Proton Resonance Studies of the Solution Equilibria of Nickel(II) Complexes with Schiff Bases Formed from Salicylaldehydes and N,N-Substituted Ethylenediamines.   I

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Proton resonance measurements have been made on CDCl₃ solutions of series of nickel(II) Schiff base complexes, of the general formula [X–SALen–N(R)R′]₂Ni. Fully octahedral forms and octahedral ⇄ planar equilibria in solution give rise to large positive and negative contact shifts. The linear dependence of contact shifts on $1/T$ for fully octahedral forms has been used for spin density calculations. Alternation in the sign and magnitude of the spin density on adjacent carbon atoms of the salicylaldimine ring is scarcely recognizable though alternation is clear in R′ = phenyl, *p*-tolyl rings. Deviations from the linear dependence of contact shifts on $1/T$ occur when an appreciable proportion of diamagnetic planar form is present at high temperatures and have been used to estimate ΔG values for planar ⇄ octahedral equilibria.

Introduction

It has been shown that nickel(II) Schiff base complexes of the general formula I, which will be referred to as [X–SALen–N(R)R′]₂Ni

I
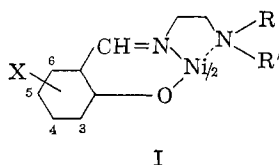
may be four- or six-coordinate according to environmental factors and the substituents X, R, and R′.[2]

When R = H and R′ = *n*-alkyl or benzyl, the solid compounds are all mustard colored and paramagnetic, with values of μ_{eff} varying from 3.05 to 3.30 BM with various substituents X (see Table I). The absorption spectra of the solids and their solutions in inert solvents are characteristic of distorted octahedral complexes. On the other hand, the compounds in which R = H, R′ = *o*-tolyl and R = methyl, phenyl, R′ = phenyl are olive-green and diamagnetic in solid form and in solution in chloroform, irrespective of the nature of the ring substituent X. They may be assigned a *trans*-planar structure on the basis of their absorption spectra and low dipole moments in benzene. It is evident that both steric and electron-withdrawing capacities play a role in preventing the ligands from acting as tridentate.

Between these extremes lies the series of complexes for which R = H, R′ = phenyl, *p*-tolyl, in which some of the green solid compounds are diamagnetic planar complexes, while other are paramagnetic and may be assigned a distorted octahedral structure. Their chloroform and benzene solutions are all paramagnetic, and the relative intensity (ϵ_1/ϵ_2) of the two bands in their absorption spectra at *ca.* 10,600–11,000 and *ca.* 17,000 cm⁻¹, respectively, is a measure of the propor-

tion of octahedral and planar forms in equilibrium. The intensity ratio ϵ_1/ϵ_2 is less than that found in the series of fully octahedral complexes and decreases, depending on the substituent X and R′, as shown in Table I, toward the very low values found for the diamagnetic solutions of planar complexes. Magnetic measurements in solution at room temperature have not been made because of low solubility problems, but the magnetic moment of [3,4-benzo–SALen–N(H)C₆H₅]₂Ni complex dissolved in dibenzyl has been found to decrease with increasing temperature from 80 to 170°. This fact indicates an endothermic rearrangement from the octahedral to the planar form. Molecular weight measurements of all the complexes cited have revealed no evidence for association, and accordingly a polymeric structure for the paramagnetic compounds in solution can be excluded.

The present investigation is concerned with measurements of the proton magnetic resonance spectra of the paramagnetic solutions in deuteriochloroform of the compounds discussed in this introduction and listed in Table I. For the majority of these compounds, especially those existing in a planar octahedral equilibrium, temperature studies were made at *ca.* 20° intervals between +60 and −50° in deuteriochloroform solutions. The spectra of the diamagnetic nickel(II) complexes and of analogous zinc(II) complexes were measured to enable the calculation of contact shifts for the paramagnetic compounds.

To date, only a few measurements of contact shifts in nickel(II) octahedral complexes have been reported[3,4] though there have been many thorough pmr studies of tetrahedral nickel(II) complexes.[5,6] It is felt that the

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(2) L. Sacconi, P. Nannelli, and U. Campigli, *Inorg. Chem.*, **4**, 818 (1965).

(3) (a) A. Chakravorty, J. P. Fennessey, and R. H. Holm, *ibid.*, **4**, 26 (1965); (b) G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 2117 (1965).

(4) E. A. LaLancette, D. R. Eaton, R. E. Benson, and W. D. Phillips, *ibid.*, **84**, 3968 (1962).

(5) D. R. Eaton, D. J. Caldwell, and W. D. Philips, *ibid.*, **85**, 397 (1963), and references therein.

(6) (a) R. H. Holm, A. Chakravorty, and G. O. Dudek, *ibid.*, **85**, 821 (1963); **86**, 379 (1964); (b) A. Chakravorty and R. H. Holm, *ibid.*, **86**, 3999 (1964); *Inorg. Chem.*, **3**, 1010 (1964).

