the most obvious difference is incorporation of Co(II) into a porphyrin, which leads to a low-spin state for Co(II).[31] Many similar mononuclear low-spin Co(II) complexes bind O_2 reversibly.[42] The O_2 adduct in cobalt-substituted hemocyanin is formulated as a (μ-hydroxo)(μ-peroxo)dicobalt(III) complex, which represents the other known structural type resulting from reaction of synthetic Co(II) complexes with O_2.[42,43] In contrast to the dicobalt site in Co_2Hr, the visible absorption spectrum of cobalt-substituted hemocyanin prior to exposure to O_2 indicates that the active-site Co(II) have a pseudotetrahedral coordination geometry and that these Co(II) centers are accessible to solvent and exogenous ligands.[41] If a (μ-hydroxo)bis(μ-carboxylato)dicobalt(II) core accurately describes the complex in Co_2Hr, then access of O_2 to both Co centers simultaneously is likely to be severely inhibited, as is the case for the diiron(II) site in native deoxyHr.[2] Thus, the dimetal site favored in Hr is not designed to accommodate either known type of adduct resulting from reaction of Co(II) with O_2.[42,43] In addition, the lack of a pH-dependent absorption spectrum and of azide binding noted above suggest a general inaccessibility of small molecules to the dicobalt site in Co_2Hr, despite the five-coordinate Co(II) indicated by the spectroscopic data. The diferrous site in deoxyHr also shows no evidence for interaction with solvent but does show evidence for complex formation with azide.[45]

Summary and Conclusions

A simple method is described for high-yield preparation of a cobalt-substituted Hr. The cobalt-substituted Hr closely resembles the native protein in polypeptide helix content and molecular weight, indicating that the protein subunit structure and intersubunit interactions have been preserved. Close to 2 Co/Hr subunit with no detectable iron is reproducibly obtained, suggesting that cobalt occupies the same coordination sites as iron in the native protein. Analysis of the EXAFS data provides proof of a dicobalt site (3.54-Å Co–Co distance) with histidine ligation. The requirement of correlated motion of the Co scatterers for observation of EXAFS implies the existence of one or more bridging ligands. Given the single distance (2.12 Å) found for the first coordination sphere donor atoms, and comparisons to synthetic complexes, a hydroxo bridge is suggested. The X-ray absorption as well as the UV/vis and near-IR absorption and CD spectra indicate that all of the cobalt in Co_2Hr is in the +II oxidation state, even in air, that the coordination spheres consist exclusively of N,O-donor ligands, and that both five- and six-coordinate Co centers are present in significant proportions. Given the five- and six-coordinate iron centers with terminal histidine ligands in the (μ-hydroxo)bis(μ-carboxylato)diiron(II) site of deoxyHr, an isostructural dicobalt(II) site is strongly suggested in Co_2Hr. The absorption spectrum of the dicobalt(II) site in Co_2Hr is unaffected by variations in pH or by the presence of azide, O_2, or H_2O_2. Apparently, even the five-coordinate Co center is inaccessible to solvent and exogenous ligands. Despite this lack of reactivity, the close structural analogies to native Hr and the stability of Co_2Hr are likely to facilitate studies of the relationship between protein folding and dimetal site assembly. This relationship will be addressed subsequently.[46]

Acknowledgment. This research was supported by NIH Grants GM40388 (D.M.K.) and GM38829 (M.J.M.). The near-IR CD/MCD spectrometer was purchased with funds from an NSF Research Training Group Award to the Center for Metalloenzyme Studies (DIR 9014281). We thank Gerald J. Colpas and Csaba Bagyinka for help in collecting the X-ray absorption spectra. We thank Michael K. Johnson for helpful discussions regarding the near-IR absorption and CD of Co_2Hr.

---

(42) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988; pp 735–738.

(43) A recently described side-on bonded superoxo complex of Co(II) results from reaction of a formally Co(I) complex with O_2.[44]

(44) Egan, J. W., Jr.; Haggerty, B. S.; Rheingold, A. L.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1990**, *112*, 2445–2466.

(45) (a) Maroney, M. J.; Kurtz, D. M., Jr.; Nocek, J. M.; Pearce, L. L.; Que, L., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 6871–6879. (b) Wilkins, P. C.; Wilkins, R. G. *Biochim. Biophys. Acta* **1987**, *912*, 48–55. (c) Reem, R. C.; Solomon, E. I. *J. Am. Chem. Soc.* **1987**, *109*, 1216–1226. (d) Hendrich, M. P.; Pearce, L. L.; Que, L., Jr.; Chasteen, N. D.; Day, E. P. *J. Am. Chem. Soc.* **1991**, *113*, 3039–3044.

