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UNIVERSITY OF FLORENCE, FLORENCE, ITALY, AND THE LABORATORY FOR PHYSICAL CHEMISTRY,
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Proton Resonance Studies of the Solution Equilibria of Nickel(II) Complexes with Schiff Bases Formed from Salicylaldehydes and N,N-Substituted Ethylenediamines. II¹

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Received September 28, 1965

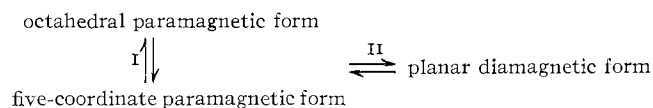
Proton resonance measurements of CDCl₃ solutions of nickel(II) Schiff base complexes have been extended to complexes of the general formula [X-SALen-NR₂]₂Ni which give rise to a paramagnetic five-coordinate species, as well as octahedral and planar forms. The proton shifts were found to be linearly dependent on the total percentage of paramagnetic species, and their temperature dependence was readily interpretable on the basis of the total free energy of formation of paramagnetic species in solution. A decrease noted in the shift of the signals from protons in the methylene groups adjacent to the nitrogen of the -NR₂ groups, relative to that of the signal from corresponding protons in fully octahedral complexes, can be interpreted as indicative of the presence of five-coordinate species. The calculated spin densities on the carbon atoms of the salicylaldehyde ring indicate that the contribution from π -spin delocalization in the five-coordinate species is greater than in the octahedral ones.

Introduction

Recently, further studies of nickel(II) complexes with Schiff bases formed from ring-substituted salicylaldehydes and N,N-substituted ethylenediamines have been published.³ Their most important result was to attribute a five-coordinate structure, in the solid state, to paramagnetic complexes of the general formula [X-SALen-NR₂]₂Ni, when -NR₂ is a diethylamino group and X = 3-Cl, 5-Cl, and 3,4-benzo. These complexes are the first reported examples of high-spin five-coordinate complexes of nickel(II).⁴ Their reflectance spectra are not compatible with either a tetrahedral or a regular or distorted octahedral structure. Furthermore, a recent X-ray structural analysis⁵ of the -NR₂ = diethylamino, X = 5-Cl complex confirms that this compound is five-coordinate and has a structure which can be regarded as a distorted square-based pyramid.

Other complexes in the series of general formula [X-SALen-NR₂]₂Ni are paramagnetic and have a distorted octahedral configuration, *e.g.*, when -NR₂ is a pyrrolidine group or diamagnetic, and have a square-planar configuration, *e.g.*, when -NR₂ is a piperidino group, in the solid state. In solution in inert solvents, however, most of them exist as mixtures of planar, octahedral, and five-coordinate forms. The magnetic moments of the complexes in solution are intermediate between 0 and 3.3 BM and give, to a reasonable degree of approximation, the total percentage of paramagnetic species in solution (see Table I: para-

magnetic % = 100 $\mu_{\text{eff}}^2/3.3^2$). They cannot, of course, distinguish between five-coordinate and octahedral forms because these have the same magnetic moment (≈ 3.3 BM). On the other hand, the intensities of characteristic bands in the absorption spectra³ give an indication, albeit not a very accurate one, of the relative proportions of five-coordinate, octahedral, and planar forms in solution. Apparently the solution equilibrium can be represented by the scheme



The proportion in the planar form is promoted by an increase in temperature and is particularly high in benzene solution. Little can be said with regard to equilibrium I, at the present, except that a greater proportion of the five-coordinated form has been found in chloroform solutions.

The present study reports measurements of the proton magnetic resonance spectra of CDCl₃ solutions of various complexes of the [X-SALen-NR₂]₂Ni series. It is an extension of the pmr studies, reported in the previous paper¹ of this series, on octahedral \rightleftharpoons planar equilibria in solutions of similar nickel(II) complexes. In the present case, large or small contact shifts have been observed, depending on the degree of paramagnetism of the solutions. Their dependence on the group -NR₂ and the substituent X in the complexes is described. For several complexes the pmr spectra were measured at various temperatures, and spin densities have been estimated from the shifts at -50° and at room temperatures where free energy (ΔG) values were available from magnetic measurements. Analysis of the spectra has followed the scheme used in the previous paper in this series,¹ and particular attention has been paid to differences which may be explained on the basis of the presence of five-coordinate species in the solution equilibria.

(1) Part I: J. D. Thwaites and L. Sacconi, *Inorg. Chem.*, **5**, 1029 (1966).

