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Comparisons of ^1H and ^{13}C NMR Chemical Shifts for Low Spin d^6 Complexes of Pyridine and Substituted Pyridines as Probes of π Back-Bonding

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Abstract: Effects of metal-to-ligand π back-bonding in pentaammineruthenium(II) and pentacyanoferrate(II) complexes have been investigated by changes in ^1H and ^{13}C nuclear magnetic resonance chemical shifts. For purposes of comparison, corresponding complexes of other low spin d^6 metal atoms, Co(III) and Rh(III), as well as the protonated ligands, have been studied. ^1H shift changes from free ligand positions upon protonation and complexation reflect current concepts of Lewis acid charge withdrawal (H^+, Co(III), Rh(III)) and π back-bonding (Ru(II) and Fe(II)) when comparisons are made for β and γ protons. The shift changes at the α positions of pyridine and substituted pyridines as ligands are not explained in this manner. Solvent effects on ^1H chemical shifts are of the same order of magnitude as changes caused by complexation (0.2 ppm vs. 0.1–1.0 ppm). ^{13}C shift changes on complexation, however, are an order of magnitude larger than the ^1H changes while solvent effects are similar. The ^{13}C shifts at the β and γ positions are consistent with π back-bonding concepts and are a much more sensitive probe than the ^1H shift changes. On an empirical basis, the γ position ^{13}C shifts of aromatic ligands appear to be a sensitive and reliable probe of π back-bonding.

Development of a means for obtaining quantitative information concerning the nature of metal-to-ligand π bonding is a matter of current interest. ^{19}F NMR results on a series of *trans*-bis(triethylphosphine)fluorophenyl complexes of nickel(II), palladium(II) and platinum(II) have demonstrated the ^{19}F nucleus, especially when in the para position, is a reasonable probe of electron density changes.[1] ^1H NMR chemical shift changes have been studied in a series of related ruthenium(II) complexes[2] and ^1H and ^{19}F changes have been compared for a series of ruthenium(II) and rhodium(III) complexes.[3] ^1H and ^{13}C NMR results have been obtained for several pentacyanoferrate(II) complexes.[4] Coulson has recently reported the results of linear least-squares multiple regression analysis of ^{13}C and ^{19}F NMR data for a series of aryl platinum complexes with a range of substituents on the phenyl ligand.[5] These studies demonstrate that chemical shift changes, especially for ^{19}F and ^{13}C nuclei, are a promising means of directly observing π back-bonding effects which have been previously deduced by other means.[6] The nature of the mechanism by which electron density alterations cause chemical shift changes in transition metal complexes is not yet clear.[7,8] Further empirical evidence is required that would compare complexes of similar structure which include metal centers that have been shown to be non-π-back-bonding as well as those which are known to participate in π back-bonding.

In the case of the ^{19}F study by Parshall,[1] a closely related series of diamagnetic d^8 complexes allows a comparison of the Ni(II), Pd(II), and Pt(II) centers but, of necessity, included no non-π-back-bonding metal centers. Coulson's study[5] included a large number of substituents but was restricted to platinum complexes. The other studies cited compared the effects of various ligands, but each was quite limited in the number and range of examples reported. In this study we report the ^1H and ^{13}C NMR spectra of diamagnetic, substitution inert d^6 complexes of Co(III), Rh(III), Fe(II), and Ru(II) with pyridine, γ-picoline and 4-benzoylpyridine. γ-Picoline and 4-benzoylpyridine were chosen to test the effect of ligands with Hammett σ constants of opposite sign (−0.17 for para methyl and +0.46 for para benzoyl) on apparent degree of back-bonding. One might expect that the more electron withdrawing substituent, para benzoyl, could cause a greater degree of back-bonding than the electron donating para methyl substituent. Spectra of the protonated ligands and of the ligands in various solvents are included as an aid in interpretation of the spectra of the complexes.

Experimental Section

Reagents. CD_3OD, CH_3OD, and D_2O (Stohler Chemical Co.), reagent grade CCl_4 (Fisher), and 4-benzoylpyridine (Aldrich) were used without further purification. Pyridine (Fisher) and γ-picoline (City Chemical Co.) were distilled and stored over molecular sieves. Methanol (Fisher) was distilled over sodium and stored over molecular sieves. Argon was bubbled through chromous ion scrubbing towers and passed through a calcium sulfate drying tower. Amalgamated zinc was prepared by adding mercuric chloride (5% by weight) to acid-washed 20-mesh zinc. Sodium trifluoromethanesulfonate was prepared by neutralization of sodium carbonate with trifluoromethanesulfonic acid (3M Co.) that was doubly distilled from all glass apparatus.

Cobalt Complexes. Aquopentaamminecobalt(III) perchlorate was used as the starting material. It was synthesized by the method of Gould and Taube[9] and gave the appropriate visible absorption spectrum (ϵ at 474 nm = 64, literature value 66). The aquopentaammine complex was converted to the dimethylformamide–pentaammine complex by addition to dimethylformamide at 95 °C.[10] Preparation of each complex was then accomplished by addition of a fivefold excess of the ligand and heating it 95 °C for 20–30 min.[10,11] Isolation was by crystallization from saturated aqueous $NaClO_4$. Extinction coefficients were within 5% of literature values.[10,11] Pyridine-*2-d*-pentaamminecobalt(III) iodide was prepared as outlined above except that the product was obtained by precipitation of the iodide salt by addition of saturated methanolic NaI. The precipitate was filtered,