(46) Zhang, J.-H.; Kurtz, D. M., Jr. Manuscript in preparation.

Contribution from the Department of Chemistry, Box CH,
Mississippi State University, Mississippi State, Mississippi 39762

Infrared and ^{13}C and ^{15}N NMR Studies of Cyano(ligand)cobaloximes: Evidence for Cobalt-to-Cyanide π-Bonding

Kenneth L. Brown* and S. Satyanarayana

Received July 19, 1991

A series of 17 cyano(ligand)cobaloximes have been prepared, including 6 with 4-substituted pyridine ligands, 6 with primary amine ligands, 3 with 4-substituted aniline ligands, the ammonia complex, and the potassium salt of the thiocyanato complex. The analogous series of complexes enriched in ^{13}C and ^{15}N in the cyanide ligand have been used to locate the cyanide ^{13}C and ^{15}N NMR resonances and the cyanide stretching frequencies in the infrared spectra. As the trans axial ligand is varied, an inverse dependence of the ^{15}N chemical shifts on the ^{13}C chemical shifts is observed, and for 14 of the complexes the chemical shift data give an excellent linear correlation with a slope of −0.614. These data, together with trends in $\delta_{^{15}N}$, $\delta_{^{13}C}$, and ν_{CN} with the basicity of the trans axial ligand, are interpreted to indicate that cobalt-to-cyanide π-bonding is important in these cyanocobalt complexes.

Introduction

In a recent report,[1] a curious inverse dependence of the ^{13}C and ^{15}N NMR chemical shifts of cyanide ion bound to cobalt corrins upon changes in inner-sphere coordination was observed. Thus, conversion of the base-on form of cyanocobalamin to the base-off form (in which the dimethylbenzimidazole ligand is replaced by water) caused a 9.6 ppm upfield shift of the cyanide ^{13}C resonance but a 8.7 ppm *downfield* shift of the ^{15}N resonance. In contrast, protonation of CN^- causes an upfield shift of both the ^{13}C and ^{15}N resonances (by 52.4 and 26.9 ppm, respectively) as expected.[1] Similarly, for eight cobalt corrin-bound cyanide species in various coordination environments, a reasonably good ($r^2 = 0.89$) linear correlation of $\delta_{^{15}N}$ with $\delta_{^{13}C}$ with a slope of −0.73 was found to exist. This correlation not only confirms the inverse behavior of the ^{13}C and ^{15}N cyanide chemical shifts of cyanocobalt corrins

---

(1) Brown, K. L.; Gupta, B. D. *Inorg. Chem.* **1990**, *29*, 3854.

Table IV. Cyanide ^{13}C and ^{15}N NMR Chemical Shifts and Infrared Stretching Frequencies for Cyano(ligand)cobaloximes

L[a]	pK_L[b]	$\delta_{^{13}C}$,[c] ppm ($\Delta\nu_{1/2}$, Hz)	$\delta_{^{15}N}$,[c] ppm ($^1J_{NC}$, Hz)	ν_{CN},[d] cm^{-1}	$\nu_{^{13}C^{15}N}$,[d] cm^{-1}	$\nu_{CN}/\nu_{^{13}C^{15}N}$
SCN^-[e]	0.85[f]	120.82 (60.3)	304.55 (8.3)	2141.9	2064.3	1.0376
CNpy	2.24[g]	114.88 (50.0)	308.30 (8.6)	2143.8	2065.2	1.0381
In-py	3.77[g]	115.91 (36.1)	307.77 (8.5)	2145.2	2065.8	1.0384
Br-py	4.10[h]	115.68 (36.3)	307.98 (8.4)	2142.0	2063.4	1.0381
py	5.51[g]	116.25 (62.3)	307.51 (8.6)	2141.0	2063.0	1.0378
CH_3py	6.63[g]	116.64 (56.7)	307.31 (8.6)	2140.0	2061.9	1.0379
NH_2py	9.40[g]	118.61 (58.9)	306.34 (8.5)	2137.0	2059.0	1.0379
DEA	8.72[g]	119.72 (69.4)	305.29 (8.5)	2145.0	2066.1	1.0382
FEA	9.19[h]	120.25 (68.7)	304.84 (8.5)	2149.2	2070.0	1.0383
NH_3	9.24[f]	122.92 (69.6)	303.83 (8.5)	2133.6	2055.5	1.0380
HEA	9.50[f]	120.89 (69.1)	304.76 (8.5)	2148.7	2069.7	1.0382
MEA	9.68[g]	120.51 (71.1)	304.84 (8.5)	2143.0	2064.7	1.0379
EA	10.63[f]	121.81 (73.2)	304.81 (8.4)	2133.3	2055.6	1.0378
PA	10.80[g]	121.53 (75.8)	304.14 (8.5)	2134.3	2056.2	1.0380
BrAn	3.91[f]	117.41 (41.1)	308.32 (8.5)	2141.5	2063.7	1.0377
An	4.60[f]	118.13 (45.8)	307.92 (8.5)	2134.6	2056.8	1.0378
CH_3OAn	5.29[f]	119.01 (47.3)	307.72 (8.4)	2133.1	2055.4	1.0378

