Nuclear Magnetic Resonance Contact Shift, Infrared, and Electronic Spectroscopic Study of Bis(stilbenediamine)nickel(II) Complexes[1a]

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Abstract: Estimates of the relative strengths of axial anionic ligands were investigated by nmr, ir, and visible absorption spectroscopy in a series of complexes of the type *trans*-Ni(*meso*-stilbenediamine)$_2$(anion)$_2$, where anion = acetate, chloro-substituted acetate, benzoate, and substituted benzoate. The various criteria for establishing the order of the relative coordinating power of the acetates are compared with that intuitively expected on the basis of the relative basicities of the anions. The effect of varying the axial ligand on the stilbenediamine proton magnetic resonance contact shifts showed that the observed contact shift increases as the axial ligand strength increases. This trend is opposite to that predicted on the basis of the inductive properties of the axial ligands. A model is presented to account for the experimental observations. This result clearly establishes pitfalls in the attempts to deduce trends in covalency or bond strength from trends in the magnitude of the contact shift. Crystal-field parameters were calculated by fitting the low-temperature mull spectrum. No simple relationship could be found between trends in the McClure $\delta\sigma$ and $\delta\pi$ parameters and the trends in bonding ascertained from the other physical measurements.

Studies of proton nmr contact shifts in paramagnetic molecules have been interpreted in terms of metal–ligand bonding interactions and mechanisms of electron delocalization through the ligand.[2] In this connection, the method has been employed to indicate trends in covalency in transition metal complexes as the ligand or the central metal ion is varied in a series of complexes. Only a few studies of this type have been reported,[3] and more work, preferably on a system where the answer is known, is needed to evaluate this application. The main question in this connection is: do trends in unpaired electron delocalization occurring mainly in nonbonding or antibonding orbitals accurately reflect trends in covalency in the mainly bonding orbitals in complicated molecules or ions? Some insight into the answer to this question can be obtained by properly designed experiments. If, for example, tetragonal complexes were to be studied in which the axial ligands were changed and the equatorial ligands held constant, changes in the electron–proton coupling constants for equatorial ligand protons could be examined to study whether or not these changes parallel changes in the axial ligand–metal interaction. One might expect that as the axial ligand donor strength increases, the equatorial ligands would be bonded less strongly because the metal positive charge would be decreased. The common drawbacks in such a study are a lack of knowledge of the magnitude of the axial ligand–metal interaction in the particular complex and uncertainties concerning the changes in the dipolar shift arising from a changing molecular **g** tensor.

The complexes chosen for this study are of the type Ni(*meso*-stilbenediamine)$_2$(anion)$_2$ where the anions are acetate, halo-substituted acetate, benzoate, and substituted benzoate ions. Stilbenediamine (stien) is 1,2-diphenylethylenediamine [H(C$_6$H$_5$)(NH$_2$)–C–C–(NH$_2$)(C$_6$H$_5$)H]. These complexes were chosen because they possess properties favorable for nmr analysis such as adequate solubility, availability of many protons in the complex, and absence of an appreciable dipolar (pseudocontact) shift. Furthermore, since the basicities of these anions have been extensively studied and substituent constants are reported, we have an intuitive feeling about trends in their σ coordinating ability. The p*K* values of the acids are summarized in Table I.

Table I. p*K* Values of Some Substituted Acetates and Benzoates

Acid	p*K*
Acetic	4.75
Monochloroacetic	2.85
Dichloroacetic	2.11
Trichloroacetic	0.70
p-Methylbenzoic	4.36
Benzoic	4.19
p-Chlorobenzoic	3.98

Complexes of the type studied here were first prepared by Lifschitz, *et al.*[4–6] The unusual magnetic behavior of these compounds, manifested by a diamagnetic–paramagnetic isomerism between yellow and blue forms, has aroused interest.[7] The solution electronic absorption spectrum of the dichloroacetate complex has been examined[8] in order to study the paramagnetic–diamagnetic equilibrium in ethanol and acetone–water solutions. The crystal structure of [Ni(stien)$_2$(CHCl$_2$CO$_2$)$_2$]$_3\cdot$2C$_2$H$_5$OH$\cdot$4H$_2$O indicates that

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[1] (a) Abstracted in part from the Ph.D. thesis of J. Zink, University of Illinois, Urbana, 1970; (b) NDEA Title IV Fellow, 1966–1969.

[2] For a review, see D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965).

[3] (a) E. A. LaLancette and D. R. Eaton, *J. Amer. Chem. Soc.*, **86**, 5145 (1964); (b) A. Chakravorty and R. H. Holm, *ibid.*, **86**, 3999 (1964); (c) B. B. Wayland and R. S. Drago, *ibid.*, 88, 4597 (1966); (d) G. N. La Mar, *Inorg. Chem.*, **6**, 1939 (1967); (e) R. S. Drago and B. B. Wayland, *ibid.*, 7, 628 (1968).

[4] I. Lifschitz, J. G. Bos, and K. M. Dijkema, *Z. Anorg. Allg. Chem.* **242**, 97 (1939).

[5] I. Lifschitz, and J. G. Bos, *Recl. Trav. Chim. Pays-Bas*, **59**, 407 (1940).

[6] I. Lifschitz and K. M. Dijkema, *ibid.*, 60, 581 (1941).

[7] J. R. Miller, *Advan. Inorg. Chem. Radiochem.*, 4, 172 (1962).

[8] W. C. Higginson, S. C. Nyburg, and J. S. Wood, *Inorg. Chem.*, **3**, 463 (1964).

one-third of the Ni(II) ions exist in diamagnetic form with planar coordination.[9] The effect produced on the magnetic properties of complexes of the type Ni(stien)$_2$L$_2$(ClO$_4$)$_2$ by varying the steric requirements and donor strength of neutral ligand L has also been recently reported.[10]

In this study, we have found that the anion is bonded to the metal ion in solution and that it undergoes rapid exchange on the nmr time scale. In chloroform solution, our complexes remain fully paramagnetic. We have proof of the *trans* configuration of our complexes from the crystal structure,[9] from solid and solution infrared studies, and from the visible absorption spectra reported here. Severe steric strain[10] prevents facile *cis–trans* equilibrium.

