occupancy of the nitrogen orbital involved in bonding to the metal as compared with carbon.

Summary

The present work shows that a simple semiempirical model based on the Townes–Dailey model can be adapted to account for changes in the field gradient at ^{14}N in phenanthroline complexes of Pd(II). There is little reason to doubt that the model should be applicable to phenanthroline complexes with other metals as well. The ^{14}N NQR data provide a measure of the effective nuclear charge of the metal, and thus provide information regarding interaction of the metal with the other ligands to which it is coordinated. The ^{14}N NQR signals due to other ligands in the complexes reveal a broad range of resonance frequencies. In many cases the ^{14}N signals are strongly indicative of structural environment, as in the distinction between S- and N-bonded thiocyanate, or the presence of a coordinated nitro group.

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References and Notes

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Carbon-13 Chemical Shifts as a Measure of π-Back-Bonding in Pentacyanoferrate(II) and -cobaltate(III) Complexes of Substituted Pyridines

Joseph E. Figard, Joseph V. Paukstelis, Edmund F. Byrne, and John D. Petersen*

Contribution from the Department of Chemistry, Kansas State University, Manhattan, Kansas 66506. *Received May 27, 1977*

Abstract: The degree of π-back-bonding in the isoelectronic pentacyanoferrate(II) and -cobaltate(III) complexes of unsaturated nitrogen heterocyclic ligands has been investigated using ^{13}C nuclear magnetic resonance. The chemical shift changes (with respect to free ligand) indicate that the π-back-bonding observed in the Fe(II) analogues is not prominent in the Co(III) complexes. The degree of π-back-bonding into remote rings in the Fe(II) complexes of the heterocyclic ligands is dependent on the ligand conformation. When the remote ring is coplanar with the bound ring (isoquinoline), π-back-bonding into the remote ring is observed. No π-back-bonding is observed into the remote ring when coplanarity is not a constraint of the ligand (4,4′-bipyridine). The best measures of the magnitude of π-back-bonding in the pentacyanoferrate(II) complexes appear to be the change in γ-carbon shift in the heterocycle upon coordination and the relative differences in the cis and trans ^{13}CN resonances as the heterocycle is varied. In general, additivity of carbon-13 shifts through the binding of similar ligands to $(CN)_5Fe^{II}$ and CH_3^+ is observed.

Introduction

The importance of substituent effects on the energy of the charge transfer to ligand (CTTL) bands for a series of pentaammineruthenium(II) species was first demonstrated by Ford et al.[1] A variety of physical methods, including ^1H NMR,[2,3] Mössbauer spectroscopy,[4] and ^{13}C NMR,[5] have been used to study the extent of π-back-bonding from the Ru(II) metal center into unsaturated ligands. Toma and Malin[6] have shown that pentacyanoferrate(II) complexes with unsaturated, nitrogen-coordinating, heterocyclic bases follow the same trend in charge transfer band maxima vs. the nature of the sixth ligand as do the analogous pentaammineruthenium(II) complexes. The presence and magnitude of the π-back-bonding interaction in the pentacyanoferrate(II) system has been studied by infrared,[7] electronic,[6,7] Mössbauer,[7] and NMR[6,8] spectroscopy.

The ^{13}C and ^1H NMR data of Malin and co-workers[8] suggest a definite correlation between the chemical shifts of the carbon and proton resonances of a few nitrogen-bound heterocyclic complexes of pentacyanoferrate(II) complexes. In this study we report the ^{13}C NMR spectra of a variety of nitrogen-coordinated bases bound to $Fe^{II}(CN)_5$ and the isoelectronic $Co^{III}(CN)_5$ metal center. The Co(III) complexes do not display CTTL bands in the near-UV or visible portion of the spectrum suggesting little or no π-back-bonding and thus will be used as model compounds for σ-bonding effects in the Fe(II) complexes. In addition, NMR data on methylated and protonated nitrogen ligands will be reported and used to discuss the role of σ and π interactions in pentacyanoferrate(II) and -cobaltate(III) complexes.

Experimental Section

Syntheses. Pentacyanoferrate(II) Complexes. Pentacyanoferrate(II) complexes of nitrogen-coordinated organic ligands were prepared by the method of Toma and Malin.[6] These complexes were recrystallized three times from deoxygenated water containing a slight excess of free ligand. Purity of the recrystallized sodium salts was determined by comparison of the electronic spectra with literature values of the absorption maxima and molar extinction coefficients for the complexes with isonicotinamide, pyrazine, N-methylpyrazinium, 4,4′-bipyridine, 1-methyl-4-(4-pyridyl)pyridinium, and 4-pyridylpyridinium. Purity of the sodium salts of pentacyanoferrate(II) with 4-cyanopyridine and isoquinoline was determined by elemental analysis and confirmed by ^{13}C NMR. The 4,4′-bipyridine bridged dimer was prepared by the method described above with an Fe(II)/4,4′-bipyridine molar ratio of 2:1.

Anal. (Galbraith Laboratories, Knoxville, Tenn.) Calcd for $Na_3[Fe(CN)_5(4\text{-cyanopyridine})]\cdot 3.7H_2O$, $C_{11}H_4N_7FeNa_3\cdot 3.7H_2O$: C, 31.0; H, 2.7; N, 23.0. Found: C, 30.9; H, 2.5; N, 23.4. Calcd for $Na_3[Fe(CN)_5(\text{isoquinoline})]\cdot 3H_2O$, $C_{14}H_7N_6FeNa_3\cdot 3H_2O$: C, 38.4; H, 3.0; N, 19.2. Found: C, 39.1; H, 3.6; N, 18.2.

The electronic spectra of the $(CN)_5Fe^{II}L$ complexes are reported in Table I.

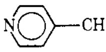
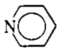
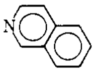
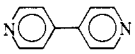
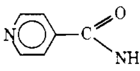
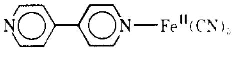
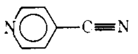
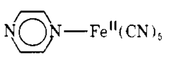
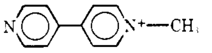
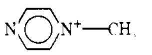
Pentacyanocobaltate(III) Complexes. Pentacyanocobaltate(III) complexes of substituted pyridines were prepared by stirring a 150-fold molar excess of heterocyclic ligand with 15 mL of a 0.02 M $Co(CN)_5H_2O^{2-}$. (The $Co(CN)_5H_2O^{2-}$ was prepared photolytically from $K_3[Co(CN)_6]$ using the procedure of Adamson[9].) Isolation of the potassium salt was accomplished by rotary evaporation and collection by filtration. Crude products were recrystallized from warm water, washed with ethanol and then ether, and dried under vacuum. Compounds were prepared by this procedure with the following heterocyclic ligands: pyridine, isonicotinamide, 4-cyanopyridine, pyrazine, 4-methylpyridine, and 4,4′-bipyridine. The pyridine complex had a UV-visible spectrum identical with that previously reported.[7] All other heterocyclic derivatives had similar UV-visible spectra with the $^1E^a$, $^1A_2 \leftarrow {}^1A_1$ transitions having maxima ~354 nm (2.82 μm^{-1}) and ϵ_{max} values of 200-300 $M^{-1}\ cm^{-1}$ (Table I). Elemental analyses for the pentacyanocobaltate complexes were satisfactory.[10]

N-Methylation Reactions. Monomethylation of pyrazine, 4,4′-bipyridine, and 4-cyanopyridine was accomplished by the standard literature procedure[11] with some minor modifications. Ten grams of the free ligand was dissolved in 20 mL of chloroform containing 1% dimethylformamide as a catalyst. A 1:1 molar ratio of methyl iodide was added and the reaction mixture was stirred in a tightly closed flask at room temperature for 3-25 days depending on the ease of methylation. The solid product which formed was collected on a sintered-glass filter, washed with chloroform to remove unreacted starting materials, washed with ether and then acetone, and dried under vacuum. The product was recrystallized from chloroform with the purity being determined by ^1H and ^{13}C NMR spectroscopy. Compounds which were successfully N-monomethylated are pyrazine, 4-cyanopyridine (pyridine nitrogen), 4,4′-bipyridine, isonicotinamide, and isoquinoline. All compounds were isolated in greater than 50% yields.

