Articles

Effects of Axial Ligand Basicity on the Isotropic NMR Shifts in Pyridine-Type Ligands Coordinated to the Paramagnetic Polyoxometalate, $[SiW_{11}Co^{II}O_{39}]^{6-}$

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Received September 6, 1996

When ^1H NMR spectra of pyridine, 4-amino-, 4-methyl-, and 4-cyanopyridine coordinated to the paramagnetic polyoxometalate, $[SiW_{11}Co^{II}O_{39}]^{6-}$ in D_2O are compared, both $\alpha-$ and $\beta-$ proton peaks are shifted upfield as the basicity of the ligand decreases. The isotropic shifts are separated into contact and pseudocontact contributions by assuming that the contact shifts are proportional to the isotropic shifts of the same ligands coordinated to $[SiW_{11}Ni^{II}O_{39}]^{6-}$. This separation reveals that the shift variations with the axial ligand basicity are dominated by changes in the magnetic anisotropy (pseudocontact shift) of $[SiW_{11}Co^{II}(ptl)O_{39}]^{6-}$ (ptl=pyridine-type ligand). The magnitude of the magnetic anisotropy in a series of pyridine-type ligands increases linearly as the pK_a of their conjugate acids decreases.

Introduction

Several years ago we discovered that the exchange rates of some ligands coordinated to a Co^{2+} ion could be varied by incorporating it in various polyoxometalates.[1,2] It has been shown that pyridine- and imidazole-type ligands coordinated to $[SiW_{11}Co^{II}O_{39}]^{6-}$ ($SiW_{11}Co$) or $[SiW_{11}Ni^{II}O_{39}]^{6-}$ ($SiW_{11}Ni$) undergo slow exchange on the NMR time scale, exhibiting separate signals for the complexes and the free ligands in their ^1H and ^{13}C NMR spectra.[1,2] Well-resolved NMR spectra of ligands coordinated to paramagnetic polyoxometalates can provide useful information on both the ligands and polyoxometalates.[3,4]

Slow ligand exchange makes it possible to measure absolute isotropic shifts directly from room temperature spectra, and hence to compare the values for various ligands. We have studied effects of ligand basicity on the isotropic NMR shifts of protons in pyridine, 4-amino-, 4-methyl-, and 4-cyanopyridine coordinated to $SiW_{11}Co$. Previously La Mar *et al.* reported effects of basicities of the same ligands coordinated to low-spin ferric tetraphenylporphyrin complexes.[5] They used the pattern of the *meso-* phenyl isotropic shifts to separate the contact and pseudocontact contributions. It was concluded that the shift variations with pyridine pK_a were dominated by changes in the magnetic susceptibility anisotropy. We have used NMR data for the $SiW_{11}Ni$ complexes to separate the isotropic shifts of the $SiW_{11}Co$ complexes into contact and pseudocontact contributions.

Experimental

$K_6[SiW_{11}Co(H_2O)O_{39}] \cdot nH_2O$, $K_6[SiW_{11}Ni(H_2O)O_{39}] \cdot nH_2O$, and $K_{12}[Ni_3(PW_9O_{34})_2] \cdot nH_2O$ were prepared according to the literature methods[6-8] and identified by their IR spectra. Pyridine, 4-amino-, 4-methyl- ($\gamma-$ picoline), and 4-cyanopyridine were purchased from Aldrich. NMR samples were prepared by dissolving a polyoxometalate and a ligand in a 1:1

molar ratio in D_2O. The typical concentration was 20 mM for each of the polyoxometalate and ligand.

^1H NMR spectra were obtained in the Fourier transform mode with a Varian Gemini-300 or -200 spectrometer equipped with a broad band, narrow-bore probe. NMR measurements were made at ambient temperature (22-25 °C). The line-broadening factor used in exponential anodization was 20 Hz. Pulses of 90° (10 μs) were used, and the acquisition time was 0.2 s. No extra delay time was introduced between pulses. The residual water resonance in each spectrum was saturated by irradiating with a single frequency pulse which was gated off during acquisition. Sodium salt of 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid (TSP) was used as an internal reference.