This series of complexes provides us with another possibility to test a proposed method for inferring details about metal ion–ligand interactions. In several recent reports from this laboratory, studies of the changes in bonding in tetragonal Ni(II) complexes have been inferred using a crystal-field and qualitative molecular orbital approach.[11,12] In these studies, the visible absorption spectra were fit using the crystal-field parameters B, Dq, Ds, and Dt. The McClure qualitative molecular orbital parameters $\delta\sigma$ and $\delta\pi$ were calculated[13] to infer changes in the magnitudes of metal–ligand σ and π bonding interactions. The complexes discussed here may be isolated in the solid state. The tetragonal splittings produce bands in excess of those needed to fit the parameters in the crystal-field calculation, so the effect of deviation from D_{4h} symmetry can be checked. Since both the nmr contact shift method and the visible absorption method can be applied in conjunction, this dual study enables us to test the interpretations proposed for the contact shift and crystal field parameters. There has been no reported study in which the results from the two different experiments have been used in conjunction and compared. In such a study, the values of the g tensor can be calculated from the known separations of the electronic levels. Armed with this knowledge, the pseudocontact shift contribution can be estimated. In this series of complexes, we have also examined the change in carboxylate stretching frequency upon coordination to a metal ion and inferred an order of bond strength in the metal–carboxyl oxygen bond. These inferences can then be compared with the results obtained from the electronic absorption study and the nmr contact shifts.

The $\delta\sigma$ and $\delta\pi$ parameters are found to have no simple interpretation in this series of compounds. It is also shown that trends in covalency cannot be naively inferred from trends in the contact shift; *e.g.*, a decreased equatorial ligand covalency does not correspond to increased axial ligand covalency. A model is proposed to explain the stilbenediamine proton contact shifts as the axial ligand is varied. The infrared results qualitatively correlate with intuitive estimates of the axial ligand coordinating ability.

Experimental Section

Preparation of Compounds. ***meso*-Stilbenediamine (stien).** This ligand was prepared by the method of Irving and Parkins.[14]

Anal. Calcd. for $C_{14}H_{16}N_2$: C, 79.25; H, 7.55; N, 13.21. Found: C, 79.18; H, 7.52; N, 13.34.

Ni(stien)$_2$(ClO$_4$)$_2$. This bright yellow complex was prepared by the method of Lifschitz, Bos, and Dijkema.[4] *Anal.* Calcd for $C_{28}H_{32}N_4Cl_2O_8Ni$: C, 49.28; H, 4.69; N, 8.22. Found: C, 49.03; H, 4.67; N, 8.03.

Complexes of the form Ni(stien)$_2$(anion)$_2$, where anion = acetate, monochloroacetate, dichloroacetate, trichloroacetate, benzoate, *p*-methylbenzoate, and *p*-chlorobenzoate, may be crystallized in both a yellow diamagnetic or blue paramagnetic form. The compounds which follow were all isolated in the solid state in the blue paramagnetic form. Unless otherwise indicated, the preparation followed that of Lifschitz.[4] All compounds were dried *in vacuo* before analysis.

Ni(stien)$_2$(CH$_3$CO$_2$)$_2$. *Anal.* Calcd for $C_{32}H_{38}N_4O_4Ni$: C, 63.92; H, 6.32; N, 9.32; Ni, 9.77. Found: C, 62.54; H, 6.14; N, 9.28; Ni, 9.86.

Ni(stien)$_2$(ClCH$_2$CO$_2$)$_2$. An aqueous solution of sodium monochloroacetate was added to a solution of Ni(*meso*-stien)$_2$(ClO$_4$)$_2$ in ethanol. After stirring for 1 hr, the solution turned blue and cloudy. The pale blue precipitate was filtered and washed with distilled water. The light blue powder was dried *in vacuo* over P_2O_5. *Anal.* Calcd for $C_{32}H_{36}N_4Cl_2O_4Ni$: C, 57.34; H, 5.37; N, 8.36; Ni, 8.76. Found: C, 56.98; H, 5.39; N, 8.33; Ni, 8.69.

Ni(stien)$_2$(Cl$_2$CHCO$_2$)$_2$. The intermediate, Ni(Cl$_2$CHCO$_2$)$_2$, was prepared by refluxing an aqueous solution of Cl$_2$CHCOOH with solid NiCO$_3$. *Anal.* Calcd for $C_{32}H_{34}N_4O_4Cl_4Ni$: C, 51.99; H, 4.60; N, 7.58; Ni, 7.94. Found: C, 51.88; H, 4.91; N, 7.27; Ni, 8.15.

Ni(stien)$_2$(CCl$_3$CO$_2$)$_2$. *Anal.* Calcd for $C_{32}H_{32}N_4O_4Cl_6Ni$: C, 47.55; H, 3.96; N, 6.94; Ni, 7.27. Found: C, 47.80; H, 3.99; N, 6.91; Ni, 7.33.

Ni(stien)$_2$(C$_6$H$_5$CO$_2$)$_2$. The method of Lifschitz, *et al.*,[4] was followed except that Ni(stien)$_2$(ClO$_4$)$_2$ was substituted for Ni(stien)$_2$Cl$_2$ and the crystals were washed with ethanol and ethyl ether rather than being recrystallized. *Anal.* Calcd for $C_{42}H_{42}N_4O_4Ni$: C, 69.54; H, 5.79; N, 7.73; Ni, 8.10. Found: C, 69.25; H, 5.84; N, 7.56; Ni, 8.13.

Ni(stien)$_2$(C$_7$H$_7$CO$_2$)$_2$. *p*-Methylbenzoic acid was neutralized with NaOH. The resulting aqueous solution was added dropwise to an ethanolic solution of Ni(stien)$_2$(ClO$_4$)$_2$. The green solution turned blue on stirring overnight, with fine blue-gray crystals separating out. The crystals were washed successively with distilled water, ethanol, and ethyl ether, and dried *in vacuo* over P_2O_5. *Anal.* Calcd for $C_{44}H_{46}N_4O_4Ni$: C, 70.14; H, 6.11; N, 7.44; Ni, 7.79. Found: C, 70.56; H, 6.35; N, 7.31; Ni, 7.85.

Ni(stien)$_2$(*p*-ClC$_6$H$_4$CO$_2$)$_2$. The same procedure as for the *p*-methylbenzoate was followed. *Anal.* Calcd for $C_{32}H_{40}N_4O_4Cl_2Ni$: C, 63.57; H, 5.04; N, 7.06; Ni, 7.40. Found: C, 63.02; H, 4.97; N, 6.89; Ni, 7.76.

Apparatus. a. Spectrophotometric Measurements. All near-infrared and visible absorption spectra were obtained using a Cary Model 14RI spectrophotometer equipped with a high-intensity source.

The solid-state mull spectra were obtained by grinding the compound in Kel-F stopcock grease until no particles were visible. The resulting mull was placed between two glass slides, suspended in a dewar, and flushed with nitrogen gas, and the dewar was filled with liquid nitrogen. A 30-min time interval was allowed for the temperature to equilibrate. Filter paper saturated with Nujol was placed in the reference beam. A beam attenuator was used to bring the pen onto the paper.