(2) Postdoctoral Fellow of the CIBA Fellowship Trust, at the Laboratory for Physical Chemistry, The Swiss Federal Institute of Technology, Zürich, Switzerland.

(3) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, **4**, 943 (1965).

(4) Recently, J. Lewis, R. S. Nyholm, and G. A. Rodley (*Nature*, **207**, 72 (1965)) have reported some five-coordinate high-spin complexes of nickel(II) with diphenylmethylarsine oxide.

(5) P. L. Orioli, L. Sacconi, and M. Di Vaira, *J. Am. Chem. Soc.*, **87**, 2059 (1965).

TABLE I
MAGNETIC,^a FREE ENERGY,^b AND PMR^c DATA FOR [X-SALCN-NR₂]₂Ni COMPLEXES

X	-NR ₂	CHCl ₃ solution		CDCl ₃ solution									
		T, °C	μ_{eff} , BM %	Param, %	ΔG , cal/mole	α	α'	β	4	6	5	3	β'
H	-N<CH ₃ CH ₃					-44.7 (-42.1)	-42.5 (-38.4)	-30.3 (-23.5)	-11.6 (-4.80)	-4.33 (+2.50)	+4.40 (+11.2)		
5-Cl	CH ₂ -CH ₂ -N<CH ₂ -CH ₂	22	3.18	94	-1500	-51.5 (-48.9)	-50.5 (-46.3)	-28.4 (-21.5)	-12.0 (-5.17)		+3.93 (+10.8)		-0.47 (+1.0)
H		23	3.23	97	-1840	-49.6 (-47.0)	-42.6 (-38.4)	-23.9 (-23.1)	-11.6 (+4.80)	-5.02 (+1.82)	+3.78 (+10.6)		-0.43 (+1.1)
5-CH ₃						-47.7 (-45.1)	-41.2 (-37.1)	-28.4 (-21.5)	-11.4 (-4.58)	[-5.97] [(-3.47)]	+3.58 (+10.4)		-0.53 (+0.97)
3-CH ₃						-46.7 (-44.0)	-41.7 (-37.6)	-32.6 (-25.8)	-11.2 (-4.40)	-3.38 (+3.45)	[-5.63] [(-3.38)]		-0.27 (+1.2)
5-Cl	-N<C ₂ H ₅ C ₂ H ₅	21	3.15	91	-1360	-30.3 (-27.7)	-26.2 (-22.1)	-25.8 (-19.0)	-13.2 (-6.33)		+1.50 (+8.33)		-0.65 (+0.85)
H		17	2.88	87	-670	-23.9 (-21.2)	-20.5 (-16.4)	-22.7 (-15.9)	-11.0 (-4.18)	-3.27 (+3.57)	-0.533 (+6.30)		-0.75 (+0.75)
5-C ₂ H ₅		21	2.53	59	-220		-17.1 (-14.5)	-17.7 (-10.9)	-9.72 (-2.88)	[-5.33] ^d [(-2.83)]	-1.92 (+4.92)		-0.82 (+0.68)
5-CH ₃		23	2.46	56	-130	-54.8 (-50.7)	-40.7 (-37.7)	-17.1 (-10.3)	-9.57 (-2.73)	[-5.68] [(-3.18)]	-2.03 (+4.80)		-0.80 (+0.70)
3-Cl		20	2.29	48	+50	-44.4 (-40.2)	-13.7 (-10.1)	-15.6 (-8.80)	-9.75 (-2.92)	-4.17 (+2.67)			-0.55 (+0.95)
3-CH ₃		23	2.06	39	+260	-31.1 (-27.0)	-9.63 (-5.47)	-13.6 (-6.80)	-8.58 (-1.75)	-4.72 (+2.12)	[-4.15] [(-1.90)]		-0.90 (+0.60)
5-Cl	-N<CH ₂ -CH ₂ >CH ₂ CH ₂ -CH ₂	23	3.14	90	-1320		-20.8 (-16.7)	-25.7 (-18.9)	-13.3 (-6.43)		+2.55 (+9.38)		-2.78 (-1.28)
H		25	2.74	69	-470	-13.7 (-11.0)	-21.5 (-17.3)	-20.0 (-13.1)	-10.3 (-3.50)	-3.67 (+3.17)	-0.92 (+5.92)		-2.57 (-1.07)
3-Cl		22	2.56	60	-240	-15.4 (-12.8)	-21.4 (-17.2)	-19.9 (-13.1)	-10.7 (-3.83)	-3.48 (+3.35)			-1.93 (-0.43)
5-CH ₃		24	2.42	54	-90	-50.9 (-46.7)	-16.7 (-12.5)	-17.1 (-10.2)	-9.52 (-2.68)	[-5.43] [(-2.93)]			-2.33 (-0.83)
5-C ₂ H ₅		25	2.41	53	-80	-47.9 (-43.7)	-16.2 (-12.0)	-16.3 (-9.50)	-9.43 (-2.60)	[-4.93] [(-2.43)]			-2.33 (-0.83)
3-CH ₃		22	2.22	45	+110	-35.5 (-31.3)	-12.9 (-8.75)	-14.9 (-8.03)	-8.88 (-2.05)	-4.40 (+2.43)	[-4.28] [(-2.03)]		-2.03 (-0.53)