Table I

Selected Magnetic and Spectrophotometric
Absorption Data[a] for [X–SALen–N(R)R']₂Ni Complexes

				Solids		CHCl₃ solution	
R	R'	X	T °C	μ_{eff}, BM	μ_M	Form	ϵ_1/ϵ_2
H	CH₃	H	24	3.13	P$_M$	O	
H	C₂H₅	H	21	3.10	P$_M$	O	
H	n-C₃H₇	H	21	3.13	P$_M$	O	
H	n-C₄H₉	H	20	3.12	P$_M$	O	
H	CH₂C₆H₅	H	25	3.28	P$_M$	O	
H	n-C₃H₇	5-Cl	23	3.16	P$_M$	O	
		H	21	3.13	P$_M$	O	
		5-C₂H₅	21	3.13	P$_M$	O	
		5-CH₃	22	3.10	P$_M$	O	
		3-CH₃	19	3.08	P$_M$	O	
H	p-CH₃C₆H₄	5-Cl	18	3.15	P$_M$	O ⇌ P	1.9
		3-Cl	19	3.11	P$_M$	O ⇌ P	1.8
		H	22	D	P$_M$	O ⇌ P	1.7
H	C₆H₅	5-Cl	22	3.10	P$_M$	O ⇌ P	1.7
		3-Cl	21	3.19	P$_M$	O ⇌ P	1.6
H	p-CH₃C₆H₄	5-CH₃	27	3.22	P$_M$	O ⇌ P	1.5
H	C₆H₅	H	22	D	P$_M$	O ⇌ P	1.4
H	p-CH₃C₆H₄	3-CH₃	22	D	P$_M$	O ⇌ P	1.3
H	C₆H₅	5-CH₃	21	D	P$_M$	O ⇌ P	1.2
		3-CH₃	21	D	P$_M$	O ⇌ P	1.0
H	o-CH₃C₆H₄	H	21	D	D	P	0.12
CH₃	C₆H₅	H	21	D	D	P	0.00
C₆H₅	C₆H₅	H	21	D	D	P	0.0

[a] Partially compiled from ref 2. Abbreviations: P$_M$, paramagnetic; D, diamagnetic; O, octahedral (distorted); P, planar; ϵ_1/ϵ_2, intensity ratio of characteristic peaks in absorption spectra.[2]

augmentation of contact shift data for octahedral nickel(II) complexes is important in view of the expected differences[7] in the nature of the bonding between nickel(II) and the ligands in octahedral and tetrahedral complexes and the effect this may be expected to have on the mechanism of transference of spin density into the ligand.[7]

Experimental Section

The preparation and characterization of all of the compounds have already been reported elsewhere,[2] except for the following new complexes with X = 3-CH₃ and 5-CH₃ substituents, which were prepared by similar methods.

[5-CH₃–SALen–N(H)C₆H₅]₂Ni.—Green crystals, mp 200–202°. *Anal.* Calcd for C₃₂H₃₄N₄O₂Ni: N, 9.95; Ni, 10.42. Found: N, 9.99; Ni, 10.49.

[5-CH₃–SALen–N(H)-p-CH₃C₆H₄]₂Ni.—Green crystals, mp 234–236°. *Anal.* Calcd for C₃₄H₄₀N₄O₂Ni: N, 9.46; Ni, 9.91. Found: N, 9.41; Ni, 9.93.

[3-CH₃–SALen–N(H)-p-CH₃C₆H₄]₂Ni.—Green crystals, mp 236–238°. *Anal.* Calcd for C₃₄H₄₀N₄O₂Ni: N, 9.46; Ni, 9.91. Found: N, 9.42; Ni, 9.80.

Absorption spectra and magnetic moments were measured as previously reported.[2]

Proton Resonance Measurements.—All of the spectra were recorded on a Varian DP60 spectrometer operating, at 60 Mc/sec, in the normal high-resolution mode. For spectra at temperatures other than room temperature, the Varian DP60 variable-temperature dewar probe was used, coupled to a cryostat of our own design. For temperatures between +10 and −50° the dewar probe was cooled by a cold stream of nitrogen gas produced by the cryostat, filled with liquid nitrogen, the boiling rate being controlled by a Trüb-Täuber regulator coupled to a copper–constantan thermocouple in the probe within 1 cm of the radio-

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

frequency coil. For temperatures near room temperature (+10, −10°) the cool nitrogen gas stream was preheated on entering the probe by coupling the low-voltage preheater coil, supplied by Varian, to the cryostat regulator. The same controlled preheater was used to warm a compressed-air stream blown through the cryostat to obtain probe temperatures above room temperature (+40, +60°). Once the Trüb–Täuber regulator was set, the corresponding temperature was achieved at the probe within 5 min and remained constant to within ±1.5°. The probe temperature was monitored by measuring the peak separation of pure methanol and the voltage from a copper–constantan thermocouple dipped into the solution in the probe.

Solutions (≃50 mg/ml, ≃0.1 M) of the paramagnetic complexes in deuteriochloroform (Fluka, Puriss 99%) showed no signs of impurities, except for the residual CHCl₃ peak and a scarcely visible broad and irregular peak in the methyl region. When stored in a refrigerator, they tended to absorb small quantities of water, but their nmr spectra remained reproducible even after several days' storage and repeated heating and cooling in the variable-temperature probe. Reasonable spectra of analogous zinc(II) complexes and the nickel(II) complexes, which remained diamagnetic in deuteriochloroform solution, were recorded despite their low solubility. The spectra were all individually calibrated, from tetramethylsilane (≃2% v/v) as an internal standard, using the normal audio-frequency side-band technique.