Results and Discussion

^1H NMR spectrum of a D_2O solution containing $SiW_{11}Co$ and 4-aminopyridine (4-NH_2-py), 4-methylpyridine (4-CH_3-py), pyridine (py), or 4-cyanopyridine (4-CN-py) is shown in Figure 1. The spectra of py and 4-CH_3-py coordinated to $SiW_{11}Co$ were reported before.[1] The free ligand peaks appear at 0-9 ppm, and the peaks originating from the complexes are easily identified on the basis of their linewidths and intensities.[1] Listed in Table 1 are pK_a values for the conjugate acids of these ligands,[9] which may be used as a measure of their σ basicities: the pyridine basicity increases as the pK_a value increases. It is seen that both a-H and $\beta-$ H peaks are shifted up field, as the basicity of the ligand decreases. The isotropic shifts change linearly as a function of pK_a, as shown in Figure 2.

The isotropic NMR shifts (δ_{iso}) in a paramagnetic system contain contact (δ_{con}) and pseudocontact shifts (δ_{dip}).

$$\delta_{iso} = \delta_{con} + \delta_{dip} \qquad (1)$$

Contact shifts occur when unpaired electron density is transferred from the metal to the ligand nucleus in question,
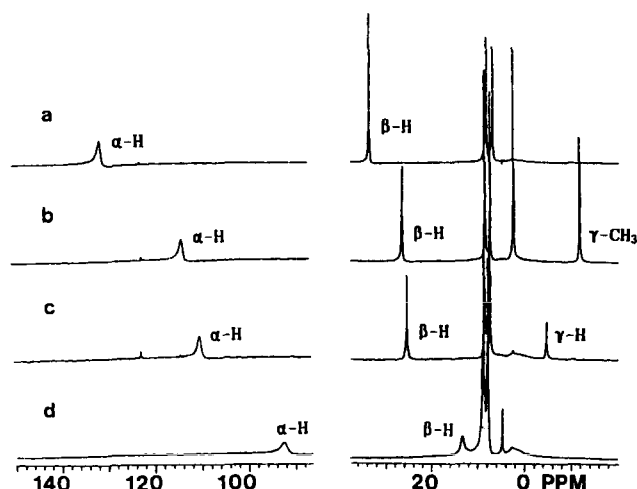
Figure 1. ^{1}H NMR spectra of D[2]O solutions containing SiW[11]Co and (a) 4-aminopyridine, (b) 4-methylpyridine, (c) pyridine, and (d) 4-cyanopyridine in a 1:1 molar ratio. The peaks originating from the complexes are labeled.
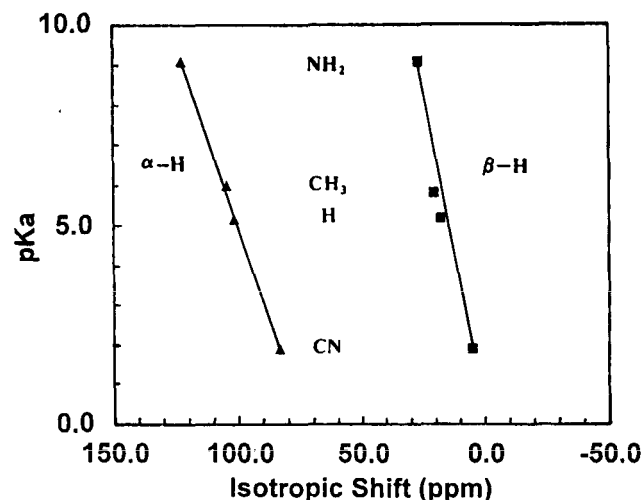

Figure 2. Isotropic shifts of protons in SiW[11]Co complexes as functions of pK_a of the ligands. Straight lines are given as guides for eyes.

