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^{13}C NMR Chemical Shifts of Diamagnetic Pyridine Complexes of Silver(I), Zinc(II), and Cadmium(II): Evidence for a Correlation of Chemical Shift and Metal Ion Polarizing Ability

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Calculations of the pK_a values for dissociation of water molecules bound in the first coordination sphere of metal ions using optical basicities derived from electronegativity values, which have been reported by Duffy and Ingram, indicate that outer-sphere solvent molecules are significant in determining experimental pK_a values. Very limited empirical data are available, however, for verifying the validity of the calculated pK_a values. The ^{13}C NMR chemical shifts for the para carbon atom of pyridine bound in the first coordination sphere of diamagnetic metal ions show an excellent correlation with calculated pK_a values, whereas they are not directly proportional to measured pK_a values, strongly supporting the hypothesis of Duffy and Ingram. For $[Ag(H_2O)_5py]^+$, $[Cd(H_2O)py]^{2+}$, $[Zn(H_2O)_5py]^{2+}$, $[Rh(NH_3)_5py]^{3+}$, and $[Co(NH_3)_5py]^{3+}$, the ^{13}C NMR chemical shift values (in H_2O, relative to Me_4Si as external standard), 140.54, 141.59, 142.10, 142.63, and 143.43 ppm, respectively, show an excellent correlation (a correlation coefficient of 0.999 with a standard deviation less than the reproducibility of the measurement, 0.025 ppm) with *calculated* pK_a values and worse correlation (a correlation coefficient of 0.917 and standard deviation of 0.41 ppm) with *measured* pK_a values. The strong correlation with optical basicities and, hence, with electronegativities is consistent with the use of ^{13}C NMR chemical shifts of the para carbon atom of bound pyridine as an empirical measure of the polarizing power of a diamagnetic metal ion. The ^{13}C chemical shifts of the ortho carbon atoms correlated well with calculated pK_a values for filled-shell (d^{10}) metal ions but not for d^6 metal ions which exhibit temperature-independent paramagnetism (Co(III) and Rh(III)). The magnitude of the chemical shift values indicates that differences between ions of different charge are readily observed but shift changes due to a change in the complement of ligands about a particular metal ion of given charge are not likely to be observable.

Introduction

The acidity of an aquo complex appears to depend principally on the polarization of the bound water molecule by the metal atom, but the influence of outer-sphere water molecules is significant. Duffy and Ingram have used calculated optical basicities to determine pK_a values that would be expected without participation by water molecules outside the first coordination sphere. Such calculated values deviate considerably from measured pK_a values.[1] They were able to obtain related experimental data to support their conclusion for the $ZnCl_2$–H_2O molten-salt hydrate system in which there is little outer-sphere hydration, but it was not feasible to obtain corresponding data for other metal ions. Duffy and Ingram also cited related work of Angell[2] involving determination of ^1H NMR chemical shifts of concentrated solutions of a number of metal ions. Angell's results are consistent with Duffy and Ingram's conclusion that bulk water greatly attenuates the acidity that would be found for aquo complexes in the absence of a large amount of bulk water. Angell's results do not, however, provide a direct probe of the first coordination sphere. In this report we present results of a ^{13}C NMR study of pyridine bound in the first coordination sphere of the diamagnetic, filled-shell ions Zn(II), Cd(II), and Ag(I) and diamagnetic, d^6 ions Co(III) and Rh(III). These data are correlated with optical basicities derived from Allred–Rochow electrostatic force considerations and with experimental pK_a values and compared to results of other studies that have indicated an empirical correlation between ^{13}C chemical shifts and polarization of bound pyridine.

