Table IV. One-Electron Orbital Energies (ev) of HF_2^-

	$R_{FF'}$ = 2.49 A	$R_{FF'}$ = 2.79 A	ΔE
$E(2)$	−18.97	−18.93	−0.04
$E(7)$	−20.24	−20.26	0.02
$E(8)$	−36.37	−36.31	−0.06
$E(9)$	−36.92	−36.98	0.06
E_F	−19.28	−19.43	0.15
$E_{F'}$	−19.08	−18.93	−0.15

cates an "antibonding" interaction of the orbitals; a straight line connecting two ao's represents a bonding interaction. The mo's labeled ψ_7 and ψ_9 are bonding with respect to both H–F and H···F′; ψ_2 and ψ_8 are H···F′ bonding and H–F antibonding. The unoccupied fifth mo is not shown. This result is obtained whenever the HF′ distance is greater than the HF distance.

It may also be noted (from the magnitudes of the eigenvectors) that ψ_2 and ψ_8 correspond to "nonbonding" orbitals *in the sense that there is little hydrogen 1s involvement.* This description is misleading, however, since these orbitals contribute significantly to the HF, HF′ overlap populations and energies.

In Table IV are given the one-electron energies of the mo's for F–F′ internuclear distances of 2.49 and 2.79 A. The effect of shortening the F–F′ distance is as follows: ψ_2 is stabilized, ψ_7 is destabilized, ψ_8 is stabilized, ψ_9 is destabilized. The stabilization of the molecule by changes in ψ_2 and ψ_8 is larger than the destabilization of the molecule by ψ_7 and ψ_9. The change in H–F bond energy must then be less than the change in H···F′ bond energy. We note that the formation of the new bond is more important than destabilization of the old bond and this, of course, is the prime reason for stability of the hydrogen-bonded adduct. Note that ψ_7 and ψ_9 include contributions from the new bond as well as the original bond. Contributions from the strength of the new bond in these molecular orbitals are less than the destabilization of the original bond since the net change in energy of both of these molecular orbitals is in a positive direction.

A comment on the nonbonding $2p_x$, $2p_y$ orbitals can be made. The data in Table IV indicate that these filled nonbonding π-type orbitals on F are destabilized to the same extent that these nonbonding orbitals on F′ are stabilized (move to lower energy). The directions of the changes are a consequence of the decreasing negative charge on F′ and the increasing negative charge on F as $R_{FF'}$ is decreased.

Acknowledgment. The authors acknowledge the generous support of this research by the National Science Foundation through Grant GP-5498.

Contact-Shift Studies and Delocalization Mechanisms of Nickel(II)–Benzylamine Complexes

Ronald J. Fitzgerald[1] and Russell S. Drago

Contribution from the William Albert Noyes Laboratory, University of Illinois, Urbana, Illinois. *Received January 14, 1967*

Abstract: The proton nmr contact shifts of $[Ni(bz)_6]^{2+}$ (bz = benzylamine, $C_6H_5CH_2NH_2$) have been investigated to ascertain whether or not unpaired spin can be delocalized in the phenyl π system when the ligand–metal interaction is essentially σ. The amino, methylene, and aromatic protons are assigned in the nmr spectrum of the complex. The contact shifts and electron spin–nuclear spin coupling constants for these protons are reported. Results obtained from the nmr data show that electron spin is delocalized into the π system of the phenyl group of the ligand. Since the bonding to the ligand is σ, this study shows that contrary to several literature reports one may not assume *a priori* that π delocalization in a phenyl ring is evidence for metal–ligand π-type bonding. A delocalization mechanism which accounts for the observed shifts is presented. The complex with the formula $[Ni(bz)_5BF_4](BF_4)$ was isolated as a solid. Spectral and conductance data are presented to substantiate that $[Ni(bz)_6]^{2+}$ is the species present when the previously mentioned complex is dissolved in nitromethane solutions containing an excess of benzylamine.

The general theory and interpretation of nmr contact shifts has been extensively discussed in a previous publication from this laboratory[2] and should be consulted along with the references therein for background information. In this paper, we are specifically concerned with using both the signs and magnitudes of the contact shift for the ligand protons to deduce information about the metal–ligand bonding. The unpaired spin in most complexes is in a molecular orbital which is essentially a metal d orbital. The extent of mixing of the ligand orbitals with this essentially d metal orbital to form a nonbonding or antibonding mo is taken as an indication of the mixing of the d orbitals with the ligand orbitals in forming the bonding molecular orbital. Hence, by looking at the contact shift, one infers information about the bonding.