Table 1. pK_a Values of Ligands and Isotropic Shifts (in ppm) for SiW[11]Co and SiW[11]Ni Complexes

4-X	pK_a	α–Proton		β–Proton	
		SiW[11]Co	SiW[11]Ni*	SiW[11]Co	SiW[11]Ni
NH[2]	9.2	122.7	130.3	26.9	32.3
CH[3]	6.0	107.7	137.0	19.3	34.4
H	5.2	101.6	133.9	17.7	36.1
CN	1.9	83.4	129.1	4.9	30.3

*Estimated from the following δ[iso] values for α–11 and β–11 in the [Ni[x](PW[9]O[34])[y]] complexes: 4-NH[2] 144.4 and 35.8 ppm; 4-CH[3] 141.8 and 35.6 ppm; 4-H, 145.4 and 38.1 ppm; 4-CN, 138.5 and 32.5 ppm.

whereas pseudocontact shifts arise from a through-space dipolar interaction between the electronic and nuclear magnetic moments.[16]

The contact and pseudocontact contributions to δ[iso] may be separated in the following way. For an octahedral nickel (II) complex, which has an orbitally non-degenerate $^3A_{2g}$ ground state with excited states far removed in energy, the orbital contribution is small and so is the magnetic anisotropy.[10] NMR studies have shown that the isotropic shifts in bis(2,4-pentanedionato)bis(pyridine)nickel(II) come mainly from the contact shifts.[10,11] In order to estimate the pseudocontact shifts in [SiW[11]Ni(ptl)O[39]][6-], in which the environment of Ni^{2+} deviates considerably from octahedral symmetry (see below), we have compared the isotropic shifts in [SiW[11]Ni(py)O[39]][6-](36.1 and 11.8 ppm for β– and γ-H, respectively)[1] with those in [Ni(py)[6]][2+], an octahedral complex. ^{1}H NMR spectrum of [Ni(py)[6]][2+] in propylene carbonate exhibits average peaks for free and complexed pyridine molecules at room temperature, indicating that the ligand exchange is fast on the NMR time scale.[12] However, separate NMR lines are observed for free and complexed pyridine molecules, when Ni(NO[3])[2] and pyridine are mixed in D[2]O. The isotropic shifts were measured for various ratios of [py]/[Ni^{2+}]. The isotropic shifts changed slightly when the ratio was increased from 1 to 6, but remained con-

stant thereafter. Since the species responsible for the NMR spectrum must be [Ni(py)[x](H[2]O)[6-n]][2+], the constant isotropic shifts for [py]/[Ni^{2+}]>6 were assumed to be equal to those in [Ni(py)[6]][2+](118, 32.9, and 9.6 ppm for α–, β–, and γ–H, respectively). It is noted that the isotropic shifts in [SiW[11]Ni (py)O[39]][6-] are slightly larger than the corresponding values in [Ni(py)[6]][2+]. If the pseudocontact shifts are significant for [SiW[11]Ni(py)O[39]][6-], all peaks are expected to be shifted upfield and hence the isotropic shifts to be decreased, as was observed for [SiW[11]Co(py)O[39]][6-]. Absence of such upfield shifts indicates that the pseudocontact contributions to the isotropic shifts in [SiW[11]Ni(ptl)O[39]][6-] are negligibly small.

Since both Co^{2+} and Ni^{2+} ions in distorted octahedral environments have two σ electrons in the d[z2] and d[x2-y2] orbitals, contact shifts due to σ– electron delocalization in the SiW[11]Co complex may be assumed to be proportional to the corresponding isotropic shifts for the SiW[11]Ni complex. Although SiW[11]Co complexes can have additional contact shifts due to π–electron delocalization, they are small for α– and β–protons[11] and may be neglected.

The pseudocontact shift may be expressed as[10]

$$\delta_{dip} = \frac{\mu_o}{4\pi r^3} \times [\,\{\, \chi_{zz} - (\chi_{xx} + \chi_{yy})/2\,\} \times (3\cos^2\theta - 1)$$
$$+ (\chi_{xx} - \chi_{yy}) \times \sin\theta\cos 2\phi] \qquad (2)$$

where χ_{zz} etc. are magnetic susceptibility components, and other symbols have their usual meaning. When the ligand rotates freely about the Co-N axis, the second term due to the in-plane magnetic anisotropy can be neglected. Pyridine-type ligands can form both σ– and π– symmetry bonds with transition metal ions, and it has been suggested that a π–bonding barrier prevents these ligands from rotating at room temperature.[14] However, recent molecular mechanics calculations (MM2*) on low-spin ferric porphyrinates have shown that the barrier to rotation of pyridine (py) in [Fe (TPP)(py)[2]][1] is extremely low (2.2 kcal/mol).[15] Similar calculations have shown that the axial imidazole (Im) rings in *trans*- [(Im)[2](NH[3])[4]Ru[III]]Cl[3] rotate freely in solution.[16] Comparison of δ[iso] values for [(Im)(NH[3])[5]Ru[III]][3+] and the cor-

