$_2$–N$_3$ | 2.872(3) | 2.879(3) | 2.851(3) | 2.851(3) |
| α[a] | 1.42(10) | 1.10(13) | 3.76(18) | 1.14(10) |
| τ[b] | 88.45(9) | 87.43(8) | 88.6(4) | 87.43(8) |

[a] Butterfly bending angle. [b] Twist angle of pyridine with respect to the line joining the midpoints of $C_1$–$C_8$ and $C_{20}$–$C_{21}$.

The δ (C=N) is known to be sensitive to any change in the axial or equatorial environment in cobaloximes. We have, therefore, monitored the change in the $\delta^{13}C$ (C=N) value to see the effect of the dpgH wing on the dmgH or chgH wing or vice versa. It is found that the $\delta^{13}C$ (C=N) dmgH in **1b**–**4b** appears upfield by about 0.6 ppm as compared to the value in **1c**–**4c**. However, the effect of the dpgH wing on the chgH wing is almost negligible [compare $\delta^{13}C$ (C=N) chgH in **11b**–**14b** versus **11c**–**14c**.

To see the effect of the dmgH/chgH wing on the dpgH wing, we find that $\delta^{13}C$ (C=N) dpgH in **1b**–**10b** and **11b**–**20b** appears upfield by about 0.2 ppm as compared to the $\delta^{13}C$ (C=N) dpgH value in **1a**–**10a** (see Supporting Information).

So it seems that there is only a small but significant effect of the one wing on the other, and the effect of the dpgH wing on the dmgH wing is more than the reverse case.

## Correlations

(Eight values are taken for each correlation (X = Me, Et, Pr, Bu, Cl, Br, $NO_2$, $N_3$.)) The trans influence of the

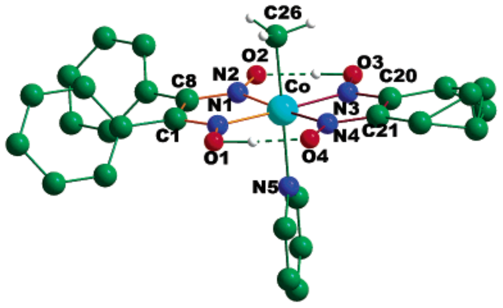


**Figure 2.** Diamond picture of structure MeCo(chgH)(dpgH)Py (**11b**) (for clarity, most of the hydrogen atoms are omitted).

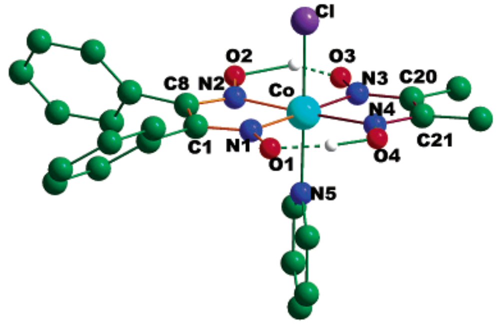


**Figure 3.** Diamond picture of structure ClCo(dmgH)(dpgH)Py (**21b**) (for clarity, most of the hydrogen atoms are omitted).

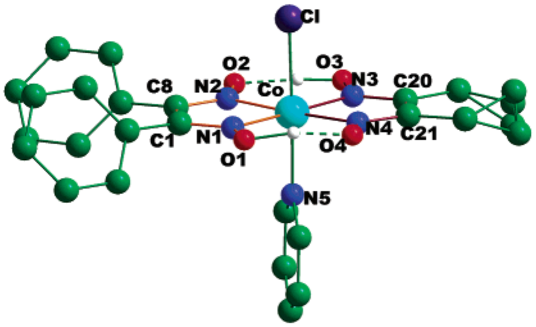


**Figure 4.** Diamond picture of structure ClCo(chgH)(dpgH)Py (**22b**) (for clarity, most of the hydrogen atoms are omitted).