Experimental Section

$Zn(ClO_4)_2{\cdot}xH_2O$, $Cd(ClO_4)_2{\cdot}xH_2O$, and $AgClO_4$ were prepared from the corresponding carbonates and doubly vacuum distilled $HClO_4$ (G. F. Smith) and recrystallized. Zinc(II) and cadmium(II) concentrations were determined by EDTA titration,[3] while silver(I) concentrations were determined gravimetrically.[4] Nitrate salts (Fisher) were dried and weighed to obtain metal ion concentrations. Water was doubly distilled, the second time from alkaline permanganate. Pyridine was distilled and dried according to published procedures.[5] Solution pH adjustment was made with $HClO_4$ for the perchlorate salt solutions and HNO_3 for nitrate salt solutions. The pH was determined using a Radiometer Model 26 pH meter. Solutions were prepared by adding appropriate amounts of each stock solution (metal ion solution, pyridine, and acid) with a calibrated microtitrator (accuracy ±0.5 μL). The concentrations of the metal ions and pyridine were generally kept at 0.50 M. the $[Co(NH_3)_5py]^{3+}$ complex was prepared as described previously,[6] and $[Rh(NH_3)_5py]^{3+}$ was generously provided by Dr. John Petersen.

The ^{13}C NMR data were obtained with a JEOL PS/PFT 100 instrument at 21 ± 1 °C. Typical pulse and delay times were 12.5 μs and 3.00 s, respectively. The samples were observed in 10-mm tubes with a concentric 3-mm capillary (Wilmad) containing Me_4Si as external standard and acetone-d_6 for deuterium lock. The number of scans ranged from 100 (for 1 M pyridine) to 25 000 (for 0.050 M pyridine).

Data for Zn(II), Cd(II), and Ag(I) complexes were fit to analytical functions by use of the Los Alamos nonlinear least-squares program[7] with an added subroutine for fitting cubic functions. Calculations were carried out using the Hunter College Computing Facility and the IBM 370/168 system of the City University of New York. The chemical shifts observed for the Co(III) and Rh(III) complexes were used directly.

Results and Discussion

A number of investigators have observed an apparent correlation of ^{13}C NMR chemical shifts of aromatic nitrogen heterocycles bound to metal ions with indicators of ligand-polarizing ability of the metal ion such as charge-transfer energies or the acidity of a bound ligand.[6,8-11] In general, the

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best correlation is found for the para carbon atom of the bound pyridine or substituted pyridine. The para carbon atom lies on the symmetry elements of the ligand and is the most distant atom of the aromatic ligand from the nitrogen atom so that anisotropic and local effects are apparently attenuated. Most of the reported correlations involve complexes of Ru(II) and Fe(II) which exhibit considerable π back-bonding to pyridine. To compare results of ^{13}C NMR experiments for a ligand in the first coordination sphere with pK_a values predicted from calculated optical basicities and with pK_a values for aquo complexes, we have chosen metal ions that are expected to polarize by σ withdrawal without π back-bonding. It is well known that large chemical shift changes for ^{13}C nuclei in ligands bound to paramagnetic metal ions are often not directly related to polarization of the ligand electrons. Therefore, only diamagnetic metal ions are suitable probes for this study. Assignment of the chemical shift of the bound pyridine ligand requires a reasonably high stability constant in a pH region where the metal ion is in a well-defined form (mononuclear aquo complexes rather than hydroxo complexes). The ions we have studied that meet these criteria are Zn^{2+}, Cd^{2+}, and Ag^+. The Hg^{2+} ion nearly fulfills the criteria but has a too low stability constant at the low pH required to prevent precipitation of the oxide.

In the pH range used for these experiments, the aquated complex of the metal ion is $M(H_2O)_6{}^{n+}$. The weakly interacting anions ClO_4^- (for Zn^{2+} and Cd^{2+}) and NO_3^- (for Ag^+) were employed to simplify treatment of ligand equilibrium expressions. The sparingly soluble nature of bis(pyridyl)silver perchlorate necessitated the use of NO_3^-. So that results obtained with ClO_4^- and NO_3^- counterions could be compared, spectra of some samples using $Zn(NO_3)_2$ and $Cd(NO_3)_2$ were compared with those using $Zn(ClO_4)_2 \cdot xH_2O$ and $Cd(ClO_4)_2 \cdot xH_2O$ and no difference in chemical shifts was observed. In the pH range studied, the pyridine-containing species are pyridine (py), protonated pyridine (Hpy^+), and a series of aquo complexes, $M(H_2O)_5py^{n+}$, $M(H_2O)_4(py)_2{}^{n+}$, and the other $M(H_2O)_{6-m}(py)_m{}^{n+}$ species. From the published values for the stepwise formation constants of pyridine complexes of Zn^{2+}, Cd^{2+}, and Ag^{2+} in aqueous solution[12-14] it is clear that at acidic pH values only the mono(pyridyl) and bis(pyridyl) complexes need to be considered in the concentration ranges we have studied. For the case of Zn^{2+}, the following relationships between formation constants and concentration hold:

