# Synthesis and Characterization of Neutral Cyano-Bridged Dicobaloximes.
## (Alkyl)cobaloxime-$\mu$-cyano-(ligand)cobaloxime

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The reaction of an alkylaquocobaloxime, Co(dmgH)$_2$(R)(H$_2$O), with a cyano(ligand)cobaloxime, Co(dmgH)$_2$(CN)(B), has been found to produce a series of cyano-bridged dicobaloximes of the general formula R–Co(dmgH)$_2$–NC–Co(dmgH)$_2$–B (I). A series of 30 such cyano-bridged dicobaloximes where R = CF$_3$, CH$_3$, C$_2$H$_5$, *n*-C$_3$H$_7$, *i*-C$_3$H$_7$, or C$_6$H$_{11}$ and B = py, py-4-NH$_2$, py-3-Cl, NH$_3$, or pip have been synthesized and isolated as crystalline solids. The complexes are characterized as dicobaloximes by means of elemental analysis and molecular weight data for selected compounds. Evidence for formulation as dicobaloximes containing a cyano ligand bridge is obtained from infrared data which show a 28–51-cm$^{-1}$ increase in $\nu_{CN}$ upon formation of the dicobaloxime from the corresponding terminal cyanocobaloxime Co(dmgH)$_2$(CN)(B). Characterization of I as the exclusive linkage isomer formed in all 30 compounds is based on electronic spectra of selected compounds and regular variations in $\nu_{CN}$ with variations in the ligands R and B. Further characterization of the bonding in the cyano-bridged dicobaloximes described here is obtained from $^1$H NMR data. The relative stabilities of the cyano-bridged dicobaloximes with respect to dissociation were found to vary with the $\sigma$ electron donating ability of the ligands R and B; the most stable cyano-bridged compounds are formed when R and B have a relatively small $\sigma$ electron donating ability, as measured by the p$K_b$ and $\sigma^*$ values for the free ligand.

## Introduction

The ability of the cyanide ligand carbon and nitrogen to coordinate simultaneously to separate atom centers has been documented previously.[1] This ambidentate behavior is evident in cyanide compounds of the main-group elements[2] and transition metal complexes.[3–11] The cyano-bridged dimetal systems have been of interest since the early recognition[12] that ligand-bridged complexes play an important role in inner-sphere electron-transfer reactions.

The present work is concerned with the synthesis and characterization of a new series of cyano-bridged dicobaloximes[13] of the general formula

$$\text{R–Co(dmgH)}_2\text{–NC–Co(dmgH)}_2\text{–B}$$
$$\text{I}$$
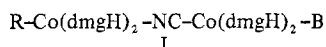
where R = CF$_3$, CH$_3$, C$_2$H$_5$, *n*-C$_3$H$_7$, *i*-C$_3$H$_7$, or C$_6$H$_{11}$ and B = py-3-Cl, py, py-4-NH$_2$, NH$_3$, or pip. These compounds are of interest because they contain a cyanide ligand that bridges two cobalt(III) metal centers by simultaneous coordination of the cyanide carbon to one cobaloxime and the cyanide nitrogen to another cobaloxime, resulting in an overall neutral dimer.

These compounds are also of interest due to the large variety of dimers that can be prepared by systematically changing the nature of the ligands R and B. In all, a total of 30 compounds of the type shown in I using all permutations of the ligands R and B have been prepared for this work. This series has been characterized by numerous physical measurements, which, as described below, allow meaningful statements to be made about the bonding of the cyanide ligand in a bridging situation. For purposes of comparison, monomeric cyanocobaloximes of the types Co(dmgH)$_2$(CN)(B) (II) and [AsPh$_4$][Co(dmgH)$_2$(R)(CN)] (III) (R and B are as defined above) were also synthesized and characterized.

In the discussions to follow, it will first be shown that the compounds listed as I are correctly formulated as cyano-bridged dicobaloximes in which a cyanide ligand simultaneously coordinates to two metal centers. It will then be shown that the cyanide ligand bridge is bound to the two cobaloxime centers in the arrangement shown in I, as opposed to the opposite linkage isomer with respect to the cyanide ligand bridge. It will be argued that the extent of $\pi$ bonding from the cobalt to the cyanide ligand $\pi^*$ molecular orbitals is relatively unimportant with respect to the $\sigma$-bonding contribution to the total cobalt–cyanide bonding scheme. As a result, all of the data presented here can be adequately ex-

plained by a cyanide ligand molecular orbital scheme which does not involve any such $\pi$ bonding. The influence of changes in the nature of R and B in complexes of types I–III will be examined and it will be seen that the data presented here allow meaningful statements to be made about many aspects of the bonding of the cyanide ligands in such complexes containing terminal or bridging cyanide. A preliminary report of some of these results has been made.[14]

## Experimental Section

**Physical Measurements.** With the exception of the three cyano-bridged dicobaloximes noted below, all physical measurements were performed on analyzed samples. Elemental analyses and molecular weight determinations (in CHCl$_3$, by vapor pressure osmometry at 37 °C) were performed by MHW Laboratories, Garden City, Mich. CHCl$_3$ used for spectroscopic measurements was dried and distilled under N$_2$ prior to use.

Infrared spectra were obtained over the region 4000–200 cm$^{-1}$ on a Perkin-Elmer 621 spectrophotometer. Solution (10$^{-3}$–10$^{-4}$ M) infrared spectra were obtained using matched 1.0-mm KBr cells for all compounds except (CH$_3$)Co(dmgH)$_2$–NC–Co(dmgH)$_2$(NH$_3$) where a 5-mm variable path length cell was used due to the low solubility of the complex. In all cases, the positions of the cyanide ligand CN stretching absorption were determined by simultaneous calibration against polystyrene (1944.0 cm$^{-1}$) and CO$_2$ (2350.0 cm$^{-1}$). CN stretching frequencies reported here represent the average of five to seven independent determinations and are reproducible to within ±2 cm$^{-1}$ (KBr disk) or ±1 cm$^{-1}$ (CHCl$_3$ solution).

$^1$H NMR spectra were obtained at 29 °C in deuterated solvents. Due to low solubility, the $^1$H NMR spectra of the cyano-bridged dicobaloximes as well as those of the compounds Co(dmgH)$_2$-(CN)(pip) and Co(dmgH)$_2$(CN)(py-4-NH$_2$) were obtained by accumulating and computer-averaging multiple spectra with a computer facility (CAT) using a Bruker HFX-10 spectrometer equipped with a Nicolet NIC-80 data processor. All other $^1$H NMR spectra were obtained with a single sweep using a Bruker HFX-10 or JEOL JNM-MH-100 spectrometer.

A Beckman Acta III spectrophotometer was used to obtain electronic spectra in CHCl$_3$ at ca. 10$^{-4}$ M for the compounds Co-(dmgH)$_2$(R)(B) and at ca. 10$^{-5}$ M for the compounds Co-(dmgH)$_2$(CN)(B) and (R)Co(dmgH)$_2$–NC–Co(dmgH)$_2$(B).

**Preparation of Complexes.** The compounds Co(dmgH)$_2$(R)(H$_2$O)[15] and Co(dmgH)$_2$(CN)(B)[16] were prepared as described elsewhere.