Dimethylation of 4,4′-bipyridine was accomplished by using a 2:1 molar ratio of CH_3I to 4,4′-bipyridine. Isolation, recrystallization, and purity determinations were performed as described above for the monomethylated species.

Nuclear Magnetic Resonance Spectra. ^{13}C NMR spectra were obtained with a Varian XL-100-15 spectrometer operating at a frequency of 25.2 MHz and equipped with a Nicolet TT-100 data system with quadrature phase detection and 20K of memory, allowing 16K data points and 8K points in the frequency domain for 6024-Hz spectra width. All spectra were measured in D_2O/H_2O (1:1 v/v) mixtures at 0.3 M concentration for the metal complexes and 1 M for the free, protonated, or methylated ligands. The flip angle was varied between 40 and 60° with a 7-s delay between pulses for the metal complexes and a 3-s delay for the free, protonated, or methylated ligands. The number of pulses required to obtain a good signal to noise ratio was sample dependent and ranged from 256 to 16 384.

Table I. Electronic Spectra of $(CN)_5Fe^{II}L$ and $(CN)_5Co^{III}L$ Complexes

L	$(CN)_5Fe^{II}L$ E_{CT},[a] μm^{-1} (ϵ, $M^{-1}\ cm^{-1}$)	$(CN)_5Co^{III}L$ E_{LF},[b] μm^{-1} (ϵ, $M^{-1}\ cm^{-1}$)
	2.81 (3.55×10^3)[c]	~28[d]
	2.76 (3.72×10^3)[c]	2.82 (260)[d]
	2.43 (2.89×10^3)[d]	
	2.32 (5.62×10^3)[c]	2.83[d]
	2.30 (4.57×10^3)[c]	2.82 (236)[d]
	2.25 (5.68×10^3)[d]	
	2.22 (5.01×10^3)[c]	2.86 (202)[d]
	2.10 (5.49×10^3)[d]	2.82 (274)[d]
	1.98[d] 2.00[c]	
	1.94 (5.62×10^3)[c]	~2.86 sh[d]
	1.80 (2.39×10^3)[d]	
	1.53 (1.20×10^4)[c] 1.52 (1.40×10^4)[d]	

[a] $^1CT \leftarrow {}^1A_1$. [b] $^1E_1$, $^1A_2 \leftarrow {}^1A_1$. [c] Reference 6. [d] This work.

All pentacyanoferrate(II) complexes were sufficiently soluble such that no residue remained in the 0.3 M solutions. The Fe(II) spectra was recorded immediately after sample preparation to prevent signals due to decomposed complex. Decomposition was not a problem with the pentacyanocobaltate(III) samples although low solubilities of some complexes led to concentrations as low as 0.15 M. The deuterium resonance of D_2O was used as the lock signal. Carbon-13 chemical shifts were measured relative to internal dioxane but are reported relative to external Me_4Si. The conversion to external Me_4Si was calculated with the relationship $\delta_{ext\ Me_4Si} = \delta_{int\ dioxane} + 67.40$ ppm. Spectral reproducibility was >±0.05 ppm.

Proton magnetic resonance spectra of the free ligands and their methylated derivatives were recorded on a Varian T-60 NMR spectrometer. All samples were run in D_2O solvent.

Results

The ^{13}C NMR chemical shifts and assignments for all ligands and adducts with H^+, CH_3^+, $(CN)_5Co^{III}$, and $(CN)_5Fe^{II}$ are listed in Table II by ligand. As will be the case throughout this paper, all ligands are listed in order of descending energy of the charge transfer to ligand band of the $(CN)_5Fe^{II}L$ complexes for consistency. A numbering scheme for representative ligands used in this study is illustrated in Figure 1. The assignments for free ligand resonances were made on the basis of literature values (where available),[5,12] analogy to known compounds when possible, or by analyzing proton-coupled spectra when necessary. Most of the pyridine derivatives used in this work were substituted at the 4 or γ

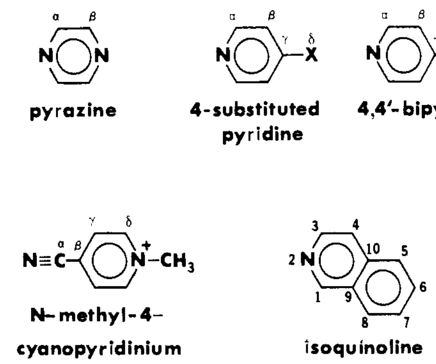


Figure 1. Labeling scheme for nitrogen base ligands.

position, retaining pseudo C_{4v} symmetry of the complex and equivalent 2,6(α) and 3,5(β) carbons. The nonsymmetrical isoquinoline molecule had nine nonequivalent carbon atoms and was assigned by comparison to literature values recorded on a neat sample.[13]

Effects of Methylation or Protonation. The chemical shifts of the methylated and protonated ligands appear in Table II with the corresponding free ligand resonances. Assignment of the resonance due to the carbon atom α to the protonated or methylated nitrogen was simplified by nuclear spin-spin coupling ($^{13}C-^{14}N$) which led to broadened or split α-carbon resonances. Coupling constants ($J_{^{13}C-^{14}N}$), when resolvable, are reported in Table II and are characteristic of quaternary nitrogen atoms.[14] The difference between the methylated or protonated chemical shifts and the corresponding free ligand chemical shifts are represented graphically in Figure 2. In all cases, methylation or protonation on a pyridine ring nitrogen leads to shielding of the α carbon and deshielding of the β and γ carbons relative to free ligand. Carbon-bound substituents attached to the γ carbon of the pyridine ring appeared upfield from free ligand in the methylated and protonated species except when the substituent was a methyl group (the only electron-donating substituent in the series). Protonation of 4-methylpyridine led to deshielding of the methyl carbon resonance by 1.5 ppm vs. the free ligand.

Although methylation of protonation of pyridine nitrogen causes large changes in the chemical shifts of α, β, and γ carbons vs. free ligand, only small perturbations were observed for most of the sites remote to the pyridine rings. The β' and α' carbons of 4,4'-bipyridine are shifted less than 1 ppm upon methylation of the nonprimed ring (Figure 1); however, the 6 and 7 carbons of isoquinoline are shifted 7.1 and 3.2 ppm, respectively.