Results

All the complexes of the general formula (I) [X–SALen–N(R)R']₂Ni cited in Table I, which give paramagnetic solutions in deuteriochloroform, have been found to manifest large positive and negative isotropic contact shifts. Typical examples of the spectra are shown in Figure 1. Shifts of the ring proton and methyl resonances, measured relative to the tetramethylsilane internal reference, and their contact shifts, relative to the normal resonance positions in analogous zinc(II) complexes and nickel(II) complexes which remain diamagnetic in solution, are presented in Table II.

The position of the signals from protons on the salicylaldimine ring are similar throughout both the fully octahedral and planar ⇌ octahedral series; consequently, signals attributable to protons on R' = phenyl, p-tolyl rings were readily identifiable by their absence in the spectra of the R' = n-alkyl series. Similarly, the assignments of the signals from the ring protons at positions 5 and 3 of the salicylaldimine ring and the *para* proton (4'-H) in the R' = phenyl ring were clear from their absence in the spectra of complexes in which X = 5 or 3 substituent or R' = p-tolyl, respectively. Assignments of the signals from the protons on both the salicylaldimine and R' = phenyl, p-tolyl rings were clarified by interpreting their partially resolved fine structure. Their line widths generally lay on the verge of resolution of their simple first-order spin–spin coupling ($J \simeq$ 6–10 cps) with adjacent ring protons, at least above room temperature, although they increased appreciably at lower temperatures. The signal due to the ring proton at position 4 of the salicylaldimine ring was one of the easiest to resolve into its J components, as the line widths of the ring proton signals tended to diminish with increasing distance from the nickel atom.[7] Line
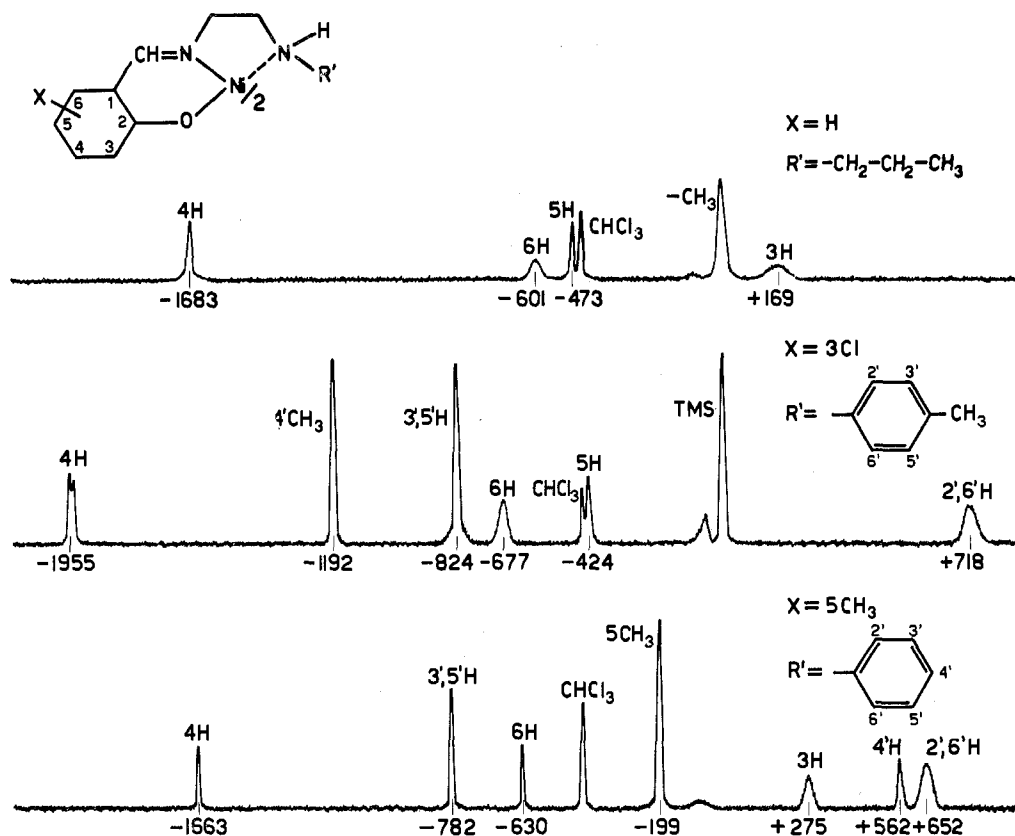
Figure 1.—Proton resonance spectra of typical paramagnetic [X–SALen–N(H)R′]₂Ni complexes in CDCl₃ solution at +27°. Frequencies are in cps at 60 Mc relative to tetramethylsilane as internal reference.

widths of the salicylaldimine ring proton signals were only slightly greater for fully octahedral complexes than those from complexes existing in an octahedral ⇌ planar equilibrium, but the signals from protons in the R′ = *n*-alkyl groups were broader, and only the terminal methyl group, for which the shifts were relatively small,[8] could be readily identified. Very broad signals from the, apparently, equivalent methylene protons between the nitrogen of the ethylenediamine chain and the aldimine proton were located at much lower fields, *ca.* −75.0 and *ca.* −100.0 ppm, respectively, in the fully octahedral complexes, decreasing, respectively, to *ca.* −46.7 and *ca.* −65.0 ppm from tetramethylsilane as internal reference, in [3-CH₃–SALen–N(H)C₆H₅]₂Ni for which the proportion in the planar diamagnetic form is appreciable. As the shifts of the broad signals were difficult to measure, the temperature–dependence studies and the discussion will be limited to the accurately measured shifts of the ring protons and methyl groups. Taken as a whole, the assignments made here are consistent with those made previously for other paramagnetic octahedral[3] and tetrahedral[6] complexes of nickel(II) with N-substituted salicylaldimines.