**Co(dmgH)(CF$_3$)(H$_2$O).** Dimethylglyoxime, 17.4 g (0.150 mol), and CoCl$_2$·6H$_2$O, 17.8 g (0.075 mol), were dissolved, while purging with N$_2$ gas and heating to 45 °C, in 200 ml of methanol in a three-necked, round-bottomed flask. NaOH, 6.00 g (0.150 mol), was added as a solution in 20 ml of H$_2$O. The resulting brown suspension was stirred for 10 min and then treated with S(CH$_3$)$_2$, 6.0 ml. This was cooled to –10 °C on a dry ice bath and stirred for 20 min, still

under an atmosphere of $N_2$ gas. Next, NaOH, 2.9 g in 15 ml of $H_2O$, was added dropwise over a period of 5 min. This was immediately followed by a solution of $NaBH_4$, 0.4 g, and NaOH, 0.1 g, in 20 ml of $H_2O$. This was stirred for 5 min and, while still at -10 °C, was sealed under an atmosphere of $N_2$ gas.

The entire reaction flask was then placed in an $N_2$ glovebag containing a high-pressure reaction vessel (Parr Instruments Co., Series 4500, 2-l. capacity). The cobaloxime solution (now green due to the presence of Co(I)) was then poured into the bomb reaction vessel, and this was tightly sealed under a pressure of $N_2$ gas. $CF_3Br$ gas (Matheson Gas Products) was introduced to the reaction by means of a stainless steel connecting tube, until the pressure reached 100 psi. This reaction mixture was heated at 40–50 °C for 5 h. The red-brown product solution was then removed from the reaction vessel and exposed to the atmosphere, and the volume was reduced by rotoevaporation. The resulting red-brown reaction mixture was cooled to 0 °C for 24 h.

Filtration yielded a quantity of red-brown, needlelike crystals and a larger amount of a water-soluble tar. The needles, being insoluble in $H_2O$, were separated from the tar by washing with large amounts of $H_2O$ and were finally washed with ethanol and ether and dried in vacuo; yield 20%.

The infrared spectrum of the product was comparable in every respect to that of $Co(dmgH)_2(CH_3)(H_2O)$, with the exception of a large, broad absorption due to the C–F stretching vibration at ca. 1050 $cm^{-1}$.

**[AsPh₄][Co(dmgH)₂(R)(CN)].** The desired alkylaquocobaloxime, $Co(dmgH)_2(R)(H_2O)$ (where R = $CH_3$, $C_2H_5$, $n$-$C_3H_7$, $i$-$C_3H_7$, or $C_6H_{11}$) was dissolved in a minimum of $H_2O$ and treated with 1 equiv of KCN, also in $H_2O$. This was heated at 40 °C to give a yellow solution after 10–20 min. The product, $[Co(dmgH)_2(R)(CN)]^-$, was precipitated by the dropwise addition of 1 equiv of $AsPh_4Cl$ in $H_2O$. The resulting yellow powder was washed with generous amounts of $H_2O$ and sparing amounts of 95% ethanol and ether and was dried in vacuo; yield ca. 90%. Infrared spectra and analytical data demonstrate the presence of water of crystallization for the compounds where R = $C_2H_5$, $n$-$C_3H_7$. Attempts to prepare the above compound when R = $CF_3^-$ resulted in a decomposition of the product, with the evolution of a gas.[17]

**Co(dmgH)₂(R)(B).** The desired alkylaquocobaloxime, $Co(dmgH)_2(R)(H_2O)$, was dissolved in a minimum of $H_2O$ at 40 °C. A slight excess of the ligand B was added, resulting in the precipitation of a yellow powder, which was washed with $H_2O$, 95% ethanol, and ether and dried in vacuo. py, py-3-Cl, and pip were added as liquids, py-4-$NH_2$ was added as an aqueous solution, and $NH_3$ was added as concentrated $NH_4OH$; yields ca. 90%.

**[Co(dmgH)₂(py)₂][ClO₄].** $Co(CH_3COO)_2 \cdot 4H_2O$, 5.74 g (2.30 × $10^{-2}$ mol), and dimethylglyoxime, 5.34 g (4.60 × $10^{-2}$ mol), were suspended in 200 ml of ethanol at 45 °C and treated with NaOH, 0.92 g (2.3 × $10^{-2}$ mol), in 20 ml of $H_2O$, to give a red-brown suspension. An excess (10 ml) of py was added, and the reaction was heated to 50 °C while aerating for 0.5 h. The resulting solution was then filtered to remove undissolved material, and the red-brown filtrate was treated with 25 ml of 6 M $NaClO_4$ to induce precipitation of the product. The resulting dark brown precipitate was recrystallized from 95% ethanol by the addition of an aqueous solution of $NaClO_4$, washed with ethanol and ether, and dried in vacuo; yield 50%.

**(R)Co(dmgH)₂–NC–Co(dmgH)₂(B).** The cyano-bridged dicobaloximes were synthesized in the following manner when R = $CH_3$, $C_2H_5$, $n$-$C_3H_7$, $i$-$C_3H_7$, $C_6H_{11}$, or $CF_3$ and B = py or py-3-Cl. The appropriate alkylaquocobaloxime, $Co(dmgH)_2(R)(H_2O)$, 2.00 × $10^{-4}$ mol, was dissolved in a minimum of $CHCl_3$ at 35 °C, to give an orange solution. The cyanocobaloxime, $Co(dmgH)_2(CN)(B)$, 2.00 × $10^{-4}$ mol, was dissolved separately in $CHCl_3$ at 35 °C to give a yellow solution. These two solutions were combined to produce an orange solution which was stirred at 35 °C for 0.5 h. The solvent was removed under reduced pressure to give a yellow powder, which was dried in vacuo to remove the now uncoordinated water. The resulting dry powder was next recrystallized from $CHCl_3/C_6H_{14}$ mixtures, the desired product being less soluble than $Co(dmgH)_2(R)(OH_2)$ but more soluble than $Co(dmgH)_2(CN)(B)$. The product of this recrystallization was washed with chloroform and hexane and dried in vacuo; yields 90%.

The compounds (R)Co(dmgH)₂–NC–Co(dmgH)₂(B), when B = $NH_3$ or py-4-$NH_2$, were synthesized in a completely analogous fashion, but using acetone instead of chloroform as the formation of the

**Table I.** Molecular Weights for the Cyano-Bridged Dicobaloximes R–Co(dmgH)₂–NC–Co(dmgH)₂–B

| R | B | Theor | Exptl[a] |
|---|---|---|---|
| $C_6H_{11}$ | py-3-Cl | 801 | 650 |
| $CH_3$ | py | 698 | 670 |
| $n$-$C_3H_7$ | py | 727 | 700 |
| $i$-$C_3H_7$ | py | 727 | 650 |
| $C_6H_{11}$ | py | 767 | 690 |
| $CH_3$ | pip | 704 | 750 |
| $C_6H_{11}$ | pip | 772 | 480 |
| $CH_3$ | $NH_3$ | 636 | 650[b] |

[a] In $CHCl_3$, $10^{-3}$ M, at 27° C by vapor pressure osmometry. [b] In $(CH_3)_2CO$.

**Table II.** Infrared CN Stretching Frequency for the Bridging Cyanide Ligand of the Cyano-Bridged Dicobaloximes R–Co(dmgH)₂–NC–Co(dmgH)₂–B in $CHCl_3$ Solution[a]

| B | R | | | | | |
|---|---|---|---|---|---|---|
| | $CF_3$ | $CH_3$ | $C_2H_5$ | $n$-$C_3H_7$ | $i$-$C_3H_7$ | $C_6H_{11}$ |
| py-3-Cl | 2196 | 2186 | 2182 | 2182 | 2180[b] | 2178[b] |
| py | 2196 | 2186 | 2182 | 2182 | 2180[b] | 2179[b] |
| py-4-$NH_2$ | 2192 | 2184 | 2182[b] | 2181[b] | 2178[b] | 2178[c] |
| pip | 2192 | 2184[b] | 2181[b] | 2181[b] | 2178[b] | 2178 |
| $NH_3$ | 2191[b] | 2183[b] | 2179[c] | 2181[c] | 2178[c] | 2175[c] |

[a] Concentration $\sim 10^{-4}$ M. [b] Partially dissociated in $CHCl_3$ solution; see text. [c] Dissociates in $CHCl_3$ to the extent that an accurate value of $\nu_{CN}$ cannot be determined for the cyano-bridged compound. The number given is that from a KBr-disk spectrum.

cyano-bridged compounds was found to be incomplete in the latter solvent; yields 60%.

