# Nuclear Magnetic Resonance Contact Shifts and Delocalization Mechanisms in Octahedral Nickel(II) Complexes

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**Abstract:** The nmr contact shifts of the octahedral Ni(II) complexes of pyridine, 3-methylpyridine, 4-methylpyridine, and 4-vinylpyridine have been determined. In an attempt to interpret the delocalization mechanism, self-consistent charge, extended Hückel molecular orbital calculations have been carried out on these ligands, and the electron–proton coupling constants have been calculated from the eigenvectors. This series of ligands provides us with a large number of proton-contact shifts enabling us to determine the amount of spin delocalization in a quantitative manner, as well as providing numerous checks on this method. The observed coupling constants require both $\sigma$ and $\pi$ delocalization. In this paper we determine the magnitude of both $\sigma$- and $\pi$-spin delocalization and show that in pyridine such a mixture reproduces the observed coupling constants. This system, therefore, provides a good test of our procedure for the quantitative interpretation of spin delocalization.

In recent years nmr contact shifts have attracted considerable interest and there have been many successful applications of this technique to problems in inorganic chemistry. The early interpretations of the shifts in terms of metal–ligand $\pi$ back bonding[2-4] have been shown to be questionable,[5a,b] and the potential for gaining information about metal–ligand bonding has not been fully realized. Only in one instance has a calculation been carried out on the entire complex and the spin densities correlated with the molecular orbital output.[6] Furthermore, there has been relatively little quantitative work done on mechanisms for spin delocalization in the ligand. The typical qualitative approach involves selecting a ligand with several different protons and inferring whether $\sigma$ or $\pi$ or some combination of these types of ligand orbitals accounts for the sign and attenuation observed in the nmr shifts. These conclusions are substantiated by substituting $-CH_3$ or $-C_6H_5$ groups at appropriate positions in the molecule and noting the direction the protons in these groups shift.[7]

We have had considerable success in calculating spin densities at protons and nitrogen atoms in a whole series of organic free radicals.[8-10] The agreement between the experimental hyperfine coupling constant and calculated values for spin density has been excellent. Except for those systems where the McConnell relation is obeyed[11] we have not been able to handle negative spin densities. This success has encouraged us to attempt a quantitative interpretation of nmr contact shifts. The requirement for such an analysis to be valid is that there be more protons in the ligands whose shifts are measured than there are unknowns, *i.e.*, molecular orbitals involved in the spin delocalization and the $g_{\parallel} - g_{\perp}$ contribution to the pseudocontact shift. One such successful quantitative calculation involved the octahedral Ni(II) complexes of methylamine and ethylamine.[12] While this system meets the above requirements, only one proton is left over as a check on the calculation. In addition this system involves only one mechanism, namely a $\sigma$ delocalization. Therefore, we were interested in testing our calculations on a system where more checks were available and where the delocalization mechanism might involve both $\sigma$ and $\pi$ orbitals. To this end we decided to investigate the six-coordinate Ni(II) complexes of pyridine and substituted pyridines. We selected the Ni(II) system because Ni(II) has a $^3A_{2g}$ ground state and in octahedral symmetry there is no possibility of pseudocontact shifts. Thus all shifts observed can be attributed to the contact shift and can be rationalized in terms of unpaired electron delocalization.

Nuclear magnetic resonance contact shifts of pyridine coordinated to Ni(II) were first reported by Happe and Ward[13] in 1963. These workers reported the relative contact shifts of pyridine, 4-methylpyridine, and 3-methylpyridine, coordinated to nickel acetylacetonates. They observed downfield shifts which became smaller as one moves away from the nitrogen donor site. This pattern, attenuating downfield shifts, has become the standard model for contact shifts caused by a $\sigma$-delocalization mechanism. In six-coordinate Ni(II), where the two unpaired electrons are in $e_g$ orbitals which have $\sigma$ symmetry, one indeed expects $\sigma$ delocalization. However, Happe and Ward also reported that the methyl group in 4-methylpyridine shifted upfield, which they suggested is indicative of a $\pi$-delocalization mechanism. Holm, Everett, and Horrocks[14] also reported an upfield shift for the methyl proton in pseudotetrahedral diiodobis(4-methylpyridine)nickel(II). Since

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(1) Abstracted in part from the Ph.D. Thesis of R. E. Cramer, University of Illinois, 1969; University of Illinois Fellow, 1965–1966; Dow Chemical Co. Fellow, 1966–1967; National Institutes of Health Predoctoral Fellow, 1967–1969.

