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Spin Delocalization in the Dipyridine Adducts of Some Heteroatom-Substituted Bis(acetylacetonate)nickel(II) Complexes

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The proton magnetic resonance spectra of the paramagnetic, dipyridine adducts of bis acetylacetonates, β-ketoimines, and monothioacetylacetonates of nickel(II) are reported. The contact shifts for the bidentate ligands are a sensitive function of the variable coordinating heteroatom, with the extent of σ delocalization increasing as $N < O < S$, while the π delocalization apparently decreases as $N > O > S$. The relative extents of σ spin delocalization are consistent with the expected ordering of the ligand field strengths of the heteroatoms in the order β-keto imine > acetylacetone > monothioacetylacetone. The dependence of the bis(β-keto imine)nickel(II) complex contact shifts on pyridine concentration indicates that the presence of pyridine shifts the tetrahedral $\rightleftharpoons$ square-planar equilibrium to the right from that observed in chloroform.

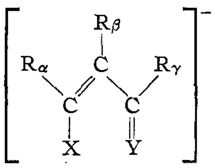
Introduction

The observation of large proton magnetic resonance shifts in paramagnetic transition metal complexes can lead to useful information on electronic structure. Thus if the isotropic shifts are dominated by the Fermi contact interaction, which reflects delocalization of unpaired metal electron into the ligand π or σ systems, as opposed to the dipolar interaction resulting from magnetic anisotropy, the nature of the metal–ligand bonding involving the metal spin-containing d orbital may be characterized in considerable detail.[2a]

Previous work with tris acetylacetonates of the first-row transition metals has shown[2b] that the spin-delocalization mechanism is very sensitive to the type of metal ion. For the lighter metals, π delocalization into the lowest antibonding orbital, LAO, is dominant, while for the heavier first-row metals, spin is delocalized into the highest bonding π orbital, HBO. Similarly, it has been suggested[3] that when complexes of the same ligand, such as salicylaldimine, can be formed for variable coordination numbers, then the low coordination number favors spin delocalization into the π HBO, while delocalization into the π LAO also may become important for high coordination numbers.

It is therefore of interest to inquire as to how the spin-delocalization mechanism for a certain complex varies as the ligand orbital energies are altered in an orderly manner. Thus by choosing a suitably large π-bonding chelate where one of the π centers can be substituted by other heteroatoms without significantly affecting the structure of the complex, the changes in the metal–ligand bonding may be monitored by observing the proton isotropic shifts in the unaltered part of the chelate.

One of the most versatile chelates in inorganic chemistry is the acetylacetonate ion,[4] AA$^-$, which can be considered to be the parent of a series of ligands designated by



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where X and Y occur in combinations with O, S, and NR, and all R are alkyl or aryl groups. Nickel(II) complexes with I with X = Y = O, acetylacetonate[4] and X = O, Y = NR, β-keto imine[5] are well known, while complexes with X = Y = S, dithioacetylacetonate,[6] X = O, Y = S, monothioacetylacetonate,[7] and X = Y = NR, β-imino imines[8] have been recently reported. Extensive contact shift studies of π delocalization for the pseudotetrahedral bis complexes with β-keto imines[5] and β-imino imines[8] with nickel(II) have been carried out; on the other hand, the bis-nickel chelates with X = Y = S[6] and X = O, Y = S[7] are completely square planar and diamagnetic in noncoordinating solvents, while the complexes with X = Y = O are associated[4] in noncoordinating solvents.

Therefore a comparison of the relative spin delocalization mechanisms for pseudotetrahedral nickel(II) complexes has to be restricted to the β-keto imines[5] and β-imino imines,[8] though the complexes with X = S, Y = NR could be added to the series.[9] The proton resonance studies have shown[5,8] that in both cases, the spin density resides primarily in the π HBO, with the relative magnitudes of π bonding, β-imino imines > β-keto imines. The possible effect of slightly different struc-

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[1] Chemical Physics Department, Shell Development Co., Emeryville, Calif. 94608.

[2] (a) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965); (b) D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).

[3] G. N. La Mar, *Mol. Phys.*, **12**, 427 (1967).

[4] J. P. Fackler, Jr., *Progr. Inorg. Chem.*, **7**, 361 (1966).

[5] G. W. Everett, Jr., and R. H. Holm, *Proc. Chem. Soc.*, 238 (1964); *J. Am. Chem. Soc.*, **87**, 2117 (1965).

[6] R. L. Martin and I. M. Stewart, *Nature*, **210**, 552 (1966).

[7] S. H. H. Chaston, S. E. Livingstone, T. N. Lockner, V. A. Pickles, and J. S. Shannon, *Australian J. Chem.*, **18**, 673 (1965); R. K. Y. Ho, S. E. Livingstone, and T. N. Lockner, *ibid.*, **18**, 1927 (1965).