Effects of Complexation to $(CN)_5Fe^{II}$ and $(CN)_5Co^{III}$. The electronic spectra of the series of pentacyanoferrate(II) and -cobaltate(III) are given in Table I. The transitions in the case of Fe(II) are assigned[6] as $^1CTTL \leftarrow {}^1A_1$ and are extremely dependent on the nature of L. The Co(III) spectra are dominated by intraligand bands in the ultraviolet with ligand field bands or shoulders occurring at approximately 2.82 μm^{-1}. The $(CN)_5Co^{III}L$ ligand field bands ($^1E^a$, $^1A_2 \leftarrow {}^1A_1$) reported in Table I are relatively insensitive to the nature of L compared to the CTTL bands of the corresponding Fe(II) complexes.

The ^{13}C chemical shifts of the nitrogen heterocycles bound to $(CN)_5Fe^{II}$ are listed in Table II with the corresponding free ligand chemical shift values. The values we obtain for 0.3 M $(CN)_5Fe^{II}L$ samples are in agreement (within 1 ppm) of data obtained by Malin and co-workers[8] for some of the same compounds. The change in ^{13}C chemical shift for the Fe(II) bound nitrogen heterocycle vs. free ligand as shown in Figure 3. The direction of the shifts are just the opposite, at the α, β, and γ carbons, of the corresponding shifts for the methylated and protonated species. Large deshielding occurs at the α carbon while shielding occurs at the β and γ carbons and in most cases carbon bound substituents at γ are shielded. As was the case in the methylated 4,4'-bipyridine, very small changes from free ligand are observed for the α' and β' carbons of bipyridine upon complexation to $(CN)_5Fe^{II}$. Small shifts are also observed (relative to free ligand) for the 5–8 carbons of $(CN)_5Fe^{II}$(isoquinoline), but the shifts are substantially different from those observed from methylation of the nitrogen.

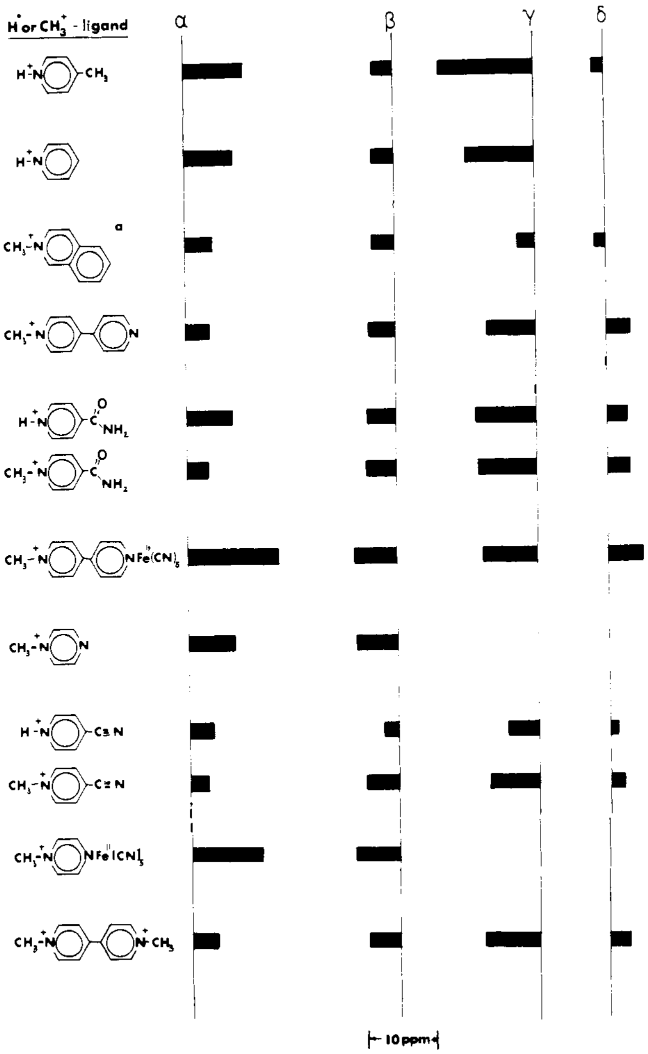


Figure 2. Carbon-13 chemical shifts of methylated and protonated ligands vs. free ligand. (a) Average shift for nonequivalent sites: α = 1.3; β = 4.9; γ = 10, and other = 5.

The ^{13}CN chemical shifts for most of the $(CN)_5Fe^{II}L$ complexes studied in this work also appear in Table II. Two cyanide peaks are observed with a relative intensity of approximately 5:1 and are assigned to $^{13}CN_{cis}$ and $^{13}CN_{trans}$, respectively. As previously reported,[8] the *trans*-CN resonance is always upfield or more shielded than the *cis*-CN resonance. When the coordinated ligand L is a neutral, pyridine-type ligand, the $^{13}CN_{cis}$ resonance is deshielded and the $^{13}CN_{trans}$ resonance is shielded with respect to the ^{13}CN resonance of $Fe(CN)_6^{4-}$ at 177.3 ppm. However, when L is *N*-methylpyrazinium, *N*-methyl-4-cyanopyridinium, and nitrosyl, both cis and trans ^{13}CN resonances are shielded vs. hexacyanoferrate(II).

The carbon-13 chemical shifts of the nitrogen heterocycles bound to $(CN)_5Co^{III}$ are listed in Table II and are compared to free ligand chemical shifts in Figure 3. The α-carbon resonances were shifted downfield with respect to the free ligand

Table II. ^{13}C Chemical Shifts for a Variety of Nitrogen Heterocycles and Their H$^+$, CH$_3^+$, (CN)$_5$Co^{III}, and (CN)$_5$Fe^{II} Adducts[a]