Table I. Electronic Spectra of Pentaammineruthenium(II), Pentaamminecobalt(III), Pentaamminerhodium(III), and Pentacyanoiron(II) Complexes

Complex	λ_{max}, nm (ϵ, M^{-1} cm^{-1})											
$[(NH_3)_5Ru(py)]^{2+}$	407	(7000)					244	(4600)				
$[(NH_3)Ru(py)]^{2+}$ [a]	407	(7700)					244	(4570)				
$[(NH_3)_5Co(py)]^{3+}$	475	(64)	348	(65)	265	(3000)	258	(4300)	253	(4700)		
$[(NH_3)_5Co(py)]^{3+}$ [b]	475	(67)	348	(68)	265	(3000)	258	(4300)	253	(4700)		
$[(NH_3)_5Rh(py)]^{3+}$			303	(170)	266	(2100)	258	(3100)	253	(2900)	228	(4900)
Pyridine									253	(3390)		
$[(NH_3)_5Ru(\gamma\text{-picoline})]$	397	(5000)							242	(3390)		
$[(NH_3)_5Co(\gamma\text{-picoline})]$	476	(65)										
$[(NH_3)_5Co(\gamma\text{-picoline})]$ [b]	476	(68)										
γ-Picoline									254	(2510)		
$[(NH_3)_5Ru(p\text{-benzoylpy})]$	535	(5180)							265	(10 500)		
$[(NH_3)_5Co(p\text{-benzoylpy})]$	474	(64)							270	(11 059)		
$[(NH_3)_5Co(p\text{-benzoylpy})]$ [b]	474	(66)							257	(10 900)		
$[(CN)_5Fe(p\text{-benzoylpy})]$	487	(3760)							257	(14 000)		

[a] Reference 13. [b] References 9 and 10.

washed with ethanol and ether, and dissolved in D_2O. The absorption spectrum matched that of pyridinepentaamminecobalt(III) cations in aqueous solutions. The pyridine-*2-d* ligand was prepared by the method of Abramovitch et al.[12] from 2-pyridyllithium and D_2O. The 2-pyridyllithium was synthesized from freshly prepared *n*-butyllithium[13] and distilled 2-bromopyridine (Aldrich).

Rhodium Complex. Pyridinepentaamminerhodium(III) Trifluoromethanesulfonate. Chloropentaamminerhodium(III) chloride (Alfa Ventron) (0.50 g; 1.7 mmol) was dissolved in 25 ml of gently boiling H_2O. Distilled pyridine (12 ml) was then added. A stoichiometric amount of mercurous nitrate (1.43 g; 5.1 mmol; Baker A.R. grade) was added. The greyish precipitate which formed readily in the refluxing reaction mixture was filtered after 10 min. Refluxing was resumed, giving slow formation of additional precipitate. After 24 h, no further precipitation was evident. The reaction mixture was filtered, cooled, diluted with 125 ml of 1:1 solution of methanol and ether, and allowed to stand at 5 °C overnight. The white precipitate was separated by filtration, 30 ml of H_2O was added, and the solution was filtered. Sodium iodide (3–4 drops of 1 M) was added to precipitate residual mercurous ion. The yellow HgI precipitate was filtered off. The filtrate was reduced in volume to 15 ml, acidified to pH 2 with 1 M distilled trifluoromethanesulfonic acid, and an equal volume of saturated aqueous sodium trifluoromethanesulfonate was added. The solution was filtered and cooled slowly to −10 °C. The crystallized complex was filtered, washed with a cold solution of methanol and ether (1:1 by volume), and air dried. Anal. Calcd for $[(NH_3)_5Rhpy](CF_3SO_3)_3$: C, 13.45; H, 2.82; N, 11.76; F, 23.94. Found: C, 13.58; H, 2.89, N, 11.54; F, 23.99. Characteristics of the absorption spectrum are noted in Table I.

Ruthenium Complexes. The ruthenium(II) complexes were prepared by the general method of combining aquopentaammineruthenium(II) with the appropriate ligand in aqueous solution according to the method of Taube et al.[14] with some modifications required by the properties of the ligands.

In a typical synthesis, 1.0 mmol of $[(NH_3)_5RuCl]^{2+}$ was reduced with amalgamated zinc under an argon atmosphere for 0.5 h, 1.0 mmol of the appropriate ligand in deaerated deuterated solvent was then added, and the reaction was allowed to proceed for 1 h. The complexes were identified by their characteristic absorption spectra.[14]

In the case of the *p*-benzoylpyridine complex, 0.4 mmol of aquopentammineruthenium(II) was produced in 2.7 ml of D_2O; 1.3 ml of CD_3OD was injected, followed by addition of 5 ml of deaerated CCl_4 containing 5 mmol of the ligand. The two-phase system was stirred vigorously for 2 h under argon. The purple complex remains in the alcohol–water layer and the excess ligand is left in the CCl_4 layer. The partition coefficient for the *p*-benzoylpyridine is approximately 80:1 for the CCl_4 vs. 2:1 water/methanol. The CCl_4 layer was removed and the water/methanol layer was extracted several times with 5-ml aliquots of CCl_4. The nature of the complex was determined by a Job's plot and the ^1H NMR spectrum verified that no observable free ligand remained.

Deaerated solutions of the complexes were injected into deaerated NMR tubes fitted with serum caps and no difficulties from oxidation were observed for the several hours required for obtaining the ^{13}C spectra.

