Proton Nuclear Magnetic Resonance Contact Shifts of Octahedral Iron(II), Cobalt(II), and Nickel(II) Imidazole Complexes

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Abstract: Proton NMR isotropic shifts have been measured for the high-spin octahedral complexes M(imidazole)$_6$(ClO$_4$)$_2$ (M = Fe^{2+}, Co^{2+}, Ni^{2+}) in methanol-d_4 in the presence of excess imidazole. For these complexes which have essentially O_h symmetry, the isotropic shifts are interpreted as being primarily contact in nature. The isotropic shifts for 4,5-H (merged because of tautomerism) and 2-H are downfield in the above three complexes. The N–H proton resonance which also is shifted downfield is not separately observed because of rapid exchange with the solvent. Using Co(Im)$_6{}^{2+}$ as a model and assuming a small trigonal distortion of not more than 2°, as implied by the known single-crystal magnetic anisotropy, the isotropic shifts for protons 2-H and 4,5-H are calculated to be approximately 95% contact and 5% dipolar. It is shown that the contact shift ratios $\Delta\nu$(4,5-H)/$\Delta\nu$(2-H) are near equal in Co(Im)$_6{}^{2+}$ and Fe(Im)$_6{}^{2+}$ but different from that in Ni(Im)$_6{}^{2+}$. Possible spin delocalization mechanisms are discussed in relation to the above ratios.

In the study of contact shifts of paramagnetic transition metal complexes, one of the more troublesome aspects has been the estimation of the magnitude of the electron magnetic dipole–nuclear magnetic dipole interaction and its resultant dipolar (pseudo-contact) shift.[1] For six-coordinate nickel(II) complexes, because of their orbitally nondegenerate ground state and approximate magnetic isotropy, it has been commonly assumed without any ensuing difficulty that a dipolar shift contribution is nonexistent. Such an assumption is not valid for octahedrally coordinated complexes having an orbitally degenerate ground state where dipolar contributions to the isotropic shifts can be substantial because of the magnetic anisotropy present.[1,2] Commonly studied paramagnetic complexes in this category are those of high spin cobalt(II) and iron(II).

In this work we wish to examine the importance of dipolar shifts in the most symmetrical of the six-coordinate complexes, i.e., those of O_h or "near O_h" symmetry, and the effect of small trigonal distortions. Using the octahedral imidazole complexes[3] or iron(II), cobalt(II), and nickel(II) and the known magnetic anisotropy[4] of Co(Im)$_6{}^{2+}$, we present evidence which suggests that for the above class of complexes, dipolar shifts are of negligible magnitude. Also of considerable interest is the question of spin delocalization in these imidazole complexes and in the related complexes containing the nitrogen donor ligands pyridine,[5-7] 2,2′-bipyridine,[8] and 1,10-phenanthroline.[9] Based on the type of molecular orbital calculation, INDO or extended Hückel, attempts have been made to rationalize contact shifts particularly for the nickel complexes of the three aforementioned ligands.[5-9] Using INDO molecular orbital calculations, the contact shifts for Ni(imidazole)$_6{}^{2+}$ are in good agreement with that expected for simple σ-delocalization and thus are consonant with the spin delocalization mechanism for Ni(pyridine)$_6{}^{2+}$ proposed by Horrocks.[6,7]

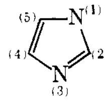
Experimental Section

The imidazole complexes were prepared by the method of Reedijk described in the literature.[3] Satisfactory analyses were obtained in all cases. The proton magnetic resonance spectra were obtained at 35° using a Varian T-60 spectrometer equipped with a wide sweep module. Solution magnetic susceptibilities were determined by the NMR method of Evans.[10] Solutions of the iron(II) and cobalt(II) complexes were prepared and handled in a nitrogen atmosphere glove bag. The solvent for all NMR spectra was methanol-d_4 (99%) purchased from Brinkmann Instruments, Inc. Electronic spectra were measured using a Cary 14 spectrometer.