X group on Py correlates well with the cis one experienced by methyl groups of the equatorial dmgH ligands in complexes **1b**–**4b**. While plotting, we have also included the corresponding inorganic cobaloximes (R = Cl, Br, $NO_2$, $N_3$).[15d]

$$\delta^{1}\mathrm{H}\ (\mathrm{dmgH}) = 2.34(1) - 0.81(5)\ (\Delta\delta^{1}\mathrm{H\ Py}_{\alpha})$$

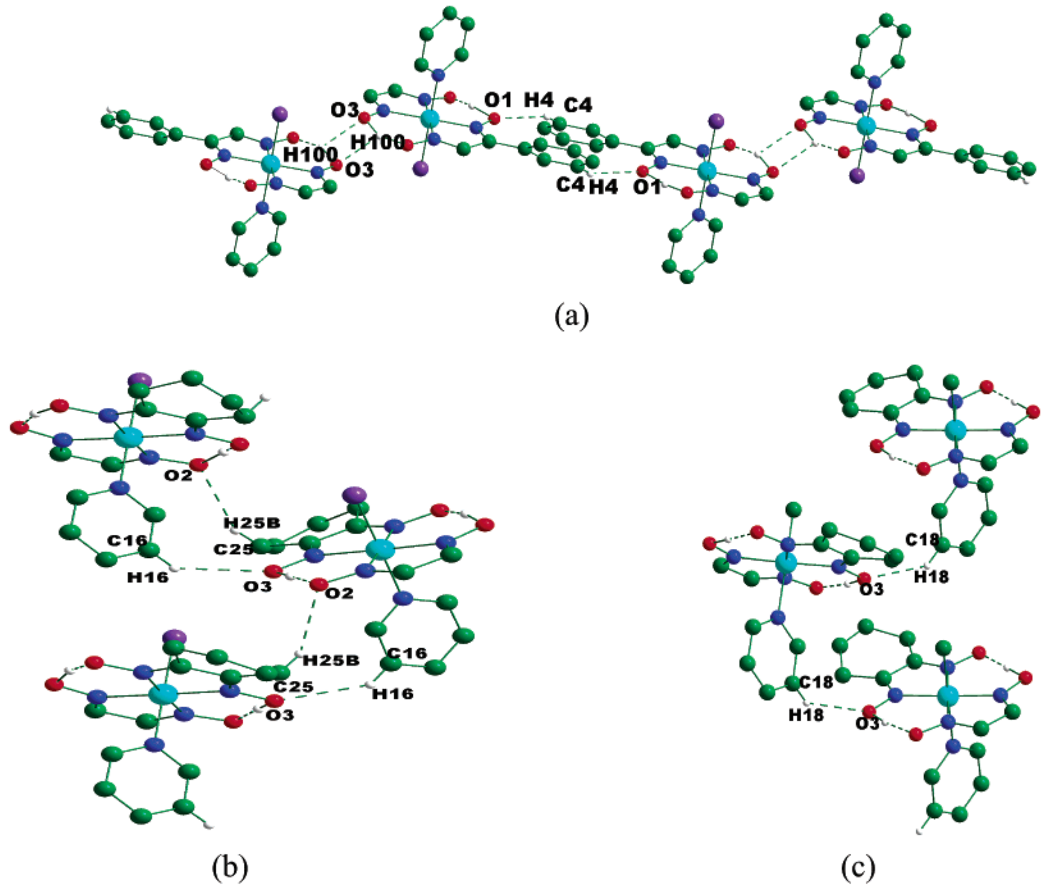
$$(r^2 = 0.98,\ \mathrm{esd} = 0.02\ \mathrm{ppm})$$

When considering the equatorial methyl groups, one would expect the magnetic anisotropy from the closer C=N double bonds to be more important than that from the cobalt atom. The fact that the chemical shifts of the axial protons, affected by the cobalt electrons, correlate with those of the equatorial methyl, affected by the C=N bonds, indicates electronic delocalization throughout the $CoN_4C_4$ system. According to the above equation, the influence of R on the chemical shifts of cis (Me of dmgH) and trans ($H_\alpha$ of Py) ligands is opposite in sign but is of the same magnitude (the slope of the least-

