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Unusual NMR Spectral Properties of the 1,2-Dicyanoethyl Alkyl Ligand in Organocobaloximes. Structure of the Organocobalt Complex *trans*-Bis(dimethylglyoximato)-(1,2-dicyanoethyl)(1,5,6-trimethylbenzimidazole)cobalt(III)

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The 1,2-dicyanoethyl ligand has been reported to exhibit unusual dynamic processes in certain organocobaloxime complexes. The crystal and molecular structures of the complex *trans*-bis(dimethylglyoximato)(1,2-dicyanoethyl)(1,5,6-trimethylbenzimidazole)cobalt(III)–0.5-ethanol, $Me_3BzmCo(DH)_2CH(CN)CH_2CN$, are reported. The compound crystallizes in space group $P\bar{1}$, triclinic, with $a = 7.721$ (1) Å, $b = 11.845$ (2) Å, $c = 15.078$ (3) Å, $\alpha = 79.09$ (2)°, $\beta = 80.65$ (2)°, $\gamma = 75.65$ (2)°, $V = 1320.0$ Å^3, $Z = 2$, $D_{measd} = 1.38$ g cm^{-3}, $D_{calcd} = 1.39$ g cm^{-3}, and $R = 0.051$ for 5261 independent reflections. The Co–C bond distance of 2.061 (3) Å is slightly shorter than that of 2.076 (2) Å found in the structure of the isopropyl analogue, whereas the Co–N(Me_3Bzm) bond length (2.031 (3) Å) is shorter than that in the isopropyl analogue (2.097 (2) Å). Hence, the 1,2-dicyanoethyl and isopropyl groups have similar bulk properties but different trans influences. The rate constants, k_1, were determined for dissociation of Me_3Bzm from six $Me_3BzmCo(DH)_2R$ complexes where R ranges from weak donors such as CH_2CF_3 to strong donors and $CH(CH_3)_2$. High-field ^1H NMR spectroscopy showed that the $CH(CN)CH_2CN$ proton pattern, which is distorted by second-order effects, is greatly affected by temperature and the trans influence of L. A deuteration study in pyridine-d_5/D_2O revealed no exchange of the $-CH(CN)CH_2CN$ after 2 months at ambient temperature. These results militate against any unusually rapid dynamic processes involving the $CH(CN)CH_2CN$ group. Rather, previous NMR spectral observations at low field could be understood as arising from the peculiar ^1H NMR spectral characteristics of these compounds.

Introduction

Organocobalt complexes of the type $LCo(DH)_2R$, where L = neutral ligand, DH = monoanion of dimethylglyoxime, and R = alkyl group, containing both substituted and unsubstituted alkyl groups have been the subject of considerable interest.[1-10] Emphasis on such systems originates from the need to understand factors that influence Co–C bond cleavage in coenzyme B_{12} and the skeletal rearrangement reaction in B_{12}-dependent enzymic processes.[1-6] The role of Co now appears to be limited to the provision of an alkyl radical, namely the 5′-deoxyadenosyl radical, which participates in H atom abstraction from substrate.[5,6] The rearrangement of substrate to product evidently does not involve cobalt.

The most persistent theme used to explain the acceleration of the Co–C bond cleavage by enzymes is the "butterfly" bending of the equatorial ligand toward the alkyl group, a process supported by structural and Co–C bond cleavage trends for cases in which $LCo(DH)_2R$ complexes contain both a bulky P-donor ligand and a relatively bulky R group, e.g. $CH(CH_3)(C_6H_5)$.[2,5] In coenzyme B_{12} holoenzymes, the enzyme probably uses its binding energy to distort the equatorial corrin ligand toward the 5′-deoxyadenosyl alkyl ligand.

Our studies aimed at detecting similar structural trends when L = N-donor have not detected a similar effect; i.e., N-donors are not effective in inducing significant butterfly bending characteristic of P-donors.[2] This is true in the case of 1,5,6-trimethylbenzimidazole (Me_3Bzm) complexes.[1] Me_3Bzm is a model for the 1-substituted 5,6-dimethylbenzimidazole ligand in coenzyme B_{12}. An effect of N-donor L bulk on Co–C bond length might be observed if the R ligand has a weak trans influence. The effective bulk of the N-donor might become manifest since the Co–N bond would be shorter. In most structural studies, the bulky ligand also has a good trans influence (e.g. $CH(CH_3)_2$, adamantyl).

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The cyano group has a large electron-withdrawing effect,[3] and cyanoalkyl moieties can be prepared by a variety of routes from Co(I) species.[2-4,7,8] Of particular interest, complexes derived from acrylonitrile and fumaronitrile have shown interesting properties either in the solid state[7] or in solution.[8]

We have chosen to examine the less well studied adducts of fumaronitrile, which are believed to have the coordinated 1,2-dicyanoethyl ligand, for several reasons. First, this ligand should be both bulky and a poor donor, thus providing an ideal situation to determine if N-donors can exhibit significant steric effects. Second, evidence exists that the group is a poor electron donor.[3] Third, the 1,2-dicyanoethyl ligand has peculiar ^{1}H NMR signal behavior, which has been attributed to dynamic processes.[8]

Experimental Section

Reagents. 5,6-Dimethylbenzimidazole was purchased from Sigma Chemicals. Chloroform-*d* (MSD Isotopes), methylene chloride-d_2 (MSD Isotopes), deuterium oxide (Aldrich), and pyridine-d_5 (KOR, Aldrich) were the solvents used for the NMR studies. All other reagents were from Aldrich and were used without further purification.

Instrumentation. ^{1}H NMR spectra of 0.05 and 0.1 M solutions ($CDCl_3$, CD_2Cl_2, and C_5D_5N) were recorded on Nicolet NB-360 (360 MHz, ^{1}H) and General Electric GN-500 (500 MHz, ^{1}H) spectrometers. ^{1}H chemical shifts were referenced to internal $(CH_3)_4Si$. The program PANIC, from Bruker, was used for the spectral simulation of the second-order proton patterns of the 1,2-dicyanoethyl group of various L-substituted cobaloximes. Spectral simulation of the strongly coupled proton pattern of the 4-cyanopyridine derivative of (1,2-dicyanoethyl)cobaloxime was achieved by analyses of its ^{1}H NMR spectra obtained at two different spectrometer frequencies, 360 and 500 MHz. 1,2-Dicyanoethyl proton chemical shift data in Table V are relative to a field frequency of 360 MHz. Additional NMR data are reported in Table VIIIs.[11] Me_3Bzm dissociation rates were monitored spectrophotometrically with a Perkin-Elmer Lambda-3B UV-visible instrument equipped with a 3600 Data Station for the slower reactions ($k_{obsd} < 1.0$ s^{-1}) and a Durrum-Gibson D-110 stopped-flow spectrophotometer for the fast reactions. Both instruments were equipped with thermostated cell compartments at 25.00 ± 0.04 °C.

Rate Measurements. Absorbance vs time data were obtained for the substitution of Me_3Bzm from $Me_3BzmCo(DH)_2R$ by $P(OCH_3)_3$ in CH_2Cl_2 as described previously.[3] The pseudo-first-order rate data were treated with the standard integrated expression for a first-order process by using linear least-squares regression analysis and yielded classical S_N1(lim) behavior.[9,10]

Preparations. Me_3Bzm and $Me_3BzmCo(DH)_2R$ (except for R = $CH(CN)CH_2CN$) and $LCo(DH)_2CH(CN)CH_2CN$ (L = py (pyridine), 4-CNpy (4-cyanopyridine), $PhNH_2$ (aniline)) complexes were prepared as reported elsewhere.[1,3] The other (1,2-dicyanoethyl)cobaloxime complexes were synthesized as follows.