[8] J. E. Parks and R. H. Holm, *Inorg. Chem.*, **7**, 1408 (1968).

[9] R. H. Holm, private communication.

tures on the delocalization mechanism could not be ascertained, though it is unlikely that major differences exist for these two sets of complexes.[8] The tris complexes of V(III) with acetylacetonate and β-keto imine have also been investigated,[10] and though it was shown that the spin delocalization for both ligands involves predominantly metal-to-ligand charge transfer into the π LAO, the complexity of the proton spectra resulting from the low symmetry of the *trans* configuration did not allow a comparison of the magnitudes of spin transfer for the two chelates.

It has been demonstrated that the bis complexes of nickel(II) with acetylacetonate,[11,12] monothioacetylacetonate,[13] and β-keto imine[14] with small N substituents will readily react with two molecules of pyridine to form the octahedral diadducts, which have been formulated to exist in the *trans* configuration, as was shown[15] to be the case for the analogous adduct with cobalt(II) bis(acetylacetonate). The nickel complexes with X = Y = S[6] do not react with pyridine, while the complexes with X = Y = NR are presently known only for bulky R groups, such that the bis chelates exist exclusively in a pseudotetrahedral arrangement.[8] The octahedral, *trans*-dipyridine adducts with X = O and Y = O, S, or NR should be isostructural and are paramagnetic,[11-14] thereby allowing a comparison of spin-delocalization characteristics between Y = O, S, and NR.

Experimental Section

The proton magnetic resonance spectra were recorded on a Varian DP-60 spectrometer, operating at 29° and using TMS as internal calibrant. The bis complexes of nickel employed in this study all have X = O, R_β = H, and R_γ = CH_3 and are designated as follows: Y = O, R_α = CH_3, AA; Y = O, R_α = phenyl, BA; Y = S, R_α = CH_3, S(AA); Y = S, R_α = phenyl, S(BA); Y = NR, R_α = CH_3, N(R)(AA); Y = NR, R_α = phenyl, N(R)(BA), where R is CH_3, phenyl, or *p*-tolyl.

Solutions of the dipyridine adducts of all complexes were prepared by either dissolving the pure bis chelate in pentadeuteriopyridine or else first isolating the adduct and then dissolving it in pyridine-d_5, to ensure complete reaction. The two methods yielded identical proton spectra, except that the pyridine resonances were absent in the *in situ* preparation, owing to the use of only fully deuterated pyridine.

The proton spectra of the bis chelates with $N(C_6H_5)(AA)$ and S(AA) were also recorded in chloroform-*d* with an increasing amount of pyridine-d_5 added to the solution. The deuterated pyridine was necessary since the use of undeuterated pyridine obliterated the spectrum of the complex when excess pyridine was present. The isotropic shifts, in ppm, are defined as the difference in resonance position between the paramagnetic adduct and the diamagnetic ligand, such that upfield shifts are positive.

Results and Discussion

The observed isotropic shifts for the nickel adducts are given in Table I. The dependence of the chemical shifts of $[N(C_6H_5)(AA)]_2Ni$ and $[S(AA)]_2Ni$ in chloroform-*d* on pyridine-d_5 concentration is illustrated in Figures 1 and 2, respectively.

TABLE I
CONTACT SHIFTS FOR $Ni[Y(AA)]_2 \cdot 2py$[a]

	Y(AA) shifts			N-substituent shifts			
Ligand	α-CH_3	β-CH	γ-CH_3	NCH_3	*o*-H	*m*-H	*p*-H or *p*-CH_3
S(AA)	−3.00	+14.54	−25.90	...	...	...	...
S(BA)	*b*	+15.05	−27.33	...	...	...	...
AA[c]	−2.95	+18.50	−2.95	...	...	...	...
BA[d]	*b*	+19.28	−3.36	...	...	...	...
$N(C_6H_5)(AA)$	−2.00	+18.90	+14.17	...	+15.27	−7.33	+14.77
N(*p*-tol)(A)	−1.10	+20.18	+15.28	...	+15.06	−7.46	−15.14
$N(CH_3)(BA)$	*b*	+18.19	+16.94	−120	....	...	...

[a] Shifts in ppm for pyridine d_5 solutions at 29°, referenced against diamagnetic ligand. [b] The α-phenyl shifts could not be assigned, but one large peak at −1.5 ppm plus some unresolved ones at −0.5 to −1.0 ppm were observed. [c] Data taken from ref 15. [d] Data taken from ref 12. The α-phenyl shifts were similar to those for the S(AA) and N(R)(AA) complexes.