Results and Discussion

Before interpreting the NMR isotropic shifts of the octahedral complexes Fe(Im)$_6{}^{2+}$, Co(Im)$_6{}^{2+}$, and Ni(Im)$_6{}^{2+}$, it is first necessary to be assured that the complexes remain intact in solution without ligand displacement by the solvent which in this case is methanol. The solid state and solution visible spectra are reported in Table I and are consistent with octahedral geometry. Solution spectra of the above complexes in methanol were run in the presence of a fivefold molar excess of ligand. Under this condition the solution spectra and mull spectra are essentially identical implying that in each case the divalent metal ion is surrounded by six imidazole molecules. This can further be substantiated by the NMR chemical shift and mole fraction plots (vide infra).

The paramagnetic octahedral complexes reported herein possess very simple proton NMR spectra. Using the common numbering system shown below



one sees three signals downfield from TMS in each complex. The 1-H proton signal in all cases was found between 360 and 380 Hz downfield from TMS. This proton is in rapid exchange with the hydroxylic methanol proton and thus shifted only slightly from the normal resonance position of the latter.[11] Successive additions of complex (any of the three) to methanol-d_4 causes the OH impurity resonance to move slightly downfield, thus indicative of a negative contact shift for the 1-H proton in these three complexes. The two remaining resonances belong to the C–H protons. The smaller of the two in area is assigned to 2-H, while the larger is assigned to 4,5-H. Note that separate signals for 4,5-H are not observed because of rapid ligand tautomerism.[12] Spectra of the three complexes in the absence of excess ligand are shown in Figure 1.

For a metal ion complex in the presence of excess ligand as is the case discussed here, the chemical shift of the ith ligand proton is given by[1]

$$\nu(i) = X\Delta\nu(i) + \nu_r(i) \qquad (1)$$

where $\nu(i)$ is the observed chemical shift of the ith proton, X is the mole fraction of complexed ligand, $\Delta\nu(i)$ is the isotropic shift for the ith proton, and $\nu_r(i)$ the chemical shift in an appropriate diamagnetic reference. A plot of $\nu(i)$ vs. X,

Table I. Electronic Spectra of the Complexes[a]

Compound	State (concn, *M*)	Absorption max, cm^{-1}
$Ni(Im)_6(ClO_4)_2$	Nujol mull	10,500; 17,200; 27,800
	Methanol (0.068)	10,500; 13,200 (sh); 17,200; 27,800
$Co(Im)_6(ClO_4)_2$	Nujol mull	19,000 (sh); 20,600
	Methanol (0.070)	19,000 (sh); 20,400
$Fe(Im)_6(ClO_4)_2$	Nujol mull	11,100
	Methanol (0.070)	11,100

[a] The solution spectra for the above complexes were run in the presence of a fivefold excess of imidazole.

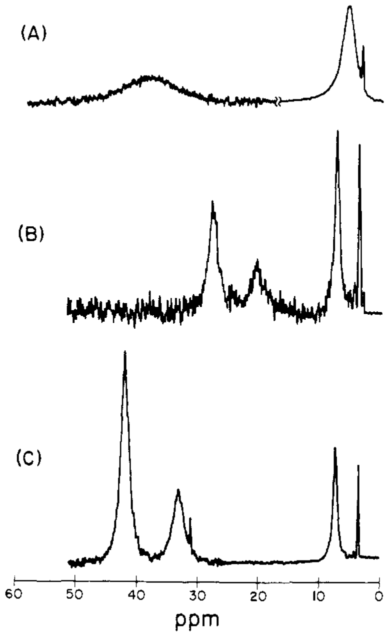


Figure 1. NMR spectra of (A) $Ni(Im)_6(ClO_4)_2$, (B) $Fe(Im)_6(ClO_4)_2$, and (C) $Co(Im)_6(ClO_4)_2$ in methanol-d_4 at 35°.