The compounds (R)Co(dmgH)₂–NC–Co(dmgH)₂(pip) were synthesized in $CHCl_3$ when R = $CF_3$, $CH_3$, $C_2H_5$, or $n$-$C_3H_7$ and in acetone when R = $i$-$C_3H_7$ or $C_6H_{11}$; yields 80%.

## Results

Crystalline samples of 30 cyano-bridged dicobaloximes of the general formula I have been prepared. With the exception of the three compounds noted below, satisfactory elemental analyses were obtained on all of these compounds. In addition, the molecular weights of certain of these compounds have been determined in $CHCl_3$ solution. These data are listed in Table I.

**Infrared Spectra.** Infrared spectra of each of these cyano-bridged dicobaloximes have been obtained in the solid state as pressed KBr disks. All of these complexes exhibit a weak, broad absorption in the region 2202–2175 $cm^{-1}$ due to the bridging cyanide ligand ($\nu_{CN}$). This absorption was sharper and more intense when the spectra were obtained in dry $CHCl_3$ solution. These data obtained in $CHCl_3$ solution are listed in Table II, where it can be seen that changes in the nature of R and B result in regular changes in the bridging cyanide ligand CN stretching frequencies ($\nu_{CN}$).

In addition to the absorption listed in Table II, the solution infrared spectra of some of the cyano-bridged dicobaloximes displayed an absorption at lower energy due to the cyanide ligand of the terminal compound $Co(dmgH)_2(CN)(B)$. As discussed below, this is due to a partial dissociation of the cyano-bridged compounds in solution.

It is this incompleteness of bridge formation in $CHCl_3$ which requires that solid samples of some of these compounds be synthesized in acetone, where bridge formation was found to be more complete. Still, analytically pure samples of the compounds $(C_6H_{11})Co(dmgH)_2$–NC–$Co(dmgH)_2$(py-4-$NH_2$), $(C_6H_{11})Co(dmgH)_2$–NC–$Co(dmgH)_2(NH_3)$, and $(i$-$C_3H_7)Co(dmgH)_2$–NC–$Co(dmgH)_2(NH_3)$ could not be obtained. Repeated recrystallizations did not remove trace amounts of the monomeric cobaloxime starting materials.
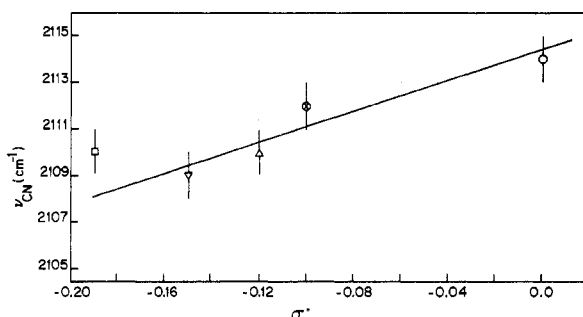
**Figure 1.** CN stretching frequency, $\nu_{CN}$, for [AsPh$_4$]-[Co(dmgH)$_2$(R)(CN)] with different alkyl ligands R (R = CH$_3$, C$_2$H$_5$, n-C$_3$H$_7$, C$_6$H$_{11}$, i-C$_3$H$_7$) plotted as a function of $\sigma^{*24}$ values for each ligand R; data obtained in dry CHCl$_3$ solution: ○, R = CH$_3$; ⊗, R = C$_2$H$_5$; △, R = n-C$_3$H$_7$; ▽, R = C$_6$H$_{11}$; □, R = i-C$_3$H$_7$.
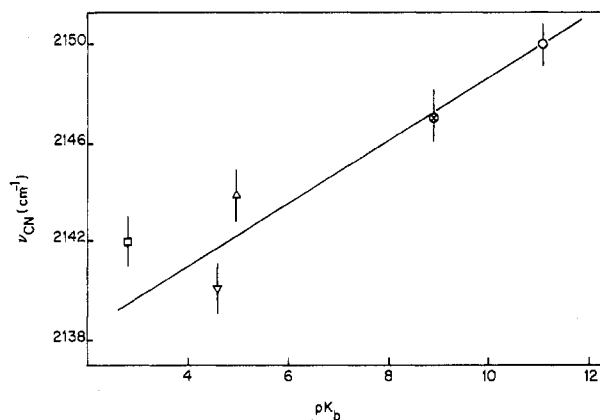


**Figure 2.** CN stretching frequency, $\nu_{CN}$, for Co(dmgH)$_2$-(CN)(B) with different nitrogen-donor bases B (B = py-3-Cl, py, py-4-NH$_2$, NH$_3$, pip) plotted as a function of p$K_b^{25}$ values for each ligand B; data obtained in dry CHCl$_3$ solution: ○, B = py-3-Cl; ⊗, B = py; △, B = py-4-NH$_2$; ▽, B = NH$_3$; □, B = pip.

**Table III.** Electronic Spectroscopic Data for the Cyano-Bridged Dicobaloximes R–Co(dmgH)$_2$–NC–Co(dmgH)$_2$–B[a]

| R | B | λ, nm | $10^{-3}\epsilon$, M$^{-1}$ cm$^{-1}$ |
|---|---|---|---|
| CH$_3$ | py-3-Cl | 445 max | 1.43 |
| | | 294 sh | 11.0 |
| | | 248 max | 34.1 |
| CH$_3$ | py | 443 max | 1.40 |
| | | 294 sh | 13.0 |
| | | 244 max | 38.2 |
| CH$_3$ | pip | 443 max | 1.35 |
| | | 294 sh | 12.0 |
| | | 244 max | 37.2 |
| n-C$_3$H$_7$ | py-3-Cl | 456 max | 1.69 |
| | | 294 sh | 12.8 |
| | | 245 max | 38.1 |
| n-C$_3$H$_7$ | py | 455 max | 1.34 |
| | | 290 sh | 11.2 |
| | | 248 max | 31.0 |
| n-C$_3$H$_7$ | pip | 455 max | 1.54 |
| | | 292 sh | 12.3 |
| | | 245 max | 38.9 |
| C$_6$H$_{11}$ | py-3-Cl | 446 max | 1.51 |
| | | 335 sh | 6.15 |
| | | 246 max | 44.6 |
| CF$_3$ | py | 350 sh | 3.51 |
| | | 248 max | 40.4 |
| CF$_3$ | pip | 350 sh | 3.18 |
| | | 247 max | 38.1 |

[a] Dry CHCl$_3$ solution.