Owing to the isotropic $^3A_2$ ground state for octahedrally coordinated nickel(II), dipolar contributions to the observed shifts are expected to be negligible. The magnetic moments[11,13,14] for $Ni(AA)_2 \cdot 2py$, $Ni[NR(AA)]_2 \cdot 2py$, and $Ni[S(AA)]_2 \cdot 2py$—∼3.3, ∼3.2, and ∼3.2 BM, respectively—are not consistent with sizable magnetic anisotropy, so the observed shifts are probably contact in origin. In addition, the calculated ratio of dipolar shifts[15] for the CH_3 and β-CH protons, (β-CH)/(CH_3) = ∼1.5, is in serious disagreement with the observed ratio for every complex. Furthermore, as previously shown, the isotropic shifts for the AA protons are essentially independent of the chemical nature of the polar ligands, L, in *trans*-$Ni(AA)_2 \cdot 2L$, and such insensitivity to the magnitude of the axial distortion is completely inconsistent with significant dipolar contributions to the shifts in any of these adducts.[15]

The Assignment of Peaks.—The broad proton resonances for the diadducts, ∼25–100 Hz at 60 MHz, preclude assignments based on multiplet structure, particularly for the N substituents. For a given adduct with Y(AA), it was always possible to assign α-CH_3, γ-CH_3, and β-CH peaks on the basis of intensities and upon comparison with the analogous Y(BA) adduct. For the N substituents, except for NCH_3, it was necessary to follow the change in contact shift of the bis complex in chloroform-*d* upon addition of pyridine-d_5. Owing to the rapid pyridine exchange rate, only an averaged spectrum over the diamagnetic complex and paramagnetic adduct is observed, as shown in Figure 1, allowing unambiguous assignments for all resonances except for the α-phenyl groups which always exhibited an unresolvable set of two to three lines with contact shifts −0.5 to −1.5 ppm.

$[N(C_6H_5)(AA)]_2Ni$ and $[N(p\text{-tol})(AA)]_2Ni$ in chloroform solution exist as approximately 99% square-planar, diamagnetic and 1% tetrahedral, paramagnetic isomers,[5] giving rise to average contact shifts of 1–3 ppm. Therefore, the slight decrease in β-CH and γ-CH_3 shifts at large pyridine: complex ratios apparently arises from the fact that the presence of pyridine shifts

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[10] F. Röhrscheid, R. E. Ernst, and R. H. Holm, *Inorg. Chem.*, **6**, 1315, 1607 (1967).

[11] J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **84**, 24 (1962).

[12] R. W. Kluiber and W. D. Horrocks, Jr., *Inorg. Chem.*, **6**, 166 (1967).

[13] S. H. H. Chaston, S. E. Livingstone, and T. N. Lockner, *Australian J. Chem.*, **19**, 740 (1966).

[14] E. G. Jäger, *Z. Anorg. Allgem. Chem.*, **337**, 80 (1965).

[15] G. N. La Mar, *J. Magn. Res.*, in press.