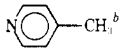
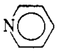
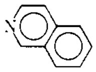
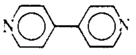
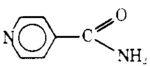
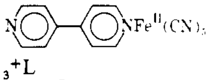
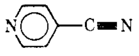
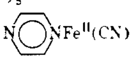
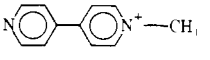
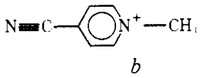
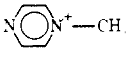
Compd	^{13}CN$_{cis}$	^{13}CN$_{trans}$	CH$_3^+$	α	β	γ	Other		
L =  [b]								γ-CH$_3$	
				149.6	125.9	149.1		21.1	
H$^+$L				140.8 (6.2)	128.6	162.4 (br)		22.6	
c				141.1	128.8			22.7	
(CN)$_5$Co^{III}L				155.1	127.3	152.6		21.0	
(CN)$_5$Fe^{II}L	179.3	176.7		156.3	125.1	148.2		20.9	
L = 				149.3	125.1	138.1			
b				149.3	125.2	138.3			
H$^+$L				141.9 (5.4)	128.2	147.9			
c				142.1	128.4	148.2			
(CN)$_5$Co^{III}L	142 (br)	126		155.9	126.4	139.8			
(CN)$_5$Fe^{II}L	180.8			157.1	124.2	136.6			
b	180.2	177.1		156.8	124.3	136.7			
L = 				1/3	9/4	10	8/5	7/6	
				152.0/142.0	128.3/120.8	135.4	127.5/126.3	127.4/130.6	
CH$_3^+$L			49.0	150.5/135.7	127.9/126.9	137.7	132.1/128.0	130.6/137.7	
(CN)$_5$Fe^{II}L	179.6			160.5/149.2	128.5/120.6	135.2	128.5/126.6	127.5/132.0	
L = 							γ′	β′	α′
				150.1	122.7	146.5	146.5	122.7	150.1
CH$_3^+$L			49.1	146.4 (6.1)	126.5	153.4	142.6	123.1	150.7
(CN)$_5$Co^{III}L	141.5			156.5	123.7	147.7	144.6	122.6	150.4
(CN)$_5$Co^{III}LH$^+$	144.1	123.8		156.9	124.4	145.6	152.7	125.8	143.9
(CN)$_5$Fe^{II}L				160.3	119.4	144.7	145.7	122.6	150.1
L = 							γ-C(O)NH$_2$		
				150.2	122.5	141.8	170.9		
b				150.0	122.8	142.1	171.2		
H$^+$L				143.3 (br)	126.4	150.4	167.7		
CH$_3^+$L			49.5	147.0 (8.4)	126.9	150.3	167.4		
(CN)$_5$Co^{III}L	141.3			156.8	123.9	143.5	169.5		
(CN)$_5$Fe^{II}L	179.9	175.4		158.0	121.2	140.1	170.9		
b	180.0	175.8		158.1	121.4	140.0	170.6		
L = 							γ′	β′	α′
				150.1	122.6	145.7	144.7	119.4	160.3
CH$_3^+$L	179.3	174.9	49.2	146.5	125.5	152.6	140.5	121.1	158.5
(CN)$_5$Fe^{II}L	180.2	175.9		157.8	121.1	144.3	144.3	121.1	157.8
L = 				145.4	145.4				
b				145.3	145.3				
CH$_3^+$L			50.3	138.8 (9.2)	151.3				
b			50.0	137.4	150.9				
(CN)$_5$Co^{III}L				150.9	146.8				
(CN)$_5$Fe^{II}L	178.4	173.8		153.5	143.1				
b	177.3	173.5		153.2	143.0				
L = 							γ-CN		
				150.5	127.0	121.4	117.6		
H$^+$L				147.0	129.2	125.8	116.5		
CH$_3^+$L			50.4 (4.8)	147.4 (9.5)	131.8	128.5	115.1		
(CN)$_5$Co^{III}L	140 (br)			156.8	128.3	123.1	116.5		
(CN)$_5$Fe^{II}L	179.2	174.3		158.2	125.2	119.0	117.6		
L = 	178.4	173.8		143.1	153.5				
b	177.3	173.5		153.2	143.0				
CH$_3^+$L	172.7	166.6	48.6	132.9 (1.7)	159.7				
b	172.3	166.2	49.0	133.2	159.8				
(CN)$_5$Fe^{II}L	178.2	173.6		150.8	150.8				
b	177.8	173		150.6	150.6				
L = 							γ′	β′	α′
			49.1	150.7	123.1	142.6	153.4	126.4	146.4 (6.1)
CH$_3^+$L			49.5	147.0	127.5	150.4	150.4	127.5	147.0
(CN)$_5$Fe^{II}L	179.3	174.9	49.2	158.5	121.1	140.5	152.6	125.5	146.5
L = 							Δ		
			50.4 (4.8)	115.1	128.5	131.8	147.4 (9.5)		
b	171.3	163.8	50.6 (4.7)	115.1	126.8	131.8	147.5 (9.2)		
(CN)$_5$Fe^{II}L			50.3	151.3	138.8 (9.2)				
L = 			50.0	150.9	137.4				

Table II (*Continued*)

Compd	$^{13}CN_{cis}$	$^{13}CN_{trans}$	CH_3^+	α	β	γ	Other
H^+L			50.2	152.4	139.8		
$(CN)_5Fe^{II}L$	172.7	166.6	48.6	159.7	132.9 (1.7)		
b	172.3	166.2	49.0	159.8	133.2		
$(CN)_6Fe^{II}$	177.3	177.3					
b	177.0	177.0					
$(CN)_5Fe^{II}NO^+$	135.0	132.8					
b	135.1	133.2					
$(CN)_5Co^{III}$	139.8	139.8					
$J_{^{59}Co-^{13}C}$	(126.6)	(126.6)					

[a] Chemical shifts reported vs. Me_4Si with dioxane (67.4 ppm) as an internal reference. Compounds containing Fe^{II} or Co^{III}, 0.3 M, all other 1 M in D_2O/H_2O (1:1 v/v). [b] Reference 8. [c] Reference 5.

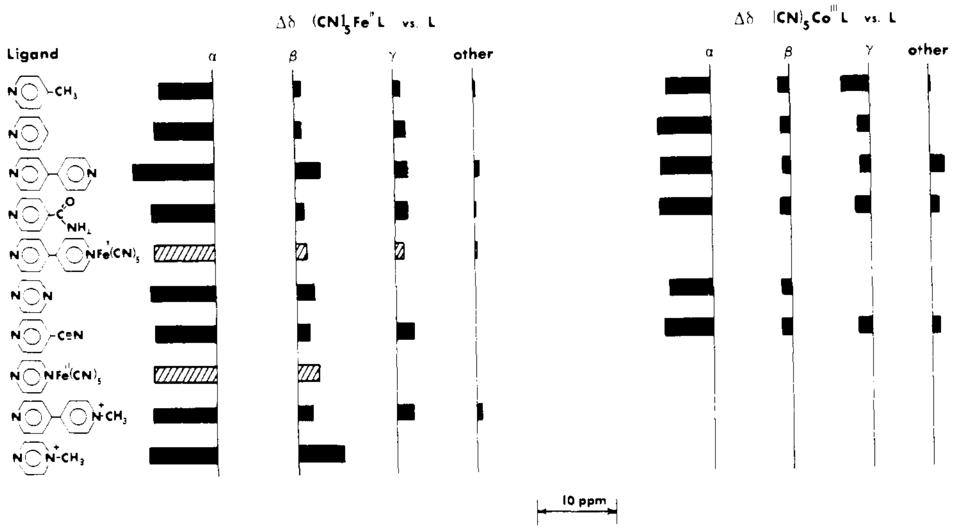


Figure 3. Carbon-13 chemical shift differences between free ligand L and $(CN)_5Fe^{II}L$ or $(CN)_5Co^{III}L$.

between 63 and 88% of the corresponding Fe(II) shift. The β- and γ-carbon resonances for $(CN)_5Co^{III}L$ are deshielded with respect to the free ligand as was observed for the methylated and protonated analogues but the opposite direction as that observed for complexation to $(CN)_5Fe^{II}$. Carbon-bound substituents on the γ carbon of the pyridine ring were shielded with respect to the free ligand resonances as was the case for the $(CN)_5Fe^{II}L$ species with the magnitude of the Co(III) shift slightly greater (more shielded) than for the corresponding Fe(II).

In most cases, the cyanide carbon-13 resonances were not observed for $(CN)_5Co^{III}L$ complexes. This was the result of short relaxation times due to quadrupolar coupling. The eight-line pattern for octahedral $Co(CN)_6^{3-}$ (δ_{CN} 139.8 ppm, $J_{^{59}Co-^{13}C}$ = 126.6 Hz) was in good agreement with previously reported data.[15,16] When cyanide resonances were observed in the pseudo C_{4v} complexes $(CN)_5Co^{III}L$, no carbon-cobalt coupling was detected in these less symmetric complexes. The loss of observed carbon-cobalt coupling in C_{4v} cyanocobaltate species has been reported by Miller and Wentworth.[15] As was the case for the pentacyanoferrate(II) complexes, the *cis*-CN carbon-13 resonance is deshielded and the *trans*-CN carbon-13 resonance is shielded with respect to the resonance in $Co(CN)_6^{3-}$.