For purposes of comparison, the infrared spectra of the compounds Co(dmgH)$_2$(CN)(B) and [AsPh$_4$][Co(dmgH)$_2$-

**Table IV.** Electronic Spectroscopic Data for Monomeric Cobaloximes[a]

| Compd | λ, nm | $10^{-3}\epsilon$, M$^{-1}$ cm$^{-1}$ |
|---|---|---|
| **A. Co(dmgH)$_2$(R)(B)** | | |
| Co(dmgH)$_2$(CH$_3$)(H$_2$O) | 447 max | 1.60 |
| | 378 max | 1.50 |
| | 288 sh | 5.95 |
| | 246 max | 13.8 |
| Co(dmgH)$_2$(CH$_3$)(py-3-Cl) | 429 sh | 0.960 |
| | 375 max | 1.81 |
| | 292 sh | 7.30 |
| | 242 max | 17.2 |
| Co(dmgH)$_2$(CH$_3$)(py) | 425 sh | 1.43 |
| | 375 max | 3.13 |
| | 288 sh | 9.81 |
| | 242 max | 17.8 |
| Co(dmgH)$_2$(CH$_3$)(pip) | 430 sh | 1.07 |
| | 380 max | 1.74 |
| | 288 max | 6.57 |
| | 242 max | 16.1 |
| Co(dmgH)$_2$(CH$_3$)(NH$_3$) | 427 sh | 0.989 |
| | 374 max | 2.08 |
| | 294 max | 6.55 |
| | 245 max | 16.3 |
| Co(dmgH)$_2$(C$_6$H$_{11}$)(py) | 440 sh | 1.30 |
| | 335 sh | 5.16 |
| | 294 max | 7.54 |
| | 245 max | 30.1 |
| Co(dmgH)$_2$(n-C$_3$H$_7$)(py) | 425 sh | 1.38 |
| | 380 max | 2.22 |
| | 296 max | 8.10 |
| | 245 max | 20.0 |
| Co(dmgH)$_2$(CF$_3$)(py) | 350 sh | 1.72 |
| | 294 sh | 5.28 |
| | 246 max | 22.4 |
| **B. Co(dmgH)$_2$(CN)(B)** | | |
| Co(dmgH)$_2$(CN)(py) | 350 sh | 1.85 |
| | 248 max | 21.8 |
| Co(dmgH)$_2$(CN)(py-3-Cl) | 350 sh | 2.00 |
| | 248 max | 20.9 |
| Co(dmgH)$_2$(CN)(pip) | 350 sh | 1.76 |
| | 248 max | 24.2 |
| **C. [AsPh$_4$][Co(dmgH)$_2$(R)(CN)]** | | |
| [AsPh$_4$][Co(dmgH)$_2$(CH$_3$)(CN)] | 345 sh | 3.35 |
| | 288 sh | 7.35 |
| | 242 max | 23.7 |
| [AsPh$_4$][Co(dmgH)$_2$(n-C$_3$H$_7$)(CN)] | 345 sh | 3.03 |
| | 288 sh | 6.31 |
| | 245 max | 22.4 |
| [AsPh$_4$][Co(dmgH)$_2$(C$_6$H$_{11}$)(CN)] | 345 sh | 4.62 |
| | 290 sh | 7.93 |
| | 248 max | 30.4 |
| **D. [Co(dmgH)$_2$(B)$_2$](ClO$_4$)** | | |
| [Co(dmgH)$_2$(py)$_2$](ClO$_4$) | 340 sh | 2.38 |
| | 244 max | 29.3 |

[a] Dry CHCl$_3$ solution.

(R)(CN)][17] have also been obtained in CHCl$_3$ solution, and $\nu_{CN}$ data for coordinated cyanide are presented in Figures 1 and 2. All of these compounds are susceptible to solid-state effects on the cyanide ligand CN stretching frequency. This is particularly dramatic in the compound Co(dmgH)$_2$-(CN)(pip) and the hydrated compounds [AsPh$_4$][Co-(dmgH)$_2$(R)(CN)], where R = C$_2$H$_5$, n-C$_3$H$_7$, or C$_6$H$_{11}$. The $\nu_{CN}$ values for coordinated cyanide obtained in CHCl$_3$ solution and shown in Figures 1 and 2 are taken to represent the true values for $\nu_{CN}$ in the absence of any hydrogen bonding.

**Electronic Spectra.** Electronic spectra of selected cyano-bridged dicobaloximes have been determined in CHCl$_3$ solution from crystalline samples of the pure bridged compounds. These data are listed in Table III. Electronic spectra have also been determined for the related monomeric compounds

**Table V.** $^1$H NMR Spectra for the Cyano-Bridged
Dicobaloximes CH$_3$-Co(dmgH)$_2$-NC-Co(dmgH)$_2$-B$^a$

| B | $\delta$(dmgH)$^{'b}$ | $\delta$(dmgH)$^c$ | $\delta$(Co-CH$_3$) |
|---|---|---|---|
| py-3-Cl | 2.17 | 2.30 | 0.59 |
| py | 2.18 | 2.29 | 0.57 |
| py-4-NH$_2$ | 2.17 | 2.27 | 0.56 |
| pip | 2.15 | 2.32 | 0.53 |
| NH$_3$$^d$ | 2.13 | 2.37 | 0.56 |

$^a$ CDCl$_3$ solution using a Bruker HFX-10 spectrometer and
TMS as an internal reference. $^b$ The 12 equivalent dimethyl-
glyoxime methyl protons at the "CH$_3$ cobalt" in CH$_3$-Co-
(dmgH)$'_2$-NC-Co(dmgH)$_2$-B. $^c$ The 12 equivalent dimethyl-
glyoxime methyl protons at the "B cobalt" in CH$_3$-Co-
(dmgH)$'_2$-NC-Co(dmgH)$_2$-B. $^d$ See ref 18.

Co(dmgH)$_2$(R)(B), Co(dmgH)$_2$(CN)(B), [AsPh$_4$][Co-
(dmgH)$_2$(R)(CN)], and [Co(dmgH)$_2$(py)$_2$][ClO$_4$], and these
data are listed in Table IV. A significant feature of the
spectra tabulated in Tables III and IV is that both the cya-
no-bridged dicobaloximes and the monomeric compounds
Co(dmgH)$_2$(R)(B) display an absorption maximum in the
visible region (425–456 nm; $\epsilon \sim 10^3$ M$^{-1}$ cm$^{-1}$) that is not
present in the electronic spectra of the compounds Co-
(dmgH)$_2$(CN)(B), [AsPh$_4$][Co(dmgH)$_2$(R)(CN)], or [Co-
(dmgH)$_2$(py)$_2$][ClO$_4$].

**Proton Magnetic Resonance Spectra.** $^1$H NMR spectra
have been determined for the dicobaloximes (CH$_3$)Co-
(dmgH)$_2$-NC-Co(dmgH)$_2$(B). These data are given in Table
V. An absorption due to the 12 equivalent protons of the
equatorial dimethylglyoxime ligands at each of the cobalt
centers of the bridged compounds is observed. These are listed
in Table V as $\delta$(dmgH)$'$ for the dmgH ligands bonded to the
cobalt which is bonded to the methyl ligand (CH$_3$) and $\delta$-
(dmgH) for the dmgH ligands bonded to the cobalt which is
bonded to the N donor ligand (B). The $^1$H NMR spectra of
the cyano-bridged dicobaloximes in Table V also exhibit a
resonance at one-fourth intensity of $\delta$(dmgH) or $\delta$(dmgH)$'$.
This is listed as $\delta$(Co-CH$_3$) and is assigned to the protons of
the methyl ligand coordinated directly to the cobalt. These
assignments were facilitated by obtaining $^1$H NMR spectra
for the appropriate monomeric cobaloximes, Co(dmgH)$_2$-
(CN)(B), where the dmgH methyl proton resonances occur
in the range $\delta$ 2.20–2.35, and Co(dmgH)$_2$(CH$_3$)(B), where
the dmgH methyl proton resonances occur in the range $\delta$
2.10–2.20.

$^1$H NMR spectra for the axial CH$_3$ ligand were also ob-
tained for the compounds Co(dmgH)$_2$(CH$_3$)(B). These data
are comparable to those reported by Bied-Charreton et al. for
a wider variety of similar complexes[19] and are shown in Figure
3 (as $\delta$(Co-CH$_3$)) along with data for the corresponding
cyano-bridged complexes.