(2) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, 37, 347 (1962).

(3) G. N. LaMar, W. D. Horrocks, Jr., and L. C. Allen, *ibid.*, 41, 2126 (1964).

(4) E. A. LaLancette and D. R. Eaton, *J. Amer. Chem. Soc.*, 86, 5145 (1964).

(5) (a) R. J. Fitzgerald and R. S. Drago, *ibid.*, 89, 2879 (1967); (b) R. W. Kluiber and W. D. Horrocks, Jr., *Inorg. Chem.*, 6, 430 (1967).

(6) M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, 91, 3432 (1969).

(7) See, for example R. W. Kluiber and W. D. Horrocks, Jr., *ibid.*, 87, 5350 (1965).

(8) R. S. Drago and H. Petersen, Jr., *ibid.*, 89, 3978 (1967).

(9) R. S. Drago and H. Petersen, Jr., *ibid.*, 89, 5774 (1967).

(10) R. E. Cramer and R. S. Drago, *ibid.*, 90, 4790 (1968).

(11) H. M. McConnell, *J. Chem. Phys.*, 24, 632, 764 (1956).

(12) R. J. Fitzgerald and R. S. Drago, *J. Amer. Chem. Soc.*, 90, 2523 (1968).

(13) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, 39, 1211 (1963).

(14) R. H. Holm, G. W. Everett, and W. D. Horrocks, *J. Amer. Chem. Soc.*, 88, 1071 (1966).

Table I. Electronic Spectral Data

| Ligand | Solvent | Assignment | $\nu$, cm$^{-1}$ | $\epsilon$ (max) | Ref |
|---|---|---|---|---|---|
| Pyridine | $CH_3NO_2$ | $^3A_{2g} \rightarrow {}^3T_{2g}$ | 9,880 | 9 | 15 |
| | | $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) | 16,500 | 15 | |
| | | $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) | 26,670 | 31 | |
| Pyridine | Propylene carbonate | $^3A_{2g} \rightarrow {}^3T_{2g}$ | 9,660 | 4 | This work |
| | | $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) | 16,500 | 11 | |
| | | $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) | 26,670 | 26 | |
| 4-Vinylpyridine | Propylene carbonate | $^3A_{2g} \rightarrow {}^3T_{2g}$ | 9,760 | 4 | This work |
| | | $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) | 16,500 | 12 | |
| | | $^3A_{2g} \rightarrow {}^3T_{2g}$ (P) | *a* | | |
| 3-Methylpyridine | Propylene carbonate | $^3A_{2g} \rightarrow {}^3T_{2g}$ | 9,710 | 5 | This work |
| | | $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) | 16,500 | 12 | |
| | | $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) | 26,670 | 30 | |
| 4-Methylpyridine | Propylene carbonate | $^3A_{2g} \rightarrow {}^3T_{2g}$ | 9,760 | 4 | This work |
| | | $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) | 16,500 | 13 | |
| | | $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) | 26,800 | 35 | |

[a] Obscured by charge-transfer band.

$\pi$ delocalization is quite possible in tetrahedral Ni(II) complexes, these authors concluded that some $\pi$ delocalization occurred in $NiI_2(4pic)_2$, but that the $\sigma$ delocalization was dominant. They were unable to calculate the observed shifts using the extended Hückel method with any combination of $\sigma$- and $\pi$-delocalization mechanisms.