All infrared spectra were recorded using a Perkin-Elmer 521 grating infrared spectrophotometer.

b. Nmr Spectra. The nmr spectra were obtained with either a Jeolco Model C-60-H or Varian Model HA-100 spectrometer. All nmr spectra were measured relative to TMS as an internal standard.

c. Magnetic Susceptibility Measurements. Solution magnetic moments were obtained using the Jeolco C-60-H following the method first reported by Evans.[15] The measured susceptibilities

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(9) S. C. Nyburg and J. S. Wood, *Inorg. Chem.*, **3**, 468 (1964).

(10) D. M. Goodgame and M. A. Hitchman, *ibid.*, 7, 1404 (1968).

(11) D. A. Rowley and R. S. Drago, *ibid.*, **6**, 1092 (1967).

(12) D. A. Rowley and R. S. Drago, *ibid.*, 7, 795 (1968).

(13) D. S. McClure, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 498.

(14) M. N. Irving and R. M. Parkins, *J. Inorg. Nucl. Chem.*, **27**, 270 (1965).

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

Table II. Magnetic Resonance Results

Complex		Nmr frequencies, ν,[a] and contact shifts, $\Delta\nu$[b]					Molar susceptibilities,[c]
		ϕ	m	p	CH	NH_2	$\chi \times 10^3$
Ni(stien)$_2$–							
Acetate		±10	±5	±5	±50	±100	
	ν	−310	−474	−380	−4817	8989	4.04 ± 0.1[d]
	$\Delta\nu$	129	−35	59	4576	9068	
Monochloroacetate	ν	−288	−464	−364	−4680	9140	
	$\Delta\nu$	151	−25	75	−4439	9219	
Dichloroacetate	ν	−294	−472	−360	−4495	9162	3.95 ± 0.1[e]
	$\Delta\nu$	145	−33	79	−4254	9241	
Trichloroacetate	ν	−291	−482	−358	−4516	9080	[f]
	$\Delta\nu$	148	−43	81	−4275	9159	
Benzoate	ν	−286	−454	−358	−4648	8948	4.17 ± 0.1[g]
	$\Delta\nu$	153	−15	81	−4407	9027	
p-Methylbenzoate	ν	−295	−456	−359	−4672	8812	
	$\Delta\nu$	144	−17	80	−4431	8891	
p-Chlorobenzoate	ν	−307	−462	−365	−5042	8623	
	$\Delta\nu$	132	−23	74	−4801	8702	
Free ligand	ν	−439 ± 2[h]			−241 ± 2	−79 ± 2	

[a] In hertz relative to TMS as an internal standard. [b] In hertz relative to the free ligand. [c] Cgs units measured in $CHCl_3$. [d] 3.70 cgs units in the solid (ref 4). [e] 3.74 cgs units in the solid (ref 4). [f] 3.72 cgs units in the solid (ref 4). [g] 3.75 cgs units in the solid (ref 4). [h] Broad singlet in $CDCl_3$.

were corrected for diamagnetism by the use of Pascal's constants.[16]

d. Calculations. The calculations used to fit the visible electronic spectra have been described.[11]

Results and Assignments

(1) Nmr Spectra. The proton nmr spectrum of stilbenediamine in deuterated chloroform was found to consist of three singlets: the phenyl protons (a broad peak), the CH_2 protons, and the NH protons. In $(CH_3)_2CO$, multiplet structure in the phenyl resonance was observed. Upon coordination to paramagnetic Ni(II), forming complexes of the type Ni(stien)$_2$(anion)$_2$, five shifted proton resonances are observed whose general pattern remains constant regardless of the axial anionic ligand used. Figure 1 contains a representative paramagnetic proton nmr spectrum of the complex Ni(stien)$_2$(CH_3CO_2)$_2$. The broad peak far upfield is clearly from the N–H proton. In all nitrogen-coordinating ligands bonded to Ni(II) studied by nmr, the amine proton resonances are shifted to high fields and are considerably broadened.[17] The farthest downfield peak is assigned to the methylene protons. A downfield shift is observed for the methylene protons in nickel(II)–alkylamine and –benzylamine complexes, and for the C–H protons in Ni(butylenediamine)$_6^{2+}$.[18–20] Since the metal e_g orbitals contain two unpaired electrons aligned with the magnetic field, mixing of these orbitals with ligand σ orbitals places positive spin density (up spin) on the ligand protons causing a downfield shift at all atoms contributing to the ligand σ orbital. The methylene protons, by virtue of their proximity to the site of unpaired electron density and their predominant σ molecular orbital character, provide the most sensitive probe of σ delocalization onto the ligand. The remaining peaks all arise from the phenyl protons. The observed pattern is that which frequently arises for phenyl protons—a π delocalization mechanism. The ratios of areas of the peaks from lower to higher field are approximately 2:1:2. The highest field peak of the three is the broadest; the middle peak the sharpest. In general, the closer the proton in question is to the source of unpaired electron spins, the broader the peak. We thus assign the broad upfield peak to the *ortho* proton. The ratios of the remaining peak areas require that the sharp middle peak be assigned to the *para* proton and the downfield peak to the *meta* proton. The ratios of the phenyl proton shifts provide evidence that our assignment is consistent throughout the series of complexes. This is treated in the Discussion section. We have here another example of a complex in which the metal–ligand bonding is essentially σ (local symmetry around Ni(II) is D_{4h}), but which exhibits a dominant π mechanism on the phenyl group. The positions of the peaks relative to TMS and the observed shifts are contained in Table II.

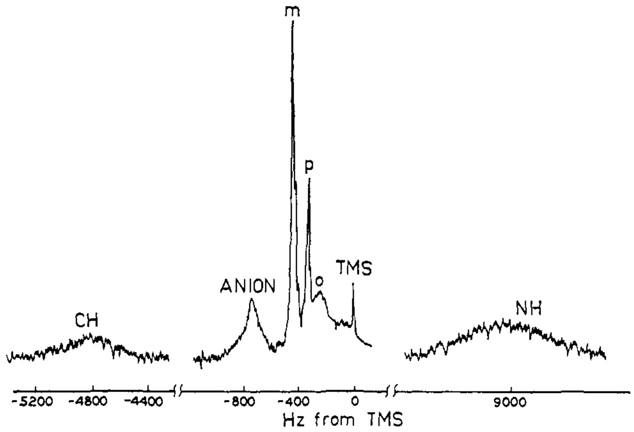

Figure 1. Photon nmr spectrum of Ni(stien)$_2$(CH_3CO_2)$_2$ in $CDCl_3$.

The assignments of the anion peaks present a more difficult problem. The acetate and dichloroacetate peaks occur in the region between the stilbenediamine *meta* phenyl and methylene protons. The monochloro-

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(16) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. Wilkins, Ed., Interscience, New York, N. Y., 1960, pp 400–454.

(17) B. F. Wayland and W. L. Rice, *Inorg. Chem.*, **6**, 2270 (1967).

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

(19) R. J. Fitzgerald and R. S. Drago, *Inorg. Chem.*, **8**, 2254 (1969).