Happe and Ward[3] have found proton contact shifts indicating a σ mechanism for delocalizing spin onto pyridine. There have been many reports in the literature,

---

[1] Abstracted in part from the Ph.D. thesis of R. Fitzgerald, University of Illinois, 1968; National Institutes of Health Predoctoral Fellow, 1966–1967.

[2] B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **87**, 2372 (1965).

[3] J. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

for example, the work of Eaton, *et al.*,[4] on the aminotroponeimineates, where unpaired electron density is delocalized into the π orbitals of conjugated ligands. The authors concluded from this study that there was considerable metal–ligand π bonding. Similarly, the magnitude and direction of the phenyl proton shifts were taken to indicate delocalization of spin into the π obitals of complexed $(C_6H_5)_3P$ in $(R_3P)_2MX_2$ complexes.[5,6] Similar shifts are found for $[Ni(C_6H_5CN)_6]^{2+}$.[7] These observations were taken as an indication of metal–ligand $d\pi$–$d\pi$ bonding in the phosphine complexes and π bonding in the nitrile complexes.

In the above ligands, the unpaired spin in the π orbitals is transmitted from aromatic ring π orbitals to the protons which are orthogonal to these π orbitals by an atomic exchange coupling mechanism.[8] Levy has proposed[9] that when a methylene group is attached to an aromatic ring, a linear combination of the atomic 1s orbitals of the methylene protons form pseudo-π-type orbitals and interact directly with the ring carbon p_z orbitals. Thus spin is placed directly on the methylene protons through a hyperconjugative-type mechanism. By considering the operation of these mechanisms in reverse, one could place unpaired spin in the π system of the ligand, even though the metal–ligand bond is primarily a σ bond.

In the $(C_6H_5)_3P$ complex, the phenyl π orbitals are not orthogonal to the phosphorus lone pair, and, if spin were placed on phosphorus by a σ interaction with the metal, it could be placed in the π system by a mechanism similar to that discussed for the methylene group above. In the case of the benzonitrile ligand, spin placed on the nitrogen by a σ interaction could enter the π system by an atomic exchange coupling mechanism similar to that discussed above for protons which are orthogonal to aromatic rings. These arguments, in principle, would offer an alternative explanation to the triphenylphosphine and benzonitrile contact shifts in the nickel(II) complexes and would cast doubt upon the previously cited conclusions regarding π-type metal–ligand bonding. It is difficult to sort out the reported interpretations and the alternatives offered here in the above complexes. In an attempt to ascertain whether or not the alternatives we have offered here are operative, we decided to investigate the contact shifts in $[Ni(bz)_6]^{2+}$.

Mixed anion–neutral ligand complexes with benzylamine have been previously reported.[10–12] However, we could find no previous report of the preparation of $[Ni(bz)_6]^{2+}$ which is described here.

Experimental Section

Apparatus. a. Nmr Spectra. The nmr spectra were obtained with Varian Models A-60A, A-56-60, and DP-60 spectrometers. All nmr spectra were measured relative to TMS as an internal standard.

b. Visible and Near-Infrared Spectra. All near-infrared and visible spectra were determined using a Cary recording spectrophotometer, Model 14.

c. Conductance Data. The conductance measurements were made on an Industrial Instruments conductivity bridge, Model RC 16B2.

d. Magnetic Susceptibility Measurements. The solution moment was determined by nmr at 28° using a method first reported by Evans.[13] The measured susceptibilities were corrected for diamagnetism by the use of Pascal's constant.[14,15]

Reagents and Solutions. Hydrated nickel(II) tetrafluoroborate (Alfa Inorganics), anhydrous reagent grade diethyl ether, and reagent grade methanol were used without further purification.

Matheson benzylamine was distilled from BaO under reduced pressure, a constant-boiling middle fraction being selected for use. Aldrich *p*-methylbenzylamine was purified in a similar manner. The ligands were stored in a desiccator containing P_2O_5.

Fisher reagent grade nitromethane was dried over Linde 3A Molecular Sieves for at least 24 hr.

All additions of ligand were carried out in a drybox equipped with an automatic continuous air flow drying system. When accurate complex concentrations were necessary the materials were weighed in stoppered volumetric flasks and addition of ligand was accomplished by use of Hamilton microliter syringes.