In both of the above cases, the authors assumed, but did not demonstrate, that pseudocontact shifts were absent. Yet pseudocontact shifts are expected for tetrahedral Ni(II) complexes and are possible in distorted octahedral Ni(II) complexes. With this in mind, it is possible to conclude that pseudocontact shifts are responsible for the upfield shift of the methyl group in these studies. Thus, in addition to calculating spin densities we were interested in learning whether an upfield shift would occur at the methyl group in the octahedral complex $Ni(4pic)_6^{2+}$. An upfield shift in this compound would indicate that some type of $\pi$ delocalization indeed occurs in these complexes and would imply that pseudocontact shifts in $Ni(AA)_2(4pic)_2$ are not dominating the shift at the methyl group.

## Experimental Section

**Reagents.** Pyridine, 4-methylpyridine, 3-methylpyridine, and 4-vinylpyridine were distilled and stored over Linde4A mole cular sieves. 4-Vinylpyridine, which decomposes in a few days, was used immediately after distillation.

**Preparation of Complexes.** All complexes were prepared by a previously described technique.[15] The complex $[Ni(4pic)_4](BF_4)_2$ is not moisture sensitive and may be handled in air. All other complexes rapidly add water and must be handled in a drybox.

*Anal.* Calcd for $[Ni(py)_4(ClO_4)_2]$: C, 41.81; H, 3.48; Ni, 10.23. Found: C, 41.96; H, 3.50; Ni, 10.19. *Anal.* Calcd for $[Ni(4pic)_4](BF_4)_2$: C, 47.66; H, 4.67; N, 9.27; Ni, 9.71. Found: C, 47.77; H, 4.73; N, 9.13; Ni, 9.71. *Anal.* Calcd for $[Ni(3pic)_4(ClO_4)_2]$: C, 45.75; H, 4.48; N, 8.89; Ni, 9.32. Found: C, 45.47; H, 4.72; N, 8.01; Ni, 9.59. *Anal.* Calcd for $[Ni(4\text{-}vinpy)_4ClO_4)_2]$: C, 49.50; H, 4.17; N, 8.26; Ni, 8.66. Found: C, 50.03; H, 4.35; N, 8.23; Ni, 8.48.

**Visible Spectral Measurements.** Electronic spectra were obtained with a Cary Model 14 recording spectrometer. The solutions in both the sample and reference beam contained the same concentration of excess pyridine.

**Nuclear Magnetic Resonance.** All nmr spectra were obtained from propylene carbonate solutions ranging from 0.1 to 0.01 *M* in complex, on a JEOLCO C-60-H high-resolution instrument at 30°. For each complex a series of spectra was obtained as a function of added free ligand. In all cases tetramethylsilane was used as an internal reference. The peaks were assigned by following the observed peak, which is an average of free and complexed pyridine peaks, as a function of increasing mole fraction of complexed ligand. The assignments are confirmed by the line widths, which are greatest for protons closest to the paramagnetic metal ion. Solution magnetic moments were obtained by the nmr method of Evans.[16]

**Calculations.** Extended Hückel molecular orbital calculations were carried out as previously described.[10] Electron–proton coupling constants were evaluated from the eigenvectors as described by Drago and Petersen.[8] A description of the treatment of results of the molecular orbital calculation is included in the Discussion.

## Results

The electronic spectra for the $NiL_6^{2+}$ complexes are reported in Table I.

The nmr contact shifts for these complexes are reported in Table II. These shifts were determined by plotting the observed shifts against the mole per cent of complexed ligand. All plots gave straight lines as required for one complex species undergoing rapid ligand exchange with excess ligand.[17a] The extrapolated values at $\chi_{\text{complex}} = 1.0$ were taken as the chemical shift of the complexed ligand protons. The contact shift is then determined by subtracting the diamagnetic ligand chemical shifts from the paramagnetic complexed ligand chemical shifts. These contact shifts were then converted into electron–proton coupling constants in gauss according to[17b]

$$A_i = -\frac{3g_n\beta_n kT\Delta H}{(g_{av})^2\beta_e^2 S(S+1)H_0}$$

where $g_n$ is the nuclear $g$ factor, $g_{av}$ is the average electronic $g$ factor, $\beta_e$ and $\beta_n$ are the Bohr and nuclear magnetons, $k$ is Boltzman's constant, $T$ is the absolute temperature, $\Delta H$ is the contact shift, and $H_0$ is the probe frequency.