[a] Ligand abbreviations given in ref 2. [b] pK_a of the conjugate acid of the ligand, L. [c] In DMSO-d_6, 25 °C. ^{13}C chemical shifts relative to external TSP, ^{15}N chemical shifts reported relative to NH_3(l). [d] KBr pellets. [e] Values for K[NCCo(D_2H_2)SCN]. For K[NCCo(D_2H_2)SCN], ν_{SC-N} was 2108.0 cm^{-1}, and for K[$^{15}N^{13}CCo(D_2H_2)SCN$], ν_{SC-N} was 2107.2 cm^{-1}. [f] Reference 14. [g] Reference 15. [h] This work.

but demonstrates that the ^{15}N resonance is nearly as sensitive (ca. 75%) to changes in the coordination environment as the ^{13}C resonance.

These results were interpreted as being indicative of the existence of dπ–pπ back-bonding in such cyanocobalt species as depicted, for example, in eq 1 by the valence-bond species **2**. Here,

$$\underset{\mathbf{1}}{\mathrm{Co{-}C{\equiv}N}} \leftrightarrow \underset{\mathbf{2}}{\mathrm{Co^{+}{=}C{=}N^{-}}} \qquad (1)$$

the effect of trans axial ligands on the cyanide ^{13}C and ^{15}N chemical shifts will include the dependence of the relative stabilization of **1** and **2** by the axial ligand. We now report the results of an NMR and IR study of a series of 17 cyano(ligand)cobaloximes with axial ligands of widely varying basicity, which permits a more detailed analysis of this phenomenon.

Experimental Section

Axial ligands were obtained in the highest purity commercially available and used without further purification. $NCSCo(D_2H_3)SCN$[2] was prepared by the method of Ablov and Syrtsova.[3,4] This complex was converted to $H_3NCo(D_2H_2)SCN$ by treatment with concentrated NH_4OH as described by Crumbliss and Gaus.[5] The latter complex was then reacted with an equimolar amount of KCN[5] to afford the salt K[NCCo(D_2H_2)SCN] in 75% yield. The $NCCo(D_2H_2)L$ complexes were then obtained in 22–82% yield by treatment of a suspension of this potassium salt in methanol with an excess of the desired ligand, L, as described by Crumbliss and Gaus.[5] The isotopically enriched complexes $^{15}N^{13}CCo(D_2H_2)L$ were similarly prepared from K[$^{15}N^{13}CCo(D_2H_2)SCN$], obtained by treatment of $H_3NCo(D_2H_2)SCN$ with $K^{13}C^{15}N$ (Isotec, 99 atom % ^{13}C, 99 atom % ^{15}N). However, no $NCCo(D_2H_2)L$ complexes could be obtained for the ligands $CF_3CH_2NH_2$, $NCCH_2NH_2$, 4-$NO_2C_6H_4NH_2$, 4-$NCC_6H_4NH_2$, CH_3CN, or C_6H_5CN.

^{1}H, ^{13}C, and ^{15}N NMR spectra were obtained on a GE QE 300 NMR spectrometer at 25 °C using a 5-mm broad-band probe. Samples contained between 25 and 50 mM $^{15}N^{13}CCo(D_2H_2)L$ in DMSO-d_6. ^{1}H and ^{13}C NMR spectra were referenced to external TSP in DMSO-d_6. ^{15}N NMR spectra were referenced to external CH_3NO_2 locked to DMSO-d_6 in a concentric insert (Wilmad). ^{15}N chemical shifts are reported relative to NH_3(l) using $\delta_{CH_3NO_2}$ = 380.23 ppm relative to NH_3(l).[6] Infrared spectra were obtained on a Midac FTIR instrument using KBr pellets.