Temperature Dependence.—Typical plots, in Figure 2, illustrate the general tendency for the contact shifts to increase more rapidly at lower temperatures. These
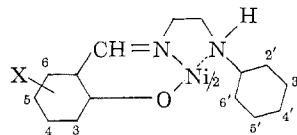
plots are indicative[9] of a much lower energy for the octahedral paramagnetic form relative to that of the planar diamagnetic form over the accessible temperature range (+60 to −50°). In consequence, the contact shifts, Δf_i, exhibit a temperature dependence closely proportional to $1/T$. Plots of Δf_i *vs.* $1/T$ were accurately linear throughout the accessible temperature range for solutions of the fully octahedral complexes, *e.g.*, [SALen–N(H)CH₂CH₃]₂Ni in Figure 3, and deviations were inappreciable for solutions in which the proportion of planar form in equilibrium with the octahedral form is expected to be small, *e.g.*, [3-Cl–SALen–N(H)-*p*-CH₃C₆H₄]₂Ni in Figure 3 and complexes down to X = 3-Cl, R′ = C₆H₅ in Table I.

Appreciable deviations from linearity of Δf_i *vs.* $1/T$ were only found for solutions of the compounds where X = 5-CH₃, R = H, R′ = *p*-tolyl to X = 3-CH₃, R = H, R′ = phenyl as listed in Table I. In all of these cases, the deviations from linearity were all toward the normal values of chemical shifts in analogous diamagnetic molecules and were only apparent at higher temperatures (*cf.* Figure 4). At low temperatures the plots of Δf_i *vs.* $1/T$ remained linear, with much the same slope as that for the fully octahedral complexes. This behavior is clearly indicative of systems in which an equilibrium exists—in this case between paramagnetic monomeric octahedral and diamagnetic planar forms—the proportion in the

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(8) R′ = –CH₂CH₃, terminal methyl signal *ca.* −7.33; R′ = –CH₂CH₂-CH₃, β′-methylene signal very broad *ca.* −0.92; terminal methyl signal *ca.* −0.27 to 0 ppm from tetramethylsilane as internal reference.

(9) *Cf.* D. R. Eaton, W. D. Philips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963), Figure 3.

TABLE II

PMR Data^{a,b} on Paramagnetic [X–SALen–N(H)R′)$_2$Ni Complexes in CDCl$_3$ Solution at Room Temperature^c

X	R′	3	4	5	6	2′,6′	3′,5′	4′
H	CH$_3$	+1.68	−27.8	−8.52	−9.78			
		(+8.02)	(−20.5)	(−1.85)	(−2.78)			
H	C$_2$H$_5$	+2.73	−27.9	−8.45	−9.92			
		(+9.07)	(−20.5)	(−1.78)	(−2.92)			
H	n-C$_3$H$_7$	+2.82	−28.0	−7.88	−10.0			
		(+9.15)	(−20.7)	(−1.22)	(−3.02)			
H	n-C$_4$H$_9$	+2.87	−28.0	−8.00	−10.0			
		(+9.20)	(−20.7)	(−1.33)	(−3.0)			
5-Cl	n-C$_3$H$_7$	+2.35	−26.1		−10.5			
		(+8.68)	(−18.8)		(−3.5)			
5-C$_2$H$_5$		+3.15	−27.5	[−3.47]^d	−9.87			
		(+9.48)	(−20.2)	[(−0.85)]^d	(−2.87)			
5-CH$_3$		+3.20	−27.5	[−3.42]	−9.83			
		(+9.53)	(−20.2)	[(−0.92)]	(−2.83)			
3-CH$_3$		[−2.62]	−32.6	−6.50	−10.0			
		[(−0.38)]	(−25.2)	(+0.16)	(−3.0)			
5-Cl	p-CH$_3$C$_6$H$_4$	+4.30	−27.8		−11.1	+12.7	−13.6	[−19.9]
		(+10.63)	(−20.4)		(−4.1)	(+19.0)	(−6.6)	[(−17.7)]
3-Cl			−32.6	−7.06	−11.3	+12.0	−13.7	[−19.9]
			(−25.3)	(−0.40)	(−4.3)	(+18.3)	(−6.7)	[(−17.7)]
H		+4.62	−29.7	−8.17	−10.6	+12.5	−13.4	[−19.4]
		(+10.95)	(−22.4)	(−1.50)	(−3.6)	(+18.8)	(−6.4)	[(−17.2)]
5-CH$_3$		+0.83	−28.8	[−3.31]	−10.5	+12.2	−13.4	[−19.1]
		(+11.2)	(−21.5)	[(−0.81)]	(−3.5)	(+18.5)	(−6.4)	[(−16.9)]
3-CH$_3$		[−2.15]	−33.6	−6.56	−10.4	+11.3	−16.6	[−18.2]
		[(+0.08)]	(−26.3)	(+0.10)	(−3.4)	(+17.6)	(−6.0)	[(−16.0)]
5-Cl	C$_6$H$_5$	+4.52	−28.0		−11.6	+12.5	−13.7	+11.2
		(+10.8)	(−20.7)		(−4.6)	(+18.8)	(−6.7)	(+18.1)
3-Cl			−32.3	−6.92	−11.3	+11.9	−13.6	+10.8
			(−24.9)	(−0.25)	(−4.3)	(+18.2)	(−6.6)	(+17.7)
H		+4.80	−29.5	−7.93	−10.7	+11.9	−13.3	+10.4
		(+11.13)	(−22.2)	(−1.27)	(−3.7)	(+18.2)	(−6.3)	(+17.3)
5-CH$_3$		+4.58	−27.7	[−3.32]	−10.5	+10.9	−13.0	+9.37
		(+10.92)	(−20.4)	[(−0.82)]	(−3.5)	(+17.2)	(−6.0)	(+16.2)
3-CH$_3$		[−2.15]	−31.2	−6.33	−10.2	+9.08	−12.3	+7.72
		[(+0.08)]	(−23.8)	(+0.33)	(−3.2)	(+15.4)	(−5.3)	(+14.6)