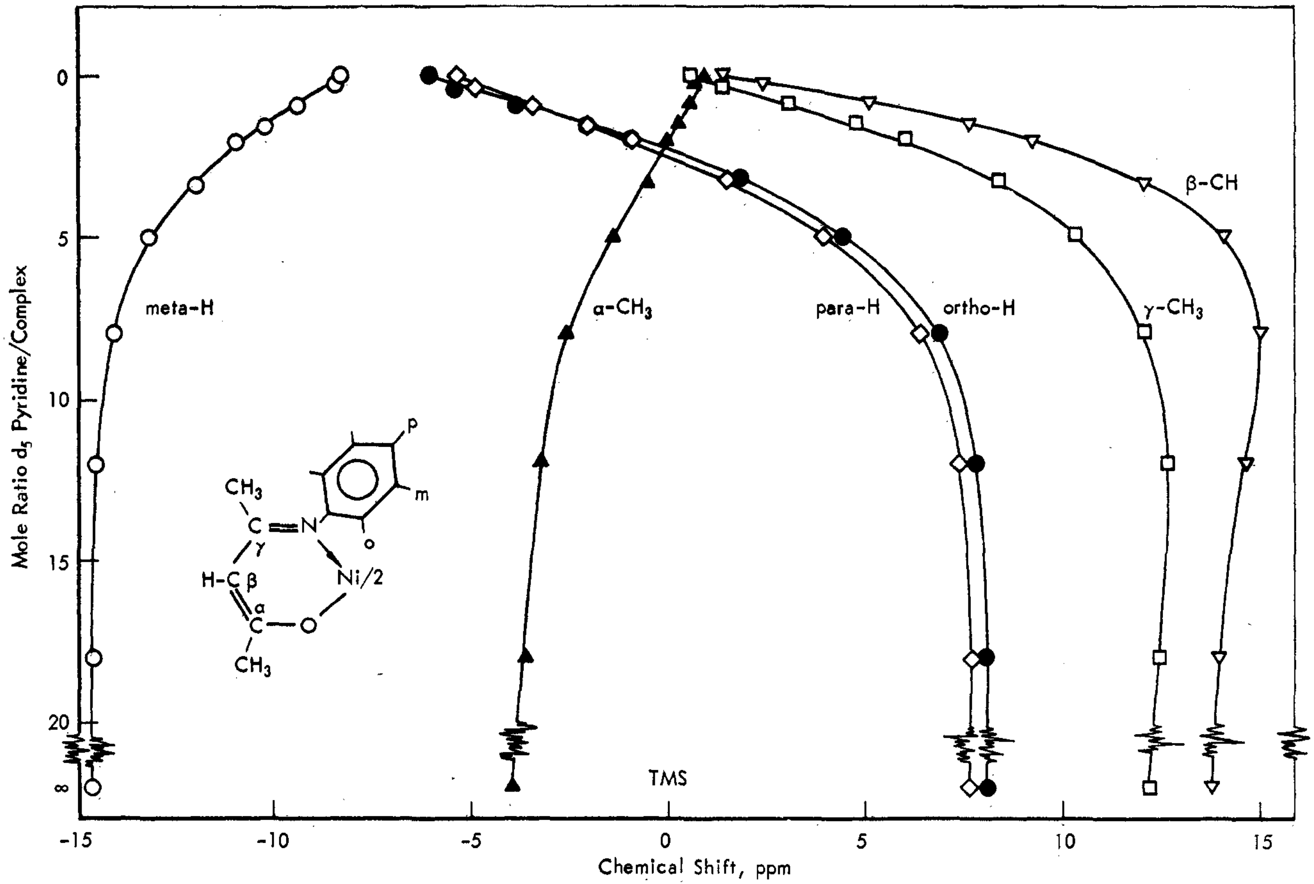

Figure 1.—Dependence of contact shifts of $[N(C_6H_5)(AA)]_2Ni$ in $CDCl_3$ on the pyridine:complex ratio, in ppm, referenced to TMS.

the solution equilibrium in favor of the tetrahedral form. Since the 99:1 diamagnetic:paramagnetic ratio in chloroform exhibits average contact shifts much smaller than those for the diadduct, it cannot account for the *decrease* in contact shifts noted in Figure 1. Molecular association is unlikely to arise at these temperatures or at these relatively low concentrations.[5] The decrease in β-CH and γ-CH_3 shifts shortly before complete diadduct formation therefore suggests that the square-planar ⇆ tetrahedral equilibrium has been shifted to the right so as to produce for the unreacted species average contact shifts larger than those for the dipyridine adduct. For $[N(CH_3)(BA)]_2Ni$, which is completely square planar and diamagnetic in chloroform-*d* solution, as indicated by the lack of any paramagnetic shifts in the absence of pyridine, the β-CH and γ-CH_3 shifts increase upon addition of pyridine-d_5, approaching their values in the diadduct without the decrease in contact shifts noted for the two slightly paramagnetic complexes. That only the diadduct for these complexes is present in pyridine-d_5 solution is evidenced by the fact that the contact shifts are independent of the concentration of the complex.

Since these deviations of the contact shifts from the simple behavior expected for a system composed only of diamagnetic complex and paramagnetic diadduct arise only at high pyridine:complex ratios, just before complete formation of the diadduct, it appears safe to rule out an intermediate monopyridine adduct, which should introduce complexities in the contact shift pattern only at very low pyridine:complex ratios, as observed[16] for the $N(C_2H_5)$–Ni(SAL)–py system.

For the S(AA) complex, the dependence of the averaged contact shift on pyridine concentration was studied primarily to ascertain the assignments for the nonequivalent methyl groups in the diamagnetic bis complex, since the methyl resonances can be unambiguously identified in the diadduct by comparison with the S(BA) adduct. Previous assignments[17] are −2.17 and −2.08 ppm for the α-CH_3 and γ-CH_3, respectively. However, as Figure 2 clearly demonstrates, the peak at −2.17 ppm moves downfield with increasing pyridine concentration, terminating at −27.98 ppm from TMS for the diadduct, and is definitely assigned to the γ-CH_3 resonance, thereby reversing the reported assignments.[17] Thus, as also shown for nickel complexes with N,N′-dimethylamides[18] and pyrazoles,[19] coordination of a diamagnetic ligand to a paramagnetic metal ion will sometimes permit the unambiguous assignment of nearly magnetically equiv-

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(16) G. N. La Mar, to be submitted for publication.

