The Influence of Halogen, Substituent, and Solvent on Spin Delocalization in High-Spin, Five-Coordinated 2,6-Diacetylpyridinebis(N-alkylimine)nickel Dihalides

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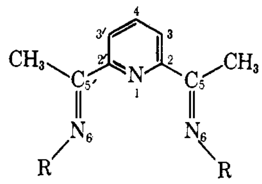
Abstract: The proton magnetic resonance spectra of a series of high-spin, five-coordinated complexes of nickel(II) dihalides with 2,6-diacetylpyridinebis(N-alkylimine) have been observed. The contact shifts reflect delocalization of unpaired spin into the ligand highest bonding π as well as σ systems. The relative extent of π/σ spin delocalization is found to depend markedly on the halogen, the nature of the alkyl substituent, and the dielectric properties of the solvent. The effect of the halogen and substituent is interpreted as arising from a steric or bulkiness effect, which induces small structural variations in the complexes, while the solvent influence produces a similar structural change due to variable solvation.

Proton magnetic resonance is now firmly established as a powerful new tool for elucidating the electronic nature of metal–ligand bonding in paramagnetic complexes.[2] A more recent application of this technique has been to monitor structural[3] or isomeric[4,5] effects in complexes, where the exact electronic origin of the isotropic shifts may not be as significant as the structural or symmetry properties of the complexes which they reflect.

The discovery of high-spin, five-coordinated nickel[6] complexes has prompted us to extend the contact shift studies[3,7] from the more conventional four- and six-coordinated nickel(II) complexes to these novel five-coordinated species. A five-coordinated complex may possess one of two highly symmetric configurations, a trigonal bipyramid, TBP, or a square-based pyramid, SBP, whose energies are sufficiently similar that small perturbations in ligand properties can alter the tendency for a given complex to adopt one or the other structure. Both crystal field theory[8] and MO-type arguments, as represented by the angular overlap model including π bonding,[9] concur in predicting that the SBP is electronically more stable than the TBP for nickel(II). However, steric strain or bulkiness of the ligand or its substituents or repulsion between bonding atoms can alter the relative energies of the two configurations,[8] such as to stabilize the TBP or some intermediate structure.

A previous proton nmr study of the paramagnetic, five-coordinated complexes,[3] $[(-OC_6H_4CH{=}NCH_2CH_2CH_2-)_2NR]Ni^{II}$, has demonstrated that small structural changes resulting from bulky substituents and variable solvation can be readily detected, though the ligand field spectra were essentially insensitive to these changes.[10] The π delocalization mechanism responsible for these novel contact shift patterns has been discussed[11] in the light of this coordinating geometry.[12]

We report here a proton nmr investigation of the high-spin, five-coordinated complexes[13] formed from the nickel(II) dihalides and the planar, tridentate chelate, 2,6-diacetylpyridinebis(imine), with structure A,



A

where the complexes are designated as $py(R)_2NiX_2$, with R = methyl (Me), ethyl (Et), *n*-propyl (*n*-Pr), isopropyl (*i*-Pr), *sec*-butyl (*sec*-Bu), cyclohexyl (*c*-Hex), or benzyl (Bz), and X = Cl, Br, or I.

Thorough characterization of these complexes[13] has shown that they are all monomeric, nonionic in noncoordinating solvents, and thus five coordinated. Their reflectance and absorption spectra are characterized[13] by bands at 8100–9000, 13,000–13,800, 18,600–19,000, and 22,500–23,800 cm^{-1}, closely resembling those of other five-coordinated nickel(II) complexes[14] for which a more or less TBP configuration has been established by X-ray analysis, and are also consistent with the calculations for a TBP using crystal

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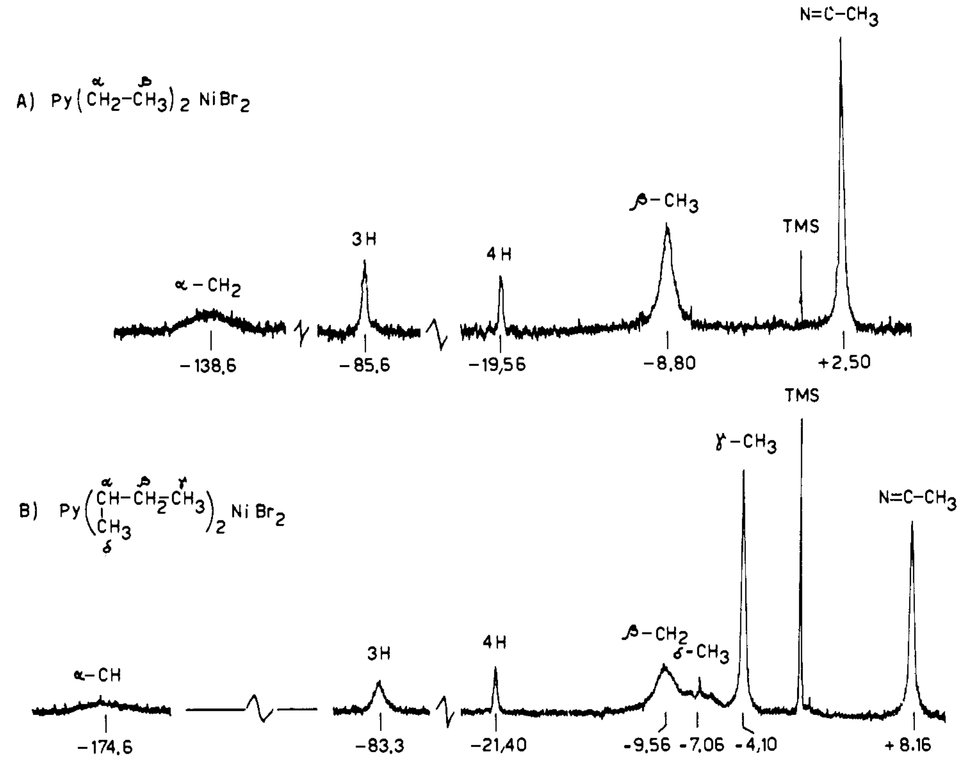

Figure 1. Nmr traces for (A) py(Et)$_2$NiBr$_2$ and (B) py(*sec*-Bu)$_2$NiBr$_2$, in CDCl$_3$, with shifts in parts per million, referenced to internal TMS.

field theory.[8,13] Thus, though the exact structure is not known, it appears safe to assume that the structure resembles a TBP much more so than a SBP, though the structure may in fact be somewhere intermediate the two extremes. Although band shifts were observed[13] upon varying the substituent, solvent, or halogen, the changes were small and too irregular to be related to any systematic structural variation. The present investigation was initiated to determine the steric or electronic influences of the alkyl substituent, halogen, and solvent on the ligand isotropic shifts.