^{a} Shifts of ring proton, [methyl] resonances, ppm from tetramethylsilane as internal reference.   General error ±1%. ^{b} In parentheses, contact shifts relative to the average shifts for corresponding protons in analogous diamagnetic complexes: 3-H, −6.33 [3-CH$_3$, −2.23]; 4-H, −7.33; 5-H, −6.66 [5-CH$_3$, −2.50]; 6-H, −7.00; 2′,6′-H, −6.33; 3′,5′-H, −7.00; 4′-H, −6.83 [4′-CH$_3$, −2.23] ppm from tetramethylsilane as internal reference. ^{c} +27° in the probe. ^{d} [−CH$_2$−]; terminal –CH$_3$, −1.00 ppm.

planar form being appreciable at higher temperatures though the complexes are ≃100% in the octahedral form at low temperatures (below −30°).

Spin Density Calculation.—Over the region of linear dependence of Δf_i on $1/T$ the basic equation

$$\frac{\Delta f_i}{f} = \frac{-a_i \gamma_e g \beta S(S+1)}{\gamma_H 6SkT} \quad (1)$$

(in which the symbols have their usual meanings[10]) for the temperature dependence of contact shifts from a single paramagnetic species (in the present case the monomeric octahedral species) is applicable, when it is assumed that pseudo-contact contributions[11] to the total contact shift are unimportant.   Equation 1 may be used to calculate spin densities (ρ_{Ci}) on the ring carbon atoms on the basis of a further assumption, namely, that for aromatic C–H fragments[12]

$$a_i = Q_{CH}\rho_{Ci} \quad (2)$$

where Q_{CH} = −22.5 gauss, a relationship requiring that the unpaired spin is placed on the ligand by a π-bonding mechanism, as distinct from a spin-polarization mechanism operating in the σ system.   Neither of these assumptions can be fully justified in the present system, but on the basis that the signs of the spin densities tend to alternate, especially around the R′ = phenyl or p-tolyl rings, as would be expected for a π-delocalized spin system,[5,6,13] and that appreciable pseudo-contact shifts do not appear to occur in nickel-(II) complexes,[13,14] they appear to be not unreasonable.[15]

The combination of eq 1 and 2 has accordingly been used here to calculate the spin density on ring carbon atoms (ρ_{Ci}) by substituting values of the corresponding ring proton contact shift measured where the complexes are ≃100% in the octahedral form, i.e., −50° in the octahedral ⇌ planar series and room temperature (+27°) for those complexes which remain fully octahedral throughout the accessible temperature

(10) D. R. Eaton, A. D. Josey, W. D. Philips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962); *Discussions Faraday Soc.*, **34**, 77 (1962).

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

(12) H. M. McConnell and D. B. Chestnut, *ibid.*, **28**, 107 (1958).

(13) W. D. Horrocks, Jr., R. C. Taylor, and G. N. LaMar, *J. Am. Chem. Soc.*, **86**, 3031 (1964).

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

(15) Many authors[5,6,13,14] have similarly assumed that pseudo-contact shifts are negligible in nickel(II) complexes and have also adopted eq 2.
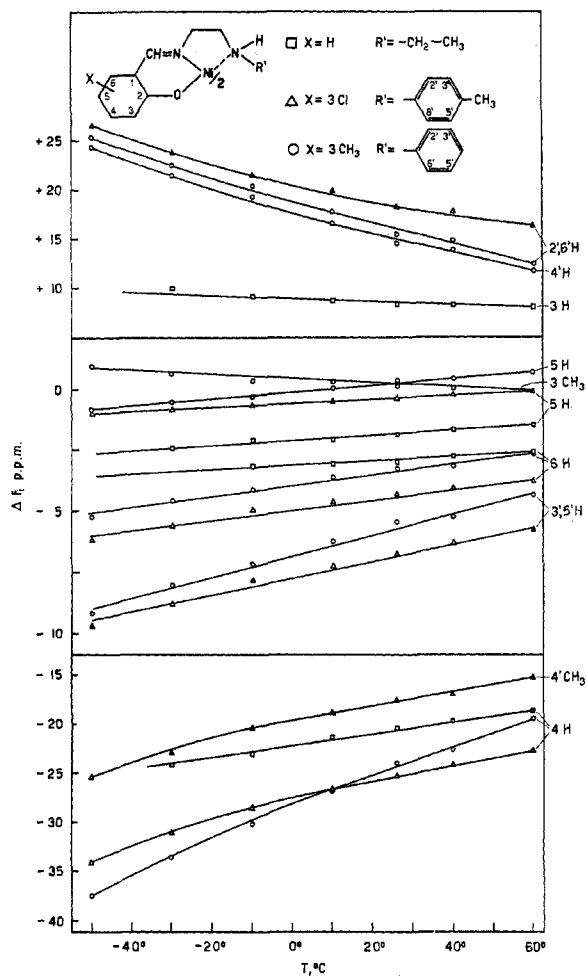
Figure 2.—Temperature dependence of the contact shifts of typical [X–SALen–N(H)R']₂Ni complexes in CDCl₃ solution.