(17) "The Sadtler Standard Spectra," Sadtler Research Laboratory, Philadelphia, Pa., nmr spectrum no. 1117M (1966).

(18) B. B. Wayland, R. S. Drago, and H. F. Henneike, *J. Am. Chem. Soc.*, **88**, 2455 (1966).

(19) E. E. Zaev, V. K. Voranov, M. S. Shvartsberg, S. F. Vasilevsky, Y. N. Molin, and I. L. Kotljareovsky, *Tetrahedron Letters*, 617 (1968).

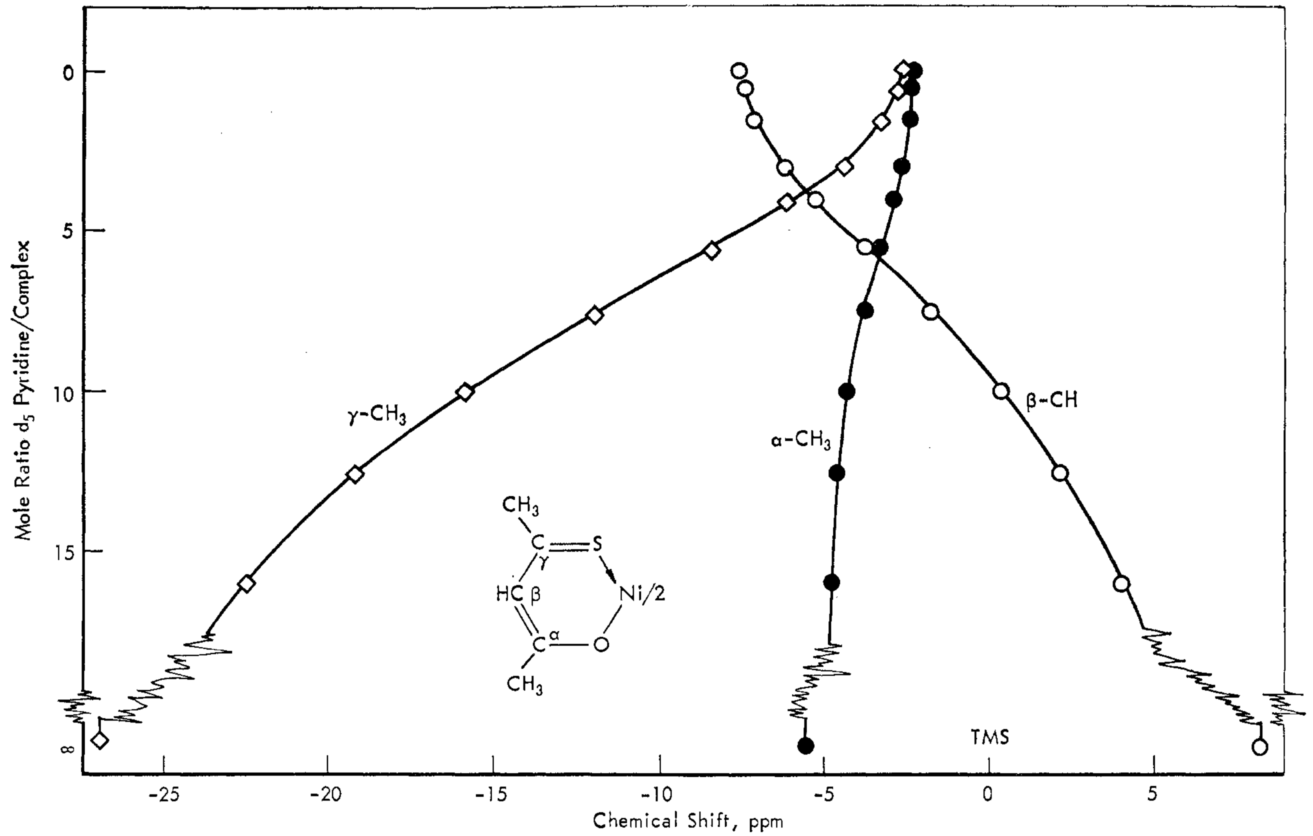

Figure 2.—Dependence of contact shifts of $[S(AA)]_2Ni$ in $CDCl_3$ on the pyridine:complex ratio, in ppm, referenced to TMS.

alent methyl peaks, not readily possible by conventional means, owing to the significant difference in their interactions with the unpaired metal electron(s).

The Delocalization Mechanism.—The contact shifts in Table I illustrate that the spin-density distributions for the ligands AA, S(AA), and N(R)(AA) differ significantly, and it would be of interest to know whether these shift variations reflect only differences induced in a given ligand molecular orbital by varying the heteroatom or whether there exist different metal–ligand spin-delocalization mechanisms for the three complexes. It is apparent that the variation of heteroatom affects primarily the γ-CH_3, causing a ~42-ppm shift from N(R)(AA) to S(AA), with the β-CH shift affected only slightly, while the α-CH_3, nearest the fixed C–O bond, is essentially constant for all complexes.