$$[Zn^{2+}]_0 = [Zn^{2+}] + [Zn(py)^{2+}] + [Zn(py)_2{}^{2+}]$$

$$[Zn^{2+}] = \frac{[Zn^{2+}]_0}{1 + K_1[py] + K_1K_2[py]^2}$$

and since

$$[py]_0 = [py] + [Zn(py)^{2+}] + 2[Zn(py)_2{}^{2+}]$$

then

$$[py] = [py]_0 - K_1[Zn^{2+}][py] - 2K_1K_2[Zn^{2+}][py]^2$$

Substituting the expression for $[Zn^{2+}]$ and rearranging, we have

$$[py]^3 + \left(\frac{1}{K_2} + 2[Zn^{2+}]_0 - [py]_0\right)[py]^2 + \left(\frac{1}{K_1K_2} + \frac{[Zn^{2+}]_0}{K_2} - \frac{[py]_0}{K_2}\right)[py] - \frac{[py]_0}{K_1K_2} = 0$$

Table I. ^{13}C Chemical Shifts for Metal-Bound Pyridine[a]

metal complex	ortho	meta	para
$[Co(NH_3)_5py]^{3+}$	154.27	129.51	143.43
$[Rh(NH_3)_5py]^{3+}$	153.28	129.11	142.63
$[Zn(H_2O)_5py]^{2+}$	149.81 ± 0.04	127.16 ± 0.05	142.10 ± 0.04
$[Cd(H_2O)_5py]^{2+}$	150.82 ± 0.03	127.15 ± 0.03	141.59 ± 0.06
$[Ag(H_2O)_5py]^+$	152.85 ± 0.04	126.70 ± 0.02	140.54 ± 0.05

[a] Indicated ranges refer to standard deviations from the mean calculated from equilibrium expressions described in the text.

Table II. Parameters Derived from Nonlinear Least-Squares Analysis

	formation constant				chemical shift	
	K_1(Mpy)	K_2(M(py)$_2$)	pK_a		free py	protonated py
Zn^{2+}	8.50	5.40		ortho	149.82	142.62
Cd^{2+}	21.4	9.30		meta	125.82	128.84
Ag^+	91.6	162		para	139.01	148.55
py			5.22			

The concentrations are related to chemical shifts by the relations

$$\delta_{obsd} = (\chi_{py})(\delta_{py}) + (\chi_{Hpy^+})(\delta_{Hpy^+}) + (\chi_{Znpy^{2+}})(\delta_{Znpy^{2+}}) + (\chi_{Zn(py)_2{}^{2+}})(\delta_{Zn(py)^{2+}})$$

$$= \left(\frac{[py]}{[py]_0}\right)(\delta_{py}) + \left(\frac{[py][H^+]}{K_a[py]_0}\right)(\delta_{Hpy^+}) + \left(\frac{K_1[py][Zn^{2+}]}{[py]_0} + \frac{2K_1K_2[py]^2[Zn^{2+}]}{[py]_0}\right)(\delta_{Zn(py)_x{}^{2+}})$$