Results

Using the synthetic route of Crumbliss and Gaus,[5] a series of 16 $NCCo(D_2H_2)L$ complexes, and their analogues isotopically enriched in the cyanide ligand, $^{15}N^{13}CCo(D_2H_2)L$, were readily obtained from the protonated, dithiocyanatocobaloxime via thiocyanato(ammine)cobaloxime and the potassium salt of cyano(thiocyanato)cobaloxime. These complexes include six derivatives with 4-substituted pyridine axial ligands, six with primary amine ligands, the ammonia complex, and three complexes with 4-substituted aniline ligands. However, for the most weakly basic of the pyridine ligands, CNpy, the yield was poor (22%, compared to 87% for py) and for the most weakly basic primary amines ($CF_3CH_2NH_2$ and $NCCH_2NH_2$) and anilines (4-$NO_2C_6H_4NH_2$ and 4-$NCC_6H_4NH_2$) with which the synthesis was attempted, no products could be obtained. All of the compounds obtained were characterized by their ^{1}H and ^{13}C NMR spectra and their infrared spectra. These data are collected in Tables I–III (supplementy material).

In addition to the anticipated resonances for the equatorial methyls, the equatorial oxime carbons, and the axial ligands, the ^{13}C spectra of the $^{15}N^{13}CCo(D_2H_2)L$ complexes contained a prominent, very broad resonance attributable to the cyanide carbon. This resonance, which appeared between 115 and 123 ppm (Table IV), was definitely assignable to the cyanide carbon as only it, and the sharp resonance near 152 ppm due to the oxime carbons, remained unchanged in the absence of ^{1}H decoupling. The broadness of these resonances ($\Delta\nu_{1/2}$ = 36–76 Hz), generally attributed to quadrupolar relaxation by the ^{59}Co nucleus ($I = {}^7/_2$),[7-12] completely obscured the anticipated ^{15}N–^{13}C coupling ($^1J_{CN} \sim 8.5$ Hz; vide infra). Gaus and Crumbliss[7] previously reported cyanide ^{13}C chemical shifts for two of these complexes ([$N^{13}CCo(D_2H_2)SCN$]$^-$ and $N^{13}CCo(D_2H_2)py$), and the current results are in good agreement with these earlier values after compensating for the differences in chemical shift reference.

The ^{15}N NMR spectra of the $^{15}N^{13}CCo(D_2H_2)L$ complexes consisted of a single, relatively sharp doublet between 303.8 and 308.3 ppm (Table IV), the unenriched equatorial and axial nitrogens being unobservable under these conditions. The ^{13}C–^{15}N coupling constants, which fall between those of CN^- and HCN (6.2 and 19.1 Hz, respectively),[1] were nearly invariant across the series of compounds varying only from 8.3 to 8.6 Hz (Table IV). Thus, as was the case for the cyanocobalt corrinoids, coordination

---

(2) Cobaloximes are bis(dimethylglyoximato)cobalt(III) complexes abbreviated here as $LCo(D_2H_2)L'$. In the neutral species, $NCSCo(D_2H_3)SCN$, the equatorial bis(dimethylglyoximato) ligand is monoprotonated. Other abbreviations are as follows: CNpy, 4-cyanopyridine; In-py, isonicotinamide; Br-pyr, 4-bromopyridine, py, pyridine, CH_3py, 4-methylpyridine; NH_2py, 4-aminopyridine; DEA, (dimethoxyethyl)amine (aminoacetaldehyde dimethyl acetal); FEA, (2-fluoroethyl)amine; HEA, (2-hydroxyethyl)amine; MEA, (methoxyethyl)amine; EA, ethylamine; PA, propylamine; BrAn, 4-bromoaniline; An, aniline; CH_3OAn, 4-methoxyaniline;

(3) Ablov, A. V.; Syrtsova, G. P. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1955**, *25*, 1247.

(4) Crumbliss, A. L.; Gaus, P. L. *Inorg. Chem.* **1975**, *14*, 2745.

(5) Crumbliss, A. L.; Gaus, P. L. *Inorg. Chem.* **1976**, *15*, 737.

(6) Srinivasan, P. R.; Lichter, R. L. *J. Magn. Reson.* **1977**, *28*, 227.

(7) Gaus, P. L.; Crumbliss, A. L. *Inorg. Chem.* **1976**, *15*, 739.

(8) Needham, T. E.; Matwiyoff, N. A.; Walker, T. E.; Hogenkamp, H. P. C. *J. Am. Chem. Soc.* **1973**, *95*, 5019.

(9) Satterlee, J. D. *Inorg. Chim. Acta* **1980**, *46*, 157.

(10) Coleman, V. M.; Taylor, L. T. *J. Inorg. Nucl. Chem.* **1981**, *43*, 3217.

(11) Brown, K. L.; Hakimi, J. M. *Inorg. Chem.* **1984**, *23*, 1756.

(12) Brown, K. L.; Peck-Siler, S. *Inorg. Chem.* **1988**, *27*, 3548.