Experimental Section

The complexes employed in this study are those reported previously.[13] The nmr spectra were recorded on a Varian DP-60 spectrometer, operating at 29°, and using TMS as internal calibrant. The spectra were recorded in chloroform-*d* solution for all complexes except those with benzyl substituents, which were insoluble. The isotropic shifts of CDCl$_3$ solutions of py(*n*-Pr)$_2$NiBr$_2$, py(*sec*-Bu)$_2$NiCl$_2$, py(*sec*-Bu)$_2$NiBr$_2$, and py(*c*-Hex)$_2$NiI$_2$ were obtained over a temperature range of -50 to 55°. Five of the complexes were also run at 29° in four additional deuterated, noncoordinating solvents, bromoform-*d*, methylene-d_2 chloride, acetone-d_6, and nitromethane-d_3. Other solvents, such as pyridine, methanol, and acetonitrile, reacted with or decomposed the complexes, forming precipitates, while carbon disulfide, carbon tetrachloride, and benzene failed to dissolve them. The complexes with benzyl substituents were sufficiently soluble only in nitromethane. In every case possible, the spectra were recorded at several concentrations, with no resultant effect on the observed shifts.

The proton nmr spectra of the analogous diamagnetic zinc complexes were recorded on the same instrument, and the isotropic shifts are defined as the difference in resonance position between the paramagnetic nickel and the diamagnetic zinc complexes, such that an upfield shift is considered positive.

Origin of Isotropic Shifts

All complexes gave well-resolved spectra, with line widths ranging from ~400 Hz for α-H, to 15–50 Hz for 5-CH$_3$ or γ-H. The three peaks at -10 to -14, -75 to -80, and 0 to $+14$ ppm, with relative areas 1:2:6, clearly result from 4-H, 3-H, and 5-CH$_3$, respectively, as they are present in all complexes. The remaining peaks are unambiguously assigned to the alkyl protons on the basis of substitution and areas, except for some of the cyclohexyl protons, which gave rise to a complex pattern of lines around -3 to -6 ppm. The nmr traces of py(Et)$_2$NiBr$_2$ and py(*sec*-Bu)$_2$NiBr$_2$ are illustrated in Figure 1. The observed isotropic shifts for all complexes in CDCl$_3$, and for five complexes in a variety of noncoordinating solvents are given in Tables I and II, respectively.

The temperature dependence of the isotropic shifts for py(*n*-Pr)$_2$NiBr$_2$, py(*sec*-Bu)$_2$NiCl$_2$, py(*sec*-Bu)$_2$NiBr$_2$, and py(*c*-Hex)$_2$NiI$_2$ exhibited a Curie behavior within experimental error (as illustrated in Figure 2), such that it is very unlikely that there exists any equilibrium between different configurations or different spin states.[15]

In order to analyze the shifts in Tables I and II more closely, it is first necessary to gauge the relative importance of the dipolar relative to the contact mechanism as the source of the sizable paramagnetic shifts. Inasmuch as the ligand field spectra suggest[13] a distorted TBP, any sizable magnetic anisotropy should be describable by a primarily axially symmetric *g* tensor, where the unique axis corresponds to the *x* axis in Figure 3. The TBP configuration[16] requires that the X-Ni-X angle be ~120°. The main distortion from an idealized

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[15] The observed Curie behavior eliminates not only any singlet–triplet equilibrium, but in all likelihood also rules out the presence of more than one geometric configuration in solution. The isotropic shifts for at least some protons will differ in different geometric isomers, and since the equilibrium would be temperature dependent, a non-Curie behavior is expected for at least some of the peaks.

[16] Since the symmetric tridentate ligand is planar, the solution structure can most probably be described by C_{2v} symmetry, which is maintained for both the SBP and TBP configurations, since they differ only in the X-Ni-X angle.