## Discussion

**Structure of the Complexes in Solution.** Previous work has shown that $[Ni(py)_4X_2]$, where X is $ClO_4^-$ or

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(15) M. R. Rosenthal and R. S. Drago, *Inorg. Chem.*, **4**, 840 (1965).

(16) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(17) (a) An examination of the line width for the *meta* proton as a function of temperature indicates this system is in the near fast-exchange region. However, the shifts appear to follow Curie law behavior as well as most of these systems do and are apparently not yet being effected by exchange. This is consistent with a linear mole fraction plot. Although exchange effects are expected to be more serious at the *ortho* proton, the percentage error introduced should be smaller and well within our capability to fit A (0.02 g). (b) H. M. McConnell and D. Chestnut, *J. Chem. Phys.*, **28**, 107 (1958).

**Table II.** $NiL_6^{2+}$ Contact Shifts, Experimental Coupling Constants, and Calculated Coupling Constants

| | | | | A, G | | |
|---|---|---|---|---|---|---|
| | | | | | Calcd | |
| Ligand | $\mu_{eff}$ | | $\Delta\nu$, cps | Exptl | $\sigma + \pi^*$ | $\sigma + \pi^b$ |
| Pyridine | 3.21 | *o* | −3820 | +0.2499 | +0.2440 | +0.2482 |
| | | *m* | −1420 | +0.0929 | +0.0937 | +0.0988 |
| | | *p* | −445 | +0.0291 | +0.2686 | +0.2699 |
| 4-Methylpyridine | 3.07 | *o* | −4570 | +0.3272 | | |
| | | *m* | −1500 | +0.1074 | +0.1311 | +0.1375 |
| | | *p*-$CH_3$ | +422 | −0.0302 | | |
| 3-Methylpyridine | 3.04 | *o* | −4320 | +0.3153 | +0.3044 | +0.3180 |
| | | *m* | −1575 | +0.1150 | +0.1136 | +0.1240 |
| | | *p* | −450 | +0.0328 | +0.3388 | +0.3259 |
| | | *m*-$CH_3$ | −313 | +0.0228 | +0.0225 | +0.0060 |
| 4-Vinylpyridine | 3.18 | *o* | −2631 | +0.1754 | +0.1700 | +0.1746 |
| | | *m* | −1236 | +0.0824 | +0.0693 | +0.0733 |
| | | $H_3$[a] | −195 | +0.0130 | +0.0059 | +0.0073 |
| | | $H_2$[a] | +53 | −0.0035 | −0.0006 | −0.0017 |
| | | $H_1$[a] | −218 | +0.0145 | +0.0263 | +0.0195 |
| | | | | Av deviation | 0.0078 | 0.0096 |

[a] $H_1$ and $H_2$ are the *gem* protons with $H_2$ being *trans* to $H_3$.

$BF_4^-$, becomes $Ni(py)_6^{2+}$ when dissolved in nitromethane with excess pyridine added.[15] The similarity of the electronic spectra of $Ni(py)_6^{2+}$ in nitromethane and the electronic spectra of $[Ni(py)_4X_2]$ dissolved in propylene carbonate with excess pyridine added indicate that the species in propylene carbonate with excess pyridine added is indeed $Ni(py)_6^{2+}$. In addition the nmr contact shift mole fraction plots, which yield straight lines in the region $\chi_{complex} = 0.05$ to 0.70, provide additional support that only one species, $Ni(py)_6^{2+}$, exists in solution. Further, the resonances of complexed and free pyridine are separated at −40°. This enables one to determine the coordination number of the $Ni^{2+}$ ion by determining the area of the free and complexed pyridine peaks. This experiment was carried out with the 4-methylpyridine complex which is a favorable case since the complexed methyl peaks are relatively sharp and occur in an area free from other peaks. This experiment yielded a coordination number of $6.05 \pm 0.45$ for an average of six determinations.