Discussion

Protonation and Methylation Effects. The pronounced upfield shifts of the α-carbon resonances upon protonation or methylation are directly in contrast to the effect observed when the heterocyclic nitrogen is bound to the Fe(II) and Co(III) metal centers and requires an explanation. Pugmire and Grant[17] have studied a series of azines and protonated cations and concluded that the observed α-carbon upfield shift is due to α-carbon-nitrogen bond polarization. The protonation or methylation of the ring nitrogen decreases the bond order (remove electrons) of the $N-C_\alpha$ bond and therefore decreases the two-center paramagnetic shielding terms associated with spin unpairing in the $N-C_\alpha$ bond. This more than compensates for the decrease in local diamagnetic shielding and increased one-center paramagnetic shielding resulting from the anisotropic charge decrease on the α carbon. The decrease in charge density on the α carbon when the pyridine nitrogen is protonated has been confirmed by extended Hückel[17] and INDO and CNDO/2[18] calculations. (A 0.2-0.4 decrease in valence electrons is observed for the protonation of the L ligands in Table I.)

The downfield shifts at the β and γ carbons upon protonation and methylation can be explained in terms of one-center diamagnetic and paramagnetic effects on the respective carbon atoms.[17,18] All carbon bound substituents on the γ position of the pyridine ring, except for methyl, exhibited upfield shifts upon protonation or methylation. These data do not parallel the charge density changes due to protonation or methylation for the γ-bound carbon determined by INDO calculations[18] (e.g., protonation of isonicotinamide leads to a 0.28 electron decrease in charge density at the amide carbon) and must be due to other factors such as bond order changes[17] or solvation effects.

Structure of the 4-Cyanopyridine Complex Anions of Pentacyanoferrate(II) and -cobaltate(III). The carbon-13 chemical differences between free 4-cyanopyridine and pentacyano-4-cyanopyridineferrate(II) anion indicate that the 4-cyanopyridine is bound to the iron by the pyridine nitrogen rather than the nitrile nitrogen. The characteristics α-carbon deshielding (+7.7 ppm) and β- and γ-carbon shielding (−1.8 and −2.4 ppm, respectively) are typical of all pentacyanoferrate(II) complexes of substituted pyridines in this study. The same conclusion can be made for the analogous cobalt(III) complex. The deshielding at the α carbon (+6.3 ppm) is larger than the deshielding at the β and γ carbons (+1.3 and +1.7 ppm, respectively) in agreement with other pyridine-bound pentacyanocobaltate complexes. In fact, the changes in chemical shift from free ligand are virtually identical for the Fe(II) and Co(III) complexes of 4-cyanopyridine and isonicotinamide (pyridine-4-carboxamide).

Toma and Malin[6] have illustrated that there is a reasonably linear correlation between the charge transfer to ligand maxima for heterocyclic ligand complexes of the $3d^6$ pentacyanoferrate(II) and the $4d^6$ pentaammineruthenium(II) metal centers. Clarke and Ford[19] have prepared the nitrile-bound and pyridine-bound pentaammine-4-cyanopyridineruthenium(II) complexes which have charge-transfer maxima at 2.35 and 2.00 μm^{-1}, respectively. Using the linear correlation of Toma and Malin,[6] predicted charge-transfer maxima energies would be 2.59 and 2.19 μm^{-1}, respectively, for the nitrile- and pyridine-bound pentacyano-4-cyanopyridineferrate(II) anion. The charge-transfer maximum for the Fe(II) analogue is 2.10 μm^{-1} (Table II) which is also in agreement with the pyridine-bound structure.

^{13}C Spectra of Fe(II) and Co(III) Complexes. The carbon-13 chemical shift differences between the $(CN)_5Fe^{II}L$ and $(CN)_5Co^{III}L$ complexes and the free ligand L are illustrated in Figure 3. Coordination of L to either metal center leads to a substantial deshielding of the α-carbon resonance (5–11 ppm). Malin and co-workers[8] have suggested that the diamagnetic anistropy of the neighboring cyano ligands may be partly responsible for the deshielding of the α carbon and α hydrogen in $(CN)_5Fe^{II}L$ complexes. This interpretation is borne out for the α hydrogen[5] which is deshielded from free ligand in $(CN)_5Fe^{II}py^{2-}$ and shielded with respect to free ligand in the non-cyano-containing $(NH_3)Ru^{II}py$ complex. However, other factors must be important in determining the α-carbon resonance since both $(CN)_5Fe^{II}py^{2-}$ and $(NH_3)_5Ru^{II}py^{2+}$ show α-carbon resonances deshielded[5] (approximately the same amount) from free ligand. Assuming that the $L_5M^{II}py$ complex ions have C_{4v} symmetry (rapid rotation around the M–N(py) bond), neighboring metal paramagnetic anisotropy arising from excited state mixing in the presence of a magnetic field is described by[20]

$$\Delta\sigma = \frac{1 - 3\cos^2\theta}{3R^3}(\chi_\parallel - \chi_\perp) \qquad (1)$$

The $\chi_\parallel$ and $\chi_\perp$ terms arise out of field induced mixing of the Fe^{II} and Ru^{II} $^1A_1$ ground states with the ^1E and $^1A_2$ ($^1T_{1g}$ in O_h) excited states, respectively.[21] Since the ^1E state is lower in energy than the $^1A_2$ state in both $(CN)_5Fe^{II}py^{2-}$ and $(NH_3)_5Ru^{II}py^{2+}$ (py has a smaller e_σ than either NH_3 or CN^- according to the angular overlap model[22]), the $\chi_\parallel - \chi_\perp$ term in eq 1 is <0. The geometric term $1 - 3\cos^2\theta$, also has a value <0 for C_α and the effect observed at the pyridine carbons is a net shielding. The magnitude of $\chi_\parallel - \chi_\perp$ is much larger for $(CN)_5Fe^{II}py^{2-}$ than for $(NH_3)_5Ru^{II}py^{2+}$ owing to the large difference in CN^- and py with respect to the difference in NH_3 and py in the spectrochemical series. Since the α carbon in $(CN)_5Fe^{II}py^{2-}$ is deshielded from free ligand exactly the same amount as the α carbon in $(NH_3)_5Ru^{II}py^{2+}$ (+7.8 ppm), the contribution to the chemical shift by the anisotropy of the cyano ligands (deshielding) must reflect the difference in shielding due to the larger $\Delta\chi$ for the Fe(II) analogue.[23]

There is a problem in accounting for the experimental NMR chemical shifts of the α carbon in pyridine bound to the d^6 metal centers $(CN)_5Fe^{II}$, $(CN)_5Co^{III}$, $(NH_3)_5Co^{III}$,[5] $(NH_3)_5Rh^{III}$,[5] and $(NH_3)_5Ru^{II}$.[5] Since all α-carbon resonances in the metal complexes are shifted downfield with respect to free ligand, there must be at least one term that leads to deshielding at α carbon in each compound. We can rule out the deshielding effect due to the cyano ligands[8] as the major contributor to chemical shift differences in all of the metal centers since three of the metal centers studied by Lavalee et al.[5] do not contain cyano ligands. The remaining terms which have been treated by others are the polarization of the N–C_α bond[17] due to σ bonding at the pyridine nitrogen (e.g., pyridinium) the temperature-independent paramagnetism due to the metal,[5] remote (metal-centered), anisotropic, diamagnetic currents, and increased electron density (change in the local diamagnetic term) due to π-back-bonding,[5,8] and *all* of these terms have net *shielding* contributions at the α carbon. The experimental observation of downfield α-carbon shifts (relative to aqueous pyridine) upon bonding to d^6 metal complexes still has not been explained.