**Discussion**

The synthetic route used in this work for the synthesis of
cyano-bridged dicobaloximes takes advantage of the lability
of the coordinated water in the alkylaquocobaloximes,[20] which
allows for substitution by the nitrogen of coordinated cyanide
as shown in eq 1. This is analogous to the method used by

$$\text{Co(dmgH)}_2(\text{R})(\text{OH}_2) + \text{NC-Co(dmgH)}_2(\text{B})$$
$$\rightarrow \text{R-Co(dmgH)}_2\text{-NC-Co(dmgH)}_2\text{-B} + \text{H}_2\text{O} \qquad (1)$$

Haim et al.[6a] in the synthesis of different cyano-bridged
compounds. The reactions represented by eq 1 were performed
in CHCl$_3$ or acetone, the displaced water being removed in
vacuo from the crystalline product.

Molecular weight data obtained for selected compounds
(Table I) support dimer formation as shown in eq 1. The
infrared spectra of the products of eq 1 show no absorptions
attributable to coordinated H$_2$O. This proves that it is the
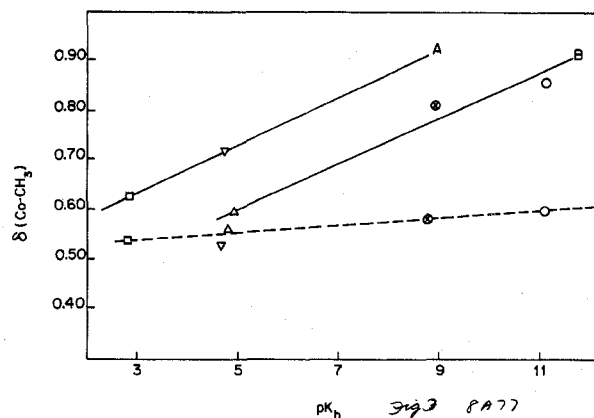H$_2$O ligand in Co(dmgH)$_2$(R)(H$_2$O) that is substituted in eq



**Figure 3.** (——) $^1$H NMR chemical shift data for the axial
methyl ligand, $\delta$(Co-CH$_3$), of Co(dmgH)$_2$(CH$_3$)(B) with
different nitrogen donor bases B plotted as a function of
pK$_b$[25] values for each ligand B. Line A and line B were
drawn according to ref 28 for non-$\pi$-bonding ligands (B =
pip, NH$_3$) and $\pi$-bonding ligands (B = py-3-Cl, py, py-4-NH$_2$),
respectively. (- - - -) $^1$H NMR chemical shift data for the
axial methyl ligand, $\delta$(Co-CH$_3$), of CH$_3$-Co(dmgH)$_2$-NC-
Co(dmgH)$_2$-B with different nitrogen donor bases B plotted
as a function of pK$_b$[25] values for each ligand B. All
chemical shift data were obtained in CDCl$_3$ at 29° and
expressed in ppm. Symbols: ○, B = py-3-Cl; ⊗, B =
py; △, B = py-4-NH$_2$; ▽, B = NH$_3$; □, B = pip.

1. The only other major difference in the infrared spectra of
the reactants and products for eq 1 is that the CN stretching
frequency of the cyanide ligand is at higher energy (28–51
cm$^{-1}$) in the product dicobaloximes than in the mono-
cyanocobaloxime reactants of eq 1 (see Table II and Figure
2). This type of increase in the CN stretching frequency upon
forming complexes containing bridging cyanide ligands from
terminal cyano complexes has been documented by Wilmarth
et al.[21] and has since been found to be a general phenomenon.
This behavior is taken here as a justification for the formu-
lation of these dimers as cyano-bridged dicobaloximes.

An analysis of the electronic spectra obtained from the
cyano-bridged dicobaloximes allows a definite linkage isomer
assignment to be made for the -CN- bridge. All of the
monomeric cobaloximes listed in Table IV display similar
ultraviolet absorptions, which have been assigned previously.[22]
In addition, the alkylcobaloximes exhibit a visible absorption
maximum in the range 425–447 nm ($\epsilon \sim 10^3$ M$^{-1}$ cm$^{-1}$). This
visible absorption has been assigned to a cobalt–carbon
charge-transfer transition.[22b] Of importance in our deter-
mination of the -CN- linkage isomer in the cyano-bridged
dicobaloximes is the empirical observation that this visible
absorption is indicative of the presence of both an alkyl ligand
R and a nitrogen donor Lewis base B on the trans coordination
axis (Table IV). This visible absorption is not observed in the
electronic spectrum of the compound Co(dmgH)$_2$(CF$_3$)(py),
presumably as a result of an effective enhancement of the
ligand field strength of py when coordinated trans to CF$_3$, thus
causing this absorption maximum to shift to higher energy
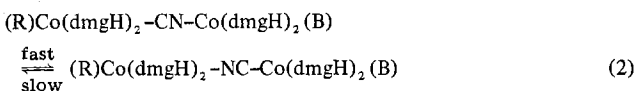where it becomes obscured by the more intense ultraviolet
absorptions.

A similar visible absorption maximum is present at 443–456
nm ($\epsilon \sim 10^3$ M$^{-1}$ cm$^{-1}$) in the electronic spectra of the
cyano-bridged dicobaloximes (Table III), again with the
exception of the CF$_3$ complexes. Thus, one of the cobalt
centers in the cyano-bridged dicobaloximes must simulta-
neously be coordinated by an alkyl ligand, R, and a trans
nitrogen donor ligand. This can only be true if these com-
pounds possess the -CN- linkage isomer structure shown above
in I, where one cobalt is coordinated by an alkyl group R as
well as by the nitrogen atom of the cyanide bridge. Conse-

quently one would expect the spectrum of the cyano-bridged dicobaloxime isomer shown in I to be approximated by the sum of the spectra of the monomeric cobaloximes $Co(dmgH)_2$-$(R)(B)$ and $Co(dmgH)(CN)(B)$. This conclusion is further supported by the observation that the nitrogen atom of co-ordinated cyanide has a ligand field strength approximately equal to that of $NH_3$.[4]

If the cyano-bridged dicobaloximes listed in Table III had the $-CN-$ linkage isomer structure opposite to that shown in I, one would not expect to observe an absorption maximum in the visible region of the spectrum for these dicobaloximes. This is because such a cyano-bridged compound would be expected to exhibit an electronic spectrum more like the sum of those of the complexes $[Co(dmgH)_2(R)(CN)]^-$ and $[Co(dmgH)_2(B)_2]^+$, neither of which exhibit visible absorption maxima (Table IV). The absence of a visible absorption maximum for the compounds $(CF_3)Co(dmgH)_2-NC-Co-(dmgH)_2(B)$ in Table III does not necessarily indicate that the $-CN-$ linkage isomer opposite to I obtains. This is due to the observation that the compound $Co(dmgH)_2(CF_3)(py)$ also does not display such an absorption maximum.

This empirical comparison of the electronic spectra of selected cyano-bridged dicobaloximes with those of the ap-propriate monomeric cobaloximes establishes the $-CN-$ linkage isomer as that shown in I for the nine cyano-bridged complexes listed in Table III. It can be argued that the same isomer holds for all of the 30 compounds listed in Table II on the basis of the regularity of the trends (decreasing $\nu_{CN}$ proceeding horizontally left to right and vertically top to bottom) in $\nu_{CN}$ with changes in ligands R and B. Had there been an alteration in the $-CN-$ isomer for one of the cya-no-bridged dicobaloximes whose electronic spectrum was not obtained, there should have been a corresponding discontinuity in the variation of $\nu_{CN}$ (Table II) for these complexes. (A justification for the order of arrangement of the compounds in Table II will be given below.)