Iron Complex. Sodium Pentacyano-*p*-benzoylpyridineferrate (II). The starting material was $Na_3[(CN)_5(NH_3)Fe]\cdot 3H_2O$, which was synthesized[15] from sodium nitroprusside (Merck) and recrystallized from cold H_2O by careful addition of distilled methanol. $Na_3[(CN)_5(NH_3)Fe]\cdot 3H_2O$ (0.4 mmol) in 4.0 ml of D_2O was combined with 5 ml of 1 M *p*-benzoylpyridine in carbon tetrachloride. The mixture was stirred for 2 h in the dark, giving a blood red upper layer containing the complex and a colorless layer of CCl_4 containing the excess *p*-benzoylpyridine. The solubility of *p*-benzoylpyridine in water is only 5×10^{-5} M, making extractions unnecessary. Job's plot analysis shows a 1:1 complex with the spectral characteristics noted in Table I. The solid complex is decomposed by light and was not analyzed. The NMR spectra support the formulation of this product as the 1:1 complex.

Nuclear Magnetic Resonance Spectra. ^1H NMR spectra were collected on a JEOL MH100 100 MHz instrument at 37 ± 1 °C. The solvent was D_2O unless otherwise indicated (as in the data in Table II). Trimethylsilylpropanesulfonic acid (Merck) was employed as internal standard. ^{13}C spectra were collected either on a 90 MHz Bruker instrument with external ^{19}F lock and Digilab data system or a JEOL 100 MHz instrument using internal deuterium lock. A low concentration of CH_3OH in the sample was used as internal standard. Proton decoupling was utilized. Data collection required from 1 to 36 h.

Visible Absorption Spectra. A Cary 14 spectrometer was used for visible and ultraviolet absorption spectra.

Results

Solvent Effects. As we will show in the Discussion section, solvent effects on the ligands themselves can be quite significant. Table II indicates the magnitude of solvent effects on chemical shift changes for both ^1H and ^{13}C NMR spectra of the uncomplexed ligands used in this study as well as for benzene. The variation in solvents was from H_2O, which should show the greatest interaction of solvent with the lone pair of electrons on the nitrogen atom, to nonpolar carbon tetrachloride. In the neat liquids the ligands may undergo significant direct interactions such as ring stacking that are less important for dilute solutions of the ligands.

^1H NMR Spectra. The proton nuclear magnetic resonance spectra of protonated and complexed pyridine and substituted pyridines are shown in Table III. The assignment of the γ proton resonance in the case of pyridine complexes is straightforward since its intensity is but one-half that of the resonances due to the α protons or the β protons. Substitution of deuterium for hydrogens at one of the α positions reduces the α proton intensity by one-half, distinguishing the chemical shifts of the α and β hydrogen atoms. The ^1H NMR spectra of pyridinepentaammineruthenium(II) cation and the corre-

Table II. Solvent Effects on the ^1H and ^{13}C Nuclear Magnetic Resonance Spectra of Pyridine, Substituted Pyridines, and Benzene

Ligand	Solvent	^1H chemical shifts[a]				^{13}C chemical shifts[b]			
		α	β	γ	Other	α	β	γ	Other
Pyridine	Neat	8.68	7.18	7.55		150.5	124.7	136.9	
	D_2O	8.55	7.46	7.88		149.3	125.2	138.3	
	Acetone	8.51	7.27	7.70					
	CCl_4	8.49	7.15	7.54		150.0	124.3	136.5	
Pyridine-*2-d*	D_2O	8.55	7.46	7.88		149.6	125.5	138.6	
					γ-CH_3				γ-CH_3
γ-Picoline	Neat	8.49	6.96		2.12				
	D_2O	8.38	7.20		2.34	149.6	125.9	149.1	21.1
	Acetone	8.40	7.16		2.30				
	CCl_4	8.31	6.97		2.29	149.7	125.3	147.7	21.5
p-Benzoylpyridine					H(2) phenyl				C=O
	4:1 CD_3OD:D_2O	8.78	7.63		7.82				
	DMSO	8.95	7.80		7.80				
	CCl_4	8.69	7.45		7.74	150.4	123.4	145.1	194.5
Benzene	Neat		7.20		Neat	128.4[c]			
	D_2O		7.45						
	CH_3OD		7.34		CH_3OH	128.5[c]			
	CCl_4		7.29		CCl_4	128.6[c]			
					CF_3COOH	128.6[c]			
					acetone	128.7[c]			

[a] Relative to internal tetramethylsilane. [b] Relative to TMS by use of CH_3OH as internal standard and $\delta_{(^{13}CH_3)_4Si} = \delta_{^{13}CH_3OH} + 50.0$ ppm. [c] C. L. Nelson, G. C. Levy, and J. D. Carjioli, *J. Am. Chem. Soc.*, **94**, 3089 (1972).

Table III. ^1H and ^{13}C Nuclear Magnetic Resonance Chemical Shifts of Protonated and Complexed Pyridine and Substituted Pyridines