^a Compiled from ref 3, Table III. ^b Total free energy values ΔG_T , cal/mole, calculated using $\Delta G = RT \ln (\mu_{\text{eff}}^2 / \mu_{\text{eff}}^2 - 1)$ where $\mu_{\text{eff}} = 3.3$ BM; estimated error $\pm 7\%$. ^c Shifts of protons, [methyl] resonances, at 27°, ppm from tetramethylsilane as internal reference. In parentheses, estimated contact shift, ppm relative to approximate shifts of corresponding protons in analogous diamagnetic complexes; i.e., aromatic protons, -6.83; 5-CH₃, -2.50; 3-CH₃, -2.25; methylene group protons: α , β , -4.17; α' , -2.67; β' -1.50; β' (methyl), -1 ppm, relative to tetramethylsilane as internal reference. ^d 5-CH₂; -CH₃, \approx -1 (0) ppm.

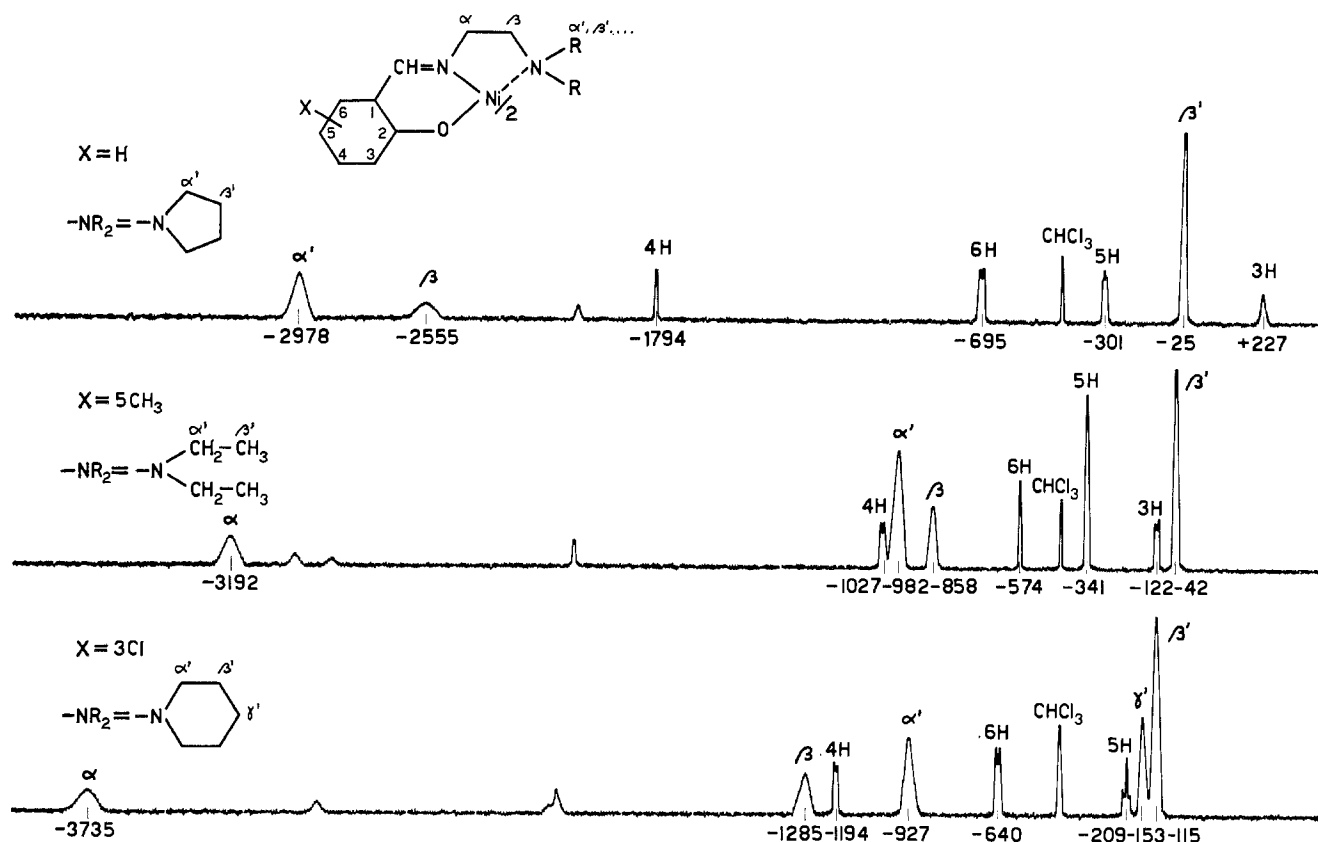


Figure 1.—Proton resonance spectra of typical paramagnetic $[X\text{-SALen-NR}_2]_2\text{Ni}$ complexes in CDCl_3 solution at $+27^\circ$. Frequencies, ppm, relative to tetramethylsilane as internal reference. Unmarked peaks due to ≈ 2000 -cps modulation in Varian base line stabilizer-integrator.

Experimental Section

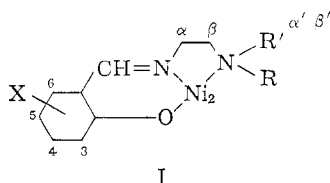
The preparation and characterization of all the compounds has been reported elsewhere,³ except for the following new complex which was prepared by an analogous method.

$[3\text{-CH}_3\text{-SALen-N}(\text{CH}_2)_4]_2\text{Ni}$.—Green crystals, mp $174\text{--}176^\circ$. *Anal.* Calcd for $\text{C}_{28}\text{H}_{38}\text{N}_4\text{O}_2\text{Ni}$: N, 10.75; Ni, 11.30. Found: N, 10.66; Ni, 11.57.

The proton resonance measurements were made, in CDCl_3 solutions (0.1 *M*) with tetramethylsilane as internal reference, as described in the previous paper in this series.¹

Results

It is convenient to divide the complexes, of the general formula