Examination of the data in Table II shows that the methyl group in the complex $Ni(4pic)_6^{2+}$ does shift upfield. Since $Ni^{2+}$ in an octahedral environment has a $^3A_{2g}$ ground state there is no possibility for dipolar or pseudocontact shifts in this complex. Therefore, the upfield shift must arise from delocalization of unpaired electron in the $\pi$ orbitals of 4-methylpyridine. Further, since the methyl hydrogens in 4-methylpyridine contribute directly to both the $\pi$ bonding and $\pi$ antibonding orbitals of 4-methylpyridine, the upfield shift must be caused by delocalization of $\beta$ spin, or spin opposed to the field, in one or both of these orbitals. Having thus established that spin is delocalized in the $\pi$ system, we then attempted to calculate the amount of unpaired spin in the ligand $\sigma$ and $\pi$ orbitals.

It would be best if we could carry out calculations on the entire molecule, $Ni(L)_6^{2+}$. However, this molecule is too large for us to handle at this time and we are uncertain about the ability of the EHT procedure to give meaningful wave functions on systems with highly charged metal atoms. For these reasons we decided to perform calculations on the free ligand and to use the output to evaluate spin densities at the different protons in the various molecular orbitals. The experimental coupling constants determined for the protons are used to "weight" the various mechanisms and to provide a check on the method. The symmetry of the ligands and the complex is employed to ascertain which ligand molecular orbitals overlap which metal orbitals. The sign of spin delocalized into each ligand molecular orbital is determined as follows. If a ligand molecular orbital mixes with a metal orbital containing unpaired spin, then $\alpha$ spin is delocalized on the ligand. If a ligand molecular orbital mixes with a filled metal orbital, spin polarization on the metal delocalizes $\beta$ spin on the ligand. This procedure is valid as long as formation of the metal–ligand bond does not greatly perturb the ratio of the hydrogen coefficients of the free ligand in the molecular orbitals with which we are concerned. Since in nickel(II) complexes of $D_{4h}$ symmetry the ratios of the Fermi contact shifts for pyridine are often similar in different complexes, this is most likely a good approximation.

The basic geometry used in this work was that of pyridine reported by Bak.[18] We used methyl–ring C–C distances of 1.53 Å and methyl–C–H distances of 1.09 Å for both 4-methylpyridine and 3-methylpyridine. In the case of 4-vinylpyridine all bond angles were set at 120° and the bond lengths were: $C_{ring}$–$C_{vinyl}$ = 1.44 Å; $C_{vinyl}$–$C_{vinyl}$ = 1.34 Å; $C_{vinyl}$–$H_{vinyl}$ = 1.08 Å. In the two methylpyridines, two conformers of the methyl group were calculated; in one of these one C–H bond lies in a plane normal to the plane of the ring, and in the other one C–H bond lies in the plane of the ring. In the case of 4-vinylpyridine, two conformers, which corresponded to a fully planar molecule and to a molecule in which the ring plane is normal to the vinyl plane were calculated.

The $\sigma$-donor eigenvector for the various ligands obtained from these calculations was then used, as previously described,[8] to calculate the coupling constant which would result if one electron were delocalized into the $\sigma$ orbital. The equation used is $A_i(G) = (1887/2S)|\Psi(0)|^2$. $\pi$ coupling constants for the ring H's and the planar vinyl H's, resulting from one unpaired electron delocalized in the lowest antibonding orbital, and resulting from one unpaired electron delocalized in the highest

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(18) B. Bak, L. Hansen-Hygaard, and J. Rastrup-Andersen, *J. Mol. Spectrosc.*, 2, 361 (1958).