Complex	^1H chemical shifts[a]				^{13}C chemical shifts[b]			
	α	β	γ	Other	α	β	γ	Other
Pyridinium ion (0.5 M)	8.81	8.10	8.66		142.1	128.4	148.2	
$[(NH_3)_5Co(py)]^{3+}$ (0.13 M)	8.33	7.75	8.21		153.5	129.1	142.7	
$[(NH_3)_5Co(py\text{-}2\text{-}d)]^{3+}$ (0.5 M)	8.33	7.75	8.21		153.6	129.1	142.6	
								(^{13}C–D at 154.4)
$[(NH_3)_5Rh(py)]^{3+}$ (0.1 M)	8.33	7.75	8.21		152.5	128.7	141.9	
$[(NH_3)_5Ru(py)]^{2+}$ (0.2 M)	8.40	7.27	7.69		157.1	126.2	134.6	
$[(NH_3)_5Ru(py\text{-}2\text{-}d)]^{2+}$ (0.2 M)	8.40	7.27	7.69		157.1	126.1	134.5	
$[(CN)_5Fe(py)]^{3-}$ (1 M)[c]	8.78	7.05	7.55		156.8	124.3	136.7	
				γ-CH_3				γ-CH_3
γ-Picoline H^+ (0.5 M)	8.62	7.92		2.69	141.1	128.8		22.7
$[(NH_3)_5Co(\gamma\text{-picoline})]^{3+}$ (0.13 M)	8.13	7.61		2.54	152.4	130.0		21.3
$[(NH_3)_5Ru(\gamma\text{-picoline})]^{2+}$ (0.1 M)	8.22	7.16		2.33	156.1	127.3		20.8
$[(CN)_5Fe(4\text{-benz})]^{3-}$ (0.1 M, D_2O)	8.60	6.95		2.30	156.3	125.1		20.9
				H(2) on phenyl				C=O
4-Benzoylpyridine H^+ (0.1 M)[d]	9.11	8.34		7.91	143.9	127.9	154.6	211.8
$[(NH_3)_5Co(4\text{-benz})]^{3+}$ (0.1 M)[d]	8.63	7.99		7.91	155.3	127.8	149.7	195.3
$[(NH_3)_5Ru(4\text{-benz})]^{2+}$ (0.1 M)[d]	8.83	7.85		7.78	158.3	124.6	*e*	189.7
$[(CN)_5Fe(4\text{-benz})]^{3-}$ (0.1 M, D_2O)	9.19	7.41		7.81	158.3	123.1	143.6	199.2
					C(1)	C(2),(6)	C(3),(5)	C(4)
					136.2	131.5	130.3	136.2
					135.8	131.5	130.1	135.8
					135.0	131.0	129.7	135.0
					136.2	131.4	129.8	135.4

[a] ppm downfield relative to TMS as internal standard. [b] ppm downfield relative to TMS by use of CH_3OH as internal standard and $\delta_{(^{13}CH_3)_4Si} = \delta_{^{13}CH_3OH} + 50.0$ ppm. [c] Reference 4. [d] 4:1 CH_3OH:D_2O for H^+ and Co(III), 2:1 CH_3OH:D_2O for Ru(II). [e] Not resolved after 121 000 pulses. [f] Solvent effect on exposed carbonyl is likely quite large; effect on acetophenone (ref 16) is δ = 196.0 (neat), 194.9 (CCl_4), 199.1 (CH_3OH).

sponding α-deuterium substituted complex have been presented previously[2] and illustrate the method of assignment. The assignments of the α and β chemical shifts for para substituted pyridines were made by comparison with the pyridine complexes. In the case of the benzoylpyridine complexes, the phenyl protons could be distinguished from the pyridyl protons by use of very consistent ^1H–^1H coupling constants. $J_{\alpha\beta}$ for the assigned peaks is 5.9 ± 0.2 Hz, while J_{23} (where phenyl hydrogen atoms 2 and 3 are ortho and meta to the carbonyl group, respectively) is 7.8 ± 0.3 Hz. The proton resonance of the hydrogen atom para to the carbonyl group is easily distinguished by its more complex coupling pattern.

Figure 1. The ^{13}C spectrum of $[(NH_3)_5Co(py\text{-}2\text{-}d)]^{3+}$ in D_2O. The α-carbon bound to the deuterium atom shows a triplet centered at 154.4 ppm downfield from tetramethylsilane with J_{CD} = 11.5 ppm. The α-carbon atom bound to a hydrogen atom is at 153.5 ppm. The γ-carbon signal is at 142.6 ppm. The β-carbon atoms show two very closely spaced signals at 129.1 and 128.9 ppm.

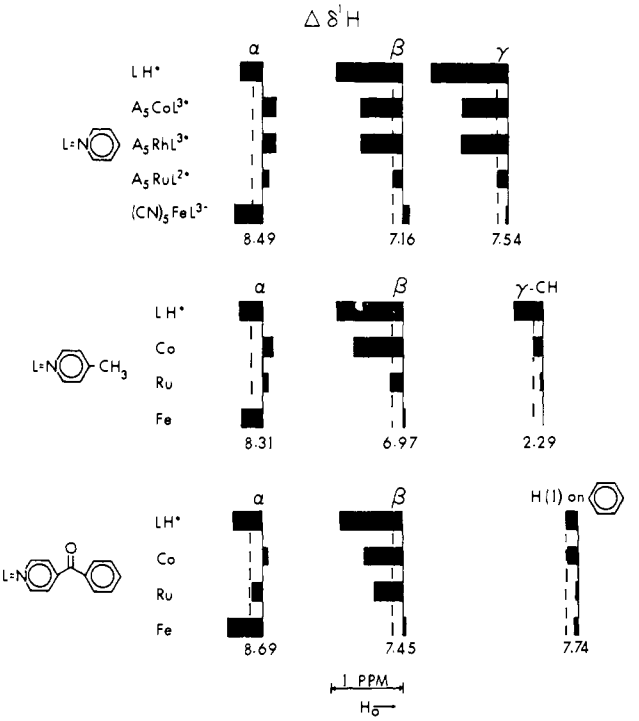

Figure 2. ^1H chemical shift changes of ligands upon complexation or protonation. In each case, the solid line indicates the NMR chemical shift of the appropriate resonance for the free ligand in CCl_4. The estimate of the downfield limit of solvent effects (+0.16 ppm downfield from the CCl_4 value) is given by the dashed line. Chemical shifts are relative to internal trimethylsilylpropanesulfonic acid.