In addition to the above electronic and infrared spectroscopic arguments, a kinetic argument may be presented in favor of the exclusive occurrence of the $-CN-$ linkage isomer given in I. The kinetic lability of the alkylcobaloximes[20] is in marked contrast with the inertness[16] of cyanocobaloximes such as $Co(dmgH)_2(CN)(B)$. For this reason, should a hypothetical equilibrium exist between the two possible $-CN-$ linkage isomers, as shown in eq 2, such an equilibrium should lie far

$$(R)Co(dmgH)_2-CN-Co(dmgH)_2(B)$$

$$\underset{slow}{\overset{fast}{\rightleftharpoons}} (R)Co(dmgH)_2-NC-Co(dmgH)_2(B) \qquad (2)$$

to the right.[23] Thus, there should be a dramatic preference for the $-CN-$ linkage isomer depicted in I above. This is in contrast to the complexes studied by Dodd and Johnson,[9] where the lability of both cobalt centers allowed for a facile equilibrium between the two possible isomers of a CN bridge.

The infrared absorption of interest with respect to the present work is the cyanide ligand $\nu_{CN}$ absorption in solution. The frequency of this absorption band was found to vary in a regular fashion in the cyano-bridged complexes $(R)Co-(dmgH)_2-NC-Co(dmgH)_2(B)$ as shown in Table II. For purposes of comparison, the infrared spectra of the monomeric cyanocobaloximes $Co(dmgH)_2(CN)(B)$ and $[AsPh_4][Co-(dmgH)_2(R)(CN)]$ have been obtained and $\nu_{CN}$ was found to vary in a regular fashion as seen in Figures 1 and 2.

The data of Figure 1 show that a decrease in the $\sigma$-electron donor strength of the ligand R (as approximated by $\sigma^*$ values for R)[24] in the complexes $[AsPh_4][Co(dmgH)_2(R)(CN)]$ results in small but regular increase in $\nu_{CN}$ for coordinated cyanide. The data point for $R = i\text{-}C_3H_7$ is displaced from the line as a result of steric interactions with the equatorial di-methylglyoxime ligands which preclude the full $\sigma$-electron

donor strength of the isopropyl ligand from being felt at the cobalt.

The same trend is apparent in the data of Figure 2, where a decrease in the $\sigma$-electron donor strength of the trans ligand B (as approximated by $pK_b$ values[25]) in the complexes $Co-(dmgH)_2(CN)(B)$ results in a regular increase in $\nu_{CN}$. The data point for $B = pip$ is displaced from the linear relationship for two reasons. First, this ligand, like the $i\text{-}C_3H_7$ case discussed above, is susceptible to steric interactions with the equatorial dimethylglyoxime ligands. Second, the value of $\nu_{CN}$ shown in Figure 2 for this compound represents an upper limit due to hydrogen bonding to the cyanide ligand. The frequency of the CN absorption for the compound $Co(dmgH)_2(CN)(pip)$ was found to decrease steadily upon dilution, reaching a value of 2142 cm$^{-1}$ in the most dilute solutions on which infrared measurements could be made. In the absence of both steric and hydrogen-bonding factors, the linearity of the data presented in Figure 2 should be improved.

In both types of monomeric cyanocobaloximes then it is concluded that a reasonably linear relationship exists between a decrease in the electron density provided to the cobalt by the trans ligand R in $[AsPh_4][Co(dmgH)_2(R)(CN)]$ and B in $Co(dmgH)_2(CN)(B)$ and an increase in $\nu_{CN}$ for coordinated cyanide. This relationship can be explained by considering the molecular orbital calculations reported for the coordination of the cyanide anion to non-$\pi$-bonding Lewis acids.[26] (An analysis of the cyano complexes reported here utilizing a bonding scheme wherein the extent of cobalt to cyanide $\pi$ bonding is relatively unimportant compared with the $\sigma$-bonding contribution is partially justified by the documented lack of importance of such $\pi$ bonding in cyano complexes of co-balt(III) in general.[27] Cobalt-cyanide $\pi$ bonding is certainly not discernible spectroscopically for these systems and further justification for its lack of importance can be obtained from a comparison of infrared and $^1$H NMR data as is discussed below.)

A result of coordination of the cyanide ligand to non-$\pi$-bonding Lewis acids is an increase in the CN stretching frequency over the value for ionic cyanide ($\nu_{CN}$ for ionic cyanide 2080 cm$^{-1}$). Purcell[26] has shown that this is a result of a stabilization (decrease in energy) of primarily $\sigma$-type molecular orbitals of the CN group. This increased $\sigma$-bond stabilization was shown to be greater for coordination of cyanide to the stronger Lewis acids, resulting in a higher CN stretching frequency. The strongest Lewis acid cobalt centers in the complexes $[AsPh_4][Co(dmgH)(R)(CN)]$ and $Co-(dmgH)_2(CN)(B)$ are provided by the weakest electron-donor trans ligands, i.e., $R = CH_3$[17] and $B = py\text{-}3\text{-}Cl$, respectively. This in turn should give rise to the highest CN stretching frequencies for these complexes, as is observed (Figures 1 and 2).

This same approach can be used to explain the further increase in the cyanide ligand CN stretching frequency that is observed (Table II) upon forming the cyano-bridged di-cobaloximes from the terminally bound cyanocobaloximes $Co(dmgH)_2(CN)(B)$. Purcell[26] has shown that either cyanide carbon or nitrogen coordination results in a decrease in the C–N overlap energy, with a corresponding increase in force constant and stretching frequency from that for ionic cyanide. In either case, these effects arise primarily from the $\sigma$ mo-lecular orbital system of the CN group, the $\pi$ molecular orbital system remaining essentially unchanged. If either cyanide carbon or nitrogen coordination to non-$\pi$-bonding Lewis acids results in a C–N $\sigma$ bond strengthening, then simultaneous coordination of both the cyanide carbon and nitrogen should result in an even greater C–N bond strengthening (presumably with a concomitant increase in the C–N force constant). This is precisely the result obtained (Table II) for the cyano-bridged

dicobaloximes, where the bridging cyanide ligand CN stretching frequency is seen to be 28–51 cm$^{-1}$ higher than in the parent monocyanocobaloximes, $Co(dmgH)_2(CN)(B)$.

An examination of the data in Table II shows that the cyanide ligand CN stretching frequency is highest for the complexes $(R)Co(dmgH)_2-NC-Co(dmgH)_2(B)$ when the ligands R and B are the weakest $\sigma$-electron donors (R = CF$_3$ and B = py-3-Cl). In addition, regular decreases in the CN stretching frequency are observed along the series R = CF$_3$ > CH$_3$ > C$_2$H$_5$ > $n$-C$_3$H$_7$ > $i$-C$_3$H$_7$ > C$_6$H$_{11}$ for a given ligand B (decreasing left to right in Table II) and B = py-3-Cl > py > py-4-NH$_2$ > pip > NH$_3$ for a given ligand R (decreasing top to bottom in Table II). With the exception of the positions of the ligands B = pip and R = $i$-C$_3$H$_7$ (which are sterically hindered; vida supra), this order parallels the relative $\sigma$-electron donor strength of the ligands R and B as suggested by $\sigma^*$[24] and $pK_b$[25] values, respectively. The result is a higher bridging cyanide CN stretching frequency in the compounds $(R)Co(dmgH)_2-NC-Co(dmgH)_2(B)$ where both the "R cobalt" and the "B cobalt" are stronger Lewis acids. The order in which the data of Table II are arranged was chosen to reflect the *effective* base strength of the ligands R and B as judged from the cyanide ligand CN stretching frequencies in the compounds $[AsPh_4][Co(dmgH)_2(R)(CN)]$ (Figure 1) and $Co(dmgH)_2(CN)(B)$ (Figure 2).