filled $\pi$ bonding orbital, were calculated using the McConnell relation

$$A_i\,(\mathrm{G}) = Q\rho_i/2S \qquad (2)$$

where $A_i$ is the coupling constant of proton i in gauss, $Q$ is a scaling factor in gauss for a $\beta$ spin,[19] and $\rho_i$ is the unpaired electron density in the $p_\pi$ orbital of the carbon to which $H_i$ is attached. The $\pi$ coupling constants for all the methyl hydrogens and the vinyl hydrogens in the nonplanar conformation of 4-vinylpyridine were evaluated by carrying out a $|\Psi(0)|^2$ analysis.[8] In all cases, the coupling constants obtained for each proton in each orbital were averaged over both conformations calculated. All three methyl hydrogen coupling constants in each orbital in each conformation were averaged to crudely account for free rotation of the methyl group. In the case of 4-vinylpyridine it is of particular interest that the two conformations show a total energy difference of only 0.1 kcal/mol. We have interpreted this to mean that free rotation of this group occurs in solution. Since we have $\alpha$ spin in the $\sigma$ orbital, those coupling constants are positive. On the other hand, $\beta$ spin in the $\pi$ orbitals produces negative coupling constants at the methyl hydrogens and nonplanar vinyl hydrogens and positive coupling constants at the ring hydrogens and the planar vinyl hydrogens. The results of this evaluation are listed in Table III.

**Table III.** Coupling Constants in Gauss for One Unpaired Electron in Various Orbitals of Pyridine Type Ligands

| Ligand | Position | A (G) | | |
|---|---|---|---|---|
| | | $\pi^b$ | $\sigma$ | $\pi^*$ |
| 4-Mepy | *o* | +1.75 | +7.23 | +2.92 |
| | *m* | +2.33 | +2.85 | +1.42 |
| | *p*-$CH_3$ | −6.80 | +0.11 | −4.31 |
| Py | *o* | +1.51 | +7.21 | +2.05 |
| | *m* | +1.60 | +2.75 | +0.87 |
| | *p* | +6.20 | +7.30 | +5.58 |
| 3-Mepy | *o* | +3.19 | +6.85 | +2.08 |
| | *m* | +2.70 | +2.50 | +1.07 |
| | *p* | +3.26 | +7.02 | +5.47 |
| | *m*-$CH_3$ | −4.17 | +0.63 | −0.49 |
| 4-Vinpy | *o* | +0.74 | +7.31 | +1.54 |
| | *m* | +1.76 | +2.90 | +0.95 |
| | $H_3$ | +1.49 | +0.13 | +0.70 |
| | $H_2$ | −1.96 | +0.16 | −1.43 |
| | $H_1$ | +1.06 | +0.70 | +2.44 |

Equipped with these coupling constants which would arise with one unpaired electron in each of several orbitals, we are now in a position to calculate the amount of unpaired electron delocalized into each of these orbitals. We do this by setting up simultaneous equations using the observed coupling constants for the *ortho* proton and the *para*-methyl protons of the 4-methylpyridine complex. As an example, we present the equations for the $\sigma$-donor orbital and the $\pi$-antibonding orbital.

$$\textit{ortho}:\ +0.3272 = +7.23x + 2.92y \qquad (3)$$

$$p\text{-methyl}:\ -0.0302 = +0.11x - 4.31y$$

Here $x$ represents the fraction of unpaired electron in the $\sigma$ orbital and $y$ represents the amount of unpaired electron in the $\pi$-antibonding orbital. Solution of this set of equations yields $x = 4.20 \times 10^{-2}$ and $y = 8.05 \times 10^{-3}$. A similar set of equations can be written for the $\sigma$-donor orbital and the $\pi$-bonding orbital. In this case the solution is $x = 4.40 \times 10^{-2}$, $z = 5.20 \times 10^{-3}$, where $z$ is the amount of electron in the $\pi$-bonding orbital. Attempts to reproduce the observed coupling constants with other combinations of orbitals gave negative values for $x$ or $y$ which is clearly impossible. In both cases, we note that the $\pi$ mechanism is about an order of magnitude less than the $\sigma$ mechanism. Since the amount of $\pi$ delocalization is so small, the $\pi$ contribution to the coupling constant is negligible at all positions except the *para* position in pyridine, the methyl group in 3-methylpyridine, and the vinyl protons in 4-vinylpyridine. The $\pi$ mechanism dominates at the methyl group in 4-methylpyridine and the proton *cis* to the ring, $H_2$, in 4-vinylpyridine.