Preparation of the Complexes. a. $[Ni(bz)_5BF_4](BF_4)$. Aquated nickel(II) tetrafluoroborate (7.5 g) was dissolved in 20 ml of methanol and then dehydrated by stirring in 50 ml of 2,2-dimethoxypropane[16] for 2 hr at room temperature. Upon addition of diethyl ether to this solution a green oil was formed, which was then redissolved in a minimal amount of nitromethane and allowed to stir again. Upon further addition of diethyl ether to the solution, a light green complex, $[Ni(MeOH)_6](BF_4)_2$, was precipitated. This compound was filtered in a drybox and dissolved in 30 ml of benzylamine and allowed to stir for 2 hr. Upon addition of diethyl ether to this solution a blue complex was precipitated. This solution was filtered in the drybox and the complex analyzed. *Anal.* Calcd for $[Ni(bz)_5BF_4](BF_4)$: C, 54.4; H, 5.87; Ni, 7.60. Found: C, 54.2; H, 5.80; Ni, 7.80. Infrared analysis detected no water.

b. $[Ni(p\text{-}CH_3bz)_5BF_4](BF_4)$ (p-CH_3bz = *p*-Methylbenzylamine). This compound was prepared by a method analogous to the preceding preparation, retaining the appropriate mole ratios, but substituting *p*-methylbenzylamine in the final step. Here a light blue complex was precipitated. *Anal.* Calcd for $[Ni(p\text{-}CH_3bz)_5BF_4](BF_4)$: C, 57.3; H, 6.61; Ni, 7.00. Found: C, 57.2; H, 6.67; Ni, 6.68. Infrared analysis detected no water.

c. $[Zn(bz)_4](BF_4)_2$. This compound is also prepared in a manner analogous to the nickel(II)–benzylamine complex. A white solid is precipitated here. *Anal.* Calcd for $[Zn(bz_4)](BF_4)_2$: C, 50.4; H, 5.44. Found: C, 49.8; H, 5.43.

Treatment of the Nmr Data. The complexes studied in this work exchange rapidly with excess ligand. In solutions containing excess ligand a single averaged line position for each proton is observed (*i.e.*, separate complexed and free ligand resonances are not detected).

Although we cooled the solution to its freezing point, −47.8°, we were unsuccessful in our attempt to stop exchange and did not see exchange broadening at this temperature. Thus one may conclude that the fast exchange condition, $1/T_c >> \Delta\nu$, where $1/T_c$ is the rate of chemical exchange and $\Delta\nu$ is the shift relative to the diamagnetic complex, is fulfilled at room temperature. The chemical shift of the complex can then be calculated from a knowledge of the stoichiometry of the complex and the chemical shift of the free ligand according[17] to

$$\nu_{\text{obsd}} = \nu_{\text{complexed}}N_{\text{complexed}} + \nu_{\text{free}}N_{\text{free}} \qquad (1)$$

where ν and N represent the resonance frequency and mole fraction, respectively.

---

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

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

[6] E. A. LaLancette and D. R. Eaton, *J. Am. Chem. Soc.*, **86**, 5145 (1964).

[7] R. W. Kluiber and W. D. Horrocks, Jr., *Inorg. Chem.*, **5**, 152 (1966).

[8] H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).

[9] D. H. Levy, *Mol. Phys.*, 10, 233 (1966).

[10] S. Prasad and V. Krishvan, *J. Indian Chem. Soc.*, **35**, 352 (1958).

[11] A. K. Mujumdar, A. K. Mukherjee, and A. K. Mukherjee, *J. Inorg. Nucl. Chem.*, **26**, 2177 (1964).

[12] M. S. Barvinok and I. S. Bukhareva, *Zh. Fiz. Khim.*, 39, 1006 (1965).

[13] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

[14] B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, pp 400–454.

[15] G. Foex, Ed., "Tables De Constants et Données Numeriques," Vol. 7, Masson and Co., Paris, 1957, pp 28, 156.

[16] K. Starke, *J. Inorg. Nucl. Chem.*, 11, 77 (1959).

[17] H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, 21, 1688 (1953).