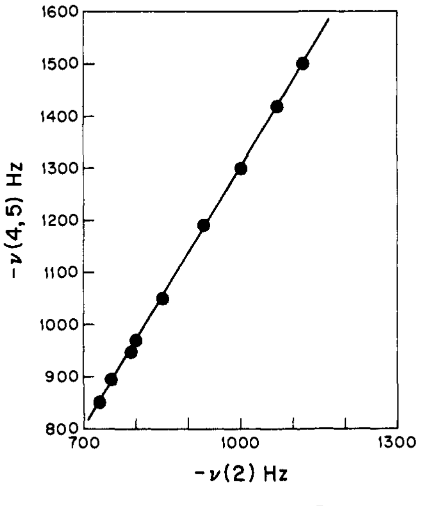


Figure 2. Plot of $\nu(4,5)$ vs. $\nu(2)$ for $Fe(Im)_6(ClO_4)_2$.

has as the slope $\Delta\nu(i)$ – the isotropic shift. Thus by plotting $\Delta\nu(4,5)$ or $\Delta\nu(2)$ vs. X, the respective isotropic shifts can be determined for these imidazole complexes. The only experimental difficulty with this method is the uncertainty in X which may result from weighing out small quantities of complex and ligand to accommodate the normally small solution volumes when using deuterated solvents. Rather than relying exclusively on the above method for generating proton isotropic shifts, we have also used a successive additions method which when applicable is experimentally much easier than the mole fraction plot. This is illustrated below for $Fe(Im)_6^{2+}$.

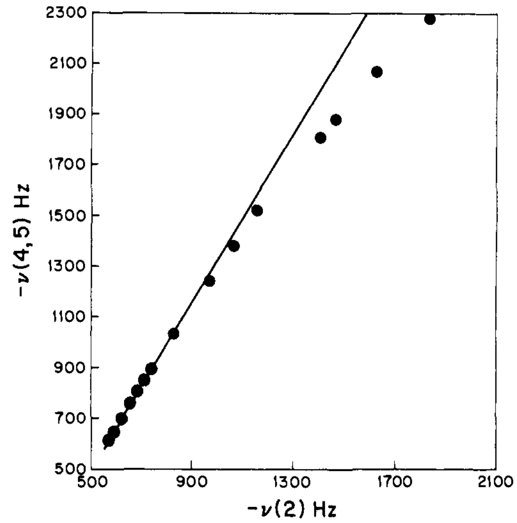


Figure 3. Plot of $\nu(4,5)$ vs. $\nu(2)$ for $Co(Im)_6(ClO_4)_2$.

$Fe(Im)_6^{2+}$. Isotropic Shifts. The isotropic shifts for 4,5-H and 2-H were determined by a method of successive additions. The NMR spectrum of $Fe(Im)_6^{2+}$ in methanol-d_4 was first recorded. A small amount of ligand (unweighed) was added directly to the NMR tube and the spectrum was recorded again. This procedure was continued thus yielding a set of NMR spectra having varied ligand concentration. The chemical shifts for 4,5-H and 2-H are expressed as follows

$$\nu(4,5) = X\Delta\nu(4,5) + \nu_r(4,5) \qquad (2)$$

$$\nu(2) = X\Delta\nu(2) + \nu_r(2) \qquad (3)$$

Combining eq 2 and 3 with the elimination of X yields

$$\nu(4,5) = \left[\frac{\Delta\nu(4,5)}{\Delta\nu(2)}\right]\nu(2) - \left[\frac{\Delta\nu(4,5)}{\Delta\nu(2)}\right]\nu_r(2) + \nu_r(4,5) \qquad (4)$$

Thus a plot of $\nu(4,5)$ vs. $\nu(2)$ should be linear with a slope of $\Delta\nu(4,5)/\Delta\nu(2)$ if fast exchange is occurring and the only paramagnetic species present in solution is $Fe(Im)_6^{2+}$. This is shown in Figure 2. A least-squares computer fit[13] for the data gives $\Delta\nu(4,5)/\Delta\nu(2) = 1.664 \pm 0.014$. The point for $Fe(Im)_6^{2+}$ (no ligand added) is very close to this line, hence we estimate that $\Delta\nu(4,5) = -1220$ Hz and $\Delta\nu(2) = -750$ Hz.[14] This is of sufficient accuracy for the purpose of this study.