where it is assumed (as supported by our experimental results) that the chemical shifts of the $Zn(py)_2{}^{2+}$ complex do not differ significantly from those of the $Zn(py)^{2+}$ complex. The expressions for the Cd^{2+} and Ag^+ equilibria are the same. As a check of the general method and the analytical curve-fitting process, ^{13}C NMR spectra of series of aqueous pyridine solutions at various pH values were obtained. The pK_a value for pyridine calculated from the ^{13}C chemical shift data is 5.22, in good agreement with literature values, which average 5.27 in an ionic strength range of 0.1-1 M ($NaClO_4$).[15] As in the case of the equilibrium of pyridine and protonated pyridine, the ^{1}H-decoupled ^{13}C NMR spectra for solutions containing Zn^{2+}, Cd^{2+}, and Ag^+ are simple. There is a single sharp resonance for each of the three types of pyridine carbon atoms since the exchange rates for bound and unbound pyridine molecules are fast on the NMR time scale. The calculated values for ^{13}C NMR chemical shifts of bound pyridine were determined by first fixing the formation constants (by using literature values[12-14]) and optimizing the shifts and then optimizing the formation constants with the shifts fixed until neither set of values varied significantly on successive cycles. These calculated formation constants are certainly within the range of formation constants found in the literature[12-14] (realizing that these constants can vary appreciably depending on the conditions used).[16] This is strong evidence indicating that our calculated formation constants are correct for the conditions used in our experiments. The final variances obtained are sufficiently small (Tables I and II) when the chemical shifts for pyridine in mono(pyridyl) and bis(pyridyl)

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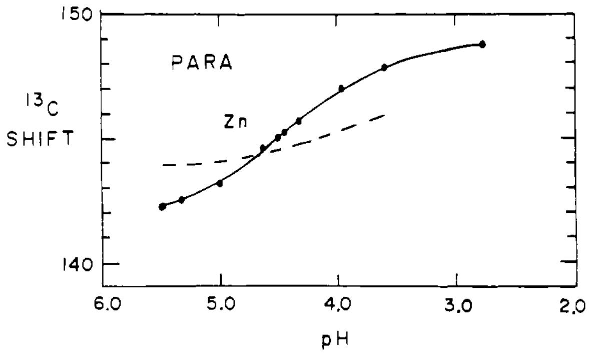

Figure 1. ^{13}C NMR chemical shift of the para carbon atom of pyridine (0.50 M) in equilibrium with Zn(II) (0.50 M) as a function of pH. The dashed line is the best fit of the experimental chemical shift data to an optimized value of the chemical shift for the bound pyridine using one set of literature values for stability constants: $K_1 = 120.2$ and $K_2 = 49.0$. The solid line represents the best fit when the equilibrium constants are optimized to give values of $K_1 = 8.50$ and $K_2 = 5.40$.

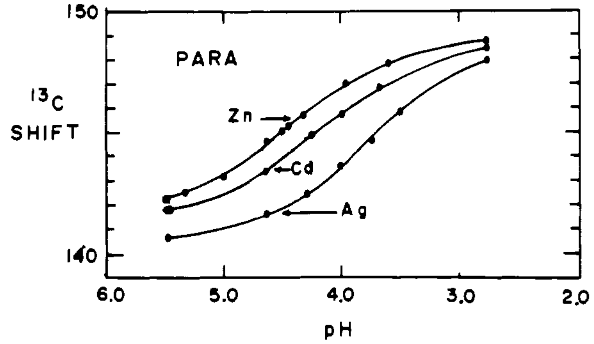

Figure 2. ^{13}C NMR chemical shifts for the para carbon atom of pyridine in equilibrium with Ag(I), Cd(II), and Zn(II) (each 0.50 M) as a function of pH. The solid lines represent the best fit of the chemical shift data to optimized values for stability constants of the metal–pyridine complexes (Table II) and the optimized value for the ^{13}C chemical shift of the metal–pyridine complexes (Table I). Larger equilibrium constants lead to a shift in the inflection point of the curve to lower pH as pyridine competes more effectively with the proton.

complexes are set equal to each other that no attempt was made to allow them to vary independently. It seems reasonable that substitution of a pyridine ligand for a water molecule in the coordination sphere of a non-π-back-bonding metal ion would not cause a large chemical shift effect (when π back-bonding is involved, however, there is an effect of one pyridine ligand on another[10]).