The temperature dependence of the contact shift is then given by the Bloembergen equation[18] (eq 2, modified for the case of protons),

$$\frac{\Delta\nu}{\nu} = -A_n \frac{\gamma_e g \beta S(S+1)}{\gamma_H 3kT} \tag{2}$$

where $\gamma_e/\gamma_H = 6.58 \times 10^2$, $g = \mu_{eff}/\sqrt{S(S+1)}$, $\beta = 9.27 \times 10^{-21}$ erg/gauss; S is the sum of the electron spins, A_n the nuclear spin–electron spin coupling constant, $\Delta\nu$ the shift relative to the diamagnetic complex, and ν the probe frequency (both in cps), the other symbols having their usual significance.

Results

(1) Nmr Data. The proton spectrum of free benzylamine in nitromethane is found to consist of three singlets. Our values for the chemical shift are consistent with those reported by earlier workers[19] for benzylamine in cyclohexane. The results of the nmr studies are contained in Table I.

Table I. Nmr Spectra in CH_3NO_2[a]

Compound	NH_2	CH_2	*ortho*	*meta*	*para*
Free $C_6H_5CH_2NH_2$	−73	−217	−428[b]	−428[b]	−428[b]
$[Zn(bz)_4](BF_4)_2$	−90	−240	−438[b]	−438[b]	−438[b]
$[Ni(bz)_6](BF_4)_2$	+6240	−2300	−350	−523	−345

[a] Chemical shifts are in cps relative to TMS as an internal standard. The temperature is 33°. [b] The *ortho*, *meta*, and *para* protons are part of an A_2B_2C system and appear as a singlet in our spectra.

The nmr contact shifts, $\Delta\nu$, and the electron spin–nuclear spin coupling constants, A, for the octahedral benzylamine complex of Ni(II) are reported in Table II.

Table II. Nmr Contact Shifts and Electron Spin–Nuclear Spin Coupling Constants for $[Ni(bz)_6](BF_4)_2$ in CH_3NO_2

Proton	$\Delta\nu$,[a] cps	$A \times 10^3$,[b] gauss
NH_2	+6330	−458
CH_2	−2060	149
ortho	+88	−6.31
meta	−85	6.15
para	+93	−6.74

[a] Shift relative to the diamagnetic Zn(II) complex at 33°. [b] Calculated from $\Delta\nu$ at 33° using eq 2 and $g = 2.39$.

The assignment of these peaks is treated in the Discussion section. In addition to the benzylamine complex, the nmr spectrum of $[Ni(p\text{-}CH_3bz)_6]^{2+}$ was studied. The peaks assigned to *ortho* and *meta* protons shifted in the same direction relative to free ligand in this complex as those in the benzylamine complex. However, the *p*-methyl peaks were shifted downfield in this complex (relative to the free ligand) while the *p*-hydrogen experienced an upfield shift in the benzylamine complex. The lower solubility of the *p*-methylbenzylamine complex precludes reporting of accurate contact shifts for this complex but approximate values of $\Delta\nu = +53$, -64, and -77 cps were obtained for the *ortho* and *meta* protons and *p*-methyl protons, respectively.

Table III. Conductance Data for $[Ni(bz)_5BF_4](BF_4)$ in CH_3NO_2

Complex	Type	Λ_{molar}	Temp, °C	Concn $\times 10^3$[a]
$[Ni(bz)_5BF_4](BF_4)$ + excess bz	2:1	169	26.4	1.08
$[Ni(bz)_5BF_4](BF_4)$	2:1	177	24.6	0.964

[a] Concentration in moles/liter of solution.

Table IV. Spectral Data for $[Ni(bz)_5BF_4](BF_4)$

Compound	Solvent	ν_{max}, cm^{-1}	Band assignment
$[Ni(bz)_5BF_4](BF_4)$	CH_3NO_2[a]	8,909 sh 9,716	$^3B_1 \rightarrow$ ^3E $^3B_2$
		16,064	$\rightarrow$ ^3E $^3A_2$
$[Ni(bz)_5BF_4](BF_4)$	CH_3NO_2 + excess bz	9,744	$^3A_{2g} \rightarrow {}^3T_{2g}$
		16,502	$\rightarrow {}^3T_{1g}$(F)
$[Ni(bz)_5BF_4](BF_4)$	DMA[b]	9,688	$^3B_1 \rightarrow$ ^3E $^3B_2$
		16,271	$\rightarrow$ ^3E $^3A_2$
$[Ni(bz)_5BF_4](BF_4)$	DMA + excess bz	9,746	$^3A_{2g} \rightarrow {}^3T_{2g}$
		16,485	$\rightarrow {}^3T_{1g}$(F)
		27,210	$\rightarrow {}^3T_{1g}$(P)

[a] When CH_3NO_2 is the solvent, the high-energy band cannot be detected due to intense solvent absorption. [b] DMA = N,N-dimethylacetamide.