$Co(Im)_6^{2+}$. Isotropic Shifts. Using the successive additions methods first, a distinct curvature was found in the $\nu(4,5)$ vs. $\nu(2)$ plot which is indicative of ligand displacement by solvent at low excess ligand concentrations. The plot is shown in Figure 3. In the linear region a least-squares analysis gives $\Delta\nu(4,5)/\Delta\nu(2) = 1.624 \pm 0.012$. Since the isotropic shifts were needed and the point for $Co(Im)_6^{2+}$ was far removed from the linear portion of the graph, a mole fraction plot was done. This is shown in Figure 4. A least-squares analysis gives $\Delta\nu(4,5) = -2250 \pm 45$ Hz, $\Delta\nu(2) = -1391 \pm 35$ Hz, and $\Delta\nu(4,5)/\Delta\nu(2) = 1.618$

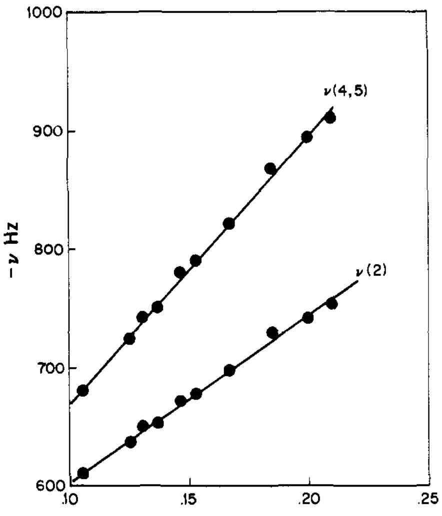


Figure 4. Plot of the mole fraction of imidazole complexed to Co^{2+} $\nu(4,5)$ and $\nu(2)$ for solutions containing $Co(Im)_6(ClO_4)_2$ in the presence of excess imidazole.

± 0.073. Obviously a successive additions plot is more precise and experimentally much simpler if one needs only relative isotropic shifts.

$Ni(Im)_6{}^{2+}$. Isotropic Shifts. The NMR spectrum of $Ni(Im)_6{}^{2+}$, shown in Figure 1, is characterized by broad and overlapping resonances for the 4,5-H and 2-H protons. Neither a successive addition or mole fraction plot will be of any value since addition of ligand can not resolve the overlap. We have, however, been able to get approximate isotropic shifts for $Ni(Im)_6{}^{2+}$ by using $Co(Im)_6{}^{2+}$ as a shift reagent in the presence of excess imidazole. For the three-component system, $\nu(i)$ is given by equation 5. For each

$$\nu(i) = X_{\mathrm{Co}}\Delta\nu_{\mathrm{Co}}(i) + X_{\mathrm{Ni}}\Delta\nu_{\mathrm{Ni}}(i) + \nu_{\mathrm{r}}(i) \qquad (5)$$

NMR spectrum, each component was first weighed so that the mole fractions could be calculated. The isotropic shifts, $\Delta\nu_{\mathrm{Co}}(i)$, used for $Co(Im)_6{}^{2+}$ were those determined above. The mole fraction plots of $\nu(i) - X_{\mathrm{Co}}\Delta\nu_{\mathrm{Co}}(i)$ vs. X_{Ni} are shown in Figure 5. Of necessity the spectra could be run only in a narrow concentration range. Too much $Ni(Im)_6{}^{2+}$ caused serious overlap of the resonances while too little imidazole could result in solvent displacement of the coordinated imidazole. The least-squares analysis yields $\Delta\nu(4,5) = -1910 \pm 160$ Hz, $\Delta\nu(2) = -1737 \pm 11$ Hz, and $\Delta\nu(4,5)/\Delta\nu(2) = 1.100 \pm 0.099$.