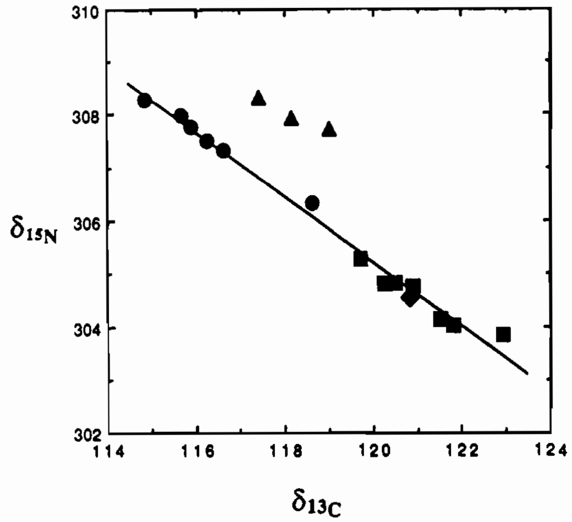


Figure 1. Plot of $\delta_{^{15}\mathrm{N}}$ vs $\delta_{^{13}\mathrm{C}}$ for the $^{15}N^{13}CCo(D_2H_2)L$ complexes. Key: (●) L = 4-Xpy; (■) L = RNH_2; (▲) L = 4-$XC_6H_4NH_2$; (◆), L = SCN^-. The solid line is a linear regression line of the 4-Xpy, RNH_2, and SCN^- data points, with slope = −0.614 ± 0.019, intercept = 378.9 ± 2.2, and $r^2 = 0.989$.

of CN^- ($\delta_{^{13}\mathrm{C}}$ = 166.9 ppm, $\delta_{^{15}\mathrm{N}}$ = 272.4 ppm)[1] to the cobaloxime cobalt center causes the ^{13}C resonance (δ = 115–123 ppm) to shift upfield but the ^{15}N resonance (δ = 303.8–308.3 ppm) to shift downfield.

Figure 1 shows a plot of the ^{15}N chemical shifts vs the ^{13}C chemical shifts of the $^{15}N^{13}CCo(D_2H_2)L$ complexes for all 16 of the complexes with nitrogeneous ligands and the thiocyanato complex. With the exception of the three aniline complexes, which seem to fall on a separate line, the remaining 14 complexes give a surprisingly good correlation ($r^2 = 0.989$) with slope −0.614. Thus, as was the case for the cyanocobalt corrins,[1] changes in the trans axial ligand cause opposite changes in the ^{13}C and ^{15}N chemical shifts, although the ^{15}N chemical shift is somewhat less sensitive relative to the ^{13}C chemical shift in these cobaloximes (61%) than was the case in the cobalt corrins (73%).

This expanded series of cyano complexes now permits an examination of the dependence of chemical shift on ligand basicity. Figure 2A shows plots of the ^{13}C chemical shifts of the $^{15}N^{13}CCo(D_2H_2)L$ complexes vs pK_L, the pK_a of the conjugate acid of the axial ligand, L. As the pK_a of ammonia does not correlate with the pK_a's of primary amines, the ammonia complex has been omitted from these correlations. For the 4-Xpy and RNH_2 ligands, reasonably good linear correlations are obtained with positive slopes (i.e., the ^{13}C resonance shifts downfield with increasing basicity of the trans ligand) with the slope of the RNH_2 correlation being about twice that of the 4-Xpy correlation. The three 4-$XC_6H_4NH_2$ complexes show a similar correlation, with a slope very similar to that of the RNH_2 correlation, but this is clearly less significant since only three compounds are available in this series.

As required by the correlations in Figures 1 and 2A, the ^{15}N chemical shifts of the 4-Xpy complexes correlate with pK_L (Figure 2B) with a negative slope (i.e., the ^{15}N resonance shifts upfield with increasing basicity of the trans ligand). Interestingly, in contrast to the ^{13}C chemical shifts, the ^{15}N resonances of the 4-$XC_6H_4NH_2$ complexes seem to correlate with those of the RNH_2 complexes and these nine complexes are very well correlated with pK_L ($r^2 = 0.994$), again with a negative slope. As with the ^{13}C chemical shift correlations, the magnitude of the slope of the correlation of $\delta_{^{15}\mathrm{N}}$ with pK_L for the RNH_2 and 4-$XC_6H_4NH_2$ complexes is about twice that for the 4-Xpy complexes. The fact that the ^{15}N chemical shifts of the 4-$XC_6H_4NH_2$ complexes correlate with those of the RNH_2 complexes but the ^{13}C chemical shifts of these two series of complexes do not correlate together suggests that the failure of the 4-$XC_6H_4NH_2$ complexes to fall on the $\delta_{^{15}\mathrm{N}}$–$\delta_{^{13}\mathrm{C}}$ correlation (Figure 1) for the remaining complexes results from an excessive downfield shift of the ^{13}C resonances of the 4-$XC_6H_4NH_2$ complexes rather than deviations of the ^{15}N resonances.