$Me_3BzmCo(DH)_2CH(CN)CH_2CN$. To a solution of $PhNH_2Co(DH)_2CH(CN)CH_2CN$ (0.4 g) in 80/20 CH_3OH/H_2O (100 mL) was added Dowex 50X8-100 cation-exchange resin (0.6 g). The solution was stirred and heated at reflux for 2 h. The resin was removed by filtration, and the solvent was eliminated by rotavaporation. $CHCl_3$ (~20 mL) was added to dissolve the oily orange residue (note: $PhNH_2Co(DH)_2CH(CN)CH_2CN$ is barely soluble in $CHCl_3$), and the solvent was again removed by rotavaporation. The oily residue was redissolved in $CHCl_3$ (~20 mL) and extracted with an equal volume of distilled water. Then a 10% excess of Me_3Bzm (based on the starting $PhNH_2$ complex) was added, and the mixture was stirred for 2 days. CH_3CH_2OH (~5 mL) was added to the solution. The resulting solution deposited an orange powder after 1 day. The solid was collected by vacuum filtration, washed with distilled water and petroleum ether, and air-dried; yield 0.20 g (35%).

Table I. Experimental Parameters for the X-ray Diffraction Study at 20 °C

formula	$CoO_4N_6C_{22}H_{29}\cdot{}^1/_2C_2H_5OH$
mol wt	551.6
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	7.721 (1)
b, Å	11.845 (2)
c, Å	15.078 (3)
α, deg	79.09 (2)
β, deg	80.65 (2)
γ, deg	75.65 (2)
V, Å^3	1320.0
Z	2
D_{measd}, g cm^{-3}	1.38
D_{calcd}, g cm^{-3}	1.39
$F(000)$	578
μ(Mo Kα), cm^{-1}	7.3
cryst size, mm	0.2 × 0.25 × 0.4
radiatn (λ, Å)	Mo Kα (0.71069)
monochromator	graphite
scan type	$\omega/2\theta$
scan speed, deg min^{-1}	variable, 0.78–4
2θ range, deg	6–60
total no. of rflns measd	7815
no. of indep rflns with $I > 3\sigma(I)$	5261
data/param ratio	15.3
R^a	0.051
$R_w{}^b$	0.062
GOF^c	1.20

$^a R = \sum(F_o - F_c)/\sum F_o$. $^b R_w = [\sum w(F_o - F_c)^2/\sum wF_o{}^2]^{1/2}$; $w = 1$. $^c \mathrm{GOF} = [\sum w(F_o - F_c)^2/(m - n)]^{1/2}$; m = number of observations, n = number of variables.

$LCo(DH)_2CH(CN)CH_2CN$ (L = 3-pic (3-Methylpyridine), 4-*t*-Bu-py (4-*tert*-Butylpyridine), 4-pic (4-Methylpyridine), 4-Me_2Npy (4-(Dimethylamino)pyridine), 1-MeImd (1-Methylimidazole)). These compounds were prepared from $PhNH_2Co(DH)_2CH(CN)CH_2CN$, on the basis of the method reported previously for the synthesis of $4\text{-}CNpyCo(DH)_2CH(CN)CH_2CN$.[3]

Elemental Analyses. C, H, N analyses were performed by Atlantic Microlabs, Inc. (Atlanta, GA), and were satisfactory for all new compounds (Table IXs).

Crystal Data. Crystals of $Me_3BzmCo(DH)_2CH(CN)CH_2CN$ were grown from CH_2Cl_2/CH_3CH_2OH. Lattice parameters were determined by least-squares refinement of 25 reflections accurately centered on an Enraf-Nonius CAD-4 diffractometer. Crystal data and details of intensity data collection and refinement are summarized in Table I. No significant change in the intensity control reflections was observed throughout the data collection. Observed data were corrected for Lorentz and polarization factors, but not for absorption, because of the small size of the crystal and the low μ value.

Structure Solution and Refinement. The structure was solved by conventional Patterson and Fourier methods. Fourier maps revealed the presence of three additional peaks, which were interpreted as a solvent ethanol molecule (O5, C23, C24) with half-occupancies. Hydrogen atoms were fixed at calculated positions (0.96 Å from the parent C atoms) with isotropic thermal parameter B equal to 1.3 times the B_{eq} value of the atom to which they are attached. The hydrogen atoms were included in the next least-squares cycles, but their positional and thermal parameters were not refined. Final full-matrix least squares converged to $R = 0.051$. Neutral-atom scattering factors were taken from ref 12. All computations were carried out on a PDP 11/44 computer, using the SDP programs.[13] Final positional and equivalent thermal parameters are given in Table II. Bond lengths and angles (Table Xs), anisotropic temperature factors (Table XIs), hydrogen atomic parameters (Table XIIs), and structure factor amplitudes (Table

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[11] s denotes that the table or figure can be found in the supplementary material.

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Table II. Atomic Positional and Equivalent Thermal Parameters for $Me_3BzmCo(DH_2)CH(CN)CH_2CN \bullet {}^1/_2C_2H_5OH$

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Co	0.20355 (6)	0.25771 (4)	0.22476 (3)	2.017 (7)	C7	0.1997 (5)	0.3472 (3)	0.0444 (3)	3.02 (8)
O1	0.5153 (3)	0.3215 (2)	0.2589 (2)	3.52 (6)	C8	0.2473 (7)	0.4068 (4)	−0.0502 (3)	4.5 (1)
O2	−0.0294 (4)	0.1320 (2)	0.3479 (2)	3.51 (6)	C9	0.3624 (6)	0.1000 (3)	0.1924 (3)	3.24 (8)
O3	−0.0933 (4)	0.1794 (2)	0.1875 (2)	3.45 (6)	C10	0.4161 (6)	0.0165 (3)	0.2724 (3)	3.66 (9)
O4	0.4405 (4)	0.3801 (2)	0.0999 (2)	3.42 (6)	C11	0.5268 (7)	0.1075 (4)	0.1231 (4)	4.5 (1)
N1	0.3758 (4)	0.2721 (2)	0.2947 (2)	2.63 (6)	C12	0.6120 (7)	−0.0087 (4)	0.0939 (4)	4.9 (1)
N2	0.1162 (4)	0.1789 (2)	0.3371 (2)	2.49 (6)	C13	0.0457 (4)	0.5257 (3)	0.2477 (2)	2.16 (6)
N3	0.0348 (4)	0.2395 (2)	0.1534 (2)	2.56 (6)	C14	0.1904 (5)	0.5795 (3)	0.2155 (3)	2.70 (7)
N4	0.2901 (4)	0.3374 (2)	0.1118 (2)	2.62 (6)	C15	0.1634 (5)	0.6997 (3)	0.2153 (3)	2.97 (7)
N5	0.0294 (4)	0.4088 (2)	0.2546 (2)	2.22 (5)	C16	0.3142 (6)	0.7615 (4)	0.1757 (4)	4.8 (1)
N6	−0.2358 (4)	0.5175 (3)	0.3027 (2)	2.65 (6)	C17	−0.0318 (7)	0.8981 (3)	0.2467 (4)	4.4 (1)
N7	0.4599 (7)	−0.0504 (4)	0.3330 (3)	6.1 (1)	C18	−0.0057 (5)	0.7667 (3)	0.2480 (3)	2.93 (7)
N8	0.6788 (7)	−0.0953 (4)	0.0709 (4)	6.4 (1)	C19	−0.1497 (5)	0.7138 (3)	0.2797 (3)	2.84 (7)
C1	0.4921 (7)	0.2226 (5)	0.4429 (3)	5.0 (1)	C20	−0.1208 (4)	0.5933 (3)	0.2782 (2)	2.24 (6)
C2	0.3593 (5)	0.2260 (3)	0.3797 (3)	3.08 (8)	C21	−0.4221 (5)	0.5466 (4)	0.3449 (4)	4.1 (1)
C3	0.2020 (6)	0.1730 (3)	0.4057 (3)	3.08 (8)	C22	−0.1405 (5)	0.4098 (3)	0.2874 (3)	2.54 (7)
C4	0.1491 (8)	0.1140 (5)	0.4999 (3)	5.1 (1)	O5	−0.1628 (7)	0.433 (1)	0.5305 (4)	8.5 (3)
C5	−0.0736 (7)	0.2813 (5)	0.0040 (3)	4.9 (1)	C23	0.035 (2)	0.4433 (8)	0.4913 (5)	12.9 (3)
C6	0.0482 (5)	0.2881 (3)	0.0696 (3)	3.03 (7)	C24	0.103 (1)	0.579 (1)	0.4800 (6)	5.6 (2)