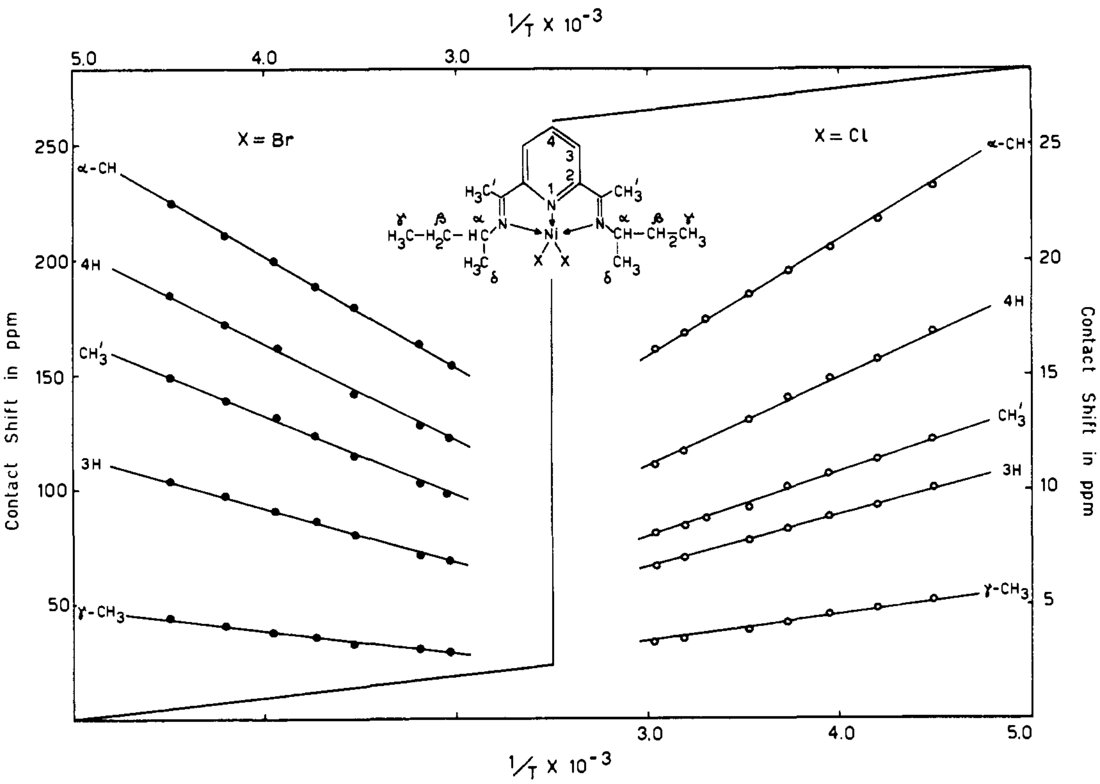


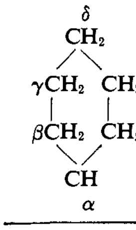
Figure 2. Curie plot for $CDCl_3$ solutions of py(*sec*-Bu)$_2$NiCl$_2$ and py(*sec*-Bu)$_2$NiBr$_2$.

TBP, aside from the difference in donor atoms, probably arises from a X-Ni-X angle greater than 120°, and from the fact that the N_1-Ni-N_6 angle is probably less than 90°.[17] The dipolar shift is given by eq 1 where all terms

$$\left(\frac{\Delta H}{H}\right) = -\frac{\beta^2 S(S+1)}{45kT}(3g_{\parallel}^2 + g_{\parallel}g_{\perp} - 4g_{\perp}^2) \times \left(\frac{3\cos^2\chi - 1}{r^3}\right) \quad (1)$$

have their conventional meaning.[2] The relative dipolar shifts for the various ligand protons are thus determined solely by their relative values of the geometric factor, $(3\cos^2\chi - 1)/r^3$; in case of significant rhombic distortion, a second geometric factor, $(\sin^2\chi \cos 2\Omega)/r^3$, must also be included.[18] Though the exact structure of the complexes is unknown, reasonable estimates to the geometric factors can be obtained,[19] and

Table I. Proton Contact Shifts for py(R)$_2$NiX$_2$ Complexes[a]

R	X	N=CCH$_3$	4-H	3-H	α-H	β-H	γ-H	δ-H
$\overset{\alpha}{CH_3}$	Br	+4.95	−11.45	−79.17	−114.5	...	...	...
$\overset{\alpha}{CH_2}\overset{\beta}{CH_3}$	Cl	+3.42	−10.64	−75.75	−135.7	−8.87	...	...
	Br	+5.02	−11.17	−77.50	−134.6	−7.27	...	...
$\overset{\alpha}{CH_2}\overset{\beta}{CH_2}\overset{\gamma}{CH_3}$	Br	+5.27	−10.95	−77.35	−135.4	−5.90	−3.57	...
$\overset{\alpha}{CH}(\overset{\delta}{CH_3})\overset{\beta}{CH_2}\overset{\gamma}{CH_3}$	Cl	+8.68	−11.78	−73.35	−175.5	−7.93	−3.65	−7.33
	Br	+10.65	−13.04	−75.80	−170.6	−7.38	−3.14	−5.38
$\overset{\alpha}{CH}(\overset{\beta}{CH_3})_2$	Cl	+8.77	−12.99	−74.25	−167.8	−8.57	...	...
	Br	+10.90	−13.63	−76.65	−165.1	−7.87	...	...
	Cl	+9.00	−13.16	−74.80	−167.6	*b*	*b*	*b*
	Br	+11.08	−13.50	−76.25	−167.0	*b*	*b*	*b*
	I	+14.26	−14.95	−77.72	−166.2	*b*	*b*	*b*

[a] Shifts in parts per million (ppm), referenced against diamagnetic zinc complex, at 29° in $CDCl_3$ solution. [b] Either not resolvable or identifiable due to complexity of spectrum.

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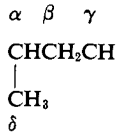
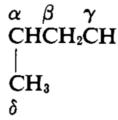
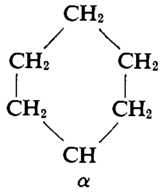
Table II. Proton Contact Shifts for py(R)$_2$NiX$_2$ in Noncoordinating Solvents[a]