(2) Evidence for the Octahedral Species in Solution. The conductance data presented in Table III are clearly indicative of a 2:1 electrolyte. The spectral data for the complexes are presented in Table IV. The spectrochemical parameters calculated from the data in Table IV are listed in Table V and the magnetic data for the complex in CH_3NO_2 solution are presented in Table VI.

Table V. Calculated Spectrochemical Parameters

Compound	Solvent	*Dq*	$\nu_{2,calcd}$	$\nu_{2,obsd}$
$[Ni(bz)_6]^{2+}$	CH_3NO_2	974	. . .	16,502
$[Ni(bz)_6]^{2+}$	DMA	974	15,971	16,485

Table VI. Magnetic Susceptibility Data for $[Ni(bz)_6](BF_4)_2$[a]

Complex	$\chi_m \times 10^6$	$\chi_{diamagnetic} \times 10^6$	χ_m (cor) $\times 10^6$	μ_{eff}, BM
$[Ni(bz)_6](BF_4)_2$	4163	−539	4702	3.38 ± 0.05

[a] The moment was determined at 28.°

Discussion

Nature of the Species in Solution. It is essential for our study to demonstrate that the species in solution is the octahedral complex, and further that there is no equilibrium in solution involving appreciable concentrations of other species.

The $[Ni(bz)_5BF_4](BF_4)$ compound is light blue. When this compound is dissolved in CH_3NO_2, the solution is green, but when excess benzylamine is added the solution turns a darker blue. On the basis of our conductance studies, both the green and blue solutions are clearly 2:1 electrolytes. An analogous process

---

(18) N. Bloembergen, *J. Chem. Phys.*, 27, 595 (1957).

(19) K. Takahaski, T. Sone, Y. Matuski, and G. Hazato, *Bull. Chem. Soc. Japan*, 36, 108 (1963).

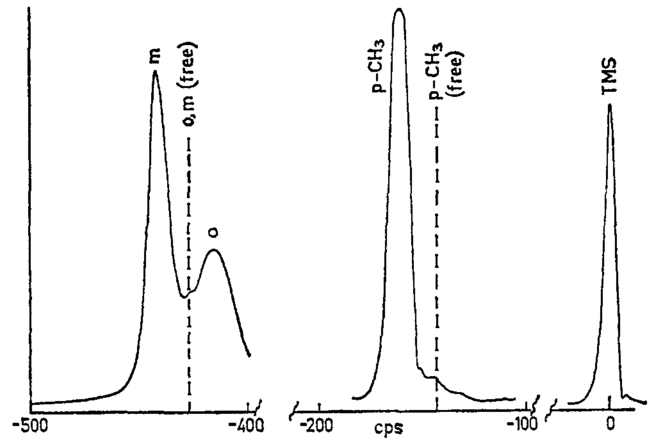

Figure 1. Nmr spectrum of $[Ni(p\text{-}CH_3bz)_6]^{2+}$ plus excess p-CH_3bz.

occurs when DMA is the solvent. We propose that two different species are formed in solution according to eq 3, and that the second reaction is essentially complete for a 1:1 mole ratio of complex and excess benzylamine.

$$[Ni(bz)_5BF_4](BF_4) \xrightarrow{\text{solvent}} [Ni(bz)_5\text{solvent}]^{2+} \xrightarrow{\text{excess bz}} [Ni(bz)_6]^{2+} \quad (3)$$

Evidence for the octahedral species is provided by the spectral data. Spectra in both CH_3NO_2 and DMA solutions containing excess benzylamine indicate that the same species is present in both solvents. Our conductance data show that BF_4^- cannot be coordinated, and therefore the only species common to both solvents must be $[Ni(bz)_6]^{2+}$. Furthermore, addition of excess ligand to a solution of $[Ni(bz)_5BF_4](BF_4)$ in a ratio greater than 3:1 does not alter the band positions. The fit of the middle band is somewhat poorer than one might expect for an octahedral complex. However, there is a charge-transfer band on the high-energy side of the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition, thus biasing the data in a manner consistent with the error.