XIIIs) have been deposited as supplementary material.

Results and Discussion

We will first discuss and present the structural results and relate these to rate processes. On this basis, we will present an analysis of the unusual spectroscopic observations reported earlier[8] based on an extensive ^1H NMR study of $LCo(DH)_2CH(CN)CH_2CN$ compounds. Next, we will discuss our studies of D exchange of the $CH(CN)CH_2CN$ ligand. Finally, we will reinterpret the previously reported results[8] on the $LCo(DH)_2CH(CN)CH_2CN$ compounds.

Description and Discussion of the Structure. The ORTEP drawing of the molecule with the numbering scheme is shown in Figure 1. The structure confirms that the product of the reaction of Co(I) compounds with fumaronitrile contains the 1,2-dicyanoethyl group. The coordination of the alkyl group to Co is characterized by Co–C9–CN and Co–C9–CH_2CN angles of 112.5 (3) and 116.5 (3)°, respectively. The C9–CN and C9–CH_2CN distances are 1.455 (5) and 1.516 (6) Å, respectively. We noticed also that the orientation of CH_2CN (C11–C12–N8) about the Co-bonded C9 atom is such that its cyano group is pointing away from the $(DH)_2$ equatorial plane to minimize steric interactions. The relative orientation of the two cyano groups about the alkyl C9–C11 bond is gauche, with a C10–C9–C11–C12 torsion angle value of 60.8 (4)°.

The $(DH)_2$ ligand occupies the four equatorial positions of a distorted octahedron around Co, the axial position being occupied by Me_3Bzm and $CH(CN)CH_2CN$ groups. The two DH units are planar within ±0.04 Å and make a dihedral angle α of 3.1°, bending toward the alkyl group. The Me_3Bzm ligand is planar within ±0.05 Å, and its orientation with respect to the equatorial moiety may be defined by the torsion angle C22–N5–Co–N*, where N* is the middle point between the two equatorial N donors on the C(22) side. The value of 3.7° in $Me_3BzmCo(DH)_2CH(CN)CH_2CN$ indicates that the Me_3Bzm plane nearly bisects the two oxime bridges. The axial fragment is characterized by Co–C and Co–N distances and a N–Co–C angle of 2.061 (3) and 2.031 (3) Å and 175.3 (1)°, respectively. As expected, the Co–N bond length is significantly shorter than that in the CH_3 analogue (2.060 (2) Å),[1] because of the appreciable electron-withdrawing effect of the CN and CH_2CN substituents at C9. The coordination of N5 to Co is characterized by the angles Co–N5–C13 = 133.7 (2)°, Co–N5–C22 = 121.1 (3)°, and C13–N5–C22 = 105.3 (3)°, values very close to those in other $Me_3BzmCo(DH)_2R$ complexes.[1,14,15] The Co–C bond length of 2.061 (3) Å is slightly shorter than that of 2.076 (2) Å found in the $CH(CH_3)_2$ analogue.[1] This difference could be ascribed to the bulk of CN and CH_2CN groups, which are slightly different from that of the CH_3 group (see next section). The similar Co–C bond lengths involving these two alkyls suggest that these groups have similar bulk.

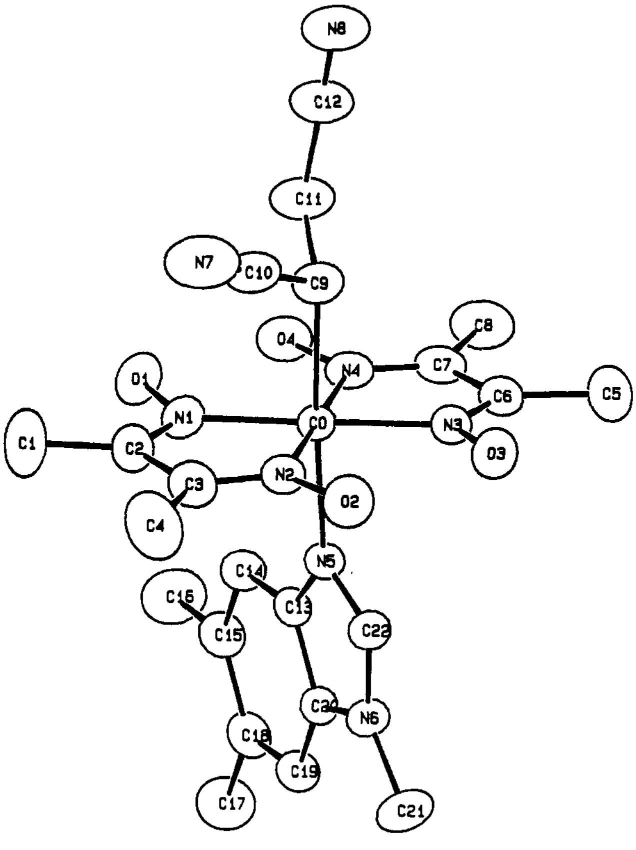

Figure 1. ORTEP drawing (thermal ellipsoids, 50% probability) and labeling scheme of $Me_3BzmCo(DH)_2CH(CN)CH_2CN$.

Table III lists relevant X-ray structural data involving the alkyl–Co–Me_3Bzm moiety of several Me_3Bzm alkylcobaloximes. The CH_3, $CH(Cl)_2$, CH_2NO_2, and CH(CN)Cl derivatives show nearly equal Co–C bond lengths (average 1.99 Å). The added bulk on substitution of at least one

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Table III. Selected Geometrical Data from X-ray Structures of Me_3Bzm Derivatives of Various Alkylcobaloximes

R	Co–N, Å	Co–C, Å	α, deg	∠Co–C–X_1, deg (X_1)	∠Co–C–X_2, deg (X_2)	∠X_3–C–X_4, deg (X_3–C–X_4)
$CH(CN)CH_2CN$[a]	2.031 (3)	2.061 (3)	3.1	112.5 (3) (CN)	116.5 (3) (CH_2CN)	109.3 (3) (C10–C9–C11)
CH(CN)Cl[b]	2.010 (3)	2.000 (5)	1.9	118.2 (3) (CN)	126.1 (3) (Cl)	115.3 (3) (C10–C9–Cl)
CH_2NO_2[c]	2.013 (3)	1.988 (5)	4.8	115.7 (4) (NO_2)		
$CH(Cl)_2$[d]	2.043 (2)	1.983 (2)	1.5	116.5 (1) (C11)	115.8 (1) (C12)	106.8 (1) (C11–C9–C12)
CH_3[c]	2.060 (2)	1.989 (2)	4.7			
$CH(CH_3)_2$[c]	2.097 (2)	2.076 (2)	4.0	114.0 (2) (C10)	114.3 (2) (C11)	112.4 (2) (C10–C9–C11)
adamantyl[b]	2.137 (4)	2.179 (5)	−6.1	110.3 (4) (C11)	111.6 (3) (C10)	109.3 (3) (Co–C9–C11) 107.8 (4) (C11–C9–C10) 109.4 (5) (C10–C9–C12) 108.4 (5) (C12–C9–C11)

[a] This work. [b] Reference 14. [c] Reference 1. [d] Reference 15.