Figure 3.—Linear dependence of contact shifts on $1/T$ for [SALen-N(H)C₂H₅]₂Ni and [3-Cl-SALen-N(H)-p-CH₃C₆H₄]₂Ni in CDCl₃ solution.
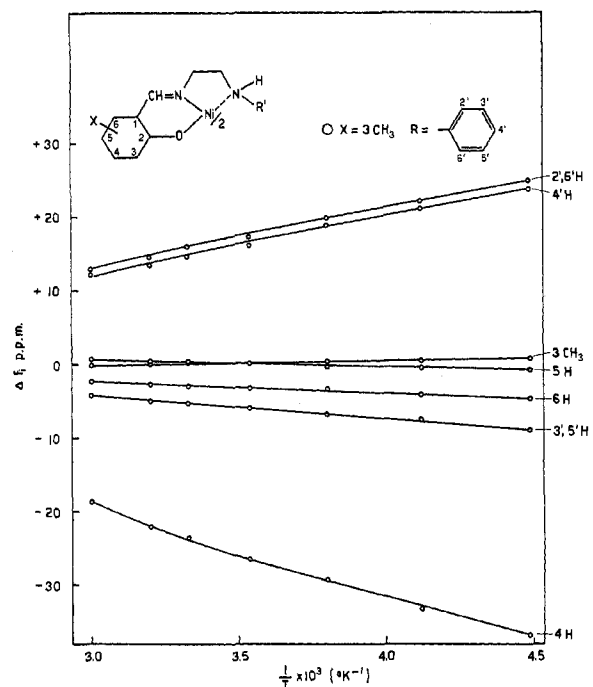
Figure 4.—Dependence of contact shifts on $1/T$ for [3-CH₃-SALen-N(H)C₆H₅]₂Ni in CDCl₃ solution.

range. As it was found that the spin density distribution was apparently similar throughout the series of complexes being investigated, the ranges within which the spin density values of each of the ring carbon atoms lie are summarized in Table III. The only cases in which spin density values, at any ring carbon atom, were distinctly different from the means of the ranges quoted were those for the complexes with a substituent (Cl or CH₃) in the 3 position on the salicylaldehyde ring. In these cases the spin density at the 4 position (and perhaps to a lesser extent at the 6 position) of the salicylaldehyde ring was consistently more negative as indicated in the footnote to Table III. These values were checked by calculating spin density values, in several cases, from the slope $(+22.5\rho_{Ci}(\gamma_e/\gamma_H) \cdot g\beta S(S + 1)/(6SK)$ of the low-temperature linear dependence of Δf_i on $1/T$, measured from graphical plots of the proton shifts from tetramethylsilane against $1/T$. The latter method has the disadvantage that it is difficult to estimate the slope accurately, as measurements could not be continued below −50° because of solubility problems. Nevertheless, it yielded values which, in view of the critical nature of errors in these
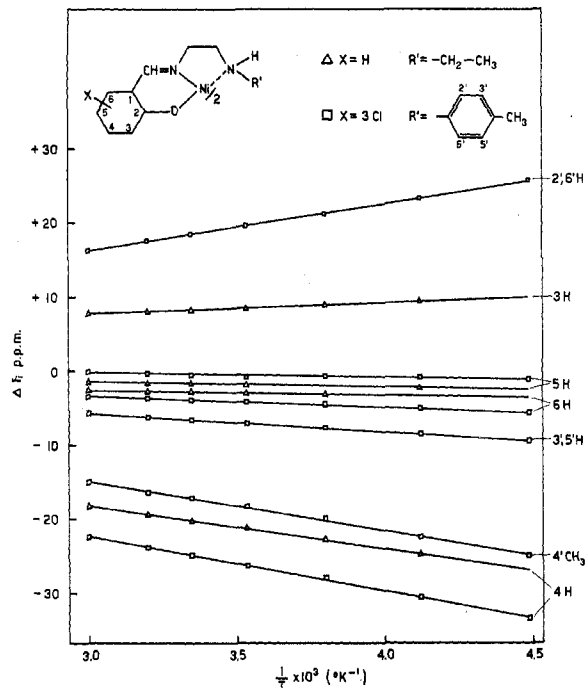
calculations, were in reasonable agreement with those calculated directly from contact shifts.