The least-squares fit is highly sensitive to the values used for the equilibrium constants. In Figure 1, the solid line represents the fit for the para ^{13}C chemical shift of pyridine bound to aquated Zn(II) with stepwise formation constants of $K_1 = 8.50$ and $K_2 = 5.40$, in agreement with literature values of $K_1 = 7.94$ and $K_2 = 4.27$ obtained by Sharma and Gaur using a potentiometric titration,[12] whereas the dotted line represents the best fit using the values of $K_1 = 120.2$ and $K_2 = 49.0$ reported by Atkinson and Bauman from a polarographic determination.[15b]

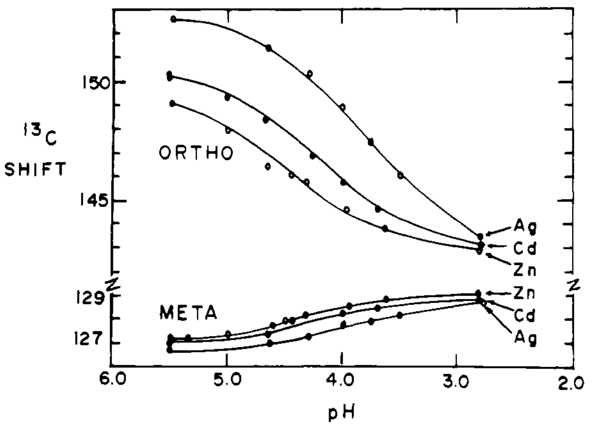

Figure 3. ^{13}C NMR chemical shifts for the ortho and meta carbon atoms of pyridine in equilibrium with Ag(I), Cd(II), and Zn(II). The solid lines are the best fit to the chemical shift data using the equilibrium constants derived from the para chemical shift data and optimized values for the ^{13}C NMR chemical shift at the ortho and meta positions for each metal complex (Table I).

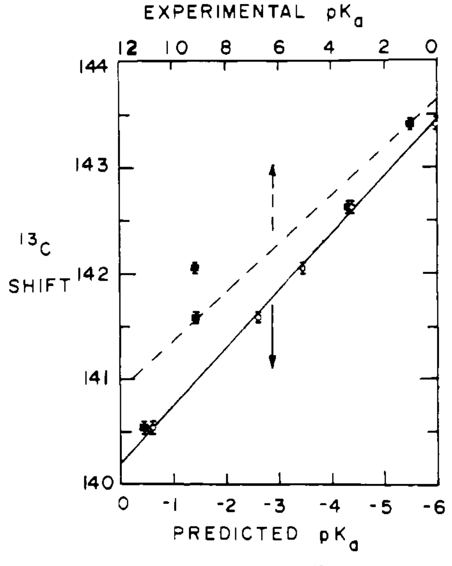

Figure 4. Comparison of correlations of the ^{13}C NMR chemical shifts for the para carbon atom of pyridine complexes of Ag(I), Cd(II), Zn(II), Rh(III), and Co(III) with experimental and predicted pK_a values. The filled points used for the plot of shifts vs. experimental pK_a values give a best fit to the dashed line. A much better correlation is found between the chemical shift values and the pK_a predicted if only inner coordination sphere polarization is considered (the open points fit to the solid line). Error bars indicate the reproducibilities of chemical shift determinations.

Table III. Electronegativity, Basicity-Moderating Parameters, Optical Basicity, and Experimental and Predicted pK_a Values of Metal–Aquo Ions

metal ion	electro-negativity[a]	γ_M[b]	λ_β[c]	pK_a exptl[d]	pK_a predicted[e]
Co^{3+}	1.70	1.96	0.328	0.98	−5.96
Rh^{3+}	1.45	1.62	0.354	3.3	−4.39
Zn^{2+}	1.66	1.90	0.371	9.13	−3.44
Cd^{2+}	1.46	1.63	0.385	9.12	−2.59
Ag^{+}	1.42	1.58	0.419	11.1	−0.60

[a] Allred-Rochow values are ref 17. [b] Basicity-moderating parameters are obtained from eq 3. [c] Optical basicity values are calculated for the conjugate base $[M(H_2O)_5(OH)]^{(n-1)+}$ from eq 2. [d] Experimental values are from data obtained in ref 16. [e] Predicted pK_a values are calculated from eq 1.