Finally plots of ν_{obsd} *vs.* N_{comp}, where ν_{obsd} is the observed nmr frequency in cps and N_{comp} is the mole fraction of ligand complexed, give straight-line plots for all the protons of benzylamine indicating that only one species is present in solution, in addition to excess ligand.

These observations lead us to conclude that in solutions of the complex with excess benzylamine the complexed species is indeed $[Ni(bz)_6]^{2+}$.

Interpretation of the Contact Shifts. The contact shifts, $\Delta\nu$ (cps), for all the protons of $[Ni(bz)_6]^{2+}$ are reported in Table II. The contact shifts are reported relative to the diamagnetic Zn(II) complex. The electron spin–nuclear spin coupling constants, A, were calculated according to eq 2 and are also listed in Table II. The assignments of the amino and methylene protons in the complex were made by adding excess ligand to the solution of the complex and tracing back to the free ligand value. Because of the line width of the complexed N–H peak, the amino peak can only be detected in solutions containing a large excess of ligand.

Integration of the aromatic proton resonances in the benzylamine complex gave an approximate 3:2 ratio of upfield to downfield peaks. Upon substituting a p-CH_3 for p-H, the p-CH_3 is shifted downfield, *i.e.*, the opposite direction of the p-H. This is an indication of a π-delocalization mechanism[20] in the phenyl group and suggests that the upfield peaks be assigned to o- and p-H and the downfield peak to m-H. This assignment is further substantiated by the fact that the peak we have assigned to the *ortho* proton in the p-methylbenzylamine complex (the upfield peak) is the broadest C–H in the spectrum, as can be seen in Figure 1. It is not possible to assign unambiguously the two upfield peaks in the benzylamine complex to the *ortho* and *para* positions because of their substantial overlap. A tentative assignment is presented, and, as will be seen, this assignment does not alter the conclusions to be drawn. Since octahedral nickel(II) complexes are of cubic symmetry and possess a $^3A_{2g}$ ground state, the g tensor should be isotropic and there should be no pseudo-contact interaction.[21] Even though the "true" point group of these complexes is not O_h, we may assume any pseudo-contact shifts to be extremely small and neglect them. We can then consider the observed contact shifts to be isotropic shifts and interpret them in terms of spin delocalization mechanisms.

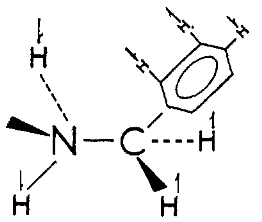

Figure 2. Spin densities on benzylamine protons.

Since there are two unpaired electrons in the metal e_g orbitals, which are aligned with the magnetic field, a σ-type metal–ligand bond with the amine would place the unpaired spin in the σ^* antibonding orbital. Thus, positive spin density (spin aligned with the field) is also placed on the nitrogen and on all other ligand atoms making a substantial contribution to the σ^* antibonding orbital. This gives rise to a downfield shift at these atoms. The spin densities on the protons, as indicated by the nmr data, are shown in Figure 2. We have the very interesting result that, in a system where the metal–ligand interaction is essentially σ, the distribution of spin density at the phenyl protons is that expected for the π-delocalization mechanism (*i.e.*, alternation of the sign of the spin densities). Clearly then, this experiment indicates that one cannot use distribution of unpaired spin in the π system of the ligand as an indication of metal–ligand π bonding as has so often been done.[5–7] Thus, unpaired spin may be delocalized onto the ligand by a σ mechanism and be placed in the π system by various mechanisms, including one that operates in the reverse of that used by Levy[9] and Copla and DeBoer[22] to explain how spin is transmitted from the phenyl ring to methylene or methyl protons.

Having established the hypothesis this experiment was designed to test, an interpretation of the contact shifts remains. As mentioned previously, the σ-bonding interaction of the ligand with nickel places positive spin density in the σ^* antibonding molecular

---

[20] A. D. McLachlan, *Mol. Phys.*, 1, 233 (1958).

[21] H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, 29, 1361 (1958).

[22] J. P. Copla and E. DeBoer, *Mol. Phys.*, 7, 333 (1963–1964).

orbitals that are formed. Thus a positive spin density is expected on the nitrogen.