The Dipolar Shift. Of the three complexes reported herein, all should have zero dipolar shifts if the complexes are perfect octahedra.[15,16] Most likely, however, there may be small distortions present which remove the O_h symmetry in favor of a lower symmetry, for example D_{4h} or D_{3d}. In either of these axial symmetries, six-coordinate nickel(II) complexes, $Ni(Im)_6{}^{2+}$ included, are expected to have negligible dipolar shifts. Likewise in D_{4h} symmetry resulting from small tetragonal distortions, dipolar shifts should be absent for $Fe(Im)_6{}^{2+}$ and $Co(Im)_6{}^{2+}$ assuming a dynamic distortion with respect to the three principal axes or assuming rapid ligand exchange in the presence of excess ligand.[15,16] In contrast, in D_{3d} symmetry resulting from a trigonal distortion, dipolar shifts are to be expected for both $Fe(Im)_6{}^{2+}$ and $Co(Im)_6{}^{2+}$; i.e., there is no dynamic process equivalent to that in D_{4h} symmetry which will average the dipolar shift to zero save a dynamic distortion in which the complexes oscillates in solution alternately between a squashed and elongated octahedron. Assuming the unlikelihood of such a dynamic process occurring, we shall now estimate the magnitude of dipolar shifts in a trigonally distorted octahedral complex, namely $Co(Im)_6{}^{2+}$.

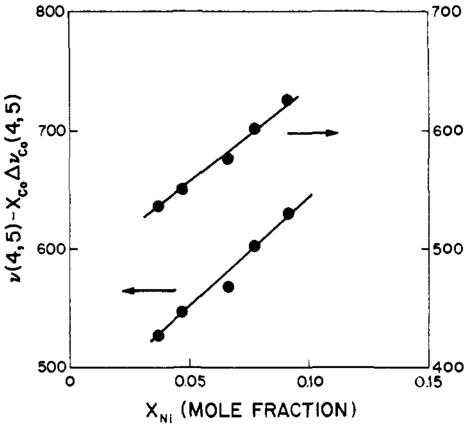


Figure 5. Plot of the mole fraction of imidazole complexed to Ni^{2+} vs. the term $\nu(4,5) - X_{\mathrm{Co}}\Delta\nu_{\mathrm{Co}}(4,5)$ for solutions containing $Co(Im)_6(ClO_4)_2$ and $Ni(Im)_6(ClO_4)_2$ in the presence of excess imidazole.

In the solid state the magnetic properties and electronic spectrum of $Co(Im)_6(NO_3)_2$ have been studied quite thoroughly by Gerloch and Quested.[4] They find that this complex is isomorphous with $Ni(Im)_6(NO_3)_2$ for which the X-ray crystal structure shows a trigonally distorted octahedron.[17] The electronic spectra of $Co(Im)_6(NO_3)_2$ is interpreted assuming a D_{3d} crystal field potential, and the trigonal distortion is estimated to be quite small: $1.2° \leq |\phi - \phi_{\mathrm{oct}}| \leq 0.8°$, where ϕ is the angle between the metal-nitrogen vector and the threefold axis. Also the single-crystal magnetic susceptibility was reported as a function of temperature over the range 80-300°K.[4]

Using the above data and assuming a static trigonal distortion for $Co(Im)_6{}^{2+}$, it is quite easy to calculate dipolar shifts for the distortions postulated above. It must be stressed, however, that we are assuming a structure in solution for $Co(Im)_6{}^{2+}$, namely that of a trigonally distorted octahedron, by relying on the solid state evidence.[4] Naturally this assumption cannot be proven but this does not detract from using $Co(Im)_6{}^{2+}$ as a paradigm for evaluating the effect of trigonal distortions on the isotropic shift and from using its known single-crystal magnetic susceptibility for the calculation of dipolar shifts.