			Dielectric constant,[b] ε				
			4.39	4.81	9.08	20.7	35.9
			Dipole moment,[b] μ				
			1.0	1.05	1.51	2.8	3.1
H	X	Position	CDBr$_3$	CDCl$_3$	CD$_2$Cl$_2$	C$_3$D$_6$O	CD$_3$NO$_2$
$\overset{\alpha}{CH_2}\overset{\beta}{CH_3}$	Br	5-CH$_3$	+6.03	+5.02	+2.86	+2.90	−0.11
		3-H	−77.94	−77.50	−77.09	−77.50	−78.28
		4-H	−11.74	−11.17	−10.49	−10.35	−9.75
		α-CH$_2$	−133.8	−134.6	−134.7	−135.2	−135.8
		β-CH$_3$	−7.01	−7.27	−7.43	−7.52	−7.92
$\overset{\alpha}{CH_2}\overset{\beta}{CH_2}\overset{\gamma}{CH_3}$	Br	5-CH$_3$	+6.08	+5.27	+2.90	+2.93	−0.17
		3-H	−77.60	−77.35	−77.50	−77.23	−78.22
		4-H	−11.10	−10.95	−10.25	−10.57	−9.12
		α-CH$_2$	−134.2	−135.4	−135.4	−135.4	−136.8
		β-CH$_2$	−5.21	−5.90	−6.27	−6.53	−6.90
		γ-CH$_3$	−3.24	−3.57	−3.80	−3.71	−4.32
 $\underset{\underset{\delta}{CH_3}}{\underset{\vert}{\overset{\alpha}{CH}}}\overset{\beta}{CH_2}\overset{\gamma}{CH_3}$	Cl	5-CH$_3$	...	+8.68	+7.70	+7.68	+6.50
		3-H	...	−73.35	−71.76	−72.40	−73.45
		4-H	...	−11.78	−11.95	−11.99	−11.44
		α-CH	...	−175.5	−175.3	−176.8	−175.4
		β-CH$_2$	...	−7.93	−8.02	−8.15	−8.47
		γ-CH$_3$	...	−3.65	−3.80	−3.85	−4.06
		δ-CH$_3$	...	−7.33	−7.63	*c*	*c*
 $\underset{\underset{\delta}{CH_3}}{\underset{\vert}{\overset{\alpha}{CH}}}\overset{\beta}{CH_2}\overset{\gamma}{CH_3}$	Br	5-CH$_3$	+10.68	+10.65	+9.80	+9.77	−8.68
		3-H	−75.98	−75.80	−74.53	−74.88	−76.27
		4-H	−13.20	−13.04	−13.00	−13.28	−12.78
		α-CH	−168.0	−170.6	−169.6	−170.7	−174.3
		β-CH$_2$	−7.27	−7.38	−7.47	−7.43	−7.68
		γ-CH$_3$	−3.12	−3.14	−3.18	−3.11	−3.35
		δ-CH$_3$	−5.13	−5.38	−5.75	−5.80	−6.20
	I	5-CH$_3$	...	+14.27	+13.75	+13.44	+12.82
		3-H	...	−77.27	−77.32	−76.24	−76.98
		4-H	...	−14.95	−14.62	−14.77	−14.34
		α-CH	...	−166.7	−166.5	−166.8	−169.9
$\overset{\alpha}{CH_2}C_6H_5$[d]	Cl	5-CH$_3$	*e*	*e*	*e*	*e*	+13.52
		3-H					−67.27
		4-H					−12.62
		α-CH$_2$					−113.4
$\overset{\alpha}{CH_2}C_6H_5$[f]	Br	5-CH$_3$	*e*	*e*	*e*	*e*	+13.75
		3-H					−67.00
		4-H					−12.95
		α-CH$_2$					−133.3

[a] Shifts in ppm at 29°, referenced against zinc complexes. [b] From "Handbook of Chemistry and Physics," 45th ed, The Chemical Rubber Publishing Company, Cleveland, Ohio, 1964. [c] Not resolvable from the β-CH$_2$. [d] Phenyl shifts are: *o*-H, +1.20; *m*-H, −0.23; *p*-H, +0.33. [e] Insoluble. [f] Phenyl shifts are: *o*-H, +1.70; *m*-H, −0.04; *p*-H, +0.48.

are given in Table III. The geometric factors for the SBP, where the unique axis is the *z* axis in Figure 3, are also included in Table III for comparison.

That the dipolar shifts are not dominant is evident from the fact that Table III predicts that for both configurations the alkyl and pyridine shifts should have opposite sign, which is contrary to observation. The maximum dipolar contribution to the negative pyridine shifts, consistent with $g_{av} = 2.33$[13] ($g_{\parallel} = 2.0$, $g_{\perp} = 2.5$), is calculated to be −3.6 ppm using eq 1. A more reasonable anisotropy of $g_{\perp} - g_{\parallel} = 0.2$ ($g_{\parallel} = 2.2$, $g_{\perp} = 2.4$) predicts a dipolar 4-H shift of 1.7 ppm with an even smaller shift of opposite sign for the 5-CH$_3$. Similar estimates result from using the SBP geometric factors, or from the rhombic geometric factors in Table III. The maximum anticipated dipolar shift for α-H is ~9 ppm.

Furthermore, the phenyl shifts in the benzyl substituents alternate in sign, and are indicative of π spin density, as previously reported for nickel complexes[20]

(19) Assumed bond distances and angles are: C—C = 1.54; C=C = 1.39, C—H = 1.09, and C=N = 1.30 Å; aliphatic angles = 109°; aromatic angles = 120°, except for the pyridine ring, for which the actual pyridine structure was used (L. E. Sutton, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions," Burlingame House, London, 1958). The Ni-N(py) distance was taken as a typical azomethine-nitrogen-nickel distance, 1.90 Å (E. C. Lingafilter and R. L. Braun, *J. Am. Chem. Soc.*, 88, 2951 (1966)). For 5-CH$_3$ and α-CH$_3$, the calculations were averaged over all angles, while for β-CH$_3$ and γ-CH$_3$, only the extended carbon chain configuration was included. The calculated geometric factors differed by less than a factor of 2 as Ni-N was varied from 1.8 to 2.0 Å.

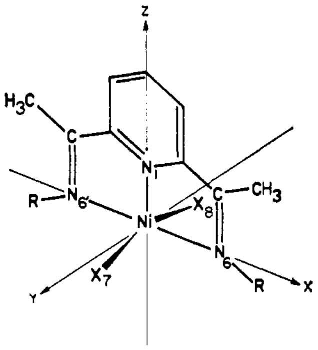


Figure 3. Coordinate system and geometry for $py(R)_2NiX_2$ complexes.