In order to ascertain whether π delocalization alone can account for the observed shifts in all complexes (either the HBO or LAO), the π eigenvectors for AA, S(AA), and N(AA) were calculated by the Hückel method, incorporating correlation by the method of McLachlan.[20,21] The Coulomb and exchange integrals were chosen[5,22] in a consistent manner, $\alpha_N = \alpha + \beta$, $\beta_{CN} = 1.2\beta$, $\alpha_O = \alpha + 1.5\beta$, $\beta_{CO} = 1.5\beta$, $\alpha_S = \alpha$, and $\beta_{CS} = 0.8\beta$, such that even though not too much emphasis should be placed on the absolute spin densities, the trends in spin densities with heteroatoms should be significant. The resultant Hückel and McLachlan spin densities are given in Table II.

Table II

Calculated π Spin Densities for Y(AA)[a]

Ligand (energy)	Pos	HBO HMO	HBO MHMO	HBO VB	LAO HMO	LAO MHMO
	O	1.162	0.144	...	0.138	0.118
AA	Cα	0.055	−0.086	...	0.362	0.480
HBO (+0.625β)	Cβ	0.565	0.883	...	0.000	0.196
LAO (−0.927β)	Cγ	0.055	−0.086	...	0.362	0.480
	O	0.162	0.144	...	0.138	0.118
	O	0.147	0.131	0.375[b]	0.132	0.138
N(R)(AA)	Cα	0.056	−0.075	−0.249	0.326	0.523
HBO (+0.580β)	Cβ	0.508	0.801	0.697	0.003	—0.204
LAO (−0.860β)	Cγ	0.032	−0.173	−0.282	0.381	0.439
	N	0.260	0.316	0.461	0.158	0.104
	O	0.102	0.102	...	0.099	0.159
S(AA)	Cα	0.077	0.051	...	0.273	0.608
HBO +0.196β)	Cβ	0.286	0.205	...	0.003	−0.221
LAO (−0.851β)	Cγ	0.030	−0.183	...	0.325	0.127
	S	0.505	0.825	...	0.288	0.327

[a] HMO designates simple Hückel spin densities, while MHMO indicates the correlated spin densities, using the methods in ref 20 and 21. The correlation parameters used are $\lambda_C = 1.8$, $\lambda_O = 2.6$, $\lambda_N = 2.2$, and $\lambda_S = 2.2$. [b] Valence bond spin densities were taken from ref 5.

Previous work with octahedral acetylacetonate complexes[2] leads us to expect predominantly π delocalization into the HBO, with the π LAO relatively

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(20) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(21) The general method outlined in ref 20 was extended to make it applicable to heteroatomic systems, where atom–bond polarizabilities must also be incorporated: G. N. La Mar and J. H. Schachtschneider, to be submitted for publication.

(22) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, New York, N. Y., 1962, Chapter 5; G. Giacometti and G. Rigatti, *J. Chem. Phys.*, **30**, 1633 (1959).

unimportant. For $Ni(AA)_2 \cdot 2py$, the positive β-CH shift is consistent with the HBO, but correlation predicts upfield shifts for the methyl groups though small negative shifts are observed. The calculated negative C_α and C_γ spin densities and thus the predicted upfield methyl shifts can be considered significant since the analogous orbital for N(R)(AA) correctly predicts the positive γ-CH_3 shift. If anything, the negative spin densities are underestimated in this type of calculation as shown by a comparison of the McLachlan and valence bond[5] spin densities in Table II. Therefore, the negative methyl shifts in AA adducts must arise from spin density in an orbital other than the π HBO.

For the N(R)(AA) chelate, it has been shown[5] by comparison with valence bond calculations that a π-HBO mechanism is primarily responsible for the observed shifts for the pseudotetrahedral nickel complexes, with the α-CH_3, γ-CH_3, and β-CH shifts all positive with α-CH_3 smallest and β-CH largest, in agreement with Table II. Thus, the observed negative α-CH_3 shift in the adduct definitely indicates at least one additional spin-delocalization mechanism. The contact shifts for the N-phenyl and N-*p*-tolyl substituents are definitely[5] of primarily π origin, as evidenced by the alteration of signs and by the shift sign reversal upon replacing *p*-H by *p*-CH_3.

No proton magnetic resonance studies of paramagnetic complexes with S(AA) have been reported. However, it is apparent that the observed shifts cannot be accounted for by either only the π HBO or π LAO, as Table II illustrates. The positive β-CH shift does show that there must be some spin density in the π HBO, since both the π LAO and σ delocalization predict negative β-CH shifts.