In order to check the validity of this procedure we then calculated the coupling constants of the remaining protons using the values of $x$, $y$, and $z$ obtained above. For example, the *meta* coupling constant of 4-methylpyridine is given by *meta* $= 2.85(4.20 \times 10^{-2}) + 1.42\cdot(8.05 \times 10^{-3})$, $\sigma$ and $\pi^*$; and *meta* $= 2.85(4.40 \times 10^{-2}) + 2.33(5.20 \times 10^{-3})$, $\sigma$ and $\pi^b$. In order to obtain the calculated coupling constants for 3-methylpyridine we used the values of $x$, $y$, and $z$ determined for 4-methylpyridine. We feel that this is justified since the base strengths of 4-methylpyridine and 3-methylpyridine are quite similar[20] and since the values of $Dq$ in Table I are quite similar. However, pyridine and 4-vinylpyridine are weaker bases.[20] We expect that the amount of unpaired spin delocalized onto the ligand will be proportional to the base strength. Hence, we expect less electron to be delocalized onto pyridine and 4-vinylpyridine than onto 4-methylpyridine. In order to take account of the lessened delocalization in pyridine and 4-vinylpyridine, we reduced the values of $x$, $y$, and $z$ for these two ligands by the ratio of the experimental coupling constants for the *ortho* position. Thus, in the case of pyridine $x$, $y$, and $z$ were reduced by the factor 0.2499/0.3272, and for 4-vinylpyridine, $x$, $y$, and $z$ were reduced by the factor 0.1754/0.3272.

One would not necessarily expect the amount of $\sigma$- and $\pi$-unpaired electron delocalization to be reduced in the same ratio. We have arbitrarily reduced $x$, $y$, and $z$ by the same ratio in all cases, and this may account for the poorer though still good agreement for the vinyl protons of 4-vinylpyridine. In other words, $\pi$ delocalization may be relatively more important in 4-vinylpyridine than in the other ligands we have studied, so the $\pi$–$\sigma$ ratio should have been changed. In order to test this postulate, we wrote and solved simultaneous equations using the measured coupling constants for the *ortho* and vinyl protons of 4-vinylpyridine. This yielded new values of $x$, $y$, and $z$ which were used to calculate the coupling constants for the remaining protons of 4-vinylpyridine. The results are given in Table IV. The values of $x$, $y$, and $z$ used for 4-vinylpyridine in Table II were: $x = 2.25 \times 10^{-2}$, $y = 4.31 \times 10^{-3}$, $x' = 2.36 \times 10^{-2}$, and $z = 2.79 \times 10^{-3}$. Comparison of the numbers used to complete Table

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[19] We used a value of 38 G for $Q$, as determined by Petersen,[8] for the benzonitrile radical anion. We also find similar values for $Q$ in the $\pi$ anion radicals of nitrosobenzene, 2,2′-bipyridine, and pyridine.

[20] A. F. Garito and B. B. Wayland, *J. Amer. Chem. Soc.*, 91, 866, (1969).

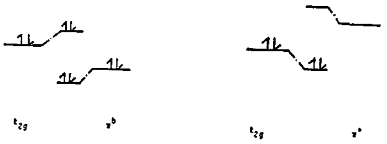

Figure 1. Diagram illustrating the interaction of a filled metal $t_{2g}$ orbital with the filled pyridine $\pi^b$ orbital, and with the empty $\pi^*$ orbital.

II with those used in Table IV shows that $\pi$ delocalization is slightly more important for 4-vinylpyridine than for 4-methylpyridine. Since the agreement between calculated and observed is nearly the same in both Tables II and IV, our procedure is not accurate enough to conclude that there is any difference in the amount of $\pi$ delocalization in 4-methyl- and 4-vinylpyridine. Our assumption of a constant $\sigma$–$\pi$ ratio appears to be justified within the accuracy of our treatment.

Table IV

| | A (G) | | |
|---|---|---|---|
| | | Calcd | |
| Position | Exptl | $\sigma + \pi^{*\,a}$ | $\sigma + \pi^{b\,b}$ |
| *meta* | +0.0824 | +0.0712 | +0.0747 |
| $H_3$ | +0.0130 | +0.0065 | +0.0086 |
| $H_1$ | +0.0145 | +0.0285 | +0.0204 |

[a] $x = 2.28 \times 10^{-2}$; $y = 5.13 \times 10^{-3}$. [b] $x' = 2.25 \times 10^{-2}$; $z = 3.67 \times 10^{-3}$.