^{13}C NMR Spectra. ^{13}C nuclear magnetic resonance chemical shifts are shown in Table III also. Assignments for the pyridine complexes were made by comparison of the spectra of the ortho deuterated pyridine species with nondeuterated pyridine species. The intensity of the ^{13}C absorbance is less when the carbon atom is bound to deuterium rather than hydrogen. The considerable nuclear Overhauser enhancement (NOE) caused by proton-carbon interaction is not as significant for deuteron-carbon interactions.[16] The spectrum of $[(NH_3)_5Co\text{-}2\text{-}d\text{-}py]^{3+}$ shown in Figure 1 illustrates the method of assignment. Replacement of one of the ortho hydrogens reduces the intensity of the peak at 153.5 ppm and gives rise to a triplet (centered at 154.5 ppm) for the carbon bound to a deuterium atom. This singlet and triplet are, therefore, the α-carbon bound to H and α-carbon bound to D, respectively. The signals for the β-carbon atoms are very slightly split (129.1 and 128.9 ppm) as a result of α-D substitution on one of the neighboring C atoms. The γ-carbon signal at 142.6 ppm is not split and has an intensity equal to the α-carbon bound to the hydrogen atom. The assignment for the γ-^{13}C resonance is consistent with changes noted for para-substituted pyridine complexes. The resonance of the para carbon is easily identified when the γ-hydrogen atom is replaced by another moiety such as the methyl group. In such cases, the nuclear Overhauser enhancement is again reduced, and the absorption due to the γ carbon atom is of much lower intensity than those of the α and β carbon atoms. Identification of the α-, β-, and γ-carbon resonances of the benzoylpyridine complexes was made by comparison with the pyridine and γ-picoline complexes. The resonance of the carbonyl carbons is far downfield from all other resonances and is marked by a low intensity expected from lack of strong NOE enhancement. The phenyl carbon resonances of the free ligand were assigned from comparison with the spectrum of acetophenone.[17] The acetophenone assignments[17] and those for the phenyl portion of benzoylpyridine (in parentheses) are: carbonyl, 194.9 (194.3); C_1, 137.4 (136.6); $C_2 = C_6$, 128.2 (130.6); C_3, 128.2 (129.1); C_4, 132.4 (133.7). The intensity of the assigned C_1 resonance is less than that of C_4 due to lower NOE enhancement. The C_2 and C_3 peaks were more intense than C_4 since there are two equivalent carbon atoms for each resonance. Identification of C_2 and C_3 resonances is based upon comparing the benzoylpyridine and benzophenone spectra and assuming that charge alternation would produce a more downfield shift of C_2, as noted for C_4, than would be found for C_3.

Discussion

Solvent Effects. Before making comparisons of the shifts found for ^{13}C and ^1H nuclear magnetic resonance signals to see if evidence for π back-bonding is forthcoming, it is necessary to choose reasonable values for the shifts of the ligands themselves. Data were obtained for the ligands neat and dissolved in various solvents as shown in Table II. Our data are very similar to those obtained by other authors.[18] It is quite apparent that solvent effects are pronounced for these nitrogen heterocycles. Quite different solvent effects will be found for pyridine or substituted pyridine which is complexed to a metal atom as compared to the free ligand. The major reason for this latter effect is likely to be the unavailability of the nitrogen atom lone pair for solvent interaction in the complexes. Effects on the remainder of the aromatic pyridine ring would be expected to be similar to those found for nonsubstituted benzene. Solvent effects on benzene are also shown in Table II. These data indicate shift changes of only 0.1 to 0.2 ppm for ^1H resonances when solvents ranging in polarity from water to CCl_4 are considered. It is most probable that specific effects on the nitrogen lone pair, especially hydrogen bonding for the case of water, cause the larger shifts found for pyridine and substituted pyridines.[19] The "solvent effect" range in which clear upfield or downfield shift changes cannot be assigned is determined to be the value for the free ligand in CCl_4 to a value 0.2 ppm downfield from the free ligand shift. Values for a complexed ligand that lie within this range are not readily interpretable, although still interesting in a relative sense.

Figure 2 indicates proton chemical shifts of complexed pyridine relative to pyridine in CCl_4. Proton chemical shifts have been shown to be related to electron density of the carbon atoms to which the hydrogen atom is bound in aromatic mol-