Table IV. First-Order Rate Constants k_1 (s^{-1}) for Me_3Bzm Exchange of $Me_3BzmCo(DH)_2R$ with $P(OCH_3)_3$ in CH_2Cl_2 at 25 °C

R	k_1	log k_1	log k_1 (4-CNpy)
CH_2CF_3	1.30 (4) × 10^{-5}	−4.89	−3.57
CH_2Br[a]	1.23 (3) × 10^{-4}	−3.91	−2.58
CH_2Cl	2.71 (3) × 10^{-4}	−3.57	−2.51
CH_3	4.19 (4) × 10^{-3}	−2.38	−1.39
$CH_2C(CH_3)(COOCH_2CH_3)_2$[b]	2.05 (6) × 10^{-2}	−1.69	−0.51
CH_2CH_3	1.13 (5) × 10^{-1}	−0.95	−0.02
$CH_2C(CH_3)_3$	1.23 (6)	0.09	1.04
$CH(CH_3)_2$	3.8 (1)	0.58	1.43
c-C_6H_{11}[a]	6.1 (2)	0.79	1.59

[a] Lopez, C. Unpublished results. [b] Bayo, F. Unpublished results.

methyl hydrogen could be detected through the dihedral angle α, between the two DH units, and the Co–C–X angle values at the Co-bonded C atom of the alkyl group. However, substitution of one methyl hydrogen by the flat NO_2 group does not seem to distort the equatorial ligands, as the α value is retained and the Co–N(Me_3Bzm) bond is shorter. On the other hand, replacement of at least one methyl hydrogen by a chloro group (e.g., CH(CN)Cl and $CH(Cl)_3$) does induce steric hindrance as the α value decreased to ~1.7°. At the same time, Table III shows, for these three cases, similar and slightly distorted Co–C–X angle values, with departure ranging from ~6 to 17° from the normal tetrahedral angle value of 109.5°. This way of relieving steric interactions is different from that in $CH(CN)CH_2CN$, $CH(CH_3)_2$, and adamantyl derivatives. The $CH(CN)CH_2CN$ and $CH(CH_3)_2$ groups are much alike with α values of 3.1 and 4.0°, respectively, and Co–C–C angle values that are much closer to the ideal tetrahedral angle value. Nonetheless, steric pressure has been decreased through lengthening of the Co–C bond. The adamantyl group is the bulkiest and the most rigid of the groups in Table III. The six angles at the Co-bonded C atom average 109.5°, the ideal tetrahedral angle value. In this case, the steric strain was relieved by further lengthening of the Co–C bond and by folding the DH units toward the neutral L donor since α has now become negative.

Rates. The Me_3Bzm ligand-exchange rate constants (k_1) were determined for six $Me_3BzmCo(DH)_2R$ compounds in the noncoordinating solvent CH_2Cl_2 (Table IV) and can be compared with other results also reported in Table IV. As expected, the stronger electron-donating alkyl groups (e.g., $CH(CH_3)_2$, $CH_2C(CH_3)_3$) lead to greater Me_3Bzm rates compared to those induced by the poorer electron-donating groups (e.g., CH_2CF_3, CH_2Cl). A plot of log k_1 for dissociation of Me_3Bzm from $Me_3BzmCo(DH)_2R$ vs log k_1 for the dissociation of 4-CNpy from 4-CNpyCo$(DH)_2$R (Figure 2) is linear, with the relationship

$$\log k_1(\mathrm{Me_3Bzm}) = [1.09\ (2)][\log k_1(\text{4-CNpy})] - 0.98$$

correlation coefficient 0.9988

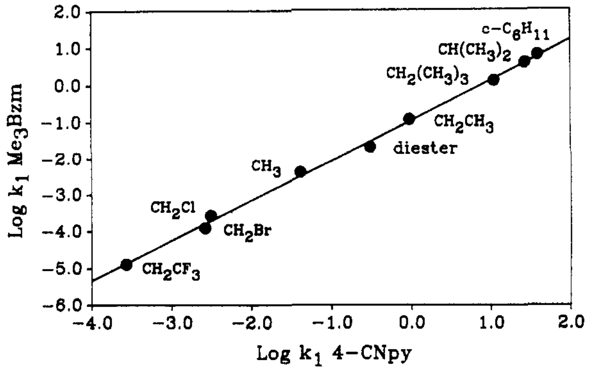
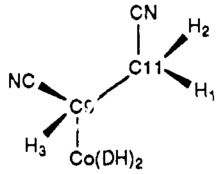


Figure 2. Plot of log k_1 of Me_3Bzm cobaloximes vs log k_1 of 4-CNpy cobaloximes.

Chart I



The k_1 values for 4-CNpy cobaloximes are roughly 10 times greater than those for the Me_3Bzm analogues, but both ligands have a similar dependence on R. Furthermore, ligand dissociation is twice as fast in $pyCo(DH)_2CH_3$ (k_1 = 0.0080 s^{-1})[2] as in $Me_3BzmCo(DH)_2CH_3$ (k_1 = 0.0042 s^{-1}). Thus, py and Me_3Bzm can be considered as ligands having similar coordinating properties and are poorer leaving groups than 4-CNpy. The results are consistent with the view from our structural studies that the C22 and phenylene sides of Me_3Bzm are less and more sterically bulky, respectively, than pyridine. The linear relationship in Figure 2 indicates also that Me_3Bzm is not particularly bulky overall. Although the dynamic and H-exchange studies reported earlier[8] were for $pyCo(DH)_2CH(CN)CH_2CN$, we were not able to obtain suitable crystals for this compound. Nevertheless, our rate and structural studies indicate that this compound must have structural features analogous to those of the Me_3Bzm compound.

Influence of L on the ^1H NMR Spectra of the 1,2-Dicyanoethyl Ligands. The three protons of this alkyl group in various L-substituted cobaloximes give rise to ^1H NMR spectral patterns that are diverse and complex. Figure 3 shows examples of $CH(CN)CH_2CN$ proton patterns from $CDCl_3$ solutions of some cobaloxime derivatives, namely, 4-CNpy, py, 4-Me_2Npy, and 1-MeImd. At high field, the pattern clearly changes from the strongly coupled ABC (4-CNpy) to the more typical ABX (4-Me_2Npy) type patterns. The 1-MeImd spectrum could be regarded as a deceptively simple second-order spectrum.