The ^{13}C NMR chemical shift data obtained by varying pH are illustrated in Figures 2 and 3 for the para and for the ortho and meta carbon atoms, respectively. The solid lines represent the least-squares fits for the data. Table III contains the parameters used to obtain the calculated curves. Chemical shift data from the $Co(NH_3)_5py^{3+}$ and $Rh(NH_3)_5py^{3+}$ complexes can be taken directly from the NMR spectra because these complexes are substitution inert. In Figure 4, the ^{13}C chemical shift values are compared with measured pK_a values and with pK_a values calculated by Duffy and Ingram from optical basicities. They have related the experimental pK_a of an acid to the calculated Lewis basicity of a conjugate base (e.g., $M(H_2O)_5OH^{(n-1)+}$) by the equation[1]

$$pK_a + 1.74 = 58.3(\lambda_\beta - 0.40) \qquad (1)$$

In this equation, $\lambda_\beta(H_2O) = 0.40$ and the term 1.74 takes into account the 55.5 M concentration of water. The optical basicity of the conjugate base, λ_β, is a measure of the Lewis basicity and can be either obtained from spectroscopic measurements or calculated from the stoichiometry and electronegativities of the constituent elements. The calculated value of λ_β is

$$\lambda_\beta = 1 - [n/2z(1 - 1/\gamma_H) + y/2z(1 - 1/\gamma_m)] \qquad (2)$$

where n and z are from an oxyanion of general formula $H_nMO_z^{m-}$ and y is the oxidation state of element M. γ_H and γ_M, the empirical "basicity-moderating" parameters for hydrogen and element M, respectively, are linearly related to electronegativity (from the Allred–Rochow effective Coulombic force on valence electrons,[17] χ, from $Z_{eff}e^2/r$) with the relationship

$$\gamma_M = 1.29(\chi - 0.26) \qquad (3)$$

In correlating the chemical shifts of complexed pyridine with calculated pK_a values, we have used Allred–Rochow electronegativities since they reflect differences in properties of the transition and post transition metals better than Pauling electronegativities. Since Duffy and Ingram used Pauling electronegativities to calculate basicity-moderating parameters,[1] γ_M, we have recalculated values of γ_M using Allred–Rochow electronegativities to ensure that correlations they found are as valid for either scale. Using the same constraints as Duffy and Ingram ($\gamma_H = 25$ on the basis of optical basicity of water with Pb(II) as the probe ion and $\gamma_{ca} = 1.00$),[19] we derived eq 3. This equation is very similar to Duffy and Ingram's ($\gamma_M = 1.36(\chi - 0.26)$). Equation 3 gives γ_β values that are consistent with expected parameters of strong acids (the NO_3^- ion has a calculated γ_β of 0.39 and is therefore less basic than H_2O) and of weak acids (all conjugate bases of weak acids have $\gamma_\beta > 0.40$). Duffy and Ingram correlated ^1H NMR chemical shifts obtained by Angell[2] for salt hydrate and nitric acid with their calculated pK_a values on the basis of Pauling electronegativities.[1] Values for pK_a using Allred–Rochow electronegativities give a correlation coefficient within 1% of what they obtained.

As can be seen from Figure 4, the fit of ^{13}C chemical shifts for the para carbon atom of bound pyridine to measured pK_a values is quite poor (a correlation coefficient of 0.918 and a standard deviation of 0.41 ppm on a range of 2.89 ppm) while the correlation with calculated pK_a values (or directly with γ_β values) is excellent (correlation coefficient 0.999 and standard deviation of the reproducibility of the measurement 0.025 ppm). This relationship lends credence to the hypothesis that the ^{13}C chemical shift of the para carbon atom of a bound pyridine ligand is a measure of the polarizing power (or "effective electron density") of a metal ion since γ_β is calculated from charge and electronegativity, accepted determinants of the polarizing power of metal ions.

For the d^{10} metal ions, not only does the para carbon atom NMR chemical shift correlate well with pK_a values predicted from electrostatic considerations but the ^{13}C chemical shift values for the ortho positions correlate well also. The ^{13}C chemical shifts for the ortho carbon atom bound to diamagnetic metal ions that are of the d^6 configuration such as Co(III) and Rh(III) (Figure 5) do not show the close correlation of chemical shift change on complexation with the expected polarizing ability of metal ion that was found for the para ^{13}C chemical shifts.[6,8-11] The origin of this local effect at the ortho position may be temperature-independent paramagnetism, which is pronounced (nearly 0.2 μ_B) for many low-spin non-d^{10} ions. As a result of participation of open-shell configurations in which unpaired electrons occupy orbitals of different symmetry, through-space contributions to the paramagnetic term of the ^{13}C chemical shift expression can be significant. These effects are expected for octahedral low-spin ions where the lowest energy configuration is t_{2g}^6, but states involving contributions from e_g orbital occupation are of relatively low energy (i.e., the observed ground state for d^6 ions exhibiting temperature-independent paramagnetism involves contributions from such configurations). Such effects are not expected for filled-shell d^{10} ions.