henceforth referred to as $[X\text{-SALen-NR}_2]_2\text{Ni}$, into series, differing according to the group $-\text{NR}_2$, and in the sequence of decreasing paramagnetism in their CHCl_3 solutions. All of the compounds which have been investigated are set out in this order in Table I together with some relevant magnetic data from an earlier paper³ and data on the proton shifts measured in CDCl_3 solutions at room temperature ($+27^\circ$ at the probe).

Reproductions of typical spectra, in Figure 1, illustrate the quality of the proton resonance spectra.

Not unexpectedly, the proton shifts and the line widths decrease as the effective paramagnetic moment of the complexes in solution decreases. The appearance of partially resolved simple spin-spin fine structure ($J \approx 6\text{--}10$ cps), even when the proportion of paramagnetic species in the solution equilibrium was still *ca.* 60%, made it easy to assign the lines due to the protons on the salicylaldimine ring. The other lines in the spectra were broader but could be clearly assigned from their relative intensities, measured by integrating the spectra. Signals from β , α' , and, in the less paramagnetic solutions, α protons (see general formula I) were identified, and it is notable that their shifts are considerably less than those of the broad and scarcely discernible signals from the corresponding protons in octahedral $[X\text{-SALen-N}(\text{H})\text{R}']_2\text{Ni}$ complexes,¹ even when the shifts of the salicylaldimine ring proton signals were of comparable magnitude. Though the signals from β and α' protons had similar shifts, they could both be distinguished in most cases, the β -proton signal lying at lower field, except in the case of $-\text{NR}_2 = \text{piperidine}$ complexes. The signal from the α protons was at even lower field and a very weak signal attributable to the aldehydic proton ($-\text{CH}=\text{N}$) was just discernible at much lower fields using high radio-frequency power and fast sweep rates. Protons at-