responding complex with 2-methylimidazole, which is sterically hindered from rotating, revealed significantly different values for 4-H but nearly identical values for 5-H.[16] This difference was attributed to rotation about the the z-axis having a negligible effect on 5-H (θ=15°) but having a large effect on 4-H (θ=40°). We have made a similar observation on SiW₁₁Co complexes of imidazole and 2-methylimidazole.[3] (Chemical shifts for 4-H and 5-H are 45.8 and 38.3 ppm for imidazole, and 75.8 and 37.0 ppm for 2-methylimidazole.) These results lead us to believe that 4-substituted pyridine ligands coordinated to SiW₁₁Co rotate freely at room temperature in solution.

If the second term in Eq. (2) is neglected, the pseudocontact shift is proportional to the geometric factor, $(3\cos^2\theta-1)/r^3$.

$$\delta_{dip} = \frac{\mu_o\{\chi_{zz}-(\chi_{xx}+\chi_{yy})/2\}}{4\pi} \times \frac{(3\cos^2\theta-1)}{r^3} \quad (3)$$

Now Eq. (1) may be expressed as

$$\delta_{iso}(Co) = C_1 \times \delta_{iso}(Ni) + C_2 \times \frac{(3\cos^2\theta-1)}{r^3} \quad (4)$$

where C_1 and C_2 are proportionality constants. Geometric factors may be assumed to be the same as those calculated for bis(2,4-pentanedionato)bis(pyridine)cobalt(II): 0.0233 for α–H and 0.0106 Å⁻³ for β–H.[17] The two unknown constants, C_1 and C_2, can be determined from measured δ values for α–H and β–H. Unfortunately signals from α–H of the SiW₁₁Ni complexes are too broad to be observed; only β–H peaks are observed.[18] However, broad α–H peaks are observable for pyridine-type ligands coordinated to [Ni₄(PW₉O₃₄)₂]¹⁰⁻ (P₂Ni₃); see Figure 3. The signals originating from α–H and γ–H consist of several peaks, which are ascribed to mono-, di-, and triligand complexes, and their monoprotonated species.[3] The spectra of coordinated pyridine and 4-methylpyridine were reported before.[3]

In order to estimate δ values for α–H in the SiW₁₁Ni complexes, we compare δ values for protons in SiW₁₁Ni and P₂Ni₃ in Table 2. Values of δ for two complexes are

roughly proportional, indicating that σ electron delocalization is the dominant mechanism contributing to the isotropic shifts. If there is considerable π electron delocalization, its contribution will be most significant at γ–H and γ–CH₃.[13] So we have assumed that the ratios of δ values for α– and β– protons are the same for the SiW₁₁Ni and P₂Ni₃complexes. Using the strongest peak in the signal for β–H in each P₂Ni₃complex.[18] we get the δ values for α–H in SiW₁₁Co listed in Table 1.

Now, using Eq. (4), one can separate the isotropic shifts in the SiW₁₁Co complexes into contact and pseudocontact contributions. The results are summarized in Table 3. It is noted that all values of δ_dip are negative. Since the geometric factors for α–, β–, and γ–H are all positive, negative δ_dip

Table 2. Comparison of Isotropic NMR Shifts[a] in SiW₁₁Ni and [Ni(PW₉O₃₄)₂]¹⁰⁻ Complexes

| Proton	SiW₁₁Ni 1	[Ni(PW₉O₃₄)₂]¹⁰⁻ 2[b]	Ratio 1/2
α–H	-	145	-
β–H	36.0	39.1	0.92
γ–H	11.8	13.7	0.86
α–CH₃[d]	-	– 13.0	-
β–CH₃[c]	7.7	8.0	0.96
γ–CH₃[d]	– 12.1	– 13.6	0.89

In ppm. [a]The data for unprotonated, monoligand complexes. [b]The data for the pyridine complex. [c]The data for the picoline complexes.