Table III. Calculated Geometric Factors for $py(R)_2NiX_2$[a]

	Trigonal bipyramid		Square-based pyramid	
Position	$\left(\frac{3\cos^2\chi - 1}{r^3}\right)^b$	Rel GF[c]	$\left(\frac{3\cos^2\chi - 1}{r^3}\right)^b$	Rel GF[c]
3-H	−0.00349	−0.144	+0.01153	+0.971
4-H	−0.00515	−0.212	+0.01030	+0.868
5-CH_3	+0.00701	+0.288	0.00000	0.000
α-H	+0.02431	+1.000	−0.01188	−1.000
β-H	+0.01115	+0.458	−0.00505	−0.426
γ-H	+0.00657	+0.270	−0.00329	−0.277
o-H	+0.00900	+0.371	−0.00569	−0.478
m-H	+0.00198	+0.082	−0.00130	−0.110
p-H	+0.00102	+0.042	−0.00003	−0.003
	$\left(\frac{\sin^2\chi\cos 2\Omega}{r^3}\right)$	Rel GF	$\left(\frac{\sin^2\chi\cos 2\Omega}{r^3}\right)$	Rel GF
3-H	+0.00603	+7.27	+0.00153	+0.127
4-H	0.00516	+6.22	+0.00000	0.000
5-CH_3	+0.00242	+2.92	+0.00476	+0.394
α-H	+0.00083	+1.000	+0.01290	+1.000
β-H	+0.00095	+1.145	+0.00573	+0.474
γ-H	+0.00144	+1.735	+0.00328	+0.272

[a] Geometric factors were calculated using the bond distances and angles in ref 19; for the TBP, the X–Ni–X angle is 120°, for the SBP, 180°. [b] Value given is $\times 10^{-24}$ cm^{-3}. [c] Rel GF designates the relative geometric factor, where the α-H dipolar shift is normalized to unity in each case.

of benzylamine, which gave approximately equal positive *o*-H and *p*-H shifts, and negative *m*-H shifts. Since this π spin density must arise from the nonorthogonality of the σ and π systems, the phenyl shift pattern in these complexes should closely resemble that of the magnetically isotropic benzylamine-nickel complex,[20] if the dipolar interaction is negligible in the five-coordinated complexes. This is indeed observed. Thus the maximum dipolar shift can only account for the slightly more positive *o*-H than *p*-H shift. Using the benzyl geometric factors[21] in Table III, the maximum dipolar contribution to the *o*-H shift consistent with the π shift pattern is calculated to be only 1 ppm. This leads to maximum dipolar contributions of +0.6 and −0.5 ppm for the 5-CH_3 and pyridine protons, respectively. The changes in isotropic shifts upon varying halogen, substituent, and solvent are only a few parts per million for most protons, and are not at all consistent with the expected dipolar behavior for either configuration, even upon including the rhombic geometric factor.[18] It therefore appears safe to attribute both the observed shifts and their X, R, and solvent dependence primarily to a contact interaction.

The appearance of both upfield and downfield shifts indicates the presence of both σ and π delocalization.[2] σ spin density results in large downfield shifts which attenuate rapidly with the number of bonds from the metal.[22–24] π delocalization[2] produces upfield shifts for protons and downfield shifts for methyl groups at aromatic centers where molecular orbital theory predicts sizable spin density, while protons and methyl groups attached to aromatic centers which experience negative spin density due to correlation effects will exhibit negative and positive shifts, respectively. The source of the contact shift can be treated in terms of the three parts of the ligand.

(a) For the pyridine ring, the downfield shifts are similar to those previously reported for pyridine in both tetrahedral[23] and octahedral[22] nickel(II) complexes, where σ delocalization has been firmly established.[23] The possibility of a sizable π contribution to the 4-H shift exists, as has been also found in other pyridine complexes of nickel.[22,23]

Table IV. Calculated π Spin Densities for $py(R)_2$[a]

	HBO[b] (A_2)		LAO (B_2)	
Position	HMO	M-HMO	HMO	M-HMO
N_1	0.000	−0.061	+0.285	+0.384
C_2	+0.140	+0.153	+0.074	+0.060
C_3	+0.191	+0.241	+0.007	−0.039
C_4	+0.000	−0.070	+0.100	+0.114
C_5	+0.014	−0.046	+0.095	+0.083
N_6	+0.155	+0.218	+0.131	+0.148

[a] Parameters used where $\alpha_N = \alpha + 0.5\beta$, $\beta_{CN1} = \beta$, $\beta_{CN6} = 1.2\beta$, with numbering as in A. Only half of the symmetric molecule is shown. [b] HMO is Hückel spin density, and M-HMO is correlated spin density using $\lambda = 1.2$. Orbital energies are: HBO, -0.856β; LAO, -0.523β.

(b) The sizable upfield 5-CH_3 shift strongly suggests a π spin density, such that the spin density at C_5 must be negative.[2] In order to determine which π orbital predicts a sizable negative C_5 spin density, a Hückel MO calculation was preformed, correcting for correlation by the method of McLachlan.[25] The calculated spin densities for the highest bonding (HBO) and lowest antibonding (LAO) π orbitals are shown in Table IV, which suggest that the unpaired spin most likely resides in the HBO, since it predicts the correct sign for C_5. It should be pointed out that the π spin density appears to dominate only at the 5-CH_3, such

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(20) R. J. Fitzgerald and R. S. Drago, *J. Am. Chem. Soc.*, **89**, 2879 (1967).

(21) The benzyl geometric factors in Table III were calculated allowing all internal rotations except those configurations where the *o*-H–Ni distance was less than 3 Å. In reality, the benzyl group is very unlikely to be free to rotate. However, the geometric factor for *o*-H varied between 0.00732 and 0.01125, indicating that the dipolar shift should be fairly insensitive to the benzyl configuration, particularly for TBP. Thus the choice of configuration does not alter the estimate to the maximum dipolar shifts for the benzyl group consistent with the observed π alternation of shift directions. For the most likely configuration, where the phenyl ring is perpendicular to the pyridine plane and points away from 5-CH_3, the calculated geometric factors are even larger than those given in Table III.

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

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

(24) D. R. Eaton, A. D. Josey, and R. E. Benson, *ibid.*, **89**, 4040 (1967).

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

that the spin densities in Table IV cannot be expected to apply to the pyridine protons. However, the HBO predicts a downfield 4-H shift, such that the observed downfield 4-H shift may well reflect both π and σ spin densities. Indeed, the effects of halogen, substituent, and solvent variation all suggest that both mechanisms contribute to the observed 4-H shift.

(c) The shifts for the alkyl substituents must reflect σ delocalization due to the absence of a π system, and closely resemble the large downfield shifts previously observed for similar substituents.[2] Though the dipolar interaction predicts a similar attenuation of shifts with chain length, it is totally incapable of accounting for the observed shift magnitudes.