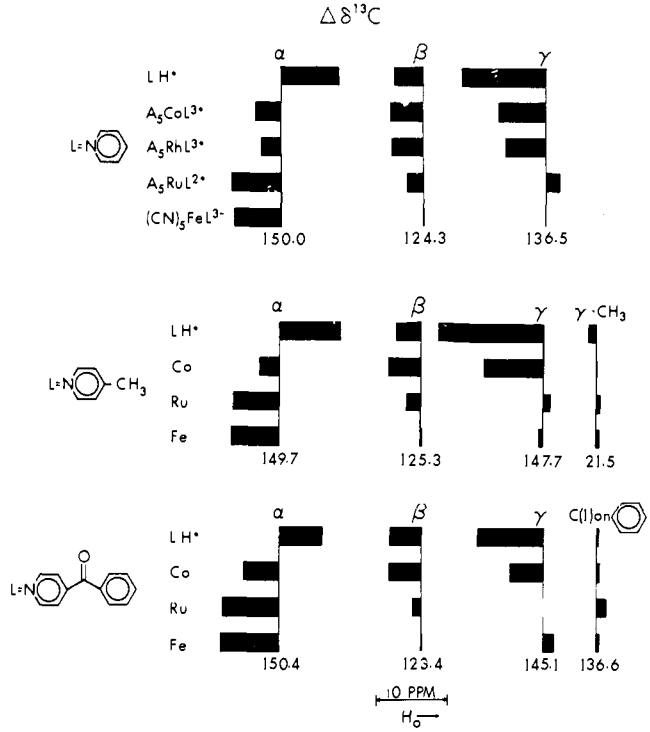

Figure 3. ^{13}C chemical shift changes of pyridine and substituted pyridines upon complexation or protonation. Note that the scale is ten times the scale for ^{1}H chemical shift changes. Since the solvent effect range is estimated to be less than 0.5 ppm, it is not indicated. Shift values are relative to tetramethylsilane by use of CH_3OH as internal standard and adding 50.0 ppm to obtain values relative to TMS.

ecules.[20] Heterocycles, however, elude such a straightforward interpretation due to the anisotropy introduced by the heteroatom. Specific local effects are expected due to changes introduced at the nitrogen site. Among these effects are the electric field effect caused by complexation or protonation and paramagnetic effects due to neighboring group anisotropy. An electric field effect would cause a downfield shift at the α hydrogen due to the polarity of the $H^{\delta+}-N^{\delta-}$ bond. This effect does not appear to be the major one for the complexes of pyridine. Neighboring group anisotropy for the cobalt(III), rhodium(III), and ruthenium(II) complexes due to their temperature-independent paramagnetism should give an upfield shift, and the results confirm this expectation. The diamagnetic effect of alkynes and nitriles[21] has been interpreted as the cause of the downfield shift found by Malin, Schmidt, and Toma for the pentacyanoferrate(II) complex.[4] This effect apparently overcomes the effect of temperature-independent paramagnetism of the Fe(II) center. The greater distance of the β and α hydrogen atoms may preclude large local effects.

The γ position is likely the best indicator of charge density changes, since local effects are attenuated to the greatest degree. The γ ^{1}H chemical shift changes indicate electron density depletion in the protonated pyridine species to be greatest, with the cobalt(III) and rhodium(III) somewhat lower and essentially equal to each other. There is essentially no change for the ruthenium(II) and iron(II) species, indicating that inductive charge withdrawal is effectively compensated by π-back-bonding.

Changes in ^{1}H NMR spectra for γ-picoline complexes, in which the methyl group shows a donation of electron density to the ring via an inductive effect, are shown in Figure 2. Corresponding data for complexes of 4-benzoylpyridine, in which electron density withdrawal occurs, are also shown in Figure 2. Quite similar changes are seen in the α and β positions, indicating the same trend as discussed for unsubstituted pyridine complexes. No γ-hydrogen atoms are available as a probe in these complexes. The hydrogen atoms of the γ-methyl group, however, indicate charge withdrawal for the protonated species and the cobalt(III) complex. The results for the Ru(II) and Fe(II) complexes are within the region of solvent effects but do show that less charge withdrawal has occurred, consistent with π back-bonding. Effects on the phenyl protons of the γ-benzoylpyridine are quite small but do indicate greater charge withdrawal by the proton and cobalt(III) center. The charge transfer bands for the complexes given in Table III are consistent with greater π back-bonding for the Ru(II) and Fe(II) complexes in the order: benzoylpyridine > pyridine > γ-picoline.

^{13}C Spectra of Pyridine Complexes. Solvent effects on ^{13}C spectra, shown in Table II, are similar in magnitude to the solvent effects on ^{1}H spectra, about 0.3 ppm for benzene in various solvents. Since the effects of complexation on ^{13}C spectra are much larger than those on ^{1}H spectra, solvent effects pose less of a limitation for interpretations. The ^{13}C data for pyridine complexes shown in Figure 3 indicate a much greater sensitivity to the effects of complexation than the corresponding ^{1}H data. The shift changes are comparable in magnitude to the ^{19}F shift changes found for the *trans*-bis(triethylphosphine)fluorobenzene complexes of Ni(II), Pd(II), and Pt(II) (2–12 ppm)[1] and those reported by Foust and Ford for organonitrile complexes of ruthenium(II) and rhodium(III) (1–5 ppm).[2] The upfield shift of the α-carbon atoms of protonated pyridine is striking. It has been interpreted as arising from a change in the bond order of the N–C bond caused by protonation.[20] Apparently, this effect is caused by a change in the electron distribution about the α-carbon atom rather than the net electron density. The polarization of electron density from the nitrogen atom toward the proton causes a polarization of density from the α-carbon which, in turn, is compensated for by a shift in density toward the α-carbon from the β-carbon. The net effect is anisotropic with respect to the α-carbon irrespective of the total electron density about this center. Such an effect is not found for the α-hydrogen atom. The spectra of the more positive or "harder" cobalt(III) and rhodium(III) complexes may manifest this process since the α-carbon shifts are not as far downfield as those of the "softer" ruthenium(II) and iron(II) complexes. The shifts at the meta positions are consistent with greater electron density withdrawal by the non-π-back-bonding species, the proton, the Co(III), and the Rh(III) centers, than by the Ru(II) and Fe(II) centers. The charge density and polarizing power of the proton is greater than that of the available coordination site of $(NH_3)_5Co^{3+}$ and $(NH_3)_5Rh^{3+}$. Therefore, a large downfield shift for the β-carbon atom of the protonated species would occur if electron density depletion were the sole criterion determining chemical shift. Electric field effects and/or paramagnetic shifts caused by anisotropy in electron distribution should cause an upfield shift at the β-carbon. These processes would have the greatest influence on the protonated species. Since the downfield shift is not as great for the proton as for the Co(III) and Rh(III) species, these upfield effects likely contribute to the net chemical shift.