Chart I shows the numbering scheme of the 1,2-dicyanoethyl protons that will be used for the remainder of

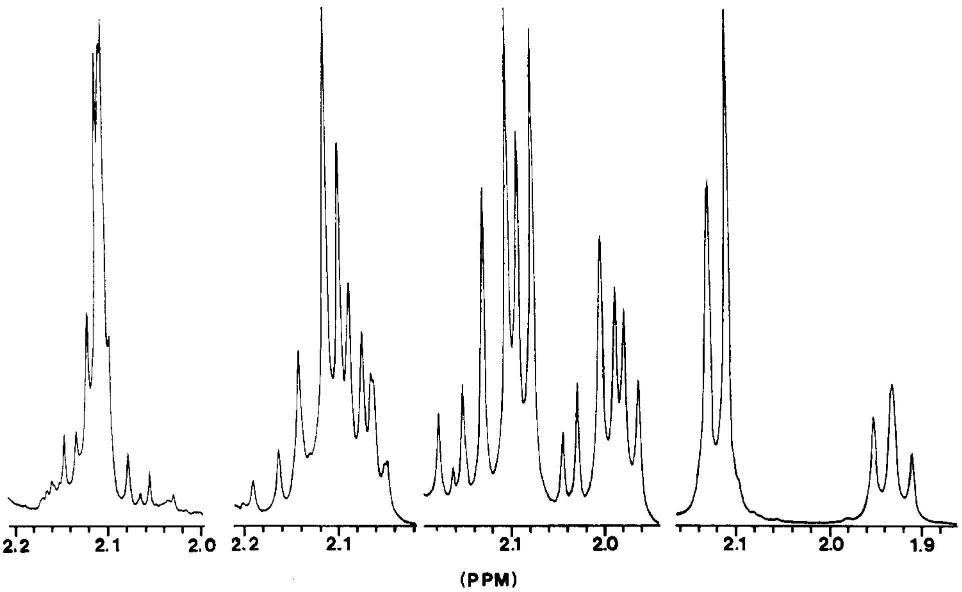


Figure 3. NMR spectral patterns of the $CH(CN)CH_2CN$ protons in (going from left to right) the 4-CNpy, py, 4-Me_2Npy, and 1-MeImd cobaloximes in $CDCl_3$.

Table V. ^1H NMR, Kinetic, and Basicity Data and Conformer Distribution of Various L Derivatives of (1,2-Dicyanoethyl)cobaloximes[a]

General Data

	L								
	4-CNpy	py	3-pic	Me_3Bzm	4-*t*-Bu-py	4-pic	1-MeImd	4-Me_2Npy	av
pK_a	1.9	5.2	5.6	5.6	6.0	6.0	6.9	9.7	
log k_1 (*i*-Pr)	1.4	0.5		0.6	−0.1		−0.9	−0.8	
δ_1[b]	765.2	772.4	771.1	779.6	773.4	770.3	763.8	769.5	
δ_2	752.2	754.9	753.2	755.8	756.6	754.1	763.3	746.7	
δ_3	765.4	748.0	748.3	746.2	737.1	739.0	698.0	716.8	
J_{12}[c]	−17.5	−17.7	−17.3	−17.3	−16.6	−17.9	−16.7	−17.4	−17.3 (4)
J_{13}	8.3	8.7	8.9	10.2	9.0	9.4	9.0	9.3	9.1 (6)
J_{23}	6.2	6.2	6.4	4.4	5.6	4.7	5.9	5.8	5.7 (7)
P_I	0.59	0.65	0.68	0.87	0.69	0.75	0.70	0.74	0.71 (8)
P_{II}	0.29	0.29	0.31	0.03	0.20	0.07	0.25	0.23	0.21 (10)
P_{III}	0.12	0.06	0.01	0.10	0.11	0.18	0.05	0.03	0.08 (5)

Chemical Shifts of $pyCo(DH)_2CH(CN)CH_2CN$ in CD_2Cl_2 and Pyridine-d_5[d]

solvent	δ_1	δ_2	δ_3	J_{12}	J_{13}	J_{23}
CD_2Cl_2	756.2	744.6	707.6	−17.7	10.4	5.3
pyridine-d_5	925.8	904.9	901.3	−16.5	11.1	5.1

[a] NMR data in Hz, in $CDCl_3$, at 360 MHz; pK_a values are from ref 16. [b] Esd's on the chemical shifts range from 0.04 to 0.7 Hz. [c] Esd's on the coupling constants range from 0.01 to 0.3 Hz. [d] 360 MHz.

the discussion. Table V lists the least-squares-fitted spectral parameters of several L-substituted 1,2-dicyanoethyl cobaloximes with some other useful related data. The chemical shifts of H_1 and H_2 derived from the fit remain relatively constant: H_1, from ~2.13 to ~2.17 ppm; H_2, from ~2.07 to ~2.10 ppm. However, the H_3 chemical shifts span more than 0.15 ppm, indicating that this proton on the Co-bonded carbon is influenced by some shielding effect.

Since, qualitatively, Figure 3 and Table V show that the $CH(CN)CH_2CN$ proton pattern simplifies as the pK_a value of L increases, the H_3 chemical shifts were plotted against the pK_a values of L (Figure 6s) and, also, against log k_1 for the dissociation of L from L-substituted isopropylcobaloximes (Figure 4). Isopropylcobaloximes were selected because the isopropyl and 1,2-dicyanoethyl groups have similar bulk, but the 1,2-dicyanoethyl complexes react too slowly to study. We can see in both plots that, except for the 1-MeImd data, the chemical shift of H_3 correlates reasonably well with the pK_a (correlation coefficient 0.981) and log k_1 (correlation coefficient 0.992) values. Thus, the H_3 shifts may be responding directly to increased electron density at C9, indirectly to changes in Co anisotropy (vide infra), or to both factors.

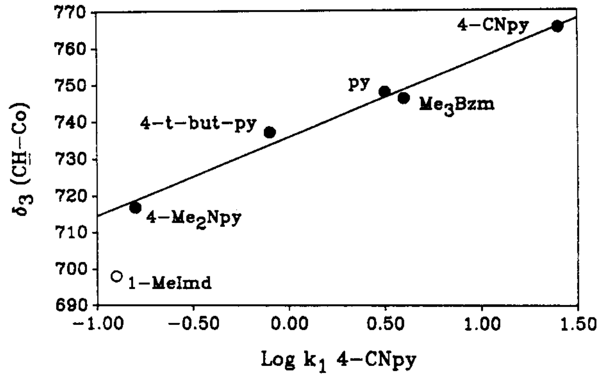
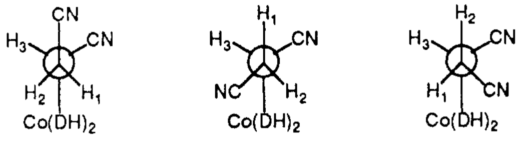


Figure 4. Plot of the H_3 chemical shifts of the related (1,2-dicyanoethyl)cobaloximes vs log k_1 of various isopropylcobaloximes.

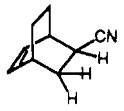
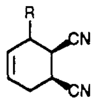
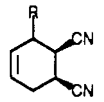
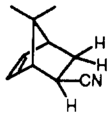
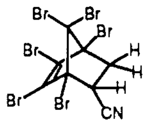
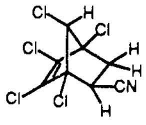
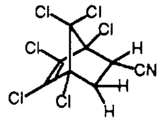
The different bulk of 1-MeImd, when compared to those of Me_3Bzm and pyridine derivatives, may explain its departure from the trend. Me_3Bzm and py are of nearly

Chart II



I II III

Table VI. Vicinal Coupling Constants of Selected Cyano-Substituted Diels-Alder Adducts[a]

compd	J^g, Hz	J^t, Hz	ref
	5		28
 	3.4	11.8	29
	4.2		30
	4.5		30
	3.4	10.6	30
	4.1	10.6	31
	4.3	11.3	32
	4.5	10.9	32
	4.4	11.5	32
	4.6	10.8	33
	4.2 (av)	11.1 (av)	

[a] Except for J^t from ref 29, the J^t values are J^{cis} values to which was added 1.5 Hz. This 1.5-Hz value was obtained from the Bothner-By modification of the Karplus equation.[17] It is the difference between J^t and J^{cis} values estimated for oriented vicinal C-H bonds with torsion angle values of 0 and 180°, respectively.

equal bulk, as their Co-N distances in various alkylcobaloximes are similar[1,14] and longer than in analogous 1-MeImd derivatives. These differences become more apparent if the 1-MeImd and 4-Me_2Npy compounds are compared. Although 4-Me_2Npy (pK_a = 9.7)[16] is roughly 500 times more basic than 1-MeImd (pK_a = 6.95),[16] it dissociates faster than 1-MeImd.