The dipolar shift equation for any proton is given by[18]

$$(\Delta\nu_{dip}/\nu) = -\frac{1}{3N}(\chi_{\parallel} - \chi_{\perp})\frac{(3\cos^2\theta - 1)}{R^3} \qquad (6)$$

Here θ is the angle between the metal–proton vector and the C_3 axis while R is the length in centimeters of the metal–proton vector. The magnetic susceptibilities $\chi_{\parallel}$ and $\chi_{\perp}$, are in van vlecks per mole units. The above equation is commonly used for octahedrally coordinated cobalt(II) complexes,[19,20] where T_{1e}, the electronic spin lattice relaxation time, is typically much shorter than τ_c, the rotational correlation time for molecular tumbling in solution and where $1/\tau_c \ll |E_{\parallel} - E_{\perp}|/h$, the Zeeman anisotropic energy.

The dipolar shift was calculated over a range of distortions by varying ϕ, the trigonal angle such that $0 < \phi < 90°$. The normal model for a trigonal distortion is shown in Figure 6. In this model both θ and R change with ϕ. The geometric factor $G(\theta,R) = \langle(3\cos^2\theta - 1)/R^3\rangle$ is given by the function

$$G(\theta,R) = \frac{(2z^2 - r^2)(3\cos^2\phi - 1)}{2(r^2 + z^2)^{5/2}} \qquad (7)$$

All terms are defined by Figure 7, and a derivation of eq 7 is presented in the Appendix. The variation of $G(\theta,R)$ with ϕ, the trigonal angle, is shown in Figure 8 for the 2-H pro-

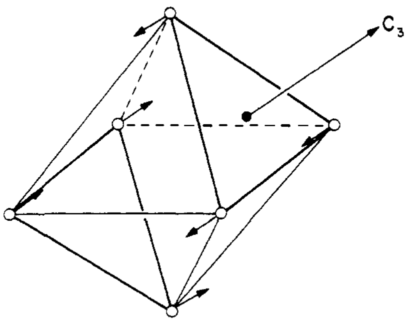


Figure 6. Model for a trigonal distortion showing a squashed octahedron.

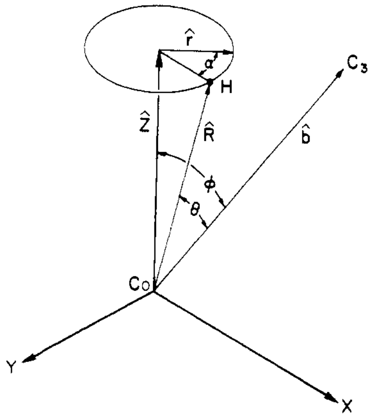


Figure 7. Geometric model for the calculation of the dipolar shift for $Co(Im)_6^{2+}$.

Table II. Isotropic Shift Components for Co $(Im)_6{}^{2+}$ [a]

ϕ	Proton	$\Delta\nu_{dip}/\nu$[b]	$\Delta\nu_{con}/\nu$	$\Delta\nu_{con}(4,5)/\Delta\nu_{con}(2)$
56.70	4,5-H	1.11	−38.61	1.566
	2-H	1.48	−24.66	
55.70	4,5-H	0.54	−38.04	1.591
	2-H	0.73	−23.91	
54.736	4,5-H	0	−37.50	1.618
	2-H	0	−23.18	
53.70	4,5-H	−0.58	−36.92	1.649
	2-H	−0.79	−22.39	
52.70	4,5-H	−1.12	−36.38	1.683
	2-H	−1.56	−21.62	

[a] All shifts are in parts per million relative to the appropriate proton resonance in imidazole. [b] The dipolar shifts were calculated at 35° with $\chi_{\parallel} = 12{,}030$ VVk/mol and $\chi_{\perp} = 9{,}550$ VVk/mol.[4] The solution magnetic susceptibility at 35°, measured by Evans' method is 10,650 VVk/mol, which is in agreement with the solid state average of 10,380 VVk/mol.

ton of $Co(Im)_6^{2+}$. A similar shaped curve is obtained for 4,5-H. Bond distances and angles necessary for calculating $G(\theta,R)$ were estimated from the X-ray structural determination of the related $Ni(Im)_6(NO_3)_2$.[17] Also shown in Figure 8 is the variation of $\Delta\nu_{dip}/\nu$ with ϕ over the range $0 < \phi < 90°$.