The degree of attenuation of local perturbations which occurs at the β position, as well as the possible results of charge alternations in aromatic heterocycles, are not sufficiently developed to allow unambiguous interpretation of the changes in β-carbon chemical shifts. A smaller downfield shift at this position, however, is consistent with a lower degree of electron density depletions by Ru(II) and Fe(II) relative to H^+, Co(III), and Rh(III).

Attenuation of local perturbations at the nitrogen binding site should produce smallest shifts at the γ position. The symmetry of this site should also minimize anisotropic electron distribution alterations which may be caused by complexation.

The values determined for ^{13}C shift changes at the γ carbon may provide a quantitative measure of electron density changes from one species to another. As one proceeds from the hardest Lewis acid, the non-π-back-bonding sequence, $H^+ > Co(III) > Rh(III)$, parallels the shift changes found at the γ-carbon: 10.7, 5.2, and 4.4 ppm *downfield* from γ-^{13}C of pyridine itself. The order of the *upfield* shift changes for the Ru(II) and Fe(II) complexes (3.1 and 1.2 ppm upfield, respectively) parallel the predicted π back-bonding tendencies.[22] Of greatest pertinence to these predictions are the studies of hydrate–carbonyl equilibria of pentacyano(4-formylpyridine)iron(II)[22] and pentaammine(4-formylpyridine)ruthenium(II).[23] The ruthenium(II) center stabilizes the carbonyl forms over the hydrate to a much greater extent than does iron(II), indicating that the unfavorable inductive effect of the positive metal center has been overcome by π back-bonding. The carbonyl/hydrate ratio for the Ru(II) complex is >10, while, under similar conditions, it is 2.1 for the Fe(II) complex. The ratio for the Fe(II) complex is only a factor of 1.5 times that of free aqueous 4-formylpyridine, indicating the small but real effect of π back-bonding in this species.

^{13}C Spectra of Complexes of Substituted Pyridines. Figure 3 demonstrates the results of complexation on ^{13}C spectra of the γ-picoline and 4-benzoylpyridine complexes. The general features are in keeping with those of the corresponding pyridine complexes. The perturbations caused by the electron donating methyl group, which should result in weaker π back-bonding, and the electron withdrawing benzoyl group which should make π back-bonding more favorable, are small but significantly reproducible. Chemical shift measurements were within ± 0.1 ppm for several spectra of different solutions of a particular complex even using different spectrometers.

The effect on the α-^{13}C resonance replacing pyridine by γ-picoline is a 0.1 to 0.8 ppm upfield change. For example, the shift caused by complexation of Ru(II) to pyridine is 7.1 ppm downfield while complexation to γ-picoline causes a 6.4 ppm downfield shift of the α-^{13}C resonance. The effects of H^+, Co(III), and Ru(II) on α-^{13}C shifts of γ-picoline are all 0.7 or 0.8 ppm less downfield than the effects on the α-^{13}C resonance of pyridine. The effects of complexation of pentacyanoferrate(II) are essentially the same (within 0.1 ppm) for each of these ligands. A comparison of the α-^{13}C shifts change on complexation for *p*-benzoylpyridine and pyridine shows that the shifts are 0.8 to 1.4 ppm downfield for all the species observed. Thus, although the alteration in ligand results in significant differences in the shifts caused by complexation, there does not appear to be a trend consistent with the π back-bonding character of the complexing species. The multitude of possible interactions at the α site precludes a satisfactory interpretation of the small effects of ligand variation.

The β chemical shift changes for three ligands on complexation are again very similar. The only discernible trend is the upfield (0.6 ppm) effect of γ-picoline replacing pyridine and the downfield (0.5 ppm) effect of *p*-benzoylpyridine replacing pyridine for the protonated species. These changes are smaller in magnitude but in the same direction as the α-^{13}C shift changes for the same species.

Of greatest interest are the changes in chemical shift at the γ carbon. Charge withdrawal appears to be substantially greater for the protonated form and the cobalt(III) complex of γ-picoline than for the pyridine moieties. This may be related to the greater charge density of the γ carbon of the free γ-picoline molecule. The shifts of the γ carbon of the Ru(II) and Fe(II) complexes are less upfield than the corresponding pyridine complexes, consistent with less π back-bonding. The shifts of the methyl carbon atom indicate charge withdrawal for the H^+ species, little effect of the Co(III) species, and an electron density increase for the Ru(II) and Fe(II) moieties. Anisotropic effects on the electron distribution about the methyl carbon atom, however, may be necessary in rationalizing these chemical shift changes.

The shift changes at the γ position for the benzoylpyridine complexes are upfield from the corresponding pyridine complex. Contrary to the γ-picoline situation, this result indicates less charge density in the free ligand. The hard Lewis acids, which are bound to the nitrogen heterocycles, appear to compensate for the initial density. Each would appear to cause a closer agreement in γ-carbon electron density among the three band ligands than is found for the free ligands. Similarly, the upfield shifts of the γ-carbon caused by Fe(II) indicate a greater degree of π back-bonding for 4-benzoylpyridine than for pyridine or γ-picoline. As one might predict from electrostatic or molecular orbital arguments, π back-bonding tends to exert a leveling effect on the electron density of a series of ligands with increasing acceptor capability. The phenyl carbon shifts are affected slightly downfield indicating charge withdrawal for all species in the order: $H^+ > Co(III) > Fe(II)$. Unfortunately, the low solubility of the complex and lack of NOE enhancement precluded unambiguous determination of the γ ^{13}C resonance position for the Ru(II) complex. The other shifts of this species, however, are consistent with the results for the other complexes with the Ru(II) complex exhibiting back-bonding like the Fe(II) complex.