As illustrated in Tables I and II, the halogen atom and substituents, as well as the solvent markedly influence the extent and nature of the spin delocalization mechanism(s). Inasmuch as the equilibrium solution structure of a five-coordinated nickel complex results from a balance between crystal field stabilization energies,[8] which stabilize the SBP, and steric interaction, which should favor the less crowded TBP, it may be anticipated that changing the size of the coordinating ligands or substituents would in some way affect the solution structure. It is therefore of interest to analyze the observed shift trends with the three variables, and determine whether these changes are consistent with variable electronic effects for fixed structure, or whether the shift trends instead parallel a steric or bulkiness effect, which would suggest slight structural changes.

Shift Variations with Halogen Atom

Certain basis trends in contact shifts as a function of halogen are evident from Tables I and II. The σ shifts in the pyridine ring increase in the order Cl < Br < I, while the 5-CH_3 π shifts increase in the same order, but at a much faster rate than the 3-H shifts, such as to produce a significant increase in the relative π/σ delocalization in the order Cl < Br < I. On the other hand, the alkyl σ shifts all *decrease* in the order Cl > Br > I. It may be noted that the 4-H shifts generally increase at a much faster rate than the 3-H shifts, and tend to resemble more the larger increases of the 5-CH_3 π shifts, suggesting that at least part of the observed 4-H shift must reflect π delocalization into the pyridine ring.

Similar variations of contact shifts with halogens have been noted for pseudo-tetrahedral bis(pyridine)cobalt(II) dihalides,[26,27] and were attributed[26] to an anion ligand field strength effect, assuming that any structural effects, if present, were negligible. The MO model employed[26] to rationalize the variable covalency was proposed for pseudo-tetrahedral C_{2v} complexes,[16] but it will be shown that a similar line of reasoning will predict the same covalency dependence on halogen atom of the present five-coordinated complexes. Following Wayland and Drago,[26] we first construct the NiX_2 fragment from the nickel 3d and the halogen σ orbitals. As indicated previously,[28] the NiX_2 antibonding acceptor orbitals capable of σ bonding with the chelate will have energies[28] Cl > Br > I.

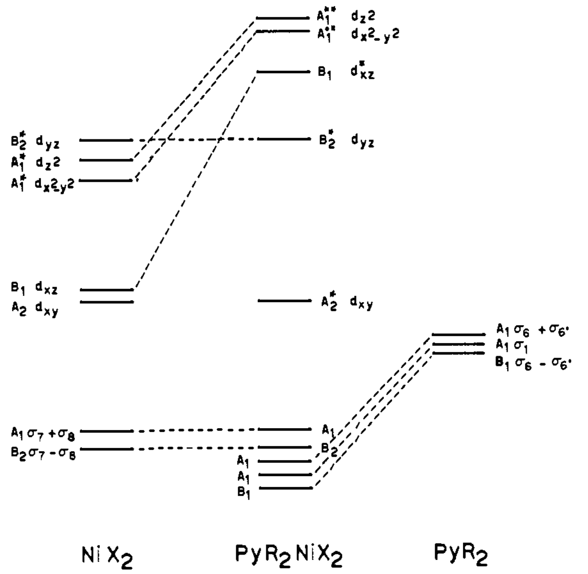

Figure 4. Energy level diagram for $py(R)_2NiX_2$, constructed from NiX_2 and $py(R)_2$ σ orbitals.

In Figure 4, we construct the energy level diagram for the five-coordinated complexes from the orbitals of the NiX_2 and $py(R)_2$ fragments. Here the analogous diagram for the tetrahedral complexes[26] differs somewhat in that we now have an additional σ orbital from the pyridine nitrogen. Using the arguments from the four-coordinated case,[26] the coordination of $py(R)_2$ results in the small contribution of the $py(R)_2$ σ orbitals to the unpaired spin containing antibonding orbitals increasing in the order Cl < Br < I. This prediction agrees with the pyridine shift variations, but contradicts the observed σ covalency trends for the alkyl substituents.[29] Though the purely electronic anion effect could cause covalency trends as observed for 3-H, the lack of consistency with the alkyl shifts indicates that observed 3-H shift trends may not be taken as evidence for the electronic effect in these complexes.

It is thus apparent that the electronic effect alone cannot account for the observed shift changes for fixed structure, such that it is considered very likely that changing the halogen atom could induce slight structural changes in solution due to the variable size of bulkiness of the anions.[27]

Shift Variations with Alkyl Substituent

The most pronounced variation in contact shifts with R again involves the extent of π delocalization, with the 5-CH_3 shifts increasing in the order Me < Et < *n*-Pr < *i*-Pr ~ *sec*-Bu < *c*-Hex < Bz, for fixed X and solvent. Very small and irregular variations are observed for the 3-H σ shifts, indicating that σ delocalization is not significantly affected. The 4-H shifts, however, again increase more or less with the 5-CH_3 shifts, confirming a π delocalization increase over the whole ligand. This substituent effect is characterized by a π/σ delocalization increase in the above order of R.

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(26) B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, 88, 4597 (1966).

(27) G. N. La Mar, *Inorg. Chem.*, 6, 1959 (1967).

(28) Figure 2 in ref 26 is applicable here, except that since the X–Ni–X angle in the five-coordinated complex is greater than 120°, the B_2 (yz) will be slightly less antibonding and the A_1 $(x^2 - y^2)$ perhaps more antibonding in the present complexes. However, the predicted energy dependence on halogen, Cl > Br > I, will be identical.

(29) Though energies of the spin containing antibonding orbitals for $py(R)_2NiX_2$ will depend on both the assumed X–Ni–X and N–Ni–N angles, the predicted covalency trends for fixed structure, Cl < Br < I, will remain the same.