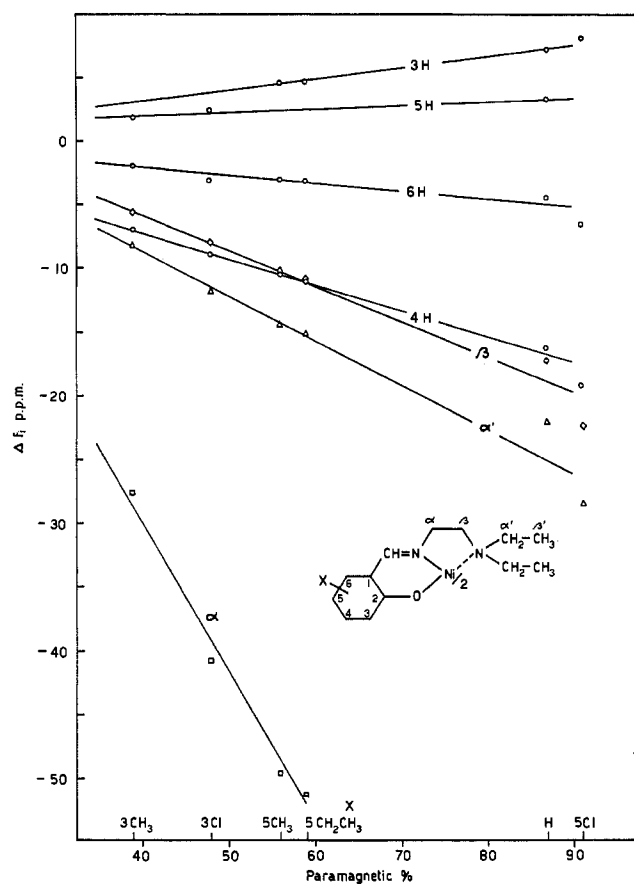


Figure 2.—Dependence of proton contact shifts on the percentage of paramagnetic species in CDCl_3 solutions of $[\text{X-SALen-N}(\text{C}_2\text{H}_5)_2]_2\text{Ni}$ complexes.

tached to carbon atoms β' to the nitrogen of the $-\text{NR}_2$ group all gave signals of characteristic intensity only slightly to low field of tetramethylsilane. In the case of $-\text{NR}_2 = -\text{N}(\text{CH}_2)_5$ compounds the γ' protons of the piperidine ring could only be distinguished from the β' protons in $\text{X} = 5\text{-Cl}$, 3-Cl complexes for which the shifts were relatively large.

The marked decrease in proton shifts, which can be seen from the data in Table I, is clearly due to the displacement of the solution equilibrium toward the diamagnetic planar form. This is confirmed by the reasonable correlation of the proton contact shifts with the total percentage of paramagnetic species (or, correspondingly, diamagnetic species) calculated from the effective magnetic moments of the complexes in their CHCl_3 solutions. The relationship, illustrated by Figures 2 and 3, is reasonably linear, except when the complexes are nearly $\approx 100\%$ paramagnetic, and the converging plots for the protons on the salicylalimine ring may be extrapolated to zero contact shift for diamagnetic solutions. Apparently, the magnitude of the contact shifts, to which the increase in the proton shifts beyond those in the diamagnetic form are due, is virtually independent of the relative proportions of octahedral and five-coordinate forms contributing to the total paramagnetism of these complexes, or, in practice, the effect of the different paramagnetic species

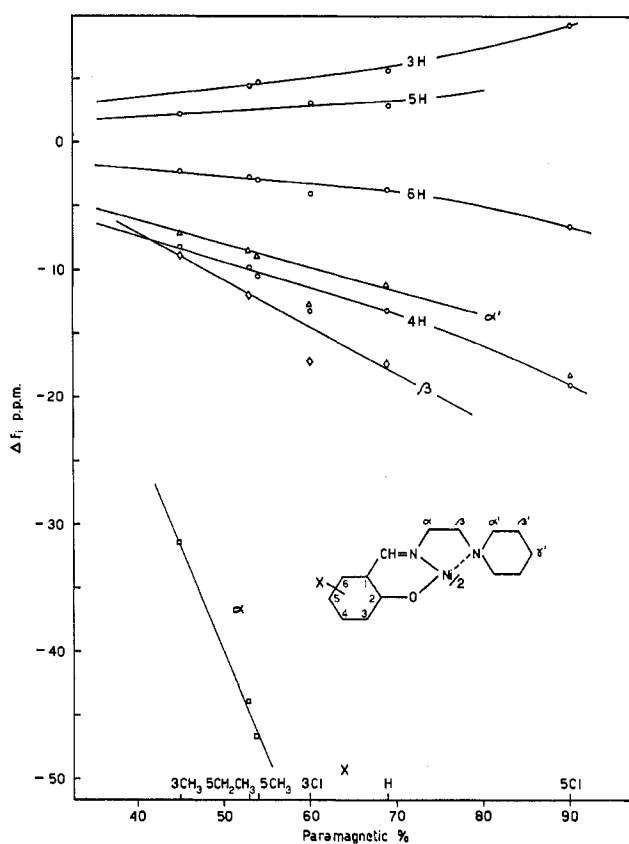


Figure 3.—Dependence of proton contact shifts on the percentage of paramagnetic species in CDCl_3 solutions of $[\text{X-SALen-N}(\text{CH}_2)_5]_2\text{Ni}$ complexes.

on the measurable shifts is disguised by the solution equilibrium.