Since the methylene protons are not orthogonal to any of the nitrogen orbitals, spin density can be placed directly on these protons (*i.e.*, the methylene protons contribute directly to the σ^* molecular orbital). This accounts for the observed positive coupling constant. Now the methylene group in benzylamine must bear the same relationship to the phenyl π system as the methylene groups in pyracene ions.[22] As discussed by Levy,[9] a linear combination of methylene protons (*i.e.*, $\pi_H = N[\phi_{1s}{}^A - \phi_{1s}{}^B]$, where π_H is the pseudo-π orbital, N is a normalization constant, and $\phi_{1s}{}^A$ and $\phi_{1s}{}^B$ are the normalized 1s atomic orbitals on the methylene protons) has the correct symmetry to interact directly with the π system of the phenyl ring. Spin in the π system is transmitted directly to the methylene protons through a hyperconjugative-type mechanism and the hyperfine coupling of methylene and methyl groups in many aromatic radicals can be explained on this basis. In benzylamine the methylene protons are now part of both the σ^* mo and this extended π system. Consequently, placing a net positive spin density on the methylene protons as described above also places spin directly in the phenyl π system. This π delocalization gives rise to positive spin densities at the *o*- and *p*-carbons and negative spin density at the *m*-carbon.[23] Spin density may then be transmitted to the aromatic hydrogens by the well-known $\sigma-\pi$, C–H spin polarization effect.[8] Thus, we expect negative spin density at the *o*- and *p*-hydrogens and positive spin density at the *m*-hydrogen. The lack of attenuation, the alteration of signs of the coupling constants for the aromatic protons, and the opposite signs of the *p*-hydrogen and *p*-methyl hydrogen shifts indicate that the electron spin is indeed in the π system of the phenyl ring.[24] It should be mentioned that a mechanism which involves the π overlap of the amino and methylene protons and the phenyl π system with the t_{2g} set of nickel orbitals would result in an opposite sign from that observed for all of the phenyl and methylene protons. Exchange interactions on nickel would place spin down on the ligand. Also, a direct overlap of t_{2g} nickel orbitals with the ring π orbitals would give rise to signs opposite to those observed for the ring protons because of exchange effects on nickel.

The large upfield shift of the amino protons is surprising when compared to the water[25] and methanol[26] contact shifts. One might expect that the amino protons would contribute directly to the σ^* mo in the complex and be deshielded by having spin placed directly on them. Instead they are observed to be shielded. The hydroxy protons in $[Ni(H_2O)_6]^{2+}$ and $[Ni(CH_3OH)_6]^{2+}$ are both deshielded[25,26] by this direct mechanism. The direction of the shift for the amino protons is similar to that reported by Wayland and Rice[27] for hexaamminenickel(II) complexes. These authors conclude that negative spin density reaches the protons by a spin polarization effect. O'Reilly,[28] in discussing spin densities in alkali metal–ammonia solutions, has proposed that the observed negative spin density on the hydrogen results from a node in the wave function of the unpaired electron near hydrogen. Consequently N–H $\sigma-\pi$ spin polarization effects, formally analogous to the more familiar C–H spin polarization effects, are reported to dominate these proton shifts. Our results are consistent with those reported by these authors.

These conclusions should not be construed to mean that we believe that metal–ligand "back-bonding" does not exist. In general, several lines of experimental evidence are required to substantiate its existence. For example, we have recently[29] reported the existence of back-bonding in some substituted pyridine N-oxide complexes of nickel(II). To draw these conclusions, it was necessary to study the infrared, electronic, and nmr spectra of the nickel complexes and the infrared spectra of some phenol adducts of the ligands.

Acknowledgment. The authors acknowledge with thanks the financial support of this research by the National Science Foundation through Grant GP-5498.

---

(23) A. Carrington, *Quart. Rev.* (London), 17, 67 (1963).

(24) D. R. Eaton and W. D. Phillips in "Advances in Nuclear Magnetic Resonance," Vol. 1, J. S. Waugh, Ed., Academic Press Inc., New York, N. Y., 1965, pp 103–148.

(25) B. B. Wayland and W. L. Rice, *Inorg. Chem.*, **5**, 54 (1966).

(26) Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 2686 (1964).

(27) B. B. Wayland and W. L. Rice, *ibid.*, **45**, 3150 (1966).

(28) D. E. O'Reilly, *ibid.*, 41, 3726 (1964).

(29) D. W. Herlocker, R. S. Drago, and V. I. Meek, *Inorg. Chem.*, **5**, 2009 (1966).