These trends are as would be expected if the bonding of the cyanide ligand is adequately described by the molecular orbital scheme[26] for coordination of cyanide to non-$\pi$-bonding Lewis acids, and all bridged complexes have the same isomeric structure (I) with respect to the bridging CN group. A comparison of the infrared spectroscopic data discussed above with $^1$H NMR data indicates that these spectroscopic results can be adequately interpreted without recourse to $\pi$-bonding discussions. This suggests that cobalt–cyanide $\pi$ bonding is of little or no importance in these systems. The transmission of an electronic trans effect can be seen in the data of Figure 3 (solid lines A and B) where the chemical shift of the axial methyl ligand protons ($\delta(Co-CH_3)$) is seen to be dependent upon the nature of the trans ligand B in the complexes Co-$(dmgH)_2(CH_3)(B)$. These data are comparable to those of Bied-Charreton et al.,[28] where a wider variety of ligands B was examined. There it was argued that the varying ability of the ligand B to enter into $\pi$ bonding with the cobalt affected the chemical shift of the trans CH$_3$ ligand bound to the cobalt by altering the magnetic anisotropy of the cobalt d-electron cloud in the proximity of the axial CH$_3$ ligand. The magnetic anisotropy was said to be different when B was a good $\pi$-bonding ligand (e.g., py-3-Cl, py, py-4-NH$_2$) than when B was a poor $\pi$-bonding ligand (e.g., NH$_3$, pip). This is reflected by the use of two lines, A and B, for the non-$\pi$-bonding and $\pi$-bonding ligands, respectively, in Figure 3.

The sensitivity of $\delta(Co-CH_3)$ to the $\pi$-bonding properties of the trans ligands B in the complexes $Co(dmgH)_2(CH_3)(B)$ should be contrasted with the inability of the cyanide CN stretching frequency to distinguish anything other than the purely $\sigma$-electron donor strength ($pK_b$) of the ligands B in the complexes $Co(dmgH)_2(CN)(B)$ (Figure 2). This presumably suggests that the cyanide ligand itself is not $\pi$ bonded to the cobalt (or that $\pi$ bonding is relatively unimportant), as a true $\pi$-bonded cyanide ligand is known to be very sensitive to competition with other ligands for metal electron density.[29]

This relative unimportance of any $\pi$-bonding tendencies for coordinated cyanide in these compounds is also shown in the data of Figure 3 for the cyano-bridged complexes (CH$_3$)-$Co(dmgH)_2-NC-Co(dmgH)_2(B)$. Data for the $\pi$-bonding and non-$\pi$-bonding ligands B fall on the same line (dotted line in Figure 3). This suggests that the bridging cyanide ligand does not enter into $\pi$ bonding with the cobaloximes and thereby

effectively insulates the CH$_3$ ligand from the $\pi$-bonding capabilities of the B ligand. Further support comes from the fact that the $^{13}$C NMR spectra of $(CH_3)Co(dmgH)_2-NC-Co(dmgH)_2(py)$ and $(CH_3)Co(dmgH)_2-NC-Co(dmgH)_2$-(pip) and related cyanocobaloximes can be interpreted without recourse to cobalt–cyanide $\pi$ bonding.[30]

One prediction made by Purcell[26] is that the coordination of the cyanide carbon to Lewis acids in general results in an increase in the Lewis basicity of the nitrogen atom of the CN group. Thus, the basicity of the cyanide nitrogen in the complexes $Co(dmgH)_2(CN)(B)$ should be greatest where B = py-3-Cl (trans ligand with lowest $\sigma$-electron donor ability as approximated by $pK_b$) and least where B = pip or NH$_3$. In terms of the stability of the cyano-bridged compounds listed in Table II, the dissociation equilibrium represented by eq 3

$$(R)Co(dmgH)_2-NC-Co(dmgH)_2(B) \rightleftharpoons (R)Co(dmgH)_2$$
$$+ (NC)Co(dmgH)_2(B) \qquad (3)$$
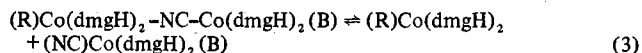
should lie farther to the left for B = py-3-Cl or py than for B = pip or NH$_3$. A second factor which should influence the position of equilibrium 3 is the Lewis acidity of the complexes $Co(dmgH)_2(R)$. For a given ligand B, equilibrium 3 should lie farther to the left when R = CF$_3$ or CH$_3$ (trans ligands with the lowest $\sigma$-electron donor ability as measured by $\sigma^*$) than when R = $i$-C$_3$H$_7$ or C$_6$H$_{11}$. Both of these trends have been confirmed in this work. As described above, the tendency of the cyano-bridged dicobaloximes to dissociate when dissolved in CHCl$_3$ is greatest when R = $i$-C$_3$H$_7$ and C$_6$H$_{11}$ as well as when B = NH$_3$, pip, or py-4-NH$_2$ (see also Table II). This qualitative trend may also explain the somewhat low experimental values for the molecular weights of some of the compounds listed in Table I. These data suggest that when B = pip, the dicobaloxime exhibits a greater degree of dissociation when R = C$_6$H$_{11}$ than when R = CH$_3$. A similar comparison holds when B = py.

The above data taken in totality allow the following general statements to be made. The variation in stability of the cyano-bridged complexes with respect to dissociation follows the order R = CF$_3$ > CH$_3$ > C$_2$H$_5$ > $n$-C$_3$H$_7$ > C$_6$H$_{11}$ for a given ligand B and the order B = py-3-Cl > py > py-4-NH$_2$ > pip > NH$_3$ for a given ligand R. These sequences also summarize the trends in $\nu_{CN}$ for the bridging cyano group.

**Registry No.** $Co(dmgH)_2(CH_3)(H_2O)$, 25360-55-8; Co-$(dmgH)_2(CH_3)(py-3-Cl)$, 59492-80-7; $Co(dmgH)_2(CH_3)(py)$, 23642-14-0; $Co(dmgH)_2(CH_3)(pip)$, 38141-71-8; $Co(dmgH)_2$-$(CH_3)(NH_3)$, 28136-46-1; $Co(dmgH)_2(C_6H_{11})(py)$, 28206-03-3; $Co(dmgH)_2(n$-$C_3H_7)(py)$, 28182-24-3; $Co(dmgH)_2(CF_3)(py)$, 28136-58-5; $Co(dmgH)_2(CN)(py)$, 23318-65-2; $Co(dmgH)_2$-$(CN)(py-3-Cl)$, 57808-58-9; $Co(dmgH)_2(CN)(pip)$, 53632-13-6; $[AsPh_4][Co(dmgH)_2(CH_3)(CN)]$, 43070-34-4; $[AsPh_4][Co$-$(dmgH)_2(n$-$C_3H_7)(CN)]$, 59492-82-9; $[AsPh_4][Co(dmgH)_2$-$(C_6H_{11})(CN)]$, 43070-38-8; $[Co(dmgH)_2(py)_2](ClO_4)$, 59492-83-0; $CH_3-Co(dmgH)_2-NC-Co(dmgH)_2-py-3-Cl$, 59492-84-1; $CH_3$-$Co(dmgH)_2-NC-Co(dmgH)_2-py$, 53533-62-3; $CH_3-Co(dmgH)_2$-$NC-Co(dmgH)_2-py-4-NH_2$, 59492-85-2; $CH_3-Co(dmgH)_2-NC$-$Co(dmgH)_2-pip$, 59573-28-3; $C_6H_{11}-Co(dmgH)_2-NC-Co$-$(dmgH)_2-py-3-Cl$, 59492-86-3; $n$-$C_3H_7-Co(dmgH)_2-NC-Co$-$(dmgH)_2-py$, 53602-60-1; $i$-$C_3H_7-Co(dmgH)_2-NC-Co(dmgH)_2-py$, 59492-87-4; $C_6H_{11}-Co(dmgH)_2-NC-Co(dmgH)_2-py$, 59492-88-5; $C_6H_{11}-Co(dmgH)_2-NC-Co(dmgH)_2-pip$, 59492-89-6; $CF_3-Co$-$(dmgH)_2-NC-Co(dmgH)_2-py-3-Cl$, 59492-90-9; $C_2H_5-Co$-$(dmgH)_2-NC-Co(dmgH)_2-py-3-Cl$, 59492-91-0; $n$-$C_3H_7-Co$-$(dmgH)_2-NC-Co(dmgH)_2-py-3-Cl$, 59492-92-1; $i$-$C_3H_7-Co$-$(dmgH)_2-NC-Co(dmgH)_2-py-3-Cl$, 59492-93-2; $CF_3-Co$-$(dmgH)_2-NC-Co(dmgH)_2-py$, 59492-94-3; $C_2H_5-Co(dmgH)_2$-$NC-Co(dmgH)_2-py$, 53533-63-4; $CF_3-Co(dmgH)_2-NC-Co$-$(dmgH)_2-py-4-NH_2$, 59492-95-4; $C_2H_5-Co(dmgH)_2-NC-Co$-