Another possible steric factor that must be considered is the variation in the geometry of the 1,2-dicyanoethyl ligand with change in L. As stated in a previous report, Co-C-C angles and Co-C distances tend to open up and lengthen, respectively, as the bulk of L increases.[2] These individual modifications or a combination of them will slightly change the position of H_3 with respect to Co and, hence, will affect its chemical shift, which may be influenced by the Co anisotropy (vide infra).

Conformational Analysis of the 1,2-Dicyanoethyl Group in Solution. Table V lists the average geminal and vicinal coupling constants between the cyanoalkyl protons. The J_{12} value of -17.3 Hz closely resembles that of -20 Hz reported for $CH_2(CN)_2$.[17] However, the J_{13} and J_{23} values of 9.1 and 5.7 Hz, respectively, are intermediate between the values of ~11 and ~4 Hz predicted from the Bothner-By modification of the Karplus equation[18] for the trans and gauche geometries found in the solid-state structure. Indeed, in substituted ethanes of the type $C(R_1)H_2C(R_2)(R_3)H$, such as the $C(CN)H_2C(Co)(CN)H$ group (see Chart I), the vicinal coupling constants J_{13} and J_{23} of a three-spin system formed by the three magnetically nonequivalent protons are weighted averages of the coupling constants of the three minimum potential energy rotamers illustrated by the Newman projections in Chart II.[19]

In rotamer III, both J_{13} and J_{23} are gauche, whereas they are gauche and trans in I and II, respectively. If we define rotamer proportions P_I, P_{II}, and P_{III} ($P_{III} = 1 - P_I - P_{II}$), J_{13} and J_{23} can then be expressed as (t = trans, g = gauche)

$$J_{13} = P_I J^t + P_{II} J^g + P_{III} J^g \qquad (1)$$

$$J_{23} = P_I J^g + P_{II} J^t + P_{III} J^g \qquad (2)$$

By rearranging these two equations and inserting suitable values for J^t and J^g, we calculate the proportions of the rotamers as

$$P_I = (J_{13} - J^g)/(J^t - J^g) \qquad (3)$$

$$P_{II} = (J_{23} - J^g)/(J^t - J^g) \qquad (4)$$

$$P_{III} = 1 - P_I - P_{II} \qquad (5)$$

This treatment was applied successfully in amino acid and peptide conformational studies[20] with J^t and J^g values of 13.6 and 2.6 Hz, respectively. However, Thomas stated in a review article that the values mentioned above, although suggested by perfectly rational arguments, seem to be suspect in that J^t, in particular, has rarely been found to be greater than ca. 12 Hz, even in systems without electronegative substituents.[21] He proposed for amino acid systems more realistic, intermediate values of 10.5 Hz for J^t and 2.7 Hz for J^g. These last two values, averaging 6.6 Hz, would be unsuitable for our (1,2-dicyanoethyl)cobaloxime system, with averaged observed J_{13} and J_{23} values averaging 7.4 Hz. Indeed, in a saturated CH-CH fragment such as $C(H_3)(Co)(CN)-C(H_1)(H_2)(CN)$, the electronegativity of the substituents will affect the value of the vicinal J_{13} and J_{23} coupling constants. It is known that $^3J_{av}$, the vicinal coupling constant in a freely rotating $CHR_1R_2-CHR_3R_4$ moiety, shows the following simple dependence on electronegativity:

$$^3J_{av} = {}^3J_0 - 0.8\sum(E_X - E_H) \qquad (6)$$

where the summation term accounts for the electronegativity differences of the groups R_1 to R_4, with respect to H.[17] $^3J_0$ stands for the ^3J value for ethane (8.0 Hz). The following electronegativity values were used for the $CH(CN)(Co)-CH_2CN$ group: Co, 1.8;[22] CN, 2.49;[23] H, 2.1.[24]

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(20) Cavanaugh, J. R *J. Am. Chem. Soc.* **1967**, *89*, 1558. Ogura, H.; Arata, Y.; Fujiwara, S. *J. Mol. Spectrosc.* **1967**, *23*, 76. Newmark, R. A.; Miller, M. A. *J. Phys. Chem.* **1971**, *75*, 505. Dezube, B.; Dobson, C. M.; Teague, C. E. *J. Chem. Soc., Perkin Trans. 2* **1981**, 730.

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(23) Cavanaugh, J. R.; Dailey, B. P. *J. Chem. Phys.* **1961**, *34*, 1099.

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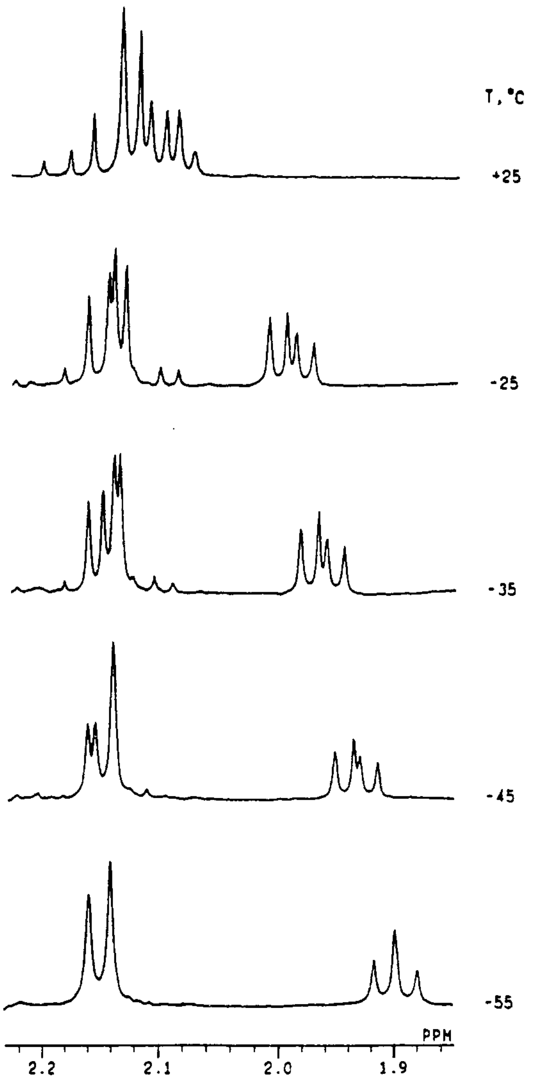

Figure 5. Series of ^1H NMR spectra of the py derivative of (1,2-dicyanoethyl)cobaloxime in $CDCl_3$ as a function of temperature.

The $^3J_{av}$ value of 7.6 Hz calculated from eq 6 compares well with the average observed value of 7.4 Hz.