The order in which the shifts decrease, from the top to the bottom of Table I, confirms the trends found from previous magnetic and spectrophotometric measurements.³ The percentage of the planar species in solution increases, for a given X substituent (and solvent) according to the $-\text{NR}_2$ group, in the order $-\text{N}(\text{CH}_3)_2 < -\text{N}(\text{CH}_2)_4 < -\text{N}(\text{C}_2\text{H}_5)_2 < -\text{N}(\text{CH}_2)_5$ and, within a given $-\text{NR}_2$ series according to the X substituents, approximately in the order $5\text{-Cl} < \text{H} < 5\text{-C}_2\text{H}_5 < 5\text{-CH}_3 < 3\text{-CH}_3$. The latter order is reminiscent of that found in systems existing in an octahedral \rightleftharpoons planar equilibrium^{1,6} except that in the present series the position of 3-Cl seems to vary (see Table I).

The proton shifts of several complexes were measured in CDCl_3 solutions at various temperatures between -50 and $+60^\circ$. In every case the shifts increased as the temperature decreased. At low temperatures the increase in line widths often prevented reliable measurements at -50° . Representative plots of contact shifts *vs.* $1/T$ in Figures 4 and 5 illustrate the two typical types of temperature dependence, which differ in the manner in which the shifts tend to decrease at higher temperatures. For plots similar to Figure 4 the curvature can be explained on the basis of a negative value for the total free energy (ΔG) of forma-

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

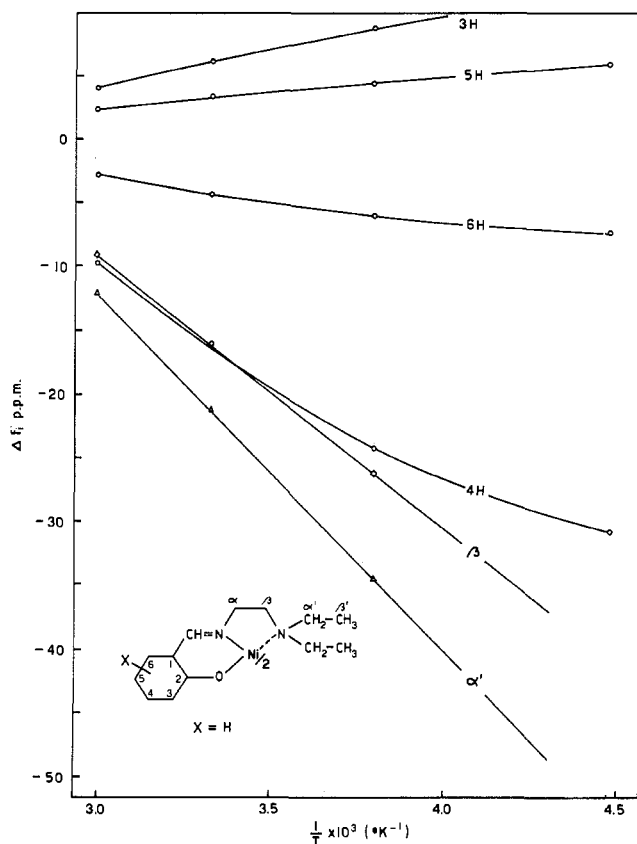


Figure 4.—Temperature dependence of proton contact shifts arising from the CDCl_3 solution equilibrium ($\Delta G_{17^\circ} = -670$ cal/mole for formation of paramagnetic species) of $[\text{SALen-N}(\text{C}_2\text{H}_5)_2]_2\text{Ni}$.

tion of the paramagnetic species (octahedral and five-coordinate forms) within the measured temperature range. In confirmation, in all cases where the curvature was as in Figure 4 the total ΔG calculable⁷ from the effective magnetic moment in solution was found to be negative. On the other hand, the reversed curvature, as illustrated by Figure 5, was found for complexes for which the total free energy of formation of the paramagnetic species in solution was positive at room temperature. Furthermore, the order in which the positive free energy values for various complexes increases agrees well with an increase in the curvature of the plots of shifts *vs.* $1/T$ as in Figure 5. The order of increasing positive total free energy values for the solution equilibria was naturally the same as that of the increase in the proportion of planar form in solution.