Of interest is the magnitude of the dipolar shift as compared to the contact shift for the protons in $Co(Im)_6^{2+}$. Considering here only small trigonal distortions, we present such a comparison in Table II for the 2-H and 4,5-H protons. It is evident that for the small trigonal distortions of the magnitude in Table II, the dipolar shift is only a minor component—less than 10%—of the isotropic shift. This is really not unexpected since one anticipates $G(\theta,R)$ to be very small in magnitude near $\phi = 54.7°$. It seems reasonable then, in the absence of evidence to the contrary, that for complexes of "near O_h" symmetry such as $Co(Im)_6^{2+}$, dipolar shifts should be quite small in the case of trigonal or tetragonal distortions whether static or dynamic.

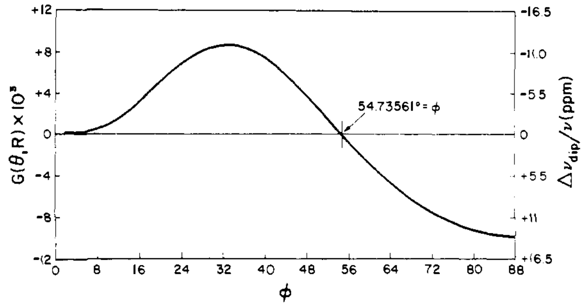


Figure 8. Plot of the geometric factor $G(\theta,R)$ and the dipolar shift, $\Delta\nu_{dip}/\nu$, vs. the trigonal angle ϕ for the 2-H proton in $Co(Im)_6^{2+}$.

Although the X-ray crystal structure and magnetic anisotropy are not known for $Fe(Im)_6^{2+}$, one would expect the above conclusions to be similarly valid for iron(II) complexes of "near O_h" symmetry; i.e., the dipolar contribution to the isotropic shift is negligible.

Most significantly it appears that the isotropic shift ratios in the above complexes, whether iron(II), cobalt(II), or nickel(II), show $|\Delta\nu(4,5)| > |\Delta\nu(2)|$. In contrast to the above three octahedral imidazole complexes which have negligible dipolar shift contributions, two imidazole complexes are known wherein substantial dipolar shifts are to be expected. For both $Co(acac)_2 \cdot 2Im$[21] and $[TPPFe(Im)_2]Cl$[22] respectively high spin cobalt(II) and low spin iron(III) complexes, a different isotropic shift pattern is observed. Here $|\Delta\nu(2)| > |\Delta\nu(4,5)|$ as would be expected for imidazole complexes with a substantial magnetic anisotropy and dominating dipolar shift contribution.[23] It seems then that the isotropic shift pattern of coordinated imidazole might very well be used as a qualitative sensor of magnetic anisotropy. This would be of particular importance in biochemically important model complexes where imidazole is coordinated to paramagnetic metal ions.

Contact Shifts. Of immediate concern is the fact that the contact shift ratio $\Delta\nu(4,5)/\Delta\nu(2)$ for $Ni(Im)_6^{2+}$ is distinctly different from that for $Co(Im)_6^{2+}$ (see Table II). There has been considerable debate[15,20,24-26] as to whether analogous cobalt(II) and nickel(II) complexes should and indeed do have identical spin-delocalization mechanisms. We do not wish to further extend these debates over the existent literature but instead would simply note that the above imidazole complexes represent a counter example to the frequent observation that delocalization mechanisms are identical in six-coordinate cobalt(II) and nickel(II) complexes. More studies with complexes of near O_h symmetry, where dipolar shifts are minimal, are clearly needed if we are to learn more about relative delocalization mechanisms in cobalt(II) and nickel(II).