More suitable J^t and J^g values can be derived if we use compounds containing properly substituted H-C-C-H systems that are fixed predominantly in a single steric arrangement. Table VI reports vicinal coupling constants found in some Diels-Alder adducts with acrylonitrile and fumaronitrile. Diels-Alder compounds are most informative in vicinal constants related to gauche and cis interactions. The resulting average J^t, 11.1 Hz, and J^g, 4.2 Hz, would seem to be well adapted to our system. These values have been used in eqs 3 and 4 to calculate P_I, P_{II}, and P_{III} (Table V). The averaged P_I, P_{II}, and P_{III} clearly indicate that isomer I, which is observed in the solid state, predominates in solution. Noteworthy is the fact that, of the three possible isomers, I shows the least amount of steric hindrance as the CH_2CN cyano group is oriented away from the $(DH)_2$ equatorial plane. In contrast, the lower abundance of isomers II and III might be explained by some steric strain involving the CH_2CN cyano group pointing toward the equatorial $(DH)_2$ plane. Such strain could be relieved by opening the Co-C9-C11 angle and/or lengthening the Co-C9 and/or the C9-C11 bond(s).

Influence of Temperature on the ^1H NMR Spectra of (1,2-Dicyanoethyl)cobaloximes. In order to elucidate the conformational behavior of the 1,2-dicyanoethyl group in solution and gain more information about the factors responsible for its ^1H NMR spectral modifications, variable-temperature ^1H NMR studies in $CDCl_3$ were undertaken on three pyridine derivatives, namely 4-CNpy, py, and 4-Me_2Npy. Spectra as a function of temperature for the py adduct are shown in Figure 5 (see Figure 7s for 4-CNpy and 4-Me_2Npy). When the temperature is lowered, the H_3 signal is upfield-shifted while the cyanomethylene (H_1 and H_2) peaks are slightly downfield-shifted, with respect to their positions at room temperature. The resulting frequency separation of signals simplified the spectrum. At -60 °C, the spectrum, which looks very similar to that of 1-MeImd at room temperature, can be interpreted by using first-order rules with $^3J_{vic} \approx 7.5$ Hz.

Table VII. ^1H NMR and ^{59}Co NMR Spectral Data for $LCo(DH)_2CH_3$

L^a	$\delta(Co\text{-}CH_3)^b$ (CH_3OH)	$\delta(Co\text{-}CH_3)^c$ $(CDCl_3)$	$\delta(Co\text{-}CH_3)^c$ (50/50 (v/v) DMSO-d_6 D_2O)
4-CNpy		0.78	0.63
CH_3OH	4110		
py	3660	0.68	0.55
4-pic	3660	0.65	0.52
4-NH_2-py			0.40
imid	3590		
PBu_3	2620		
$P(OCH_3)_3$	1580		

[a] Abbreviations: 4-NH_2-py = 4-aminopyridine; imid = 1-(2-(trifluoromethyl)phenyl)imidazole; PBu_3 = tributylphosphine. [b] In ppm, against $Co(CN)_6{}^{3-}$ as an external reference.[27] [c] In ppm, against $(CH_3)_4Si$ as an internal reference.[2]

If lowering the temperature had resulted in sets of signals for each individual conformer with an intensity distribution based on the proportions evaluated from the room-temperature spectrum, we should have observed a low-temperature spectral pattern more complex than that of Figure 5. Thus, rotation about the C9-C11 bond is not prevented (the rotational energy barrier of a C_{sp^3}-C_{sp^3} bond is very low, ca. 3-5 kcal/mol).[17] Another possibility would have been the observations of the spectral pattern of the more abundant and geometrically favorable conformer I, with vicinal coupling constants matching its geometry. However, we again find a deceptively simple second-order spectrum with $^3J_{vic} \approx 7.5$ Hz, which is the average of the J_{13} and J_{23} values deduced from the analysis of the spectra taken in $CDCl_3$, at room temperature. This finding suggests a conformer distribution similar to that at room temperature. This variable-temperature study shows that the spectral simplification obtained at room temperature upon increasing the "effective" trans influence of L transmitted through Co can be observed also upon lowering the temperature for any given L-substituted (1,2-dicyanoethyl)cobaloxime, except 1-MeImd.

Explanation of the Temperature Dependence of the ^1H NMR Signals of the 1,2-Dicyanoethyl Ligand. A reasonable explanation for such behavior is found in the Co anisotropic contribution to the chemical shift. McConnell's equation can be used to estimate such a contribution:

$$\sigma = \Delta\chi[(1 - 3\cos^2\theta)/3R^3]$$

where σ, the shielding contribution, is a function of $\Delta\chi$, the magnetic susceptibility of the contributing atom (for instance, Co), and a geometric term (see ref 25 for a full description). If we assume the same average geometry of

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(25) McConnell, H. M. *J. Chem. Phys.* **1957**, *27*, 226. Pople, J. A. *Proc. R. Soc. London, Ser. A* **1957**, *239*, 550.

the Co–CH(CN)CH_2CN group at all temperatures, then the increasing shielding effect with lower temperature is directly linked to an increase in $\Delta\chi$. Levy reported that the ^{59}Co shift of $Co(acac)_3$ was also shifted upfield upon cooling.[26] Also, as summarized in Table VII, a ^{59}Co NMR study of methylcobaloximes with various L's showed that the cobalt signal was shifted upfield as the electron-donating power of L increased.[27] The ^1H NMR shifts of the Co-bonded methyl group of methylcobaloximes (Table VII) also show the same upfield-shifting trend.[2] Thus, changes in the magnetic anisotropy of the Co center resulting from ligand substitution and temperature variation appear to explain our findings. Furthermore, such a complex dependence of spectral pattern on temperature could easily be incorrectly attributed to dynamic processes, as was done previously.[8]

Deuterium-Exchange Study. Schrauzer et al. mentioned briefly that the three 1,2-dicyanoethyl protons of the pyridine derivative underwent full deuterium exchange in a D_2O/pyridine-d_5 solvent mixture.[8] We have decided to reinvestigate qualitatively this deuterium-exchange reaction. In comparison with our spectra recorded in $CDCl_3$ and CD_2Cl_2, the spectrum of pyCo$(DH)_2$CH(CN)CH_2CN in py-d_5 is quite different. First, it is shifted downfield with respect to other spectra. Second, the spectral dispersion is smaller in py-d_5. Using py-d_5 obtained from Aldrich and a batch supplied by KOR, we found no deuteration when D_2O was added. For example, in one study, a 0.05 M solution of pyCo$(DH)_2$CH(CN)CH_2CN in py-d_5 (1 mL) was monitored by ^1H NMR spectroscopy daily for 10 days after addition of D_2O (50 μL). The 12 protons of the four DH methyl groups, assumed not to be deuterated, were used as an integration standard. No loss in signal intensity was observed. An additional 50 μL of D_2O was added and, after 2 months, no exchange was detected. No exchange was observed also with py-d_5/D_2O solutions. In one case, partial exchange was noted over several days but this reaction could not be reproduced. Clearly, no facile exchange process occurred, especially on the NMR time scale.