**Table 7. C−H···O and O−H···O Interactions in 21b, 22b, and 11b**

| bond | distance (Å) | | | angle (deg) | symmetry |
|---|---|---|---|---|---|
| | D[a]−H | H···A[b] | D···A | D−H···A | |
| | | | Compound **21b** | | |
| C4−H4−O1 | 0.9557 | 2.5153 | 3.3781 | 150.20 | −*x*, 2−*y*, 1−*z* |
| O3−H100−O3 | 1.1143 | 2.3481 | 2.7804 | 100.75 | 1−*x*, 1−*y*, −*z* |
| | | | Compound **22b** | | |
| C16−H16−O3 | 0.9459 | 2.5818 | 3.3523 | 138.84 | 3/2−*x*, −1/2+*y*, 1/2−*z* |
| C25−H25B−O2 | 0.9552 | 2.5549 | 3.3769 | 144.30 | 3/2−*x*, 1/2+*y*, 1/2−*z* |
| | | | Compound **11b** | | |
| C18−H18−O3 | 0.9511 | 2.5617 | 3.3450 | 139.81 | 3/2−*x*, −1/2+*y*, 1/2−*z* |

[a] D = donor atom. [b] A = acceptor atom



(a)

(b)

(c)

**Figure 5.** C−H- -O and O−H- -O interactions in (a) ClCo(dmgH)(dpgH)Py (**21b**); C−H- -O interaction in (b) ClCo(chgH)(dpgH)Py (**22b**) and (c) MeCo(chgH)(dpgH)Py (**11b**). Co = cyan, Cl = violet, O = red, N = blue, C = green, H = white. (Phenyl rings, disordered carbon atoms in cyclohexane ring, and all other hydrogen atoms are not shown for clarity.)

squares line is ca. −1.0). This fact is in sharp contrast with the usual trends in the NMR spectra of transition metal complexes or organometallic compounds, for which trans influences are much more important than the cis. This difference can be explained by considering that in most complexes the cis and trans influences on the chemical shifts arise from an inductive effect, whereas in the present case the prevailing effect seems to be the existence of a ring current associated with an aromatic-like metallabicyclic system.[11a,b] Similarly, $\delta^1$H (dmgH) correlate well with the coordination shift of pyridine ($\Delta\delta^1$H Py$_\beta$).

$$\delta^1\mathrm{H}\ (\mathrm{dmgH}) = 3.12(16) - 2.81(53)\ (\Delta\delta^1\mathrm{H\ Py}_\beta)$$
$$(r^2 = 0.87,\ \mathrm{esd} = 0.05\ \mathrm{ppm})$$

A fairly good correlation between the $\delta^{13}$C (dmgH) with the $\Delta\delta^1$H Py$_\alpha$ is observed.

$$\delta^{13}\mathrm{C(dmgH)} = 12.78(1) - 3.13(8)\ (\Delta\delta^1\mathrm{H\ Py}_\alpha)$$
$$(r^2 = 0.99,\ \mathrm{esd} = 0.03\ \mathrm{ppm})$$

This means one can get the same information using either $^1$H or $^{13}$C chemical shifts. The chemical shifts $^{13}$C C=N (dmgH) and $^{13}$C C=N (dpgH) correlate well with the coordination shift of pyridine ($\Delta\delta^1$H Py$_\alpha$). $\delta^{13}$C (dmgH) correlate well with the coordination shift of pyridine ($\Delta\delta^{13}$C Py$_\beta$ and $\Delta\delta^{13}$C Py$_\gamma$) (Supporting Information with the author).