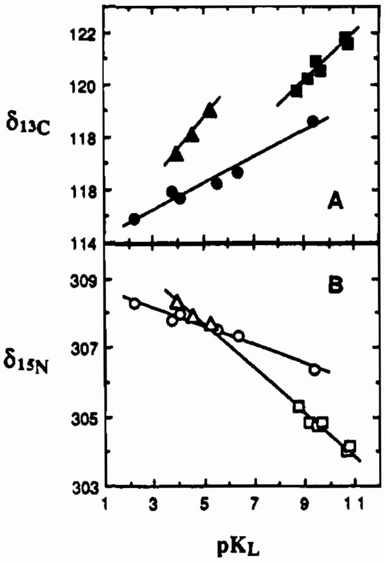


Figure 2. (A) Dependence of the ^{13}C chemical shift of the $^{15}N^{13}CCo(D_2H_2)L$ complexes on pK_L, the pK_a of the conjugate acid of the ligand, L. The solid lines are linear regression lines. Key: (●) L = 4-Xpy, slope = 0.499 ± 0.045, intercept = 113.7 ± 0.3, $r^2 = 0.968$; (■) L = RNH_2, slope = 0.926 ± 0.142, intercept = 111.8 ± 1.4, $r^2 = 0.915$; (▲) L = 4-$XC_6H_4NH_2$, slope = 1.16 ± 0.07, intercept = 112.9 ± 0.3, $r^2 = 0.997$. (B) Dependence of the ^{15}N chemical shift of the $^{15}N^{13}CCo(D_2H_2)L$ complexes on pK_L, the pK_a of the conjugate acid of the ligand, L. The solid lines are linear regression lines. Key: (○) L = 4-Xpy, slope = −0.269 ± 0.022, intercept = 308.9 ± 0.1, $r^2 = 0.934$; (□) L = RNH_2, (△) L = 4-$XC_6H_4NH_2$, slope = −0.640 ± 0.02, intercept = 310.9 ± 0.2, $r^2 = 0.994$.

In the infrared spectra of the $NCCo(D_2H_2)L$ complexes, the cyanide stretching band was readily identified by comparison to the spectra of the $^{15}N^{13}CCo(D_2H_2)L$ complexes. For a given ligand, L, all of the IR features occurred within a few cm^{-1} for the labeled and unlabeled complexes (Table III, supplementy material) except ν_{CN}, near 2060 cm^{-1} in the unlabeled complexes, which was displaced by 78–84 cm^{-1} in the labeled complexes (Table IV). The ratio of ν_{CN} to $\nu_{^{13}\mathrm{C}^{15}\mathrm{N}}$ was very nearly constant across the series of 17 complexes with an average value of 1.0380 ± 0.0002. As this value is very close to the square root of the ratio of the reduced masses (1.0393), the force constants in the labeled and unlabeled complexes are not appreciably different. Previously reported values for ν_{CN} for three of these complexes (L = NH_3, py, 4-NH_2py)[5,13] deviate from our values by about 6 cm^{-1} for reasons which are unclear.

Inspection of the values of ν_{CN} and $\nu_{^{13}\mathrm{C}^{15}\mathrm{N}}$ in Table IV shows that ν_{CN} and $\nu_{^{13}\mathrm{C}^{15}\mathrm{N}}$ tend to decrease with increasing basicity of the ligand, L, within each series of ligands as is shown graphically in Figure 3, for $\nu_{^{13}\mathrm{C}^{15}\mathrm{N}}$. While there is substantially more scatter in these correlations of $\nu_{^{13}\mathrm{C}^{15}\mathrm{N}}$ with pK_L than in the correlations of $\delta_{^{15}\mathrm{N}}$ and $\delta_{^{13}\mathrm{C}}$ with pK_L (Figure 2), omission of the badly deviant point for L = DEA from the RNH_2 correlation improves this correlation substantially (to $r^2 = 0.956$; Figure 3, dashed line). Once again, the magnitude of the slope of the correlation for the 4-Xpy complexes is significantly smaller than that for the RNH_2 and 4-$XC_6H_4NH_2$ complexes. Most importantly, the C–N force constant in the $NCCo(D_2H_2)L$ complexes clearly decreases with increasing basicity within each series of ligands.