This alkyl group effect on shifts can be analyzed first in terms of purely electronic effects, where the basicity of the coordinating azomethine nitrogens is altered by the σ inductive effect of R.[30,31] This inductive effect can be estimated from the Taft[31] σ^* values for R, which are listed in Table V. If the shift variations, particularly the π/σ delocalization, are of purely electronic origin, a more or less linear, or at least monotonic dependence of contact shift on Taft σ^* values would be expected.[30,31] However, as can be seen from a comparison of the shifts in Tables I and II, particularly for py(R)$_2$NiBr$_2$ in either CDCl$_3$ or CD$_3$NO$_2$, and the σ^* values in Table V, no such correlation exists. The deviations are most obvious for the cyclohexyl and benzyl groups, for which the largest π shifts are observed, though their σ^* values predict the smallest π shifts for benzyl, and some intermediate shift for cyclohexyl. R is not expected to significantly influence the π spin density in the complexes for fixed structure.[32]

Table V. Electronic and Steric Parameters for R

R	Taft σ^* parameter[a]	Well's steric parameter[b]
Benzyl	+0.215	−0.38
Methyl	0.00	0.00
Ethyl	−0.10	−0.07
n-Propyl	−0.115	−0.36
Cyclohexyl	−0.150	−0.79
Isopropyl	−0.190	−0.47
sec-Butyl	−0.215	. . .

[a] Data taken from ref 31. [b] Data taken from ref 33.

However, the shift variations with R do tend to follow a trend expected on the basis of increasing bulkiness or steric hindrance of R.[27] Indeed, the changes in contact shifts tend to parallel increases in the steric parameters for R, given by Wells,[33] which are also included in Table V. The only numerical deviation from the ordering of the steric constants relative to the shift changes is for the benzyl group, which should fall between *n*-Pr and *i*-Pr. However, molecular models[34] of the benzyl complex indicate that even incomplete rotation of the phenyl group at the tetrahedral angle about the N–C axis would interfere more seriously with the halogen atoms than do the methyl groups in the isopropyl substituent.

It is interesting to note that the magnitude of the σ shifts for the α-protons in alkyl substituents seems to depend only on the *number* of protons attached to C$_\alpha$, and not on the exact nature of R. Whether this reflects an inherent dependence of the C–H covalency on the number of other protons on that carbon is being investigated currently.

Shift Variations with Solvent

For the five noncoordinating solvents employed in this study, the 5-CH$_3$ shifts generally experienced a marked decrease in shift in the order CDBr$_3$ > CDCl$_3$ > CD$_2$Cl$_2$ > C$_3$D$_6$O > CD$_3$NO$_2$. Again, a similar decrease in 4-H is noted, reflecting its π shift contribution, while the 3-H σ shifts remained the same within experimental error. In addition, the alkyl σ shifts generally increase in the order CDBr$_3$ < CDCl$_3$ < CD$_2$Cl$_2$ < C$_3$D$_6$O < CD$_3$NO$_2$, opposite to the trends for the π shifts. Since a more or less proportional increase in shifts is observed for all alkyl protons, a variable dipolar shift can be definitely eliminated.

In this situation, a direct electronic effect is improbable, since the complexes remain five-coordinated[13,35] in each solvent, and the solvent does not experience any isotropic shift. However, the systematic changes in contact shifts, especially the relative π/σ delocalization, may reflect slight structural changes due to variable solvation effects. Such an effect could be expected[3] to depend on the solvating properties of the solvent, such that the contact shift trends should parallel changes in solvent dielectric strength or dipolar moments. The dielectric constant, ϵ, and the dipole moment, μ, for the five solvents are included in Table II, where it is apparent that the observed shift trends, such as decrease in π/σ covalency, do generally parallel increases in solvent dielectric strength.

Discussion

It thus appears that the observed shift trends are inconsistent with variable electronic effects of either X or R for a fixed structure. We have no *a priori* knowledge as to what shift changes can be expected on the basis of a given structural modification in these complexes. On the other hand, it is possible to postulate the most probable effect on structure on increasing the steric effect or bulkiness of the ligand. For any equilibrium structure intermediate between a SBP and TBP for arbitrary X and R, it would be expected that increasing the size of X or R would stabilize the sterically less crowded TBP, while decreasing the size of X or R would favor the electronically more stable SBP.[8] It would therefore be expected that increasing the size of X or R will have the same effect on the contact shift if similar structural changes result from the substitutions.

Table VI summarizes the observed effects of R and X on contact shifts for various parts of the ligand. Increasing the size of X indeed alters the contact shifts for the various protons in the same direction and with approximately the same relative magnitude as does increasing the bulkiness of R.

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(30) R. S. Drago and B. B. Wayland, *Inorg. Chem.*, 7, 628 (1968).

(31) R. W. Taft, "Steric Effects in Organic Chemistry," John Wiley & Sons. Inc., New York, N. Y., 1956, Chapter 13.

(32) An additional reason for discarding purely electronic effects of R to explain the sizable changes in π delocalization is that similar nmr studies on bis(aminotroponimine) and bis(salicylaldimine) complexes of nickel(II), which exist as an equilibrium mixture of square-planar and tetrahedral isomers in solution, have unequivocally shown that variation of the azomethine nitrogen substituent *does not* noticeably affect the extent of π delocalization, though the steric properties of R greatly determine the extent of conversion into the sterically more favorable tetrahedral form: D. R. Eaton, A. D. Josey, and W. D. Phillips, *J. Chem. Phys.*, 37, 347 (1962), and references therein; R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, 7, 83 (1966).

(33) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963), in particular, Table VI.

(34) Model employed is "CPK Atomic Models," The Ealing Corporation, Cambridge, Mass.

(35) The absorption spectra in all solvents here concur with a five-coordinated structure, though small band shifts are observed, and are inconsistent with spectra expected for an octahedral nickel complex. For example, for py(*sec*-Bu)$_2$NiBr$_2$, the low energy bands (with extinction coefficients) are: diffuse reflectance, 8000, ~8800, 12,500 cm^{-1}; in C$_2$H$_4$Cl$_2$, 8400 (22), 13,400 (46); CHCl$_3$, 8500 (23), ~9200 (sh), 13,800 (42); C$_3$H$_6$O, 8300 (21), ~9300 (sh), 13,300 (42); CH$_3$NO$_2$, ~8000 (sh), 9300 (19), 13,500 (30). The typically octahedral bands, such as observed for py(*sec*-Bu)$_2$Ni(NO$_3$)$_2$ at 10,200 (43) and 16,000 cm^{-1}, are absent for the halogen complexes in all solvents considered here.