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

acetate peak occurs as a shoulder on the broad *ortho* ring proton peak of stilbenediamine. These assignments were confirmed by integration of peak areas and by the disappearance of the peak in the trichloroacetate complex, with retention of the very similar stilbenediamine peak pattern. The benzoate and substituted benzoate peaks have not been completely assigned. In the case of the benzoate anion, three peaks should be observed, but only one could be found. Its integrated area suggests that it is either from the *ortho* or *meta* ring protons. Coordinated *p*-methylbenzoate gives two resolved peaks, one at the same frequency as benzoate and the other well upfield. The upfield peak has a larger area and is much sharper than the downfield one. It is tentatively assigned to the methyl group. The *p*-chlorobenzoate protons give rise to only one resolved peak (at almost the same frequency as benzoate), and there is the suggestion of another hidden under that of the broad *ortho* proton on stilbenediamine. We tentatively suggest that the large resolved peak found in the benzoate and substituted benzoate spectra is from the anion's *meta* ring proton and that the *ortho* and *para* peaks, when present, are obscured by the more intense stilbenediamine ring proton resonances. Neither the positions nor assignments of the anion proton peaks affect the conclusions to be presented in this paper.

(2) **Magnetic Properties in Solution.** Since it is known that $Ni(stien)_2(Cl_2CHCO_2)_2$ undergoes diamagnetic–paramagnetic equilibrium in some solvents,[8] we must show that such an equilibrium does not occur for our complexes in $CDCl_3$. Higginson, *et al.*,[8] report from optical spectral results that in acetone and chloroform $Ni(stien)_2(Cl_2CHCO_2)_2$ is tetragonally coordinated and paramagnetic. Our magnetic susceptibility measurements in solution (Table II) indicate that in solution the molar susceptibilities of our complexes are as great or greater than their susceptibilities in the solid state. Solubility problems prevented us from obtaining susceptibility data for all the complexes. In all the cases reported here, the maximum bulk susceptibility shift of TMS was less than 10 Hz. These small shifts are responsible for the large error limits reported.

The temperature dependence of the C–H proton shifts falls on a straight line when $\Delta\nu$ is plotted *vs.* $1/T$. The linear behavior observed is that expected for a complex undergoing no chemical reaction. If a spin-paired–spin-free equilibrium were occurring, a curved line would be obtained. It is of interest to note that none of the plots extrapolates to zero shift at infinite temperature, as required by our present theories. Most of the complexes reported in the literature exhibit this anomalous temperature behavior.

(3) **Effects of Axial Ligand Exchange.** Experimental evidence described below indicates that the axial ligands undergo rapid exchange in solution. We show, however, that this exchange does not affect the resonance positions of the stilbenediamine protons. In a solution containing $Ni(stien)_2(CH_3CO_2)_2$ and tetraethylammonium acetate, only one acetate resonance is observed. Its resonance position (−630 Hz) is between the free acetate (−419 Hz) and complexed acetate peaks (−786 Hz), indicating rapid or intermediate axial ligand exchange. Significantly for our purposes, the resonance frequencies of the stilbenediamine protons did not change within experimental error upon addition of excess anion. This information, together with the conclusions drawn from the susceptibility measurements, strongly indicates the absence of a spin-free–spin-paired equilibrium and allows us to safely use our observed contact shifts to explain trends in bonding.

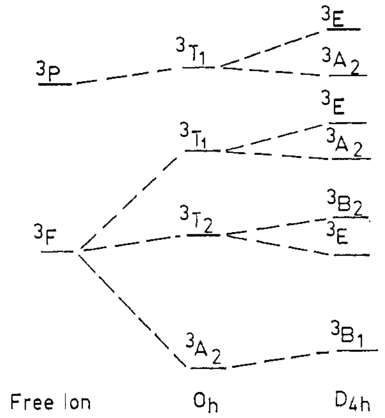

Figure 2. Correlation diagram for the triplet states of a d^8 configuration. The subscript g has been left off for states in O_h and D_{4h} for clarity in presenting the diagram.

(4) **Infrared.** The results of our studies of the symmetric and asymmetric carbonyl stretching frequencies are presented in Table III. All frequencies of complexed anionic species were obtained in an approxmately 1% solution of complex in $CHCl_3$. The stretching frequencies of the free acids were either obtained from the data of Gillette[21] or from the Sadtler listings. The interpretation of these results in terms of metal–anion bonding appears in the Discussion section.

Table III. Ir Frequencies[a]

Complex	Symmetric carbonyl stretch ν_{acid}	$\nu_{complex}$	Asymmetric carbonyl stretch ν_{acid}	$\nu_{complex}$
$Ni(stien)_2$–				
Acetate	1435	1400	1721	1560
Monochloroacetate	1433	1385	1736	1610
Dichloroacetate	1428	1365	1751	1640
Trichloroacetate	1416	1330	1764	1670
Benzoate	1426	1375	1678	1600
p-Methylbenzoate	1425	1372	1667	1596
p-Chlorobenzoate	1425	1396	1664	1590

[a] All values reported in cm^{-1}. ν_{acid} pertains to a dimeric molecule in solution, so the trend observed is very qualitative.

(5) **Visible Spectra.** Table IV contains visible spectra data obtained at liquid nitrogen temperature. The assignment of the transitions will be described below. For convenience, the correlation diagram for triplet states of a d^8 configuration is presented in Figure 2.

As an illustrative example of the band assignment procedure, consider the spectrum of $Ni(stien)_2(ClCH_2CO_2)_2$ in Figure 3. The two peaks of the low-energy band located between 7000 and 11000 Å are assigned to $^3E_g(^3T_2)$ and $^3B_{2g}(^3T_2)$. The small shoulder on the high-energy side of this band is probably due to a spin-forbidden transition to a low-energy singlet state. The

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[21] R. H. Gillette, *J. Amer. Chem. Soc.*, 58, 1143 (1936).

Table IV. Mull Spectra[a]

Complex		Transition $^3B_{2g}$ →					
		^3E_g	$^3B_{2g}$	$^3A_{2g}$	^3E_g	$^3A_{2g}$	^3E_g
Ni(stien)$_2$–							
Acetate	Calcd	10050	12230	16859	18132	29036	29876
	Obsd	10010	12190	16892	18180	28980	29850
Monochloroacetate	Calcd	9881	11481	16219	17036	26854	27397
	Obsd	9881	11481	16207	17036	26882	27397
Dichloroacetate	Calcd	9725	12100	16775	17640	28940	29742
	Obsd	9775	12136	16728	17544	28986	
Trichloroacetate	Calcd	9369	12603	16000	18310	29030	30449
	Obsd	9300	12453	16000	18380	29070	
Benzoate	Calcd	9800	12250	16683	17790	28443	29311
	Obsd	9900	12151	16653	17789	27100	29412
p-Methylbenzoate	Calcd	9688	11955	16222	17922	28895	29927
	Obsd	9756	11834	16949	18051	28986	29940
p-Chlorobenzoate	Calcd	10280	12631	16827	18216	27759	28503
	Obsd	10150	12453	17544	18342	27624	29326

[a] All values in cm^{-1}.