Conclusions

Investigations of chemical shifts in proton NMR and ^{13}C NMR spectra of a series of related complexes of pyridine and substituted pyridines lead to several conclusions regarding reasonable interpretations. Perhaps most important is the observation that changes in proton chemical shifts on complexation to highly charged "simple" Lewis acids, Co(III) and Rh(III), or lower charged π back-bonding Lewis acids, Ru(II) and Fe(II), are similar in magnitude to solvent effects. ^{13}C shift changes, on the other hand, are generally considerably larger than solvent effects and are, therefore, much less ambiguous.

The heteroatom and specific location of charge at the heteroatom significantly alter interpretation of changes in pyridine-containing species from simple cyclic carbon compounds. The greatest complexity occurs at the α position at which local effects from the nitrogen bound moiety probably predominate over the charge density effect. For proton NMR shifts, the magnetic anisotropy of the bound species predominates. This results in a paramagnetic (upfield) shift for the α proton of pyridines coordinated to pentaammine Co(III), Rh(III), and Ru(II) complexes and a diamagnetic shift due to the cyano groups of pentacyanoferrate(II). The α-carbon chemical shift is probably affected by anisotropy of bonding electrons as well as by electric field and electron density changes.

The effect on the β-^1H and ^{13}C shifts of various perturbations caused by complexation have not been sufficiently delineated, but the shifts generally parallel those found at the γ position. Shifts at the γ position appear to correlate most strongly with chemical evidence for π back-bonding. Electron density changes may be the most important parameter in determining shift changes at this position, since effects of the anisotropy of the bound moiety and electric field effects should be least. Also, the symmetry about the γ-carbon atom should minimize anisotropy of bonding electrons. Unfortunately, changes in the ^1H NMR spectra of Ru(II) and Fe(II) complexes of pyridine are only on the order of solvent effects. The downfield shifts of hydrogen atoms on complexation of pyridine and other nitrogen heterocycles to pentaammineruthenium(II) were cited in an earlier study[2] (in which solvent effects were not considered) as evidence for electron density depletion. The ^{13}C shift changes, however, are much larger than a reasonable

range of solvent effects and demonstrate that π back-bonding from ruthenium(II) can indeed increase electron density at remote ligand sites. The protonated species, as well as the Co(III) and Rh(III) complexes, manifest significant charge withdrawal. The γ-carbon resonances are much larger than solvent effects and indicate electron density depletion in the order $H^+ > Co(III) > Rh(III)$ and increase with Ru(II) > Fe(II).

The effect of substituents indicates that the extent of charge delocalization by π back-bonding is greatest for the ligand which is most depleted in electron density. Thus, one expects that *N*-methylpyrazinium and the pyrazinium ion would be more stabilized than pyrazine by the π back-bonding of pentaammineruthenium(II), as found by Malin et al. for the corresponding pentacyanoferrate(II) complexes,[4] supporting an earlier conclusion[2] that the most important factor in causing the increased basicity of pyrazine when it is complexed to Ru(II) is the stabilization of the protonated pyrazine by the ruthenium center.

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Structural–Vibrational Effects in Magnetic Circular Dichroism Spectra[2]

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Abstract: The magnetic circular dichroic intensity of a locally symmetry forbidden transition generated by structural (static) perturbations, vibrational perturbations, and their interactions, is investigated. It is shown that through second order the contributions of such static and vibrational perturbations are additive. The lowest order effects of static–vibrational interactions are first order in the static and second order in the vibrational perturbations.

It is well established that the magnetic circular dichroism (MCD) associated with an electronic transition which is locally symmetry forbidden is sensitive to the molecular environment of the chromophore involved. It is thus potentially possible to obtain information of stereochemical and spectroscopic interest about such systems from MCD data. Studies of this type have been made, for example, on saturated ketones[3-7] and nitroalkanes.[8]

A theorem[9] which is central to the development of some methods of analysis of MCD spectra of forbidden transitions may be stated as follows: The MCD associated with an electric-dipole symmetry-forbidden transition is of second or higher order in the vibrational and structural perturbations through which the transition gains intensity. Also for such transitions, through second order, the contributions to the MCD which arise from perturbations belonging to different irreducible representations of the chromophoric point group are additive.

Although applications of the above theorem to the analysis of MCD data are in principle straightforward, serious practical difficulties are frequently encountered. These difficulties arise from the fact that vibrational and structural (static) perturbations contribute on an equal footing to the MCD. Attempts to separate the effects of the two types of perturbation, and to describe their interactions, have until now been made by applying qualitative physical arguments to the processes involved in the induction of MCD intensity. While this approach has had some success, we found during the course of some recent work[10] on the MCD of saturated ketones that an extension of the analytical protocol was required. It is the purpose of the present paper to consider further the interactions of static and vibrational perturbations and to lay the theoretical groundwork for the analyses which are presented in the following paper.[10]

Theory

The fundamental theoretical quantity which describes the MCD associated with a nondegenerate[11] vibronic transition $|Aa\rangle \rightarrow |Jj\rangle$ is the magneto-optical B term. This quantity is given by[12,13]