**UV−Vis Spectra.** The complexes **1b**−**10b** and **11b**−**20b** show a Co−C CT band between 447−460 nm and 445−463 nm, respectively, with intensity (log $\epsilon$) in the range 3.20−3.50 (Tables 1 and 2). The position of the Co→C CT band depends on the dioxH ligand. The variation observed in $\lambda_{Co-C}$ in [Co(dioxH)$_2$(CH$_3$)(Py)] (405.0, 440.8, 445.0, 445.8, 447.7, 473 nm for dioxH = gH, dmgH, chgH-dpgH, chgH, dmgH-dpgH, dpgH, respectively)[2,19] can be explained in terms of the electron-donating ability of the dioxH ligand.

**X-ray Crystallographic Studies. Description of the Structures 1b, 11b, 21b, and 22b.** The diamond diagrams of complexes **1b**, **11b**, **21b**, and **22b** are shown in Figures 1–4. Selected bond distances and angles are presented in Table 6. The cobalt atom is linked to four nitrogen atoms belonging to the equatorial plane. Out of this, two nitrogen atoms belong to the diphenylglyoximato (dpgH) ligand and the other two to the dimethylglyoximato (dmgH) or 1,2-cyclohexanedionedioximato (chgH) ligand. The Co atom deviates 0.0509(13) Å from the mean equatorial CoN$_4$ plane toward the neutral pyridine ligand in **1b**, while the deviation is 0.0454(13), 0.0218(13), and 0.0276(13) Å in the compounds **11b**, **21b**, and **22b**, respectively. The displacement is toward pyridine in all cases. A methyl or chloro group and nitrogen of the pyridine ligand occupy the axial positions, thus completing the octahedral coordination sphere of the cobalt atom.

The pyridine ring is practically planar and parallel to the glyoxime C–C bonds, its conformation being defined by a twist of 88.6(4)°, 87.14(9)°, 88.45(9)°, and 87.43(8)° in the complexes **1b**, **11b**, **21b**, and **22b** respectively.

The Co–C$_{24}$ (Co–Cl for the compounds **21b** and **22b**) and Co–N$_5$ axial bonds are perpendicular (90°) to the equatorial plane, as seen in the Neq–Co–C$_{24}$, Neq–Co–Nax, and C$_{24}$–Co–Nax bond angles (Table 6). The Co–N$_5$ bond distance in **21b** and **22b** is similar to the corresponding value in ClCo(L)$_2$Py (1.959(2) and 1.965(3) Å for L = dmgH and dpgH, respectively),[14c,21b] but it is slightly shorter than in **1b** and **11b**. The Co–Neq bond distance in compounds **21b** and **22b** is somewhat longer than those in **1b** and **11b**. There is no significant change in the Co–C and Co–Cl bond lengths in **1b**, **11b**, **21b**, and **22b** when compared with the previously known structures **1a**,[14a] **1c**,[21a] **11c**,[13d] ClCo(dmgH)$_2$Py,[21b] and ClCo(dpgH)$_2$Py.[14c]

The butterfly bending angle ($\alpha$) in **1b** is 3.76°, while it is 1.42°, 1.10°, and 1.14° in **21b**, **22b**, and **11b** respectively.

The structures of compounds **21b**, **22b**, and **11b** show some interesting properties. In structure **21b**, the dimeric structure is formed due to C–H···O nonclassical intermolecular hydrogen bonding. This propagates further as a one-dimensional polymeric sheet through O–H···O (though the bond angle is acute, bond lengths are within the range)[21c] classical intermolecular hydrogen bonding. Structures **22b** and **11b** propagate as a one-dimensional zigzag polymeric sheet through C–H···O nonclassical intermolecular hydrogen bonding. The importance and the nature of the nonclassical intermolecular hydrogen bonding have recently been described by Desiraju.[21d,e] The hydrogen bonding parameters are given in Table 7. The intermolecular C–H···O and O–H···O interactions in these structures are shown in Figure 5. This kind of intermolecular interaction in the cobaloxime complexes has been observed for the first time.

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**Supporting Information Available:** This material is available free of charge via the Internet at http://pubs.acs.org.

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