Discussion

The linear dependence of the proton shifts on the total percentage of paramagnetic species and the simple interpretation of their temperature dependence on the basis of the total free energy of formation of paramagnetic species both indicate that the observed proton shifts are apparently not substantially affected by variations in the relative proportions of five-coordinate

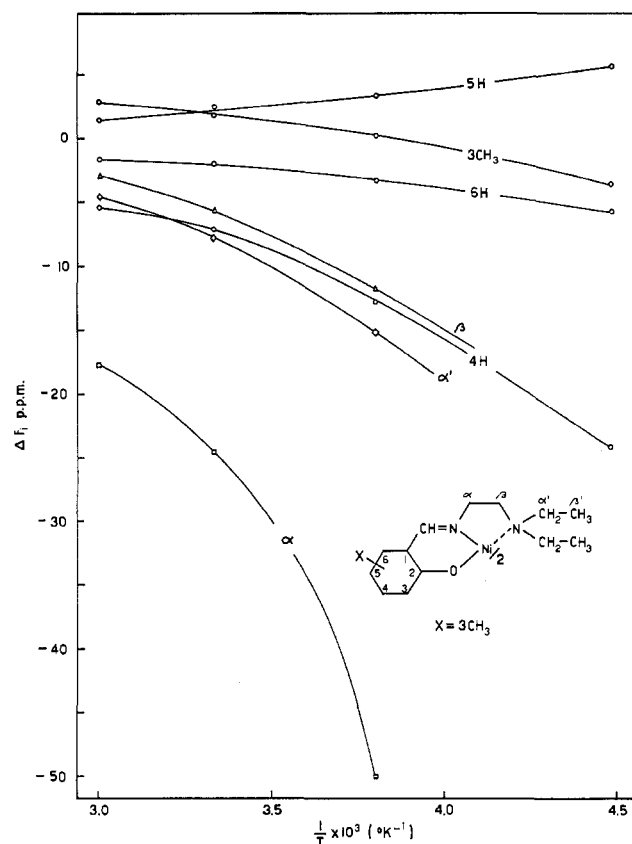


Figure 5.—Temperature dependence of proton contact shifts arising from the CDCl_3 solution equilibrium ($\Delta G_{23^\circ} = +270$ cal/mole for formation of paramagnetic species) of $[3\text{-CH}_3\text{-SALen-N}(\text{C}_2\text{H}_5)_2]_2\text{Ni}$.

and octahedral forms. This is not, however, particularly surprising as there are several possible reasons. For instance, if the equilibrium in solution, among octahedral, five-coordinate, and planar forms, is rapid, then the observed shift will be a mean of that in three forms, and variations will be correspondingly reduced. Furthermore, under these circumstances the major factor determining the observable shift will probably be the large difference between the shifts in the paramagnetic (octahedral and five-coordinate) and diamagnetic (planar) forms. The difference between the shifts in the octahedral and five-coordinate forms may be expected to be small because the spin density distribution on the ligand is unlikely to be very different, in view of the similarities which exist even between octahedral^{1,8} and tetrahedral⁹ nickel(II) complexes of the N-substituted salicylaldimine type. Ultimately, perhaps, the variations in the relative proportion of the octahedral and five-coordinate forms are, simply, not sufficiently large among the complexes studied. Previous spectrophotometric measurements cannot prove or disprove this because they are only a rough guide,³ but one deviation from the general trend may be important. This is the solution of the complex $\text{X} = 3\text{-Cl}$, $-\text{NR}_2 = -\text{N}(\text{CH}_2)_5$ for which the proportion

(8) A. Chakravorty, J. P. Fennessey, and R. H. Holm, *Inorg. Chem.*, **4**, 26 (1965).

(9) R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, **86**, 379 (1964).

(7) See footnote to Table I and eq 8 of W. D. Horrocks *J. Am. Chem. Soc.*, **87**, 3779 (1965).

of five-coordinate form relative to the octahedral form is appreciably less than in other cases.⁸ Strikingly, it is just for this complex that the shifts are appreciably greater than those which would fit the linear dependence of shifts on paramagnetic per cent in Figure 2, for the 60% paramagnetic species estimated for this compound from magnetic measurements. This increased shift may be due to the predominance of the octahedral form.