Table 3. Separation of Isotropic NMR Shifts (in ppm) in SiW₁₁Co Complexes

4-X	α–Proton δ_iso	α–Proton δ_con	α–Proton δ_dip	β–Proton δ_iso	β–Proton δ_con	β–Proton δ_dip
NH₂	122.7	139.7	– 17.0	26.9	34.6	– 7.7
CH₃	107.7	145.7	– 38.0	19.3	36.6	– 17.3
H	101.6	147.0	– 45.4	17.7	38.5	– 20.8
CN	83.4	150.0	– 66.6	4.9	35.2	– 30.3
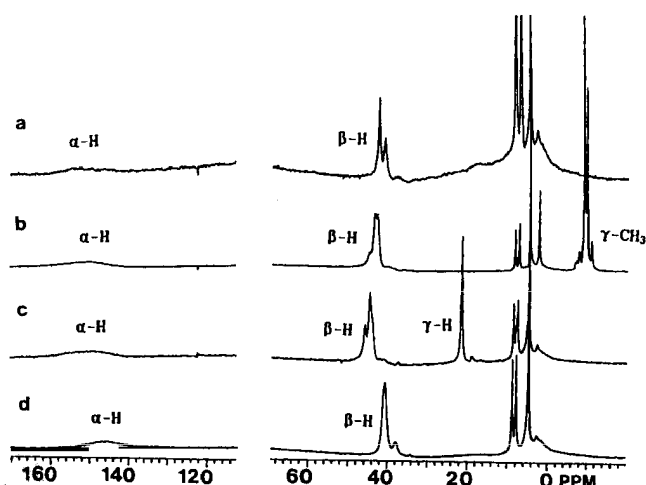
Figure 3. ¹H NMR spectra of D₂O solutions containing [Ni₄(PW₉O₃₄)₂]¹⁰⁻ and (a) 4-aminopyridine, (b) 4-methylpyridine, (c) pyridine, and (d) 4-cyanopyridine in a 1:1 molar ratio.
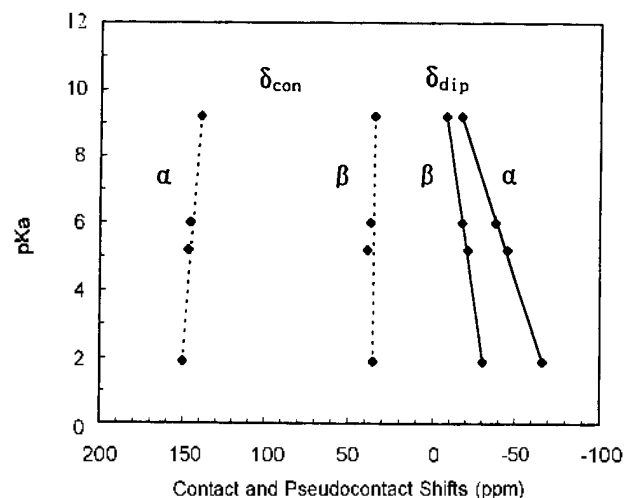
Figure 4. Contact (...) and pseudocontact shifts (–) of protons in the SiW₁₁Co complexes as functions of pK_a of the ligands. Straight lines are given as guides for eyes.

means $(\chi_{\parallel} - \chi_{\perp}) < 0$.

Values of δ_{con} and δ_{sp} for $SiW_{11}Co(ptl)$ are plotted as functions of pK_a in Figure 4. The change in δ_{con} is relatively small: an increase of 10 ppm is observed for ct-protons on going from 4-NH$_2$-py to 4-CN-py. Values of δ_{con} for $SiW_{11}Ni$ (ptl) in Table 1 are similar and exhibit no trend as a function of pK_a. These results suggest that the axial ligand basicity causes relatively small effects on the contact shifts.