Examination of Table II shows that both mechanisms, that is, a combination of $\sigma$- and $\pi$-antibonding delocalization or a combination of $\sigma$- and $\pi$-bonding delocalization, yield the correct sign in all cases and usually give an excellent estimation of the magnitude of the coupling constant. In addition, examination of all the data shows that both mechanisms reproduce the experimental coupling constants with about the same degree of accuracy. This fact makes it very difficult to decide which one of the two mechanisms is correct. The failure of this calculation to fit the *para* position of pyridine and 3-methylpyridine was expected since this type of calculation always predicts too great a coupling at the *para* position.[14,10,8,21,21a] Apparently this restriction does not apply to groups substituted in the *para* position since our results for the 4-methyl and 4-vinyl groups are very good. From the data available, we cannot determine which of the two types of $\pi$ delocalization is occurring, or whether both of them are occurring. We can say, however, that there is a small but significant amount of $\pi$ delocalization in these octahedral Ni(II) complexes.

In order to account for the $\pi$ delocalization which we observe, the following mechanism need be considered. The filled $t_{2g}$ orbitals of the metal can interact with either or both the $\pi$-bonding and $\pi$-antibonding orbitals of the ligand. The separate mechanisms are illustrated in Figure 1. We see that in both cases we have in the complex molecule a pair of electrons in a molecular orbital which is mostly an atomic orbital of the metal $t_{2g}$ set. The unpaired electrons in the metal $e_g$ orbitals will interact *via* spin exchange with this pair of electrons and cause an excess of $\alpha$ spin to build up on the metal. This will leave behind a small amount of $\beta$ spin distributed in the ligand molecular orbital. This mechanism is expected to be small, but we need only $10^{-3}$ unpaired electron in the ligand $\pi$ orbital to account for our observations. Also this mechanism predicts the observed $\beta$ spin in the $\pi$ orbitals.

## Conclusion

From our results, it appears that this type of treatment utilizing the crude extended Hückel approach is of considerable value in understanding the mechanism of spin delocalization in paramagnetic complexes. In addition we have shown that $\pi$ delocalization is indeed possible in octahedral Ni(II) complexes, although in the case of pyridine we are unable to tell whether the $\beta$ spin is in the highest bonding $\pi$ orbital, the lowest antibonding $\pi$ orbital, or both. In any case, the predominant delocalization is due to spin in the pyridine $\sigma$ donor orbital.

This work has shown that spin-delocalization mechanisms are considerably more complex than application of the simple qualitative arguments involving attenuation, or alternation of shifts might indicate. A detailed explanation of the spin delocalization in these systems which were thought to be simple $\sigma$ systems requires us to include a small but significant amount of $\pi$ delocalization. Since there is little reason to believe that pyridine is unique in this regard, we believe that mixed delocalization is probably quite common. Hence, papers which glibly rationalize contact-shift observation in terms of simple $\sigma$ or $\pi$ bonding are to be looked upon with caution. In order to say anything definite and significant about the spin delocalization in a certain complex we feel that it is necessary to carry out molecular orbital calculations on either the ligand or the entire complex.

It is also apparent from this work that electron exchange effects on the metal (*i.e.*, spin polarization) can be important and should not be overlooked.

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(21) G. A. Petersson and A. D. McLachlan, *J. Chem. Phys.*, **45**, 628 (1966).

(21a) NOTE ADDED IN PROOF. Kasai, *et al.*, have recently been successful in calculating the *para* coupling constant of the phenyl radical by using an INDO method. The small coupling constant at the *para* position is due to "spin polarization" of the lower filled orbitals. However, this "spin polarization" is only important at the *para* position: P. H. Kasai, E. Hedaya, and E. B. Whipple, *J. Amer. Chem. Soc.*, **91**, 4364 (1969).