The shifts and the dependence of Δf_i *vs.* $1/T$ for signals from protons in methyl groups attached to the aromatic rings indicate that some spin density is distributed to them. This should be proportional to the

TABLE III

SPIN DENSITIES (ρ_{Ci}) ON THE RING CARBON ATOMS IN OCTAHEDRAL [X–SALen–N(H)R']$_2$Ni COMPLEXES

	Position						
	3	4	5	6	2',6'	3',5'	4'
Sign	+	–	–	–	+	–	+
Range ($\times 10^4$)	31–42	73–110	3–9	11–18	73–79	27–29	70–75
Mean ρ_{Ci}	0.0037	0.0081	0.0005	0.0013	0.0077	0.0028	0.0073
Std dev	0.0003	0.0004^a	0.0002	0.0002	0.0002	0.0001	0.0002

^{a} Excluding ρ_{C_4} 0.0099 for X = 3-Cl and ρ_{C_4} 0.0109 for X = 3-CH$_3$, which differ distinctly from the mean ρ_{C_4}.

spin density on the ring carbon to which the methyl group is attached, and a relationship similar to eq 2, namely

$$a_{iCH_3} = Q_{CCH_3}\sigma_{Ci} \qquad (3)$$

may be written[13] for the hyperfine interaction of each methyl group. a_{iCH_3} is the hyperfine interaction constant of the ring methyl protons and can be calculated using eq 1 as in the spin density calculations described above. Thereafter, on the assumption that spin densities on the ring carbon atom are unaffected by methyl substitution, the following values of Q_{CCH_3} were calculated using eq 3: 3-CH$_3$, +1 to −1; 5-CH$_3$, +11; 4'-CH$_3$, +23 gauss. Though their accuracy is low (<10%), it is clear that, except in the case of 4'-CH$_3$ methyl groups, they deviate widely from the value of Q_{CCH_3} = +27 gauss, obtained by epr measurements[16] on systems in which the unpaired spin is predominantly in the π system. The proportionality constant Q_{CCH_3} has previously been found to vary considerably in magnitude (+5 to +30 gauss)[13] in various ring systems, but the negative value found here for X = 3-CH$_3$ group is extreme.

Estimation of the Free Energy Changes.—As has already been mentioned, the deviations at high temperature of plots of contact shift Δf_i vs. $1/T$ from linearity are due to an increase in the proportion of planar form in equilibrium with octahedral form. Under these circumstances the contact shifts Δf_i will have an explicit dependence on the free energy ΔG of the equilibrium which may be expressed by[17]

$$\frac{\Delta f_i}{f} = \frac{-a_i\gamma_e}{\gamma_H}\frac{g\beta S(S+1)}{6SKT}(1 + e^{\Delta G/RT})^{-1} \qquad (4)$$

ΔG values may be calculated from eq 4 by fitting[9] it to the curved region of plots of Δf_i vs. $1/T$, by substituting values of a_i calculated for the fully octahedral form, or, alternatively, by combining eq 1 and 4 to give

$$\Delta G = RT2.3 \log\left(\frac{\Delta f_0 T_0}{\Delta f_i T_i} - 1\right) \qquad (5)$$

where Δf_0 is the contact shift of the fully octahedral forms at low temperatures (T_0 = −50°). In the present case where the deviations from linearity of Δf_i vs. $1/T$ were never very large (cf. Figure 4), the latter method, using eq 5, was used as it is the most favorable mathematically. Even so, owing to the

Figure 5.—Temperature dependence of the free energy changes for the planar $\rightleftarrows$ octahedral interconversion of [X–SALen–N(H)R']$_2$Ni complexes in CDCl$_3$ solution.

logarithm, small errors in contact shifts produce large errors in ΔG, and meaningful values[18] could only be estimated from the large shifts of protons 4-H and 2',6'-H in the last three compounds in Table I, with an appreciable proportion of planar form at room temperature. For these compounds ΔG (planar $\rightleftarrows$ octahedral) is negative throughout the accessible temperature range (+60 to −30°) and appears to be linearly dependent on T (cf. Figure 5). The increasingly negative values of ΔG as temperature decreases are in agreement with the displacement of the planar $\rightleftarrows$ octahedral equilibrium toward the octahedral forms at low temperatures.[2] Furthermore, at a given temperature the order, among these substances, in which ΔG is increasingly negative, is the same as that of the increase in the proportions in the octahedral form at room temperature, indicated by the rise in the intensity ratio ϵ_1/ϵ_2 of bands in the absorption spectra,[2] as presented in Table I.

Discussion

Previous physical measurements[2] on solutions of [X–SALen–N(H)R']$_2$Ni complexes have indicated that the position of the paramagnetic (octahedral) $\rightleftarrows$ diamagnetic (planar) equilibrium is apparently influenced by the substituent X on the salicylaldehyde ring and

(16) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

(17) Equation 4 was adopted in view of the desirable corrections recently made by W. D. Horrocks, *J. Am. Chem. Soc.*, **87**, 3779 (1965).
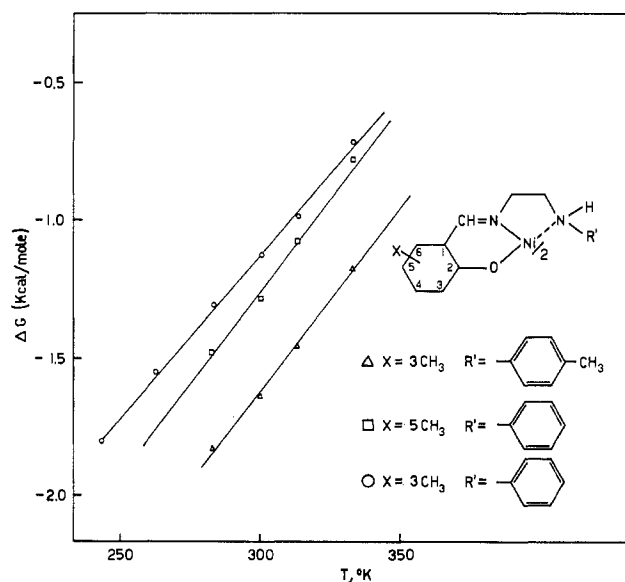
(18) The discrepancy between values of ΔG calculated from contact shifts to 4-H and 2',6'-H was generally 0.005 to 0.20 kcal, the value from 2',6'-H always being the least negative. Mean values are plotted in Figure 5.