On the other hand, the magnitude of the pseudocontact shift increases remarkably as the axial ligand basicity decreases. (Since values of δ_{sp} are negative, they cause upfield shifts.) If the geometric factors are assumed to be the same for all complexes, the magnetic anisotropy, $\{\chi_{zz} - (\chi_{xx} + \chi_{yy})/2\}$ or $(\chi_{\parallel} - \chi_{\perp})$, should be altered by the ligand basicity. Below we consider why $(\chi_{\parallel} - \chi_{\perp})$ is negative and why the magnitude of the magnetic anisotropy increases as the axial ligand basicity decreases. It is more convenient to consider $(g_{\parallel}^2 - g_{\perp}^2)$ which is roughly proportional to $(\chi_{\parallel} - \chi_{\perp})$.[19]

The theory for the high spin d^7 configuration in axially distorted octahedral field was first worked out by Abragam and Pryce,[20] and a simplified account was given by Griffith.[21] In an octahedral field the ground term is $^4T_{1g}$, to which the following Hamiltonian is applied,

$$\hat{H} = -\frac{1}{3}\gamma\zeta L \cdot S - \delta\left(L_z^2 - \frac{2}{3}\right) + \mu_B B\,(\gamma L + 2S) \qquad (5)$$

where γ satisfies $? \; 1.5 \leq \gamma \leq ? \; 1.0$, ξ is the spin-orbit coupling parameter, δ is the tetragonal distortion parameter, and other symbols have their usual meaning. The ground term, having a threefold orbital degeneracy and a fourfold spin degeneracy, splits into six Kramers doublets. And the following expressions for g values are derived from the lowest level.

$$g_{\parallel} = 2 + 4(2-\gamma) \times \left\{\frac{3}{x^2} - \frac{4}{(x+2)^2}\right\}/f \qquad (6)$$

$$g_{\perp} = 4\left\{1 - \frac{2\gamma}{x+2} + \frac{12}{x(x+2)}\right\}/f \qquad (7)$$

$$f = 1 + \frac{6}{x^2} + \frac{8}{(x+2)^2}$$

$$\delta = \frac{1}{3}\gamma\zeta\left\{\frac{x+3}{2} - \frac{3}{x} - \frac{4}{x+2}\right\} \qquad (8)$$

In sites of strict octahedral symmetry ($\delta=0$), g is isotropic with $g_{\parallel} = g_{\perp} = 4.0$-4.3. For octahedral coordination with small tetragonal distortion, g becomes very anisotropic: $g_{\parallel} > g_{\perp}$ when $\delta > 0$, and $g_{\parallel} < g_{\perp}$ when $\delta < 0$. The magnetic anisotropy for $SiW_{11}Co(ptl)$ indicates that $\delta < 0$.

The effects of axial ligand basicity on the magnetic anisotropy can be explained qualitatively based on the ordering of the d orbitals. The geometry around the cobalt ion in $SiW_{11}Co(ptl)$ deviates considerably from octahedron. The six oxygen atoms surrounding a tungsten atom in $[SiW_{12}O_{40}]^{4-}$ can be classified into four types: one O_a atom shared between three WO_6 groups and the central SiO_4 tetrahedron, two O_b atoms shared between adjacent W_3O_{13} units, two O_c atoms shared between two WO_6 octahedra in the same W_3O_{13} unit, and one O_d atom linked to one tungsten atom. The bond lengths are $W-O_a$ 2.35, $W-O_b$ 1.92, $W-O_c$ 1.93, and $W-$

O_d 1.71 Å.[22] It is noted that the axial O_a atom is located 0.4 Å farther than O_b and O_c atoms which form a square plane. In $SiW_{11}Co(ptl)$ one of the twelve $W-O_d$ groups has been replaced by $Co(ptl)$. Since the ionic radius of Co^{2+} is 0.16 Å larger than that of W^{6+}, the Co^{2+} ion should lie 0.8 Å **above** the square plane.[23] Therefore, the $Co-O_a$ bond, if it exists, must be very weak, and the geometry around the Co^{2+} ion may be considered to be square pyramidal.

The d orbitals have the ordering $d_{xz}, d_{yz} < d_{xy} < d_{z^2} < d_{x^2-y^2}$ for some square pyramidal Co(II) complexes,[24] and $d_{xy} < d_{xz}, d_{yz} < d_{z^2} < d_{x^2-y^2}$ for some square pyramidal nickel, palladium (II), and platinum complexes.[25] When $\delta < 0$ in a C_{4v} field, the term $-\delta(Lz^2 - 2/3)$ in Eq. (5) splits the T_{1g} term into A_2 and E states, the doubly degenerate E state being above the orbitally nondegenerate A_2 state. If the d_{xz}, d_{yz} orbitals are below d_{xy}, the ground electronic configuration is $(d_{xz}, d_{yz})^4 (d_{xy})^1(d_{z^2})^1(d_{x^2-y^2})^1$, and the excited electronic configurations, $(d_{xz}, d_{yz})^3(d_{xy})^2(d_{z^2})^1(d_{x^2-y^2})^1$, are degenerate in agreement with the prediction for $\delta<0$. Of course, these states are further split by electrostatic repulsion and spin-orbit coupling. If the d_{xz}, d_{yz} orbitals were above d_{xy}, the energies of the electronic configurations would be reversed.