Table V. Crystal-Field Parameters[a]

Complex	*B*	Dq_{xy}	*Ds*	*Dt*	Dq_z	$\delta\sigma$	$\delta\pi$
Ni(stien)$_2$–							
Acetate	976 ± 10	1223 ± 10	370 ± 15	235 ± 10	812	−996	33
Monochloroacetate	838 ± 5	1148 ± 10	213 ± 15	176 ± 10	840	−650	121
Dichloroacetate	1004 ± 5	1210 ± 10	201 ± 15	262 ± 10	752	−793	354
Trichloroacetate	1022 ± 10	1260 ± 15	721 ± 15	334 ± 10	675	−1708	−247
Benzoate	953 ± 10	1225 ± 10	288 ± 20	267 ± 15	758	−933	236
p-Methylbenzoate	1006 ± 10	1196 ± 15	550 ± 20	237 ± 15	781	−1269	584
p-Chlorobenzoate	827 ± 20	1263 ± 15	321 ± 30	254 ± 10	791	−958	154

[a] All values reported in cm^{-1}.

low-energy peak of the asymmetric band centered at about 5900 Å was assigned to the $^3E_g(^3T_1, {}^3F)$ transition. The position of the $^3B_{2g}$ transition, assigned to the high-energy side of the band, was allowed to vary over a 500-cm^{-1} range until the calculation produced a good fit. Of the three transitions which appear superimposed on the charge-transfer band, only two are resolved. The high-energy one was assigned to a spin-forbidden transition; subsequent calculations confirmed this assignment. The middle peak was assigned to the $^3A_{2g}(^3T_1, {}^3P)$ transition and the shoulder to the $^3E_g(^3T_1, {}^3P)$. Our calculation produced a good fit of all these bands as shown in Table IV. Because of the similarity between the electronic structure of the complex used here as an example and all the others discussed in this study, the assignments of transition in the other spectra proceeded along almost identical lines. In some of the complexes, the $^3E_g(^3T_1, {}^3F)$ and the $^3A_{2g}(^3T_1, {}^3F)$ transitions were completely resolved, while, in others, the two highest in energy both occurred as shoulders on the charge-transfer band. For all spectra reported here, convergence of at least four of the calculated peak positions to within experimental error of the measured peak positions was obtained. The two remaining peaks' frequencies were then compared to those calculated. Agreement to within experimental error of these final two calculated frequencies with those observed was a mandatory requirement for acceptance of the calculation. To determine the error limits of the calculated parameters *B*, *Dq*, *Ds*, and *Dt*, either five or six of the peaks were arbitrarily varied ±100 cm^{-1}, and the range within which the parameter varied was chosen as the error. The calculated parameters and their uncertainties are reported in Table V.

Discussion

(1) Relative Strengths of Axial Ligand Bonding. In the studies reported here, we have two independent measurements which have been suggested to provide estimates of the order of the relative strengths of the axial ligands. First, the infrared measurements of changes in the stretching frequencies of COO$^-$ groups bonded to nickel(II) can be explained. We can estimate the relative strengths of the O–H bonds in the substituted acetic acids from substituent constants and p*K* values. The observed decrease in the symmetric and the increase in the asymmetric carbonyl stretching frequencies of the dimeric COO–H species as the O–H bond strength decreases should give a parallel trend in the carbonyl frequencies for the series of COO–Ni species if the differences in the interaction of nickel with the

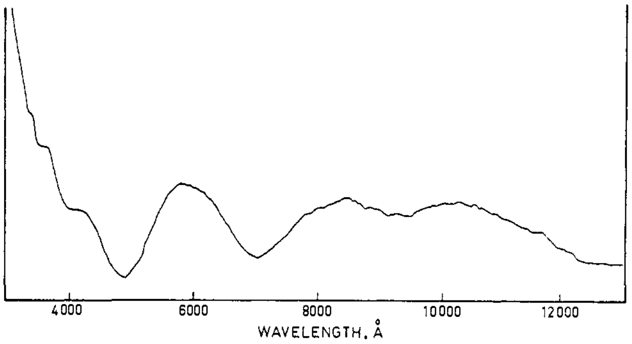

Figure 3. Mull spectrum of Ni(stien)$_2$(CH$_2$ClCO$_2$)$_2$ at liquid nitrogen temperature.

various acetates are essentially dominated by σ effects in the complexes. As can be seen from the data in Table III, both the symmetric and asymmetric stretching frequencies show the same trend for the nickel(II) complex as is shown for the proton. Of the two carbonyl stretches, the antisymmetric is the most sensitive to changes in the bonding.[22] Using the trend in frequencies for the dimer acid to establish how the frequency will vary with anion basicity, a very reasonable order of the nickel–oxygen bond strength in the acetate series results: acetate > monochloroacetate > dichloroacetate > trichloroacetate. Since the asymmetric stretching frequency increases in this order, significant changes in bonding contributions from metal to ligand π back-bonding in the chloroacetates can be eliminated, for this would cause a frequency decrease. The frequency shifts in the benzoate and substituted benzoate anions are unreasonable and indicative of complications involving the vibrational problem (*e.g.*, coupling). This is not surprising in view of the closeness in energy of the carbonyl and ring vibrations and in view of the small differences in frequency in the series. The symmetric frequency indicates a different ordering of the benzoates relative to the chloroacetates than does the asymmetric stretch. The ordering based on the asymmetric stretching frequency is quite unreasonable. Another possible complication could involve a different mode of coordination for the carboxylate group in the benzoate series. The ir frequencies were also obtained in the solid state from mull spectra with almost identical results.

With the exception of the benzoates, which cannot be ordered, the infrared ordering is that intuitively expected on the basis of the inductive effect. This is significant because if there were extensive metal-to-ligand back-bonding causing a reordering of the donor strengths of the acetates, this would be reflected in the infrared order because back-bonding into the carbonyl π^* orbital would result in a decrease in the frequency. This is the most significant conclusion that can be drawn from this infrared work.