Discussion

It is difficult to explain the opposite dependence of $\delta_{^{15}\mathrm{N}}$ and $\delta_{^{13}\mathrm{C}}$ on the nature of the trans axial ligand (Figure 1) in the

---

(13) Crumbliss, A. L.; Gaus, P. L. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 485.
(14) Jencks, W. P.; Regenstein, J. *Handbook of Biochemistry*; Chemical Rubber Co.: Cleveland, OH, 1970; pp J187–J226.
(15) Brown, K. L.; Chernoff, D.; Keljo, D. J.; Kallen, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 2297.

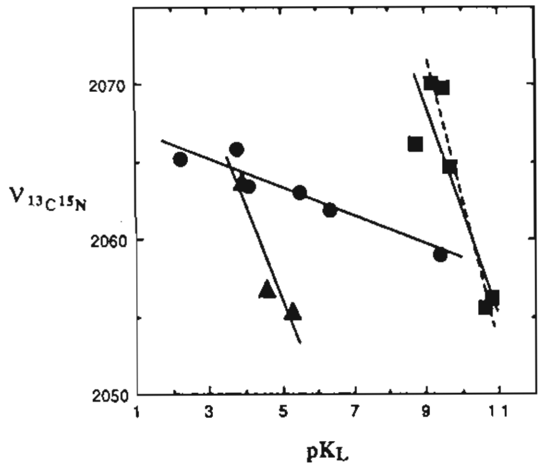
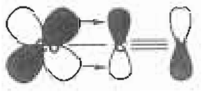


Figure 3. Dependence of $\nu_{^{13}C^{15}N}$ of the $^{15}N^{13}CCo(D_2H_2)L$ complexes on pK_L, the pK_a of the conjugate acid of the ligand, L. The solid lines and the dashed line are linear regression lines. Key: (●) L = 4-Xpy, slope = −0.934 ± 0.153, intercept = 2067.9 ± 0.9, $r^2 = 0.853$; (■) L = RNH_2, solid line, $N = 6$, slope = −6.80 ± 2.0, intercept = 2130.1 ± 19.1, $r^2 = 0.752$; (dashed line) (L = DEA omitted, $N = 5$), slope = −9.63 ± 1.19, intercept = 2159.1 ± 11.8, $r^2 = 0.956$; (▲) L = $4\text{-}XC_4NH_2$, slope = −6.01 ± 2.30, intercept = 2086.3 ± 10.7, $r^2 = 0.872$.

$^{15}N^{13}CCo(D_2H_2)L$ complexes without invoking metal-to-cyanide π-bonding. Further support for such an interaction comes from the dependence of $\nu_{^{13}C^{15}N}$ on ligand basicity within each of the three series of nitrogeneous axial ligands. Since cobalt-to-carbon dπ–pπ electron donation must lower the charge on the metal (as depicted in eq 1), this interaction would be expected to be enhanced by stronger trans axial donors. Indeed, within each series of ligands, $\nu_{^{13}C^{15}N}$, and hence the cyanide C–N force constant, decrease with increasing basicity of the trans ligand (Figure 3). Such decreases in $\nu_{^{13}C^{15}N}$ have previously been associated with increased π-bonding in metal cyanides[16-18] and are clearly consistent with the partial population of the cyanide π*-antibonding orbital and the consequent decrease in the C–N bond order in the π-bonded species. This idea is also supported by the substantially reduced dependence of $\nu_{^{13}C^{15}N}$ on pK_L for the pyridine ligands as compared to the primary amine and aniline ligands. As the pyridine ligands are potential π-acceptors, they should be able to compete with cyanide for cobalt d-electron density, thus decreasing cobalt-to-cyanide π-donation. As the substituted pyridines must be expected to become poorer π-acceptors as they become better σ-donors (i.e., as electron density on the pyridine nitrogen increases), the net effect is a decreased dependence on $\nu_{^{13}C^{15}N}$ on pK_L for this series of ligands.