It is therefore obvious for all complexes that, though the π HBO must contain some unpaired spin due to the positive β-CH shifts for each adduct, at least one additional spin-transferral mechanism must exist and that its magnitude differs with the heteroatom. The most likely candidates for this secondary mechanism are either metal-to-ligand spin transfer into the π LAO[2,3] or ligand-to-metal β-spin transfer, with the resultant spin imbalance in the ligand σ HBO.[23] It is considered most likely that only the latter mechanism can contribute to the observed shifts, as opposed to a significant contribution from the former mechanism for the following reasons.

(a) The energies for the π LAO are essentially the same for AA, S(AA), and N(R)(AA), as shown in Table II, such that significant differences between the chelates in the extent of interaction with this orbital are not to be expected.

(b) Octahedral nickel does not possess any π-bonding (t_{2g}) unpaired electrons, though a minute unpairing of the t_{2g} electrons could occur *via* spin–orbit coupling;[3] thus, a metal–ligand π-spin transfer of the magnitude needed to account for the S(AA) γ-CH_3 shift is deemed most unlikely.

(c) Downfield σ shifts have been observed[5] in the pseudotetrahedral $[N(R)(AA)]_2Ni$ chelates, where the negative γ-H shift was much larger than expected from only π-HBO spin density.

(d) The α-CH_3 shifts, attached to the fixed C–O fragment, are essentially identical in AA, S(AA), and N(R)(AA), indicating that the shift is determined by a delocalization mechanism depending primarily on the CH_3–C–O–Ni bonds. The γ-CH_3 shifts, on the other hand, vary considerably with heteroatom, again reflecting a localized effect in the CH_3–C–Y–Ni bonds. Significant changes in π-delocalization mechanisms would manifest themselves in shift changes at all π positions in the chelate, as predicted in Table II.

(e) The α-phenyl shifts experience only σ spin density, as evidenced by downfield shifts[12] for all phenyl protons, since any π delocalization would have resulted in upfield shifts for at least some phenyl protons.

(f) It seems very unlikely that just a combination of spin density in the π LAO and π HBO can account for the S(AA) methyl shifts, since the former orbital predicts a large negative α-CH_3 shift, and the latter predicts a sizable positive γ-CH_3 shift, neither of which is observed.

Qualitative justification for invoking ligand-to-metal spin transfer into the σ system can be derived from an analysis of the eigenvectors of an extended Hückel calculation.[24] Such a calculation was performed for AA, S(AA), and N(H)(AA) using a computer program yielding eigenvectors for a self-consistent charge distribution.[25,26] From a population analysis of the σ HBO, situated only ~0.5 eV from the π HBO, the proton spin densities were calculated and are listed in Table III.

Table III

Calculated Proton σ Spin Densities for Y(AA)

Ligand	Orbital energy, eV	Methyl proton spin densities $\times 10^6$ α-CH_3	γ-CH_3
N(H)(AA)[a]	−7.446	118	26
AA[b]	−7.690	108	108
S(AA)[c]	−7.401	54	148

[a] $\rho(O) = 0.904$, $\rho(N) = 0.023$. [b] $\rho(O) = 0.464$. [c] $\rho(O) = 0.293$, $\rho(S) = 0.638$.

Thus for AA, for example, the σ eigenvector correctly predicts downfield shifts for the methyl protons but has no effect on the β-CH, since the σ-HBO has a node through that position. For the S(AA) and N(H)-

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(23) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963); R. H. Holm, G. W. Everett, Jr., and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, **88**, 1071 (1966).

(24) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(25) J. H. Schachtschneider, R. Prins, and P. Ros, *Inorg. Chem. Acta*, **1**, 467 (1968).

(26) The AA geometry reported for $Fe(AA)_3$ was used: R. B. Roof, *Acta Cryst.*, **9**, 781 (1956). The C=N and C=S distances were estimated as 1.3 and 1.7 Å, respectively, from L. M. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions," Burlingame House, London, 1958. The orbital coefficients were taken from E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963), and the valence state ionization potentials and their charge dependencies were abstracted from E. Clementi, *IBM J. Res. Develop.*, **9**, 2 (1965).

(AA) ligands, similar negative σ shifts for all methyl groups are predicted. Though not too much reliance should be placed on the absolute spin densities, the relative spin densities for different heteroatoms should be significant. The β-CH proton in S(AA) and N(R)(AA) should also experience some downfield σ spin density, owing to the displacement of the node in the σ HBO in the lower ligand symmetry. However, the calculated spin densities at that position, unlike that for the methyl groups, were a very sensitive function of input parameters, so as to make their values rather meaningless.