Where data are available for the $(CN)_5Fe^{II}$ and $(CN)_5Co^{III}$ complexes with the same L, the α carbon is deshielded more upon coordination to the iron center than to the corresponding cobalt center. This observation should not be due to changes in the temperature-independent paramagnetism of the metal ($\chi_\parallel$ and $\chi_\perp$ in eq 1 should be smaller for Co(III) than for Fe(II)) but may arise, as previously suggested,[5] from an increase in the N–C_α bond polarization in going from Fe(II) to Co(III) with the result than the α-carbon resonance follows the order

$$\text{Fe(II)} > \text{Co(III)} > \text{H}^+ \text{ shielding} \rightarrow$$

The lack of knowledge, at this time, regarding all of the factors influencing the α-carbon resonance prevents any possible assessment of the π-back-bonding trends in these systems.

The chemical shift changes of the β and γ carbon atoms upon coordination should be easier to interpret in terms of d_π–p_{π^*} interaction than the α carbon shifts. Both the β and γ carbon atoms are removed further from the metal center than the α carbon so that anisotropic terms due to the cyano ligands and the metal center, which diminish as a function of R^{-3}, are less important. A comparison of the INDO[18] and extended Hückel[17] calculations to the β- and γ-carbon chemical shift differences between protonated and free ligand (Figure 2) indicates a reasonable correlation of the magnitude and direction of the chemical shift with the change in local electron density. (Protonation of 4-methylpyridine, pyridine, isonicotinamide, and 4-cyanopyridine leads to decreases in γ-carbon charge densities by 0.088, 0.087, 0.079, and 0.095 electrons, respectively.[18])

The β- and γ-carbon chemical shift changes between free ligand L and $(CN)_5Co^{III}L$ are reasonably insensitive to the nature of L and the resonances for the Co(III) complexes are deshielded with respect to the L resonances. This is not the case for the $(CN)_5Fe^{II}L$ complexes in which the β and γ carbons are shielded with respect to L. Also the chemical shift differences between free ligand and Fe(II) complexes are sensitive to the nature of L. As is the case with the pentaammineruthenium(II) complexes of L, the energies of the $d_\pi(Fe^{II}) \rightarrow p_{\pi^*}(L)$ CTTL transitions (Table I) have been used to establish an order of π-back-bonding to L[6] which increases as 4-methylpyridine ≤ pyridine < isoquinoline < 4,4′-bipyridine ≤ isonicotinamide < pyrazine < 4-cyanopyridine < *N*-methyl-4,4′-bipyridinium < *N*-methyl-4-cyanopyridinium < *N*-methylpyrazinium. As noted in previous work,[8] there is a tendency toward greater shielding at the β and γ carbons as the energy of the charge-transfer band decreases. This has been interpreted[8] as evidence that increased charge density at the β and γ carbons through d_π–p_{π^*} interaction is the predominant

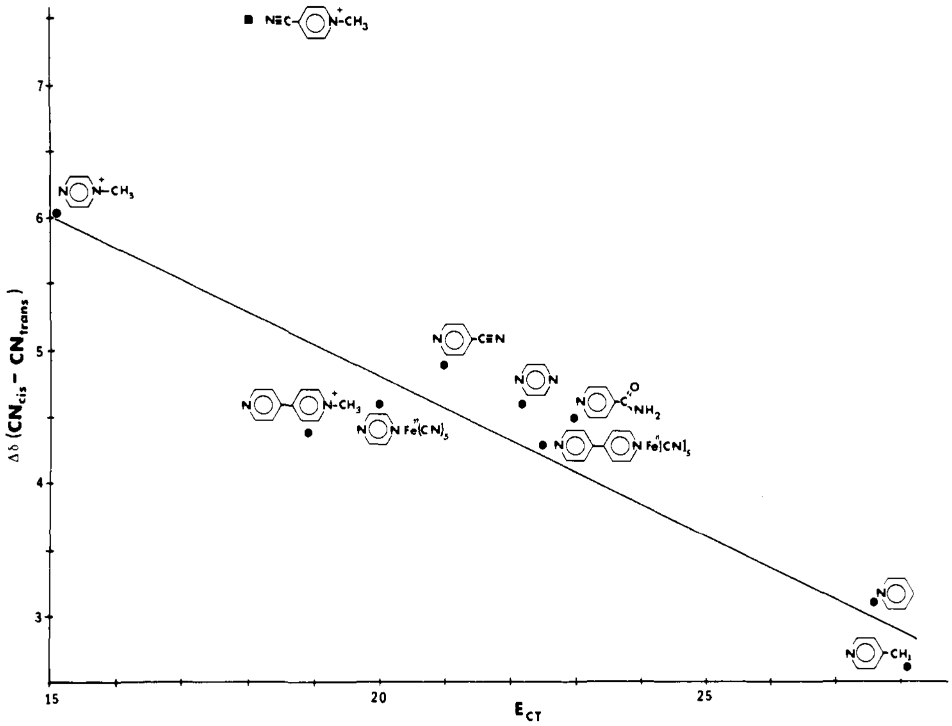


Figure 4. Relationship between the $\Delta\delta(CN_{cis} - CN_{trans})$ and CTTL maxima for $(CN)_5Fe^{II}L$.

term in the shielding of the β- and γ-carbon resonances of L upon complexation with $(CN)_5Fe^{II}$. Figure 3 indicates that the correlation of π-back-bonding from CTTL maxima in the electronic spectra to π-back-bonding as a function of the magnitude of β- and γ-carbon upfield shifts for $(CN)_5Fe^{II}L$ complexes is not definitive. The increase in upfield shift at the β carbon in going from L = 4-methylpyridine to L = *N*-methylpyrazinium is substantial but follows no orderly progression. The γ-carbon shifts for $(CN)_3Fe^{II}L$ vs. free ligand are better behaved but still show some derivations from a progressive increase in upfield shift going from top to bottom in Figure 3. In decreasing order of the energy of the CTTL maxima, the γ-carbon chemical shift differences from free ligand are as follows:

4-methylpyridine (−0.9 ppm) >
pyridine (−1.5 ppm) > 4,4′-bipyridine (−1.8 ppm) >
isonicotinamide (−1.8 ppm) > 4-cyanopyridine (−2.4 ppm)
> *N*-methyl-4,4′-bipyridinium (−2.1 ppm)

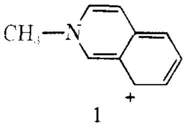
Since the CTTL energy is a property of the entire molecule and δ is a property of one atom in that molecule, the small deviation from a progressive increase is not unexpected. The actual deviation may be due to the difference in the σ bonding of the various L ligands to the metal center, which is ignored in this treatment,[24] or changes, upon coordination, of the anisotropy of the γ-bound substitutents.