A similar effect is seen on the dependence of $\delta_{^{15}N}$ and $\delta_{^{13}C}$ on trans axial ligand basicity (Figure 2). Once again, the dependence of chemical shift on ligand basicity is significantly lower for the π-accepting pyridine ligands than for the purely σ-donating primary amines and anilines. However, the trends of the ^{13}C and ^{15}N chemical shifts with ligand basicity do not appear to agree with the description of the π-bonded species as the valence-bond representation, **2**. Both the increased electron density on the cyanide carbon and the hybridization of **2** suggest that stabilization of this species should cause the ^{15}N resonance to shift downfield. Thus, the ^{15}N resonances of the terminal nitrogens of diazo compounds, which resemble the hybridization of **2**, occur downfield from the resonances of the terminal nitrogens of diazonium salts, whose hybridization resembles that of **1**.[19] In the $^{15}N^{13}CCo(D_2H_2)L$ complexes, in contrast, stabilization of the π-bonded species by increasing trans donation causes the ^{15}N resonance to shift upfield. This suggests that the valence-bond structure, **2**, is a poor representation of the π-bonded species in the cyano(ligand)cobaloximes. Since the π-bonded species involves a transfer of electron density from a filled metal orbital into the carbon-centered member of the cyanide π*-antibonding orbital (as in **3**), most of the electron density donated from the metal to the cyanide ligand would be expected to reside on the cyanide carbon. Thus, stabilization of the π-bonded species by increased electron donation across a given series of axial ligands should shift the cyanide ^{13}C resonance downfield, as observed. Similarly, the reduction in C–N bond order in the π-bonded species, **3**, would be expected to be accompanied by an upfield shift of the ^{15}N resonance. Such upfield shifts are common in tautomerizing systems where a unit reduction in C–N bond order may be associated with an upfield shift of the ^{15}N resonance of 100 ppm or more.[20]



3

In their original work on cyano(ligand)cobaloximes and cyanide-bridged dicobaloximes, Gaus and Crumbliss interpreted trends in $\delta_{^{13}C}$[7] and ν_{CN}[21] without recourse to cobalt-to-cyanide π-bonding. Citing molecular orbital calculations[22-24] on the interaction of cyanide with Lewis acids, these authors rationalized trends in the ^{13}C chemical shifts of $N^{13}CCo(D_2H_2)L$ complexes[7] from the prediction that coordination of CN^- to a non-π-bonding Lewis acid results in an increase in electronegativity on the cyanide carbon. Thus, the weakest trans donor provides the strongest Lewis acid cobalt center and the most polarization of the cyanide π_x and π_y orbitals toward the metal. A similar argument was used to rationalize trends in ν_{CN} in cyanocobaloximes and cyanide-bridged dicobaloximes.[21] In addition, potentially π-accepting trans ligands were not found to behave significantly differently from purely σ-donating ligands. The successful explanation of these trends without recourse to metal-to-cyanide π-bonding led these authors to conclude that such bonding was unimportant in cyanocobaloximes.

However, increased polarization of the cyanide π-orbitals toward the cyanide carbon also accompanies protonation of the cyanide ion. Such protonation causes both the ^{13}C and ^{15}N resonances of cyanide ion to shift upfield.[1] The fact that coordination of cyanide ion to cobaloxime or corrin-chelated cobalt centers causes the ^{13}C resonance to shift upfield but the ^{15}N resonance to shift downfield, and the extensive ^{13}C and ^{15}N chemical shift data in Table IV, show that these spectroscopic data cannot be explained without recourse to cobalt-to-cyanide π-bonding. Since the trends in ν_{CN} with axial ligand basicity and, particularly, the "leveling" effect of the π-accepting ability of the substituted pyridine ligands on these trends are also consistent with cobalt-to-cyanide π-bonding, we conclude that such π-bonding is, indeed, important in these cyanocobalt complexes.

Acknowledgment. This research was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation (Grant No. RII-89-02064), the State of Mississippi, and Mississippi State University.

Supplementary Material Available: Tables I–III, listing the ^1H, ^{13}C, and IR spectral data for the $NCCo(D_2H_2)L$ complexes (3 pages). Ordering information is given on any current masthead page.

---

(16) Nakagawa, I.; Shimanouchi, T. *Spectrochim. Acta* **1962**, *18*, 101.
(17) Jones, L. H. *Inorg. Chem.* **1963**, *2*, 777.
(18) Griffith, W. P.; Turner, G. T. *J. Chem. Soc. A* **1970**, 858.
(19) Witanowski, M.; Stefaniak, L.; Webb, G. A. *Annu. Rep. NMR Spectrosc.* **1981**, *11*, 1.
(20) Witanowski, M.; Stefaniak, L.; Webb, G. A. *Annu. Rep. NMR Spectrosc.* **1986**, *18*, 1.
(21) Gaus, P. L.; Crumbliss, A. L. *Inorg. Chem.* **1976**, *15*, 2080.
(22) Purcell, K. F. *J. Am. Chem. Soc.* **1967**, *89*, 247.
(23) Purcell, K. F. *J. Am. Chem. Soc.* **1967**, *89*, 6139.
(24) Purcell, K. F. *J. Am. Chem. Soc.* **1969**, *91*, 3487.