Now that the ordering of the d orbitals has been established, the energy difference between the $d_{x^2-y^2}$ and d_{z^2} orbitals, or that between the d_{xy} and d_{xz}, d_{yz} orbitals may be used as a measure of deviation from the octahedral field and hence the magnetic anisotropy. When the axial ligand basicity increases, the d_{z^2} and d_{xz}, d_{yz} orbitals are destabilized, reducing the energy differences and hence the magnetic anisotropy. The coordinated 4-NH$_2$-py, which has the largest basicity, exhibits the smallest absolute value of δ_{sp} in agreement with this prediction.

Values of the magnetic anisotropy, $(\chi_{\parallel} - \chi_{\perp})$, can be determined from the proportionality constant C_i: 4-NH$_2$-py, -1317; 4-CH$_3$-py, -2946; py, -4055; 4-CN-py, -5167 in units of 10^{-6} cgsu/mol. The magnetic anisotropy of bis(2,4-pentanedionato)bis(pyridine)cobalt(II) determined from single crystal magnetic measurements is -3065 x 10^{-6} cgsu/mole in reasonable agreement with our values.[17]

A similar study on the same ligands coordinated to low-spin ferric tetraphenylporphyrin complexes also revealed that the shift variations with the axial ligand basicity were dominated by changes in the magnetic anisotropy.[5] However, the pseudocontact shifts in these complexes cause downfield shifts for the protons in pyridine-type ligands, indicating $(\chi_{\parallel} - \chi_{\perp}) > 0$. In addition, the magnetic anisotropy decreases as the pyridine basicity decreases.

The ground state of low-spin ferric porphyrins is known to have the d_{xz} and d_{yz} levels above d_{xy}.[26] For such systems it was shown[16] that $g_{\parallel} > g_{\perp}$ in agreement with $(\chi_{\parallel} - \chi_{\perp}) > 0$. The energy difference, δE, between the d_{xz}, d_{yz} orbitals and the d_{xy} orbital is a measure of the magnetic anisotropy. Therefore, the variation in the magnetic anisotropy can be interpreted in terms of the effect of the axial ligand on δE. Here the (s-type interactions between the metal and the axial ligands are of less importance to the energies of the d$_\pi$ orbitals of the complexes than are the energies of the π bonding and antibonding orbitals of the ligand atoms. It has been shown that the d$_\pi$ orbitals of iron(III) lie slightly above the energy of the π orbital of the high basicity pyridines and slightly below the $\pi*$ orbital of the low-basicity py-

ridines.[27] Thus, high-basicity pyridines interact with iron(III) by π donation from the filled pyridine π orbital to the singly occupied d $_z$ orbital of iron(III). This interaction destabilizes the d $_z$ orbital, increasing the magnetic anisotropy. On the other hand, π back-donation occurs from the filled d $_\pi$ orbital of iron(III) to the empty π^* orbital of the pyridine for low-basicity pyridines, stabilizing the d $_z$ orbitals, hence reducing the magnetic anisotropy.

In summary, we have shown that axial ligand basicity causes strong effects on the isotropic NMR shifts of pyridine-type ligands coordinated to $SiW_{11}Co$ by altering the magnetic anisotropy of the complex. We have also determined absolute values of the magnetic anisotropy for some $SiW_{11}Co$ complexes.

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19. Ref 5. However, $(\chi_{\parallel} - \chi_{\perp})$ and $(g_{\parallel}^2 - g_{\perp}^2)$ are not proportional, for the second-order Zeeman terms in Van Vleck's expression for paramagnetic susceptibility are not included in the latter expression; see Horrocks, W. DeW., Jr. *Inorg. Chem.* **1970**, *9*, 690.

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