Qualitatively, some conclusions can be made regarding the relative back-bonding ability of pentacyanoferrate(II) and -cobaltate(III) complexes of substituted pyridines. The dependence of the Δδ values for the β and γ carbons in the pyridine on the nature of the ligand and the rough correlation of Δδ values to the charge-transfer energies for the Fe(II) system strongly suggest substantial π-back-bonding from Fe(II) to substituted pyridine. The β and γ carbon Δδ values for the isoelectronic Co(III) complexes are virtually ligand independent and appear to reflect only σ-inductive and $(CN)_5Co^{III}$ anisotropic contributions to the chemical shift changes. The fact that the Δδ values for the β and γ carbons (Figure 3) show a shielding for $(CN)_5Fe^{II}L$ and deshielding for $(CN)_5Co^{III}L$ complexes vs. free ligand is not enough evidence to conclude that there is no π-back-bonding in the Co(III) homologue. The β- and γ-carbon ligand resonances of the Co(III) complexes, although deshielded vs. free ligand resonances, are shielded when compared to protonated or methylated ligand resonances. Whether the π charge density at the β and γ carbons is increasing or not increasing for the Co(III) complexes cannot be decided by comparing the Co(III) complexes' ligand resonances to a model where either no σ-inductive correction (free ligand) or too much σ correction is made (protonated or methylated ligand). The strongest evidence suggesting that there is little or no π-back-bonding from Co(III) to the nitrogen heterocycle still remains the insensivitity of the β- and γ-carbon Δδ values in Figure 3 for all L ligands.

^{13}CN Chemical Shift Differences. The chemical shifts for cis and trans cyano ligands of most of the pentacyanoferrate(II) complexes were resolvable and are listed in Table II. In all cases the cis cyano resonance is deshielded with respect to the corresponding trans cyano resonance. In addition, in every case, except when L is *N*-methyl-4-cyanopyridinium or *N*-methylpyrazinium, the cis and trans cyano resonances appear on the downfield and upfield side, respectively, of the single cyano resonance in $(CN)_6Fe^{II}$ (177.3 ppm). The positively charged ligands *N*-methyl-4-cyanopyridinium and *N*-methylpyrazinium exhibit cis and trans cyano resonances both of which are shielded with respect to the hexacyanoferrate(II) resonance. This upfield shift of cyano carbon resonances is amplified for the nitrosyl complex, $(CN)_5Fe^{II}NO^+$ where the cis and trans CN resonances appear at 135.0 and 132.8 ppm which approaches the resonance in hexacyanoferrate(III) at ~ 129 ppm.[25] The large shielding of the cyano resonances in $(CN)_5Fe^{II}NO^+$ is consistent with reduced cyano π-back-bonding by increased π-back-bonding into NO^+.[26] There is no correlation between the cis or trans CN and the degree of π-back-bonding (E_{CT}). However, there is a slight correlation between the difference in the cis and trans cyano carbon resonances ($\Delta\delta(CN_{cis} - CN_{trans})$) vs. the energy of the CTTL band (Figure 4). The larger Δδ values correspond approximately to the smaller E_{CT} values and the greater π-back-bonding. The lack of an absolute correlation in Figure 4 is not surprising considering the problem in rationalizing α-carbon shifts, and may be due to the importance of both σ and π bonding of L in determining the cyano carbon chemical shifts. The angular overlap model[22] would predict that the d_{z^2} orbital energy, which is used in forming the σ bond to L, interacts four times as much with the trans cyano ligand as with each cis cyano ligand. The result is that the presence of L unequally affects the σ bonding between the metal and the cis and trans cyano ligands. The largest deviation from the line in Figure 4 occurs when L is *N*-methyl-4-cyanopyridinium. This is not surprising in that this is the only ligand in the series bound through a nitrile linkage and not a pyridine nitrogen.

Remote Effects of π-Back-Bonding. Previous discussion of the chemical shift changes as a ligand (L) is bound to pentacyanoferrate(II) has been confined to the pyridine ring carbons or the carbon-bound substituent in the γ position. In this section we will discuss the chemical shift changes (i.e., π-back-bonding) at carbon atoms more than one atom removed from the metal-bound pyridine ring. The ligands used in this discussion are 4,4′-bipyridine, 1-methyl-4-(4-pyridyl)pyridinium, isoquinoline, and *N*-methyl-4-cyanopyridinium. When L is 4,4′-bipyridine or 1-methyl-4-(4-pyridyl)pyridinium, the α, β, γ, and γ′ carbons are all coplanar while the β′ and α′ carbons are not in the plane due to free rotation around the γ-γ′ bond and the two rings are not conjugated. Therefore, we would not expect shielding of the β′ and α′ carbons due to extended π-back-bonding into the remote ring. This is observed for the β′ and α′ carbons in the 4,4′-bipyridine complex of pentacyanoferrate(II) and -cobaltate(III) where the change in chemical shift upon coordination is 0.1 ppm or less (Table II). The changes in chemical shift for the β′ and α′ in the 1-methyl-4-(4-pyridyl)pyridinium complex of pentacyanoferrate(II) are also small (0.9 for β′ and 0.1 for α′) even though they are larger than the corresponding shifts in 4,4′-bipyridine. We can conclude from these results that the small σ-inductive and π-resonance effects transmitted into the second ring when the two rings are not coplanar are not substantial enough to influence the C-13 shifts.

The pentacyano(isoquinoline)ferrate(II) anion has two rings which are fused at the 9 and 10 carbons (Figure 1) and all nine carbon atoms are coplanar and well conjugated. A comparison of the ^{13}C resonances of the free and methylated isoquinoline shows dramatic differences from the same comparison with 4,4′-bipyridine. Monomethylation of 4,4′-bipyridine does not affect substantially the resonances on the remote ring. This is not the case for isoquinoline. Large shifts are observed in the remote ring upon methylation. Carbon 6 in isoquinoline is five bonds away from the N atom by the shortest pathway and is deshielded 7.1 ppm upon N-methylation. The β′ carbon in 4,4′-bipyridine is five carbons away from the nitrogen in the unprimed ring and is deshielded only 0.4 ppm upon N-methylation. Therefore, we feel that the largest perturbations in the chemical shifts in the remote ring of isoquinoline upon N-methylation are due to π-electron density changes. The largest deshielding in the remote ring of *N*-methylisoquinoline occurs at the 8 and 6 positions (+4.6 and +7.1 ppm, respectively, vs. free ligand) and will be interpreted as changes in the π-electron density due to resonance structures **1** and **2**. Positions 7 and 5 do not have positive charges in any of the resonance structures and deshielding is smaller (+3.2 and +1.7 ppm, respectively, vs. free ligand).



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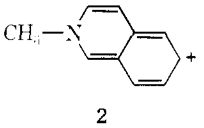
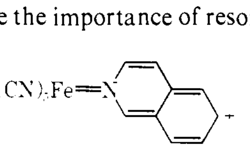


2

Complexation of isoquinoline to $(CN)_5Fe^{II}$ results in large deshielding at the 1 and 3 positions (α carbons) with respect to free ligand. The 10(γ) and 4(β) carbons are shielded which coincides with the types of shifts observed for the substituted pyridine complexes. The 9(β) carbon is slightly deshielded as are the carbons (5–8) in the remote ring. The implication is that π-back-bonding is not being transmitted into the remote ring because of deshielding of the carbon-13 resonances at positions 5–8. We feel that this is not the case and will use the 4,4′-bipyridine once again for a comparison.