In an attempt to identify the mode of spin delocalization in these imidazole complexes we have carried out open shell INDO molecular orbital calculations[27] on imidazole with a carbon atom substituted at the three position. This gives a σ-radical and is analogous to using the phenyl radical as a model for pyridine.[6,7] The resulting s orbital spin densities are $\rho(2) = 0.0101$, $\rho(4) = 0.0196$, $\rho(5) = 0.0121$, and $\rho(4,5)/\rho(2) = 1.56$. This should be compared to the isotropic shift ratios in Table III. Because of the reasonable agreement between the experimental and calculated ratios, it is clear that all three metal complexes to a great degree in-

Table III. Isotropic Shifts (Hz) for Octahedral Imidazole Compexes

Complex	$\Delta\nu(4,5)$	$\Delta\nu(2)$	$\Delta\nu(4,5)/\Delta\nu(2)$
$Fe(Im)_6{}^{2+}$	−1220	−750	1.664
$Co(Im)_6{}^{2+}$	−2250	−1391	1.624
$Ni(Im)_6{}^{2+}$	−1910	−1737	1.100

volve σ-spin delocalization. It would be impossible, however, considering the nature of the calculations, to go further and specify whether spin delocalization in $Ni(Im)_6{}^{2+}$, for example, were 100 or 90%, etc. At best what can be said is that the mechanism for $Ni(Im)_6{}^{2+}$ is different from that in both $Co(Im)_6{}^{2+}$ and $Fe(Im)_6{}^{2+}$, and that one might expect $Ni(Im)_6{}^{2+}$ to "predominantly" utilize σ-spin delocalization because its unpaired spin residues in the e_g (σ-bonding) subset only. One would expect more π-delocalization in $Co(Im)_6{}^{2+}$ and $Fe(Im)_6{}^{2+}$ since both have unpaired spin in the t_{2g} subset.

It is interesting to compare contact shifts for $Ni(py)_6{}^{2+}$ and $Ni(Im)_6{}^{2+}$ since both ligands are planar, aromatic, and imine nitrogen donors. In both cases using INDO molecular orbital calculations,[6,7] the contact shifts can be adequately explained by σ-delocalization as one would expect for a metal ion with a $(t_{2g})^6(e_g)^2$ configuration. The related nitrogen donor complexes $Ni(bipy)_3{}^{2+}$ and $Ni(phen)_3{}^{2+}$, however, are different in that both σ- and π-delocalization are allowed in D_3 symmetry.[8,28,29] Using the less reliable extended Hückel calculations, the contact shifts at all four proton positions could not be adequately explained solely by σ-delocalization. In these cases some π-delocalization or spin polarization was proposed to occur simultaneously with the dominant σ-delocalization mechanism.[8,9] It remains to be seen whether this conclusion about $Ni(bipy)_3{}^{2+}$ and $Ni(phen)_3{}^{2+}$ can still be justified using INDO molecular orbital calculations.

Appendix

Using Figure 7, the geometric factor $G(\theta,R)$ for the imidazole protons can be calculated as follows. Let $\mathbf{R} = \langle r\cos\alpha, \sin\alpha, z\rangle$, $\mathbf{b} = \langle\sin\phi, 0, \cos\phi\rangle$, and $\|b\| = 1$. It follows that

$$\cos\theta = \frac{\mathbf{a}\cdot\mathbf{b}}{\|a\|\cdot\|b\|} \tag{1}$$

$$= \frac{r\cos\alpha\sin\phi + z\cos\phi}{(r^2 + z^2)^{1/2}} \tag{2}$$

$$\langle\cos^2\theta\rangle = \int_0^{2\pi} \frac{(r^2\cos^2\alpha\sin^2\phi + 2rz \times \cos\alpha\cos\phi\sin\phi + z^2\cos^2\phi)\mathrm{d}\alpha}{2\pi(r^2 + z^2)} \tag{3}$$

$$= \frac{r^2 - \cos^2\phi(r^2 - 2z^2)}{2(r^2 + z^2)} \tag{4}$$

$$G(\theta,R) = \left\langle\frac{3\cos^2\theta - 1}{R^3}\right\rangle = \frac{3\langle\cos^2\theta\rangle - 1}{(r^2 + z^2)^{3/2}} \tag{5}$$

$$= \frac{(2z^2 - r^2)(3\cos^2\phi - 1)}{2(r^2 + z^2)^{5/2}} \tag{6}$$

References and Notes

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