The second series of observations used to ascertain an order of relative coordinating power of the anions is the visible spectra results. The parameter Dq_z, obtained from the low-temperature mull spectrum and the crystal-field calculation, represents the Dq of the axial ligand. It is defined by eq 1, where Dq_{xy}, the Dq

$$Dq_z = Dq_{xy} - {}^7/_4 Dt \tag{1}$$

of the ligands in the xy plane, and Dt, the crystal-field splitting parameter, have units of cm^{-1}. From Table V, where error limits of ± 20 are placed on Dq_z, it is found that in the acetate series the general order of the axial ligand strengths is essentially that found from the ir studies except that either monochloroacetate is slightly higher than expected or acetate lower. The benzoate series is about the same as dichloroacetate in coordinating power. The ordering within the benzoate series again is surprising. Although the Dq_z values all lie very close to each other, the result p-Cl > H is indeed surprising. Factors other than the basicity of the ligand appear to make it impossible to interpret Dq_z differences of ± 20. Such a conclusion gives rise to the following order: $CH_3COO^- \sim CH_2ClCOO^- > p\text{-}XC_6H_4COO^- > CHCl_2COO^- > CCl_3COO^-$. Apparently, Dq_z is not very sensitive to the difference in the inductive properties of the CH_3, CH_2Cl, and C_6H_5 substituents, and the order may be dominated by the existence of subtle π-bonding changes. Steric effects would not account for the surprisingly low value of acetate, but this may result from a π back-bonding into the chloroacetate antibonding orbitals influencing Dq_z more than it influences the infrared frequency shifts. A composite of the above studies would support the following ordering of ligand donor strengths for the above anions: $CH_3COO^- > CH_2ClCOO^- > HCCl_2COO^- > CCl_3COO^-$. The location of benzoate in this series is uncertain. In view of possible steric effects, we cannot depend upon the pK value of benzoic acid. The value of Dq_z permits us to say no more than it is greater than dichloroacetate.

(2) **The Absence of Appreciable Dipolar Shifts.** In order to discuss the observed proton nmr shifts on the basis of electron delocalization into the bonding properties of the ligands, we must show that the effects arising from a through-space dipolar mechanism may be neglected. The magnitude and direction of the dipolar shift may be calculated from eq 2, where ν and $\Delta\nu$ are

$$\Delta\nu = -\left\{\beta^2\nu\,\frac{S(S+1)}{3kT}\left[\frac{3\cos^2\chi - 1}{r^3}\right] \times \left[\frac{(3\mathbf{g}_\parallel - 4\mathbf{g}_\perp)(\mathbf{g}_\parallel - \mathbf{g}_\perp)}{15}\right]\right\} \tag{2}$$

the probe frequency and shift frequency in hertz, χ is the angle between the highest fold symmetry axis and the nucleus in question, and all other symbols have their usual meanings.[23,24] The molecular g factors may be calculated from the crystal-field data of Table V using eq 3.[25] k is the orbital reduction factor, λ_0 is the

$$\mathbf{g}_\parallel = 2(1 - 4k^2\lambda_0/10Dq_\parallel) \tag{3a}$$

$$\mathbf{g}_\perp = 2(1 - 4k^2\lambda_0/10Dq_\perp) \tag{3b}$$

free-ion spin-orbit coupling constant, and $Dq_\perp$ and $Dq_\parallel$ are the $^3B_{1g} \rightarrow {}^3B_{2g}$ and $^3B_{1g} \rightarrow {}^3E_g$ transition energies, respectively. Using a representative value for k of 0.9 and for λ_0 of 315 cm^{-1},[26] we calculate $\mathbf{g}_\parallel = 2.20$ and $\mathbf{g}_\perp = 2.17$. Only a knowledge of χ is needed in order to calculate the dipolar shift. Since we are seeking an upper limit of $\Delta\nu$ for the stilbenediamine protons, we choose $\chi = 90°$. The structural factor $3\cos^2\chi - 1$ has its maximum at $\chi = 0°$ and a minimum at $\chi = 55°$. Since the protons of interest lie at a $\chi > 55°$, we choose χ such that the structural factor has the largest absolute magnitude in this region. For r = 4 Å, $\Delta\nu = 1.9 \times 10^2$ Hz as an upper limit. The phenyl protons at a greater distance from the metal have a calculated dipolar shift maximum of 20 Hz. For all protons except those on the anions and the stilbenediamine nitrogens, we can safely ignore the dipolar shift. Furthermore, because of the similar geometries and Dt's of our series of complexes, the

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dipolar shift for a particular proton will be roughly equal for all members of the series.

(3) **Effects of the Axial Ligands on the Stilbenediamine Proton Nmr Contact Shifts.** In past years, trends in the bonding of equatorial ligands upon variation in the axial ligand in tetragonal systems have been explained in terms of a "ligand inductive effect." According to this explanation, as the strength of the axial ligands becomes greater (*i.e.*, higher Dq_z), the formal charge on the metal becomes smaller and Dq_{xy} decreases. For the systems reported in the literature and the data in Table V, the ligand inductive effect explains the trends in the spectrochemical parameters quite well. Based on this ligand inductive effect, one might naively expect that as Dq_z becomes larger, the observed resonance shifts for protons on the ligands in the xy plane would decrease. This decrease occurs because as Dq_{xy} becomes smaller and the metal–ligand bond strength weaker, the extent of mixing of the equatorial ligand and the metal ion orbitals would decrease. This is essentially the line of reasoning invoked in earlier studies[3b–e] where, in some instances,[3d] bond weakening was attributed to steric effects. In the work reported here, the contact shifts are not those predicted from this line of reasoning. Using the methylene protons as the most sensitive probe of electron delocalization in the ligand for reasons previously discussed, it is evident from Table II that as the axial ligand becomes stronger, the contact shift becomes larger instead of smaller. This discrepancy between the results predicted on the basis of a simple inductive argument and our experimental results is indicative of the complexity of the information provided by the contact shift experiment. Certainly in the present case, a simple interpretation, as has been previously utilized (perhaps incorrectly), is incorrect We can rationalize the experimental results by qualitative molecular orbital theory This rationalization, though after the fact, is important because it points out one of the problems neglected in a simple inductive type of interpretation of the shift data. An increased inductive effect from the axial ligand is expected to raise the energies of the metal d orbitals relative to the ligand σ orbitals as the formal charge on the metal is decreased. The increased energy difference between the ligand σ orbitals and the metal $d_{x^2-y^2}$ orbitals results in less mixing and less unpaired electron density on the ligand. This is the essence of the inductive effect argument, and is depicted in Figure 4a. However, at the same time, the splitting within the e_g set becomes smaller since the difference between the strengths of the axial and equatorial ligands is becoming smaller. As shown in Figure 4c, a stronger axial ligand will decrease the splitting of the $d_{x^2-y^2}$ and d_{z^2} orbitals and, more importantly for the contact shift experiment, could decrease the energy separation between the $d_{x^2-y^2}$ metal orbital and the σ ligand orbital. This will result in more extensive mixing. Consequently, the trend in the contact shift will depend on whether the total raising of the d-orbital energies (Figure 4a) or the change in tetragonal field splitting (Figure 4c) is larger. In the case of the Ni(stien)$_2$(anion)$_2$ system reported here, the lowering of the $d_{x^2-y^2}$ orbital energy relative to that of the stien ligand σ orbital due to the decreased splitting dominates the raising of metal orbitals due to the increasing formal charge on the metal. Our calculated values of B, Ds, and Dt support this contention. In the acetate and substituted-acetate complexes, B changes by a maximum of 180 out of 1000 cm^{-1}, while the splitting of the e_g set, which varies as $4Ds + 5Dt$, changes by over 800 cm^{-1}. Thus, according to our model, the net effect will be a decrease in separation between the ligand σ orbitals and the metal $d_{x^2-y^2}$ orbitals resulting in increased mixing and increased delocalization.