(dmgH)$_2$-py-4-NH$_2$, 59492-96-5; *n*-C$_3$H$_7$-Co(dmgH)$_2$-NC-Co-(dmgH)$_2$-py-4-NH$_2$, 59492-97-6; *i*-C$_3$H$_7$-Co(dmgH)$_2$-NC-Co-(dmgH)$_2$-py-4-NH$_2$, 59492-98-7; C$_6$H$_{11}$-Co(dmgH)$_2$-NC-Co-(dmgH)$_2$-py-4-NH$_2$, 59492-99-8; CF$_3$-Co(dmgH)$_2$-NC-Co-(dmgH)$_2$-pip, 59531-96-3; CF$_3$-Co(dmgH)$_2$-NC-Co(dmgH)$_2$-NH$_3$, 59493-00-4; C$_2$H$_5$-Co(dmgH)$_2$-NC-Co(dmgH)$_2$-NH$_3$, 53667-49-5; *n*-C$_3$H$_7$-Co(dmgH)$_2$-NC-Co(dmgH)$_2$-NH$_3$, 53533-65-6; *i*-C$_3$H$_7$-Co(dmgH)$_2$-NC-Co(dmgH)$_2$-NH$_3$, 59493-01-5; C$_6$H$_{11}$-Co-(dmgH)$_2$-NC-Co(dmgH)$_2$-NH$_3$, 59493-02-6; C$_2$H$_5$-Co(dmgH)$_2$-NC-Co(dmgH)$_2$-pip, 59573-29-4; *n*-C$_3$H$_7$-Co(dmgH)$_2$-NC-Co-(dmgH)$_2$-pip, 59573-30-7; *i*-C$_3$H$_7$-Co(dmgH)$_2$-NC-Co(dmgH)$_2$-pip, 59493-03-7; Co(dmgH)$_2$(CF$_3$)(H$_2$O), 59493-04-8; Co(dmgH)$_2$-(C$_2$H$_5$)(H$_2$O), 26025-30-9; Co(dmgH)$_2$(*n*-C$_3$H$_7$)(H$_2$O), 28182-23-2; Co(dmgH)$_2$(*i*-C$_3$H$_7$)(H$_2$O), 30974-89-1; Co(dmgH)$_2$(C$_6$H$_{11}$)(H$_2$O), 52970-74-8; py, 110-86-1; [AsPh$_4$][Co(dmgH)$_2$(C$_2$H$_5$)(CN)], 59493-05-9; [AsPh$_4$][Co(dmgH)$_2$(*i*-C$_3$H$_7$)(CN)], 59493-07-1; Co(dmgH)$_2$(CN)(py-4-NH$_2$), 57808-59-0; Co(dmgH)$_2$(CN)(NH$_3$), 19570-05-9; Co(dmgH)$_2$(CH$_3$)(py-4-NH$_2$), 38685-14-2; CH$_3$-Co-(dmgH)$_2$-NC-Co(dmgH)$_2$-NH$_3$, 53533-64-5.

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(13) The term cobaloxime is used to denote complexes containing the planar bis(dimethylglyoximato)cobalt(III) moiety. Abbreviations: dmgH, dimethylglyoximato anion, [CH$_3$C(=NOH)C(=NO)CH$_3$]$^-$; *n*-C$_3$H$_7$, *n*-propyl ligand; *i*-C$_3$H$_7$, isopropyl ligand; py, pyridine; py-3-Cl, 3-chloropyridine; py-4-NH$_2$, 4-aminopyridine; pip, piperidine.
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(18) The $^1$H NMR spectrum of the compound (CH$_3$)Co(dmgH)$_2$-NC-Co(dmgH)$_2$(NH$_3$) warrants additional comment. This compound was found to be only sparingly soluble in CHCl$_3$ to give a hazy solution. A $^1$H NMR spectrum of such a solution was obtained in spite of this haziness, and these are the data listed in Table V. In addition to the resonances listed for this compound, another dmgH resonance was observed and assigned to the dimethylglyoxime protons of pentacoordinate Co(dmgH)$_2$(CH$_3$). This material was present in solution as a result of a dissociation of the cyano-bridged dicobaloxime to give Co(dmgH)$_2$(CH$_3$) and Co(dmgH)$_2$(CN)(NH$_3$). The latter compound is insoluble in CHCl$_3$ and was responsible for the haziness of the above solution. This was shown by isolating the precipitated material from a solution of (CH$_3$)Co(dmgH)$_2$-NC-Co(dmgH)$_2$(NH$_3$) and then obtaining its infrared spectrum.
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# Isolation and Absolute Configuration of the Optically Active Isomers of Bis(1,10-phenanthroline)- and Bis(2,2'-bipyridine)cobalt(III) Complexes Containing L-(+)- or D-(−)-Tartrate Ion

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The configurationally optically active isomers of the tartratobis(1,10-phenanthroline)cobalt(III) and tartratobis(2,2'-bipyridine)cobalt(III) complexes are isolated by column chromatography using SP-Sephadex. The electronic absorption and circular dichroism spectra are measured over the range of visible–ultraviolet regions and the absolute configurations of the complexes are assigned by empirical and nonempirical methods. The properties of the tartrate in the complexes are discussed on the basis of ir spectra and the pH titration. The chromatographic behavior of these isomers is also described. Appreciable stereoselectivity in the formation of the configurationally optically active isomers is observed.

## Introduction

In the previous paper we have reported on the preparation and absolute configuration of both diastereoisomers of L-(+)-tartratobis(1,10-phenanthroline)cobalt(III) complexes.[1] We have further investigated the isolation and CD spectra of compounds of the type [Co(tart)(phen or bpy)$_2$]$^+$, where tart is the dianion of L-(+)- or D-(−)-tartaric acid, and phen and

bpy are 1,10-phenanthroline and 2,2'-bipyridine, respectively. During the course of our investigations, we found surprising the claim for the presence of only one diastereoisomer.[2] In the present paper it is shown that the species isolated in ref 2 is a mixture of two diastereoisomers and the reported preference for only one diastereoisomer could not be observed by our experiments. The absolute configurations of our