Reinterpretation of Previous Results. Schrauzer et al. used several lines of evidence to suggest that dynamic valence tautomerism involving a π–σ transition state was occurring in the CH(CN)CH_2CN ligand.[8] We will present this evidence and then offer our alternative explanation. First, the pattern of ^1H coupling of the ^1H NMR signal of CH(CN)CH_2CN collapsed in py-d_5. We have pointed out that ^1H NMR chemical shifts of cobaloximes are influenced greatly by dramatic aromatic solvent induced shifts.[2]. The relatively positive periphery of the py plane, i.e. the region with the H (or D), will preferentially solvate the negative end of the polar cobaloximes, in this case the alkyl group. Since the in-plane region of the anisotropic py ring is downfield-shifting, the alkyl signals are shifted downfield. Under circumstances where the solvations of protons under observation are slightly different, e.g. for H_1, H_2, and H_3, then the signals will have either greater or lower dispersion than in, for example, $CDCl_3$. Since H_3 is on the C bound to cobalt, it should be the most electron-rich H in the alkyl group. It is also upfield, and solvation by py-d_5 will shift H_3 relatively more downfield than it will shift the H_1 and H_2 signals. Such collapse of signal dispersion would be expected of a dynamic process and was incorrectly attributed to rapid H exchange. Second, the ^1H NMR signals were temperature-dependent. We have explained this by changes in Co anisotropy. Third, $(n\text{-Bu})_3$PCo$(DH)_2$CH(CN)CH_2CN ($(n\text{-Bu})_3P$ = tri-*n*-butylphosphine) had a more disperse coupled alkyl signal than the py compound. This was attributed to π-bonding by the $(n\text{-Bu})_3P$ ligand that destabilized a putative π-bonded alkyl intermediate needed for the dynamic process. We attribute this greater dispersion to the difference in Co anisotropy due to the greater electron donation by $(n\text{-Bu})_3P$ than by py. 1-MeImd can not π-bond in the same way but has an effect on the spectrum similar to that of $(n\text{-Bu})_3P$. Fourth, the CH(CN)CH_2CN group undergoes D exchange. We have also observed this result once, for one batch of py-d_5 from KOR. In other batches of py-d_5 from KOR and Aldrich, no exchange was observed in days to months. A dynamic process would require exchange to take place in a matter of minutes, although we do not know why exchange was observed in one batch of py-d_5 from KOR (a company no longer in business). Even in this case, the exchange process was too slow to be consistent with a dynamic process on the NMR time scale.

Conclusions

The characterization of the Me_3Bzm derivative of (1,2-dicyanoethyl)cobaloxime by X-ray crystallography allowed us to establish beyond question the identity of the alkyl group. In addition to being a weak electron donor similar to CH_2CN and CH(CN)Cl, as demonstrated by the short trans Co–N bond, the CH(CN)CH_2CN group has a steric bulk which closely resembles that of the strong electron-donating isopropyl group. The k_1 rate data for dissociation of Me_3Bzm from $Me_3BzmCo(DH)_2R$ compounds indicated that Me_3Bzm has coordination and steric properties similar to those of pyridine type ligands, in agreement with the X-ray results.

Assignment of the 1,2-dicyanoethyl ^1H NMR signals and coupling constants by second-order and least-squares analyses revealed that the alkyl proton pattern is greatly affected by the trans influence of L, especially the proton of the Co-bonded carbon. The resulting shielding phenomenon can be explained in terms of transmission through the $Co(DH)_2$ moiety of the electron-donation power of L. A similar shielding behavior is also observed upon lowering the temperature and is attributed to a change in Co anisotropy. The complex nature of these observations deceptively suggests that the CH(CN)CH_2CN group is involved in an unusual dynamic exchange process. In no case was a rapid deuteration process observed.

Independent of the factors influencing these shifts, we have shown that the (1,2-dicyanoethyl)cobaloximes exist in solution as an unequal mixture of conformers, with the conformer found in the solid state the most abundant. Our results, on the other hand, are quite understandable in terms of standard organocobaloxime chemistry. Finally, on the basis of our analysis of coupling patterns, the proportion of conformers does not appear to depend greatly on L. However, this study was confined to N-donor L groups, which are relevant to coenzyme B_{12}. We have shown that P-donor ligands can cause much greater distortions of the $Co(DH)_2$ moiety, and a study of such compounds might reveal a dependence of CH(CN)CH_2CN conformation on the bulk of P-donor L.

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Supplementary Material Available: Tables of elemental analyses, ^{1}H and ^{13}C NMR data of $LCo(DH)_2CH(CN)CH_2CN$, bond lengths and angles, H atomic parameters, and anisotropic temperature factors and two figures related to the NMR discussion (7 pages); a listing of structure factors (22 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of Novel Palladium(II) Cyclometalated Complexes of 2-Vinylpyridine Derivatives[1a]

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Novel dimeric cyclometalated complexes of 2-vinylpyridine derivatives [e.g., bis(μ-chloro)bis[2-(2-pyridinyl)-3-acetoxypropenyl-*C*,*N*]dipalladium(II)] that possess Pd–C_{sp^2} σ-bonds have been synthesized and characterized by ^{1}H and ^{13}C NMR spectroscopy. The pyridine and PPh_3 monomers of these complexes were also synthesized, and the existence of the Pd–C σ-bond was proven by an X-ray crystal structure determination of chloro[2-(2-pyridinyl)-3-acetoxypropenyl-*C*,*N*](triphenylphosphine)palladium(II) ($PdClC_{28}H_{25}NO_2P$): $a = 9.5939$ (10) Å, $b = 29.702$ (4) Å, $c = 9.0964$ (16) Å, $\beta = 100.045$ (11)°, monoclinic, $P2_1/c$, $Z = 4$.

Introduction

Although five-membered N,C-cyclometalated σ complexes, where the carbon bonded to the metal is sp^2 hybridized, are well-known, examples with pyridine as the N donor are rather limited[2] and most reports have used 2-arylpyridines. Considering the greater reactivity of an isolated carbon–carbon double bond compared to an aryl moiety, cyclometalation of 2-vinylpyridine (2-vp) should be more facile than 2-phenylpyridine, for example. However, to the best of our knowledge, reports of cyclometalated 2-vp (or derivatives) are also limited.[3] This can be rationalized by considering the accepted mechanism of the reaction. The first step is the straightforward formation of the M–N bond. Next, electrophilic attack of the metal on the double bond (2-vp) or aromatic ring (2-arylpyridine) occurs, generating a positive charge on the carbon α to the pyridine. In 2-arylpyridines, this positive charge is stabilized by delocalization in the carbocyclic ring, but in 2-vp, delocalization would result in disruption of the aromaticity of the pyridine ring. Thus, the charge resides mostly on the α-carbon, which is a secondary carbocation possessing an electron-withdrawing group (pyridine), which destabilizes the cation even further. To circumvent this, a very electrophilic metal must be used or the cation intermediate must be stabilized by suitable electron-donating substituents (R). The final step in the mechanism is deprotonated at the β-position to regenerate a double bond.

We tested this hypothesis by studying the cyclometalation reactions of suitably α-substituted 2-vinylpyridines with $PdCl_2$ and found that cyclometalation readily occurs, at 25 °C, to give the dimeric complexes $\{\overline{\mathrm{Pd[pyC(R){=}C}}\mathrm{H]}(\mu\text{-Cl})\}_2$ (R = CH_2OH, CH_2OAc).[4]

Results and Discussion

Dichloropalladium(II) does not readily undergo cyclometalation with 2-vp because of the formation of an intermediate secondary carbocation (see Figure 1). To circumvent this problem, the α-substituted derivative **1** was chosen for cyclometalation for two reasons: (1) α-substitution would generate a more stable tertiary cation in the intermediate; (2) a functionalized α-substituent would allow such uses as polymer functionalization, synthesis of dinuclear complexes, and easy ligand modification.

Ligand **1a** was easily synthesized by the method of Bohlmann et al.[5] from the commercially available[6] 2-(2-pyridinyl)-1,3-propanediol. Treatment of the propanediol with acetic anhydride at reflux for 6 h yielded (94%) **1a**,

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