In view of the foregoing discussion, the proton resonance spectra of these $[X-SALen-NR_2]_2Ni$ complexes cannot be expected to yield substantial evidence of the presence of five-coordinated species in equilibrium with considerable proportions of octahedral and planar forms. A difference between the pmr spectra of $[X-SALen-NR_2]_2Ni$ complexes and fully octahedral complexes¹ of the type $[X-SALen-N(H)R]_2Ni$ has, however, been noted which is basically that which would be expected if there is a considerable proportion of five-coordinate species in the solution equilibrium. This difference, which has already been described in the analysis of the spectra, is the reduced shift of the signals from protons (symbolized as β and α' in the general formula I) in methylene groups adjacent to the nitrogen of the $-NR_2$ groups, relative to the position of the signal from equivalent protons in fully octahedral complexes. The observable shift of these β - and α' -proton signals is presumably the mean shift, determined by the position of the solution equilibrium, from those expected when the nitrogen of the $-NR_2$ groups is coordinated or not coordinated to the central nickel atom. A decreased shift would therefore be expected when uncoordinated $-NR_2$ groups are present because the spin density transmitted to the β and α' protons through the $N-CH_2-CH_2-NR_2$ chain would be less than that transmitted through the nitrogen in $-NR_2$ when it is coordinated to the central nickel atom. Accordingly, as the decrease in the shift of β and α' protons persists even when the magnitudes of the shifts of signals from the salicylaldehyde ring protons are of comparable magnitude with those in octahedral complexes and the per cent planar form is small, it may be interpreted as due to the presence of five-coordinate species in equilibrium with octahedral species. The further rapid decrease in the shifts of β and α' signals, as the proportion of planar form in the solution equilibrium increases, is, of course, accompanied by a reduction in the shifts of the ring proton signals (*cf.* Figures 4 and 5). At present, however, the pmr shift data cannot be treated quantitatively in the absence of exact knowledge of the relative proportions of octahedral, five-coordinate, and planar species in solution.

In the previous paper¹ in this series, spin densities on the carbon atoms of the salicylaldehyde ring were calculated from contact shifts which are linearly dependent on $1/T$ at low temperatures. As the solution equilib-

rium was simply between octahedral and planar forms, the contact shifts and spin densities were clearly those corresponding to the octahedral form. In the present case, owing to the complexity of the solution equilibria for $[X-NiSALen-NR_2]_2Ni$ complexes, it is impossible to know the contribution of each paramagnetic species to the observed contact shifts. There is however a basic similarity between the contact-shift dependence on $1/T$ for these systems and the octahedral \rightleftharpoons planar systems, and, prompted by the availability of values for the total free energy ΔG of formation of paramagnetic species (Table I), spin densities have been estimated using the normal equations given in paper I in this series¹ and taking $Q_{CH} = -22.5$ gauss.¹⁰ On this basis, spin density (ρ_{C_i}) values falling within the following ranges were obtained: ρ_{C_6} , +0.0030 to +0.0040; ρ_{C_1} , -0.0065 to -0.0085; ρ_{C_2} , +0.0010 to 0.0020; ρ_{C_3} , -0.0015 to 0.0025; and Q_{CCH_3} for $X = 3-CH_3$ is ≈ 13 , and for $X = 5-CH_3$ is ≈ 25 gauss.

Despite the admission that it is not clear to which paramagnetic species these spin density estimates refer, they are interesting because of the general consistency they exhibit among themselves and their general similarity to those reported for other salicylaldehyde nickel (II) complexes.^{1,8,9} It is also interesting to note that the spin density at position 5 is positive whereas it was negative in basically octahedral complexes;¹ furthermore, the alternation even with respect to magnitudes is relatively good, and the Q_{CCH_3} value estimated for the $X = 5-CH_3$ group approaches the value of +27 gauss.¹¹ This may be indicative of a greater contribution from π -spin delocalization in these five-coordinate species than was found in the distorted octahedral complexes. A greater relaxation of the symmetry requirements preventing the spin-containing d orbitals from mixing with the ligand π orbitals is consistent with the lower symmetry of the square-pyramidal geometry of the five-coordinate species. The present system is, however, too complicated, and the distortions of the basically octahedral symmetry of the complexes previously studied¹ are not known in sufficient detail for firm comparison to be made. The relevance of the present data should increase when further systems containing paramagnetic five-coordinate nickel(II) complexes are studied.

Acknowledgments.—J. D. Thwaites gratefully acknowledges the financial support of the CIBA Fellowship Trust, London. This research was partially supported by the Italian National Research Council (CNR). The authors also wish to thank Professors H. H. Günthard and H. Primas, of the Eidgenössische Technische Hochschule, Zürich, for use of a Varian DP 60 spectrometer and laboratory facilities.

(10) H. M. McConnell and D. C. Chestnut, *J. Chem. Phys.*, **28**, 107 (1958).

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