the nitrogen substituent R'. From the present pmr measurements an indication of the position of this equilibrium can be gained by interpretation of the temperature dependence of the contact shifts (Δf_i) of the ring protons. Plots of Δf_i *vs.* $1/T$ were linear for all of the R' = alkyl complexes, which are fully octahedral, and for all of the R' = phenyl, *p*-tolyl complexes at low temperatures where they are apparently ≃100% in the octahedral form. The magnitude of the deviations from this low-temperature linearity of Δf_i *vs.* $1/T$ plots may be interpreted as a reasonable criterion of the proportion of planar forms present at higher temperatures. Interestingly, the order in which deviations from linearity increase to the maximum deviation found for [3-CH₃–SALen–N–(H)C₆H₅]₂Ni (Figure 4) is in agreement with the variation in the percentage of octahedral form (*cf.* planar form) with the substituent X, in approximately the order 5-Cl > 3-Cl > H > 5-CH₃ > 3-CH₃, and R', *p*-tolyl > phenyl, estimated from absorption spectra.[2] A similar trend is also recognizable in the occurrence of diamagnetism in the solid complexes (with the exception of X = H, R = H, R' = *p*-tolyl; see Table II). The estimated values of ΔG (planar ⇌ octahedral) presented in Figure 5 are also in accordance with this order and the greater stability of the octahedral form relative to the planar form at lower temperatures.

The measurements of proton contact shifts, reported in this paper, are of further interest because of the expected difference in the nature of the bonding between nickel and the ligand in octahedral and tetrahedral complexes[7] and the effect this may be expected to have on the mechanism of transference of spin density to the ligand.[7,13,14] The alternation of large high- and low-field contact shifts of pmr signals from the aromatic ring protons in several tetrahedral nickel(II) complexes,[5,7] including bis(N-*sec*-alkylsalicylaldimine)-nickel(II) complexes,[6] has been considered to be substantially in agreement with the proposed spin density transfer through nickel–ligand π-bonds. On the other hand, in regular octahedral complexes spin density transmission to the ligand has been expected to proceed only by polarization of σ electrons,[7] as the unpaired spins reside in the nickel e_g d orbitals which do not have the correct symmetry for π bonding with the ligand. If this were the case, the proton contact shifts would be expected[7,14] to be uniformly to low field and to decrease rapidly with increasing distance of the proton from the nickel atom.

For the compounds studied here, the observed pattern of contact shifts, to high and low field, is clearly not in accordance with that expected for solely σ-electron polarization. In the salicylaldimine ring, even though alternation is scarcely recognizable and the proton shifts have a negative bias, spin density distribution through the π orbitals is apparently important because the contact shift and therefore the spin density at position 3 of the salicylaldimine ring is clearly posi-

tive and its negative sign and magnitude at positions 4 and 6 are reminiscent of those observed for tetrahedral bis(N-*sec*-alkylsalicylaldimine)nickel(II) complexes.[6] Furthermore, the contact shifts of the ring protons and the spin densities on the ring carbon atoms of the R' = phenyl, *p*-tolyl rings are clearly alternant.

At present, the mechanism of spin density distribution in these complexes is not understood. The distinct π distribution on the R' = phenyl, *p*-tolyl rings is difficult to explain because no mechanism of π-electron transfer through the β-nitrogen atom with sp³ hybridization can be accepted. It is plausible, however, to consider that the N–H bond may be partially ionized so that back π bonding from nickel to the β-nitrogen atom is possible. Conductivity measurements in 10^{-3} *M* CHCl₃ solutions of paramagnetic complexes of this type compared with those obtained for similar solutions of the square-planar [SALen–N(CH₃)C₆H₅]₂Ni complex seem to support this hypothesis.[19] With regard to spin density distribution in six-coordinated nickel(II) complexes as a whole, at least two possible mechanisms have been proposed[3] whereby unpaired spin density in the nickel e_g d orbitals can be transferred to the ligand π system. It seems likely that the considerable distortion of the basic octahedral symmetry of these complexes will have a marked influence on the manner and extent of delocalization of unpaired spin.[3] This suggestion is supported by the observation (see Table III) that there is a tendency for the negative spin density at position 4 (and, to a lesser extent, at position 6 of the salicylaldimine ring) to increase when there is a substituent in the 3 position. This tendency is greatest for X = 3-CH₃ which also promotes the planar form of the complex, presumably because of steric and inductive effects of the 3-CH₃ group. It seems unlikely, however, that the distortion of symmetry from that of the regular octahedron can entirely account for the different spin density distribution in the individual salicylaldimine and R' aromatic rings. The individual characteristics of each coordinated group may be as important as that of the ligand as a whole. This conclusion is supported by the observations that pyridine-type bases coordinated to nickel acetylacetonates[14] accept spin density only into their σ-orbital system while triphenylphosphines[13] receive spin density into their π system in the analogous situation.

(19) We are indebted to Dr. G. N. La Mar for this suggestion.