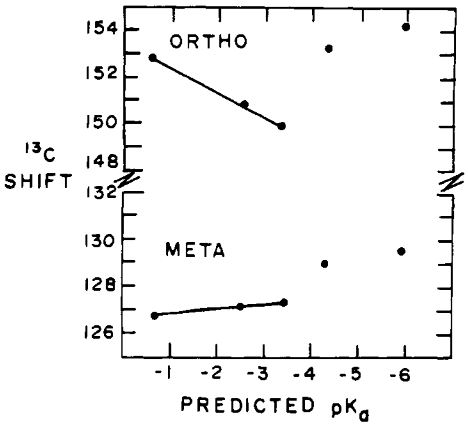

Figure 5. Correlations of ^{13}C NMR chemical shifts for ortho and meta carbon atoms of pyridine complexes of Ag(I), Cd(II), Zn(II), Rh(III), and Co(III) with predicted pK_a values. The ortho ^{13}C chemical shifts of the d^{10} ions Ag(II), Cd(II), and Zn(II) correlate strongly while those of the d^6 ions Rh(III) and Co(III) do not. The meta ^{13}C shifts are so similar for the d^{10} ions that there is no meaningful correlation with the predicted pK_a.

The correlation of the ^{13}C NMR chemical shifts with predicted pK_a values supports the concept that the polarization of ligands in the first coordination sphere is proportional to the electrostatic potential of the metal ion. Thus, if the pK_a of an aquo complex were due simply to the polarization of the bound water molecule, the pK_a could be directly related to the optical basicities derived by Duffy and Ingram.[1] The considerable effect of water molecules outside the first coordination sphere obviates the validity of explanations of pK_a's based solely on inner-sphere effects.

Although the correspondence of ^{13}C NMR chemical shift values of bound pyridine with optical basicity values is gratifying in light of earlier empirical correlations,[6,8-10] the relatively small differences in the measured values for various metal ions limits the general utility of applying this empirical correlation. A variation in polarizing ability comparable to the difference in optical basicity values of species of different charge such as that between Ag^+ and Cd^{2+} is readily evident in the ^{13}C chemical shift values, but the effect of replacing one ligand by another on a particular metal ion of given charge (as in the replacement of a water molecule by pyridine) is not likely to lead to a chemical shift change that is interpretable in terms of altered ligand polarization in the two complexes. The empirical correlation of ^{13}C NMR chemical shifts of bound pyridine may be of some interest, however, to investigate the difference in polarizing ability of metal atoms of different oxidation states that are involved in oxidative-addition/reductive-elimination mechanisms of homogeneous catalysis. Systems of some interest in this regard are pyridine-containing complexes of Rh(I) and Rh(III) and of Ir(I) and Ir(III) for which olefin hydrogenation catalysis has been observed by

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Crabtree and Morris.[20,21] The relative effectiveness of the rhodium and iridium catalysts and a comparison with the reactivity of Wilkinson's catalyst, $[RhCl(PPh_3)_3]$, in these reactions[22] might be related to the ability of the metal ions to polarize the ligand differently in the two oxidation states.

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Registry No. $[Co(NH_3)_5py]^{3+}$, 31011-67-3; $[Rh(NH_3)_5py]^{3+}$, 60118-45-8; $[Zh(H_2O)_5py]^{2+}$, 45985-08-8; $[Cd(H_2O)_5py]^{2+}$, 20154-57-8; $[Ag(H_2O)_5py]^+$, 78370-96-4.