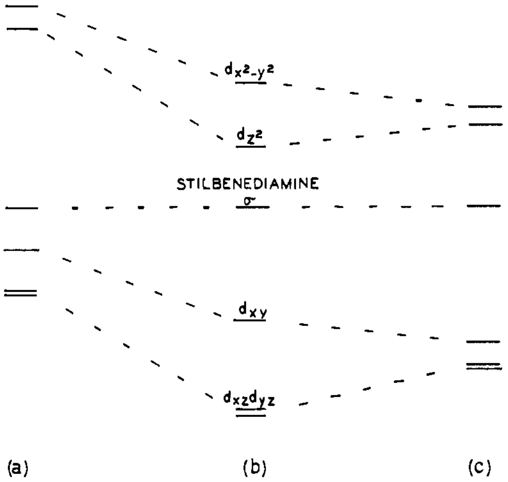

Figure 4. Changes in metal ion d orbital energies in D_{4h} symmetry with axial ligand variation: (a) splitting pattern for Ni(stien)$_2$(CH$_3$CO$_2$)$_2$ with the inductive effect predominating, (b) splitting pattern for Ni(stien)$_2$(CCl$_3$CO$_2$)$_2$, (c) predicted change for Ni(stien)$_2$(CH$_3$CO$_2$)$_2$ with inductive effect less significant.

The value of Dq_{xy} remains relatively constant throughout our series of complexes. The constancy arises from the nature of the transition from which the parameter is measured The energy of the $^3B_{2g}(3A) \rightarrow {}^3B_{2g}(^3T_2, F)$ transition (arising from the transition from $d_{xy} \rightarrow d_{x^2-y^2}$) is $10Dq$. Hence, in our scheme, the $d_{x^2-y^2}$ and d_{xy} orbital energy changes parallel each other upon variation of the axial ligand.

An interesting experimental test of the effects discussed here would be the direct measurement by means of the contact shifts of the relative amounts of unpaired spin density placed on the axial ligands. In the absence of a complete molecular orbital calculation on the various anions, the observed shifts of the anion protons provide no meaningful data for this type of comparison. For example, even if the amount of delocalization into the acetate and monochloroacetate ligands were the same order of magnitude, the presence of the chlorine could cause a large change in the coefficients of the proton atomic orbitals in the molecular orbital primarily involved in the delocalization mechanism causing the contact shift for that proton to be far different from that of the corresponding proton in the unsubstituted anion. Thus, the observed anion contact shifts in this study unfortunately do not by themselves provide valid criteria for furthering our understanding of the effects of the axial and equatorial ligands on each other.

Because low solubility prevented accurate measurement of the solution magnetic susceptibility for several of the compounds, we could not calculate a complete list of the coupling constants. The susceptibilities which we could accurately measure were equal within experimental error. Hence, the trends in shifts are

Table VI. Ratios of Shifts in $Ni(stien)_2X_2$

X	*o*:*p*	*o*:*m*	*p*:*m*	CH:*o*	CH:*m*	CH:*p*
Acetate	1.9 ± 0.3	−4.7 ± 1.0	−2.5 ± 0.5	35.5 ± 2.5	131 ± 25	78 ± 5
Monochloroacetate	1.7 ± 0.3	−3.5 ± 1.0	−1.1 ± 0.5	29.3 ± 2.5	178 ± 25	59 ± 5
Dichloroacetate	1.8 ± 0.3	−4.4 ± 1.0	−2.4 ± 0.5	29.3 ± 2.5	129 ± 25	54 ± 5
Trichloroacetate	1.8 ± 0.3	−3.4 ± 1.0	−1.9 ± 0.5	28.9 ± 2.5	99 ± 25	53 ± 5
Benzoate	1.9 ± 0.3	−10.2 ± 1.0	−5.4 ± 0.5	28.8 ± 2.5	294 ± 35	54 ± 5
p-Methylbenzoate	1.8 ± 0.3	−8.5 ± 1.0	−4.7 ± 9.5	30.8 ± 2.5	261 ± 25	55 ± 5
p-Chlorobenzoate	1.8 ± 0.3	−5.7 ± 1.0	−3.2 ± 0.5	36.4 ± 2.5	209 ± 25	65 ± 5

expected to parallel the trends in coupling constants. We have based our arguments on the trends in shifts.

(4) Visible Spectral Results. The information gained from the solid-state visible spectral studies raises serious question about the meaning of some of the crystal-field parameters for tetragonal complexes. The parameters Dq_{xy}, Dt, and Dq_z will be discussed first because they may be obtained directly from the absorption spectrum. The values obtained from Dq_z apparently accurately reflect trends in the axial ligand strength, as has been previously discussed. When Dq_z is plotted *vs.* Dq_{xy}, all of the points except those for the acetate and *p*-chlorobenzoate complexes fall on a straight line with a negative slope. The decrease in Dq_{xy} with an increase in Dq_z suggests that an inductive effect is operative. An inductive effect in the crystal-field spectra is not inconsistent with its absence in the contact shifts. In the nmr experiment, we are concerned primarily with metal orbitals containing unpaired spin, while in the visible absorption spectrum, all of the metal orbitals, including the d_{xy}, d_{yz} orbitals, contribute to the Dq's.

The fact that the *p*-chlorobenzoate point falls off of the line may probably be attributed to the relatively poor fit we were able to obtain for this complex. The result for the acetate complex is surprising. From the point of view of the linear behavior of Dq_{xy} and Dq_z, it appears that the Dq_z for acetate is too low rather than the Dq_z for dichloroacetate being too large, since the latter point falls on the line. It must be remembered that the values of Dq_z for the two complexes overlap within experimental error.