Thus a combination of spin delocalization into the π HBO and σ HBO seems to be able to account for the observed shifts for all of the complexes of interest here, since the shift patterns differ primarily in the extent of the downfield bias on the methyl peaks. The σ spin densities in Table II predict larger α-CH_3 than γ-CH_3 downfield shifts for N(R)(AA) and larger γ-CH_3 than α-CH_3 shifts for S(AA) in accordance with the observed relative shifts. From the magnitude of the downfield bias for the γ-CH_3 shift with Y, it is apparent that the extent of σ delocalization increases appreciably in the order $Y = N < O < S$. This increase in σ delocalization with Y could result from two distinct effects—either from changes in covalency in the C–Y bond or in the Y–Ni bond or from both. The calculated spin densities at α-CH_3 differ by a factor of 1.1–1.3 between $Y = N$ and O, and by 1.6–5 between $Y = N$ and S for γ-CH_3 depending on the choice of input parameters, but always increasing as $N < O < S$, in agreement with observation.

For the N(R)(AA) adducts, agreement of the relative γ-CH_3 and β-CH shifts with calculated spin densities and with the shifts observed in the tetrahedral isomers, where primarily the π HBO contained the unpaired electron,[5] indicates that the γ-CH_3 protons experience no σ shifts. For the α-CH_3 in that adduct, comparison with the valence bond calculation[5] or the known spin density distribution leads to the expectation of $\sim +10$ ppm shift in the absence of any σ delocalization at that position. For the methyl groups in AA, the calculated spin densities predict positive shifts of the same order of magnitude as predicted for the α-CH_3 in N(R)(AA) and observed in the tetrahedral complexes,[5] which would be $\sim +10$ ppm. For the S(AA) ligand, π-HBO delocalization predicts an even larger upfield γ-CH_3 shift relative to the β-CH shift than for the N(R)(AA) ligand, such that, in the absence of σ delocalization in the S(AA) adducts, a γ-CH_3 shift of ≥ 10 ppm is expected. Thus a semiquantitative estimate to the magnitudes of the minimum downfield shifts for the γ-CH_3 protons resulting from σ spin density is obtained, with ~ 0 for N(R)(AA), ~ 12 ppm for AA, and ≥ 35 ppm for S(AA).

The calculated differences in spin density at the γ-CH_3, which only reflect differences in covalency within the ligand, primarily within the C–Y bond, can account for only part of the changes in σ spin density with variable Y, the maximum calculated variation for $Y = N$, O, or S being ~ 1, 1.5, or 5, even for a variety of input parameters. It is thus suggested that there must also exist a larger increase in covalency for the σ HBO in the Y–Ni bond, in the order $N < O < S$.

Owing to the possible presence of sizable σ spin density at the β-CH in the adducts with both S(AA) and N(R)(AA), it is not possible to determine the relative amounts of π delocalization with any degree of confidence, except that the apparent trend is opposite to that deduced for σ delocalization, $S < O < N$. Since octahedrally coordinated nickel possesses no unpaired π-bonding electrons, it is likely that π spin densities observed on the ligands arise from the nonplanarity of the ligand, such that the Ni–ligand σ orbitals are not orthogonal to the ligand π orbitals.[27] Even if significant unpairing of the t_{2g} electrons occurs,[3] it would still be hazardous to relate the π shifts to π covalency.[28]

The low-energy transitions in the d–d absorption spectra for the S(AA) and N(R)(AA) adducts have been reported[13,14] and fall in the range $10{,}500 \pm 200\ \text{cm}^{-1}$, such that the differences in ligand field strengths with Y are not sufficient to allow the unambiguous detection of the spectrochemical ordering[29] of the ligands from the optical spectra for the dipyridine adducts. For the square-planar chelates, $[S(AA)]_2Ni$ and $[N(R)(AA)]_2Ni$ in chloroform-*d*, the first absorption band for the former complex appears at $\sim 15{,}600\ \text{cm}^{-1}$ and is shifted to $\sim 16{,}200\ \text{cm}^{-1}$ for the latter chelate, indicating $N > S$ as expected.[29]

The postulated spectrochemical ordering[29] of the donor atoms O, N, and S, based on decreasing ionic radii of the donor, is $S < O < N$, though S has been found to occupy positions between O and N in some complexes.[30] However, in a similar electronic configuration of valence electrons for O and S, which is certainly the case for the AA and S(AA) chelates, it is expected[30] that the ordering will be $S < O$.

Thus the observed increase in σ spin delocalization parallels the expected decrease in ligand field strength of the donor atoms. This indicates that, as the energy of the antibonding e_g (σ^*) orbital is raised (leading to increased ligand field splitting[31]), the ligand contribution to the spin-containing orbital is decreased.

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