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Metal–Nitroxyl Interactions. 21. Conformational Effects on Spin–Spin Interaction in Three Spin-Labeled Copper Porphyrins

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Electron–electron spin–spin interaction has been observed in the room-temperature solution EPR spectra of three spin-labeled copper porphyrins. For a piperidine nitroxyl attached to a porphyrin pyrrole position, the electron–electron coupling constant, *J*, was greater for an ester linkage than for an amide linkage which correlates with greater porphyrin–side-chain conjugation in the ester derivative than in the amide derivative. The larger temperature dependence of *J* for the ester derivative than for the amide derivative is consistent with the greater flexibility of ester linkages than of amide linkages. When a pyrrolidine nitroxyl was attached to the porphyrin by an amide linkage, *J* was strongly temperature dependent which was attributed to conformational mobility of the pyrrolidine ring or of the amide–nitroxyl ring linkage.

Introduction

The widespread use of nitroxyl radicals as spin labels in biological systems has led to increased interest in the nature of spin–spin interactions between nitroxyls and transition-metal ions.[1] To increase our understanding of the factors which influence the exchange component of spin–spin interactions, we have prepared the spin-labeled porphyrins I–III, obtained from IV,[2] and the corresponding copper complexes V–VII. Porphyrin IV was chosen for study because of its similarity to naturally occurring porphyrins, the possibility of inserting a variety of metal ions, and the presence of a single reactive side chain for attachment of a nitroxyl group. In the initial studies with this porphyrin, copper complexes V–VII were prepared in order to assess the effect of ester and amide linkages and of five- and six-membered nitroxyl rings on spin–spin-exchange interactions. Some preliminary EPR studies of V have been reported.[3]

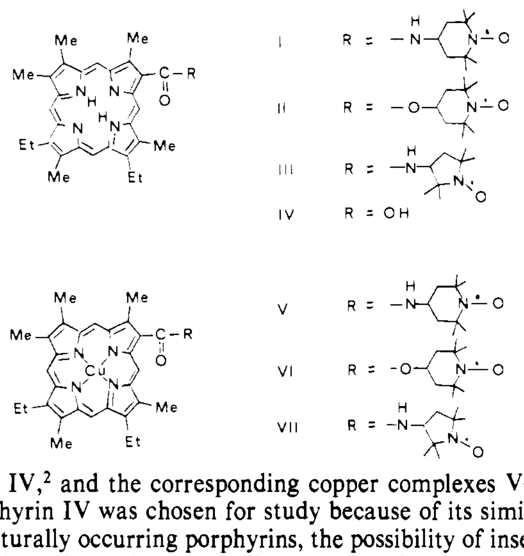

Table I. Electron-Electron Coupling Constants at Room Temperature[a]

complex	solvent	*J*, G	$10^4 J$, cm^{-1}
V	$CHCl_3$	$78^{b,c}$	74
V	C_2HCl_3	$81^{b,c}$	77
V	CH_2Cl_2	$82^{b,c}$	78
V	ethyl acetate	82^{b}	78
V	toluene	83^{b}	79
V	$CHBr_3$	84^{b}	80
V	benzene	85^{b}	81
V	Me_2SO	87^{b}	83
V	DMF	88^{b}	84
V	pyridine	90^{b}	86
V	CS_2	92^{b}	88
VI	$CHCl_3$	$210^{c,d}$	201
VI	$CHBr_3$	215^{d}	206
VI	CH_2Cl_2	$220^{c,d}$	210
VI	C_2HCl_3	220^{d}	210
VI	1:1 toluene/THF	220^{d}	210
VI	pyridine	220^{d}	210
VII	$CHCl_3$	$\sim 100^{c}$	~96
VII	CH_2Cl_2	$\sim 100^{c,e}$	~96
VII	C_2HCl_3	$\sim 100^{e}$	~96
VII	pyridine	$\sim 100^{e}$	~96

[a] Values of *J* based on computer simulation of X-band EPR spectra unless otherwise noted. [b] Uncertainty ±1 G. [c] Spectra simulated at both X band and Q band. [d] Uncertainty ±5 G. [e] Uncertainty ±15 G.

Experimental Section

Infrared spectra were obtained in Nujol mulls on a Perkin-Elmer 337 grating spectrometer. Electronic spectra were obtained in

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