Table VI. Effects of R, X, and Solvent on Contact Shifts

Position	Decrease in size of X	Decrease in size of R	Increase in solvent dielectric strength
5-CH$_3$	D (l)[a]	D (l)	D (l)[b]
4-H	D (m)	D (m)	D (m)[b]
3-H	D (s)	Irreg[c]	Irreg[c]
α-H	I (s)	...	I (s)
π/σ	D (l)	D (l)	D (l)

[a] D and I indicate a decrease and increase, respectively, in contact shifts at any position upon varying X, R, or solvent in the listed manner. In parentheses is indicated the magnitude of the change in contact shift for the range of the variable, where (s) small, (m) medium, and (l) large represent changes of 0–5, 6–15, and over 16%, respectively. [b] For variable solvent, the magnitude of the change in the π shifts depends on the size of X and R. The smaller X and R, the larger the percentage change. [c] The contact shift changes at this position are too small and irregular to characterize.

The most plausible relationship between the increasing sizes of X or R and the structure would involve changes in the X–Ni–X angle. For variable X, the 3-H and alkyl σ shifts vary only 3–4%, while for variable R, the constancy of the α-CH and α-CH$_2$ shifts and the insensitivity of the 3-H σ shifts with R attest to a more or less fixed geometry for the py(R)$_2$Ni part of the complex.

Interpretation of the solvent effect on the contact shifts in terms of slight structural variations cannot directly involve either electronic or steric effects. However, as there is no evidence for direct solvent coordination to the complexes,[35] it seems likely that a variable solvation effect might influence the solution structure. In a previous analysis of five-coordinated nickel complexes,[3] it has been shown that increasing the solvent dielectric strength tended to favor the more highly solvated SBP over the TBP. Similar preferred solvation tendencies have been invoked[36] to explain the solvent dependence of the free energy for the equilibrium between the better solvated square planar over the tetrahedral forms of the nickel(II) bis(aminotroponimines).

Should superior solvating properties induce slight structural changes in the direction of a SBP, which would correspond to increasing the X–Ni–X angle, it might be expected that increasing the solvent dielectric strength and/or dipole moment would produce changes in the observed ligand contact shifts comparable to changes resulting from decreasing the size of either X or R. The summary in Table VI illustrates that there is a surprisingly good correlation between the shift trends, in both direction and relative magnitude, for the various protons as X or R is reduced in size or the solvent dielectric strength is increased.

Support for postulating a structural variation with variable solvent dielectric strength can be drawn from the fact that the effect of varying the solvent on any complex depends very much on the size of R and X, being largest for complexes with small X and R. The solvent changes CDCl$_3$ → CD$_2$Cl$_2$ → C$_3$D$_6$O → CD$_3$NO$_2$ decrease the 5-CH$_3$ π shifts in py(Et)$_2$NiBr$_2$ by 100%; in py(*sec*-Bu)$_2$NiCl$_2$ by 25.1%; in py(*sec*-Bu)$_2$NiBr$_2$ by 18.5%; and in py(*c*-Hex)$_2$NiI$_2$ by only 10.2%. As anticipated, the steric effects of the smaller R or X, ethyl or Cl, are more readily overcome by solvation effects than for the larger groups, cyclohexyl or I, as observed previously.[3]

Unfortunately, it is not possible to relate the observed contact shift changes to the magnitudes of the proposed variation in the X–Ni–X angle within the present status of our understanding of spin delocalization. Our analysis suggests that π contact shifts increase and alkyl σ spin densities decrease with decreasing X–Ni–X angle. In view of the minute fraction of an unpaired electron which resides in the ligand π orbital (<0.01), only very slight changes in bond overlaps or covalencies, of the order $\sim$1%, could account for the observed shift changes.

The different dependence of the π and σ spin densities on R, X, and solvent indicate that two distinct delocalization mechanisms exist, such that any nonorthogonality[20,37] of the ligand π and σ systems does not give rise to the 5-CH$_3$ π shifts. Crystal field calculations have indicated that the unpaired spins in five-coordinated nickel(II) reside in the d$_{x^2-y^2}$ and d$_{z^2}$ orbitals in both the SBP and TBP. The only d orbital capable of π bonding in C$_{2v}$ symmetry is the doubly occupied d$_{xy}$(A$_2$). It thus seems likely that some unpairing of the d$_{xy}$ electrons must occur by some spin–orbit coupling mechanism,[11,38] where the extent of unpairing depends on the energy separation between d$_{xy}$ and the spin containing orbitals. Since the changes in structure will alter this spacing, as is observed[11,35] in the absorption spectra upon varying R, X, or solvent, the amount of unpaired spin available in d$_{xy}$ may well depend on R, X, and solvent. The observed π shift changes could therefore reflect differences in the extent of unpairing of the d$_{xy}$ orbital rather than changes in the nickel–ligand covalency.[39]

Acknowledgments. The support of NATO through a postdoctoral fellowship to G. N. L., as well as the hospitality of the Swiss Federal Institute of Technology, are gratefully acknowledged.

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(36) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963).

(37) R. W. Kluiber and W. D. Horrocks, Jr., *Inorg. Chem.*, **6**, 430 (1967).

(38) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 6.

(39) NOTE ADDED IN PROOF. A recent X-ray structure of the pseudo-tetrahedral complex, bis(triphenylphosphine)nickel(II) dibromide (J. A. J. Jarvis, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc.*, 1473 (1968)), has yielded the angles, Br–Ni–Br = 126.3° and P–Ni–P = 110.4°. The previously reported data for the analogous chloride (G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, *ibid.*, 3625 (1963)) are Cl–Ni–Cl = 123° and P–Ni–P = 117°. Thus the X–Ni–X angle increases significantly and the P–Ni–P angle decreases on going from Cl to Br. The increase in the X–Ni–X angle is interpreted as arising from increased halogen–halogen repulsion, which apparently also causes the P–Ni–P angle to decrease. Thus the neglect of structural changes with halogen in the interpretation of covalency changes with halogen in pseudo-tetrahedral complexes[26,31] appears to be unjustified.