Unlike Dq_{xy} and Dt, the McClure parameters $\delta\sigma$ and $\delta\pi$ depend on a quantity, Ds, which must be calculated from a fit of all of the bands. Any deviations from pure D_{4h} symmetry from either ligand or lattice effects would thus be expected to cause large uncertainties in Ds. Our fitting program presupposes D_{4h} symmetry. Our complexes, on the other hand, have D_{2h} symmetry or lower. Nyburg and Wood found a mean N-Ni-N bond angle of 82.3° and a N-Ni-O bond angle of 89.9° in $Ni(stien)_2(CHCl_2CO_2)_2$.[9] The lowering of symmetry from D_{4h} results in a further splitting of the bands. The splitting was too small to be resolved. As a result, the bands were broadened, making it difficult to assign the maximum with less than $\pm 100\ cm^{-1}$ error. Furthermore, it was assumed that the band maximum was the vibrational $0 \rightarrow 0$ transition, although this is not nesessarily correct.[27] The ambiguities in the peak positions arising from the effects discussed above make the uncertainties in the $\delta\sigma$ and $\delta\pi$ parameters much larger than those for Dq_{xy}, Dq_t, and Dt. No reasonable interpretation of the $\delta\sigma$ or $\delta\pi$ parameters for the entire series of complexes can be offered.

This study has illustrated that considerable caution must be employed in the interpretation of the McClure parameters and the results from the nmr contact shift experiment. Many subtle influences, some of which have been elucidated here, have pronounced effects on the magnitude of these parameters, which are not directly related to and often mask influences relative to the strength of the metal–ligand interaction.

The Ratio Method for Evaluating Pseudocontact Shifts. It has been proposed[28] that one can assume similar delocalization mechanisms in cobalt(II) and nickel(II) complexes and then, assuming nickel(II) is isotropic, determine the pseudocontact contribution to the shift in the cobalt(II) complex; a procedure referred to as the *ratio method*. In a study of some trisbipyridyl complexes,[29] it was shown that the delocalization mechanism is different in six-coordinate cobalt(II) and nickel(II) complexes. It was concluded that, in octahedral complexes containing unpaired spin in the t_{2g} set, one could not, in general, expect a similar delocalization mechanism in that complex and in a nickel(II) complex. In a subsequent article,[30] it was pointed out that, in order for the ratio method to work, the spin must be delocalized in an identical MO or through an identical exchange polarization mechanism in both complexes. If this requirement were ever met, the ratio method would work. It was claimed[30] that this requirement held for a whole series of previously reported complexes on which the ratio method had been employed. The complexes reported in this study show that it is very dangerous to ever make this assumption. If ever an assumption of constant delocalization mechanism should be good, it should be in a series of tetragonal complexes in which the metal ion, in-plane ligands, and symmetry are held constant. One might logically expect the $Ni(stien)_2X_2$ complexes to satisfy this requirement, and since the pseudocontact shift is small in nickel(II), the constancy of delocalization ratios can be tested directly from the observed shifts.

The ratios of the various proton shifts are shown in Table VI, from which it is clear that a constant delocalization mechanism cannot be assumed. While the *ortho-para* ratio is excellent, the other protons invariably give ratios which are outside of experimental error in spite of attempting to select an ideal system for a constant delocalization mechanism. Different sets of protons fail in the different complexes. Invariably, it will be true that, in a complex, more than one MO of the ligand will either mix with the metal orbitals

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or will be involved by spin polarization. In a conjugated phenyl π system dominated by π but including some σ delocalization, the *ortho* proton will be influenced mainly by π but to some extent by σ, the *para* proton almost solely by π, and the *meta* proton largely by σ delocalization. If, for example, the σ mechanism is affected differently than the π mechanism by the rotation and the orientation of the phenyl group in the different complexes, this subtle effect could cause the basic assumption of the ratio method to fail.

Next, we might consider judiciously selecting protons where only one delocalization mechanism will dominate. This is the approach most recently[30] utilized in the application of the ratio method to some bipyridyl complexes. For assumed rapid tumbling, the pseudocontact shift at the 3-proton of trisbipyridylcobalt(II) calculated from single-crystal magnetic susceptibility data is -13.8 ppm, compared to a value of -14.3 ppm from the ratio method. This agreement indicates the initial selection of protons was good. As shown by a recent publication from this laboratory,[31] it was recently incorrectly concluded[32] that the contact shifts in trisbipyridyliron(III) are dominated by a σ delocalization mechanism. If we, for the moment, accept the assumption that σ delocalization is dominant and apply the ratio method using the same "judicious selection" of protons as was used in the cobalt(II) case,[30] we calculate a dipolar shift at the 3,3′ position of $+118$ cps. In this complex, the **g**-tensor anisotropy can be determined from the esr,[32] and the correct dipolar shift is found to be -406 cps. The reason for the failure is obvious. The delocalization mechanisms are very different in the two complexes and no judicious selection of protons will come to the rescue. Thus, the basic assumptions and approximations of the ratio method cannot "be kept firmly in mind"[30] for they are practically impossible to evaluate. Unless the answer is known from some other source, the validity of the assumptions cannot be tested at present and, if it is known from some other source, the ratio method is not needed. Certainly, in any application of the ratio method on a system where the pseudocontact contribution is not available from another source, all of the protons (preferably several) in the molecule should stand up to the criteria required by Wicholas and Drago[29] to prove that spin is delocalized by the same molecular orbitals in both complexes.

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Hydrogen Bonding of Sulfur Donors with Various Phenols[1]

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Contribution from the W. A. Noyes Laboratory, University of Illinois,
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Abstract: We report calorimetrically determined enthalpies of interaction of sulfur donors with phenyls in poorly solvating media. The results are nicely incorporated by the *E* and *C* correlation previously reported from this laboratory. The enthalpy of interaction and infrared frequency shift of the O–H stretching vibration of phenol upon complexation do not obey a previously reported correlation for oxygen and nitrogen donors. This emphasizes a point made earlier that the infrared correlation cannot be extended to new classes of donors without first ascertaining that the general class obeys the relationship. A model is offered to rationalize the deviation of sulfur donors. A significant, specific interaction of sulfur donors with carbon tetrachloride is observed.

In an earlier report[2] from this laboratory, a double-scale enthalpy equation

$$-\Delta H = E_A E_B + C_A C_B \qquad (1)$$

was proposed to correlate and predict enthalpies of interaction for various donors and acceptors. The acid parameters E_A and C_A and the base parameters E_B and C_B are empirically determined to best reproduce the experimental enthalpies when substituted into eq 1. The enthalpies of interaction of phenol with various sulfur donors previously used in this correlation were not measured calorimetrically, but were estimated from the constant-acid enthalpy–infrared frequency shift relationship which has been shown to exist for oxygen and nitrogen donors.[3] Since the infrared relationship should not be used with a new class of donors whose enthalpies had not been directly determined calorimetrically and shown to obey this correlation, we have calorimetrically determined enthalpies of interaction of several phenols with diethyl sulfide and tetrahydrothiophene. These data allow sulfur donors to be incorporated into the *E* and *C* correlation and test the extension of the infrared correlation to this class of donors. In addition, the enthalpies were determined in different solvents in order to detect any specific interaction with the solvents.[4]

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