The large change in chemical shifts at the remote ring in isoquinoline when either CH_3^+ (or $(CN)_5Fe^{II}$ is bonded to the nitrogen makes comparisons of the iron complex data to free ligand difficult. However, as described earlier, the correlations discussed in this paper do not rely on using specifically the free ligand or the protonated (methylated) ligand as a reference chemical shift. (Regardless of which form of the ligand is used as a reference, the iron complexes will exhibit a downfield shift at α carbon atoms and an upfield shift at β and γ carbon atoms. The selection of free ligand as a reference instead of protonated or methylated ligand in earlier discussions was a result of having chemical shift data for all entries in Table I only as free ligands.) To deduce the importance of resonance structure **3**,



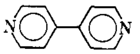
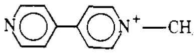
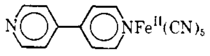
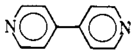
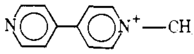
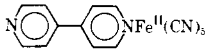
3

we will compare the 6-carbon resonances in *N*-methylisoquinoline and pentacyano(isoquinoline)ferrate(II) to the β′-carbon resonances in *N*-methyl-4,4′-bipyridine and pentacyano-4,4′-bipyridineferrate(II). Replacing *N*-methyl by pentacyanoferro in 4,4′-bipyridine causes a β′-carbon net shielding of 0.5 ppm, which is too small to interpret unambiguously. The corresponding shift for the 6 carbon in isoquinoline is 5.7 ppm upfield. We interpret this large shielding of the 6 carbon (also observed to a lesser extent for carbons 5, 7, and 8) to substantial back-bonding between the $(CN)_5Fe^{II}$ metal center and the remote ring in isoquinoline.

Additive Effects. Table III contains a series of 4,4′-bipyridine derivatives and the effect on the carbon-13 chemical shift through binding to CH_3^+ or pentacyanoferrate(II). The upper portion of Table III reports the changes in chemical shift from free ligand (column 1) upon methylation of 4,4′-bipyridine, 1-methyl-4-(4-pyridyl)pyridinium, and pentacyano(4,4′-bipyridine)ferrate(II). The changes at the α carbon are indistinguishable for the three compounds and the β, γ, and γ′ chemical shift changes are all of the same direction and approximately the same magnitude. Shifts at the β′ position are all in the same direction (deshielding when methylated) but vary in magnitude. The α′ position shows the largest scattering in the series when the unprimed ring of the ligand is methylated with deshielding (0.6 ppm) vs. free ligand for 4,4′-bipyridine and 1-methyl-4-(4-pyridyl)pyridinium and shielding (1.8 ppm) vs. free ligand for pentacyano(4,4′-bipyridine)ferrate(II). This derivation in shift in the primed ring system, which is largest at the α′ carbon atom, occurs to the greatest extent when the primed ring substituent group is the highly anisotropic $(CN)_5Fe^{II}$ functionality.

The lower portion of Table III reports the changes in chemical shift from free ligand upon complexation of 4,4′-bipyridine, 1-methyl-4-(4-pyridyl)pyridinium, and pentacyano(4,4′-bipyridine)ferrate(II) to pentacyanoferrate(II). The additivity is not as straightforward as the upper portion of Table III but chemical shifts in the same direction and of similar magnitude are observed for α, β, γ, and γ′ carbons in the three complexes. Once again larger deviations occur at the β′ and α′ positions with changes in the sign of the chemical shift occurring at both the β′ and α′ carbons when the primed ring substituent is $(CN)_5Fe^{II}$. With the exception of the α′ and β′

Table III. Chemical Shifts of CH_3^+L and $(CN)_5Fe^{II}L$ vs. L Where L Contains 4,4′-Bipyridine

L[a]	α	β	γ	γ′	β′	α′
		Δδ CH_3^+L vs. L				
	−3.7	+3.8	+6.9	−3.9	+0.4	+0.6
	−3.7	+4.4	+7.8	−3.0	+1.1	+0.6
	−3.6	+2.9	+6.9	−4.2	+1.7	−1.8
		Δδ $(CN)_5Fe^{II}L$ vs. L				
	+10.2	−3.3	−1.8	−0.8	−0.1	0.0
	+7.8	−2.0	−2.1	−0.8	−0.9	+0.2
	+7.7	−1.5	−1.4	−0.4	+1.7	−2.5

[a] α, β, and γ in the text refer to the ring on the left side. α′, β′, and γ′ refer to the ring on the right. Addition of CH_3^+ or $(CN)_5Fe^{II}$ is confined to the unprimed (left) ring.

carbon atoms in Table III additivity of carbon-13 chemical shifts is occurring in this series of 4,4′-bipyridine compounds.

This same sort of additivity described above for 4,4′-bipyridine and its derivatives is also observed for pyrazine and its derivatives. For example, the free ligand pyrazine has a single ^{13}C resonance at 145.4 ppm. Complexation to pentacyanoferrate(II) shifts the α carbon 8.1 ppm downfield and the β carbon 2.3 ppm upfield. Adding a second equivalent of pentacyanoferrate(II) to give the iron dimer, by additivity, should result in a single pyrazine resonance at 151.2 ppm. The observed resonance is at 150.8 ppm and demonstrates that there is an additivity of chemical shifts in the carbon-13 spectra of pentacyanoferrate(II) complexes.

Conclusions

Carbon-13 chemical shifts can be used as a measure of the relative π-back-bonding ability in nitrogen heterocyclic complexes of pentacyanoferrate(II) and -cobaltate(III). When the nitrogen heterocyclic ligand is a pyridine derivative, the γ carbon is the best measure of π-back-bonding ability. However, anisotropic contributions of the pyridine substituents and the inability to factor out the σ effects on the chemical shift greatly complicate the interpretation of spectral results.

Qualitatively the upfield shift of the γ carbon of a pyridine derivative bound to pentacyanoferrate(II) from free ligand increases with the degree of π-back-bonding. The chemical shift difference between the cis and trans cyano ligands also increases with an increase in π-back-bonding but the exact interpretation is complicated by σ-bonding effects. The degree of π-back-bonding into the homologous pentacyanocobaltate(III) species is much smaller than that of the corresponding iron(II) complexes, owing to an insensitivity of the Δδ value of the γ carbon of the pyridine derivative as the ligand is varied.

The π-back-bonding of pentacyanoferrate(II) to nitrogen heterocyclic ligands is not transmitted through a carbon-carbon single bond in the case of 4,4′-bipyridine and its derivatives. However, there appears to be π-back-bonding from the $(CN)_5Fe^{II}$ metal center into the remote ring of isoquinoline.

Chemical shifts in related complexes in this study showed a tendency toward additivity. In general, complexation to CH_3^+ or $(CN)_5Fe^{II}$ gave the predicted chemical shift changes regardless of the substituent group of the ligand. The deviation from additivity at the carbon atoms closest to the ligand substituent could be rationalized in terms of substituent solvation influences.

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(23) This assumes that there are no other differences in the two complexes that affect the chemical shifts in different ways.
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