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Studies on Nickel(II) Complexes. VI.¹ The Conformational Equilibria of Bis(*o*-hydroxynaphthaldimine) Complexes

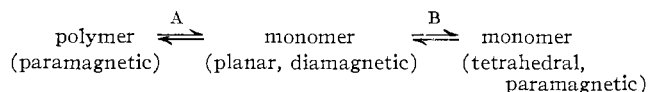
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The existence of a planar \rightleftharpoons tetrahedral structural equilibrium in solutions of three isomeric groups of bis(*o*-hydroxynaphthaldimine)-Ni(II) complexes has been established from studies of magnetic susceptibilities, ligand field spectra, and proton magnetic resonance spectra. Like the related salicylaldimine complexes,¹ these naphthaldimine complexes manifest isotropic hyperfine contact shifts in their proton resonance spectra. The assignment of these spectra is discussed. The signs of the contact shifts and spin densities are shown to be in agreement with a qualitative valence bond model of spin delocalization. The use of the contact shift effect in obtaining *cis* spin-spin coupling constants is illustrated for one *o*-hydroxynaphthaldimine system.

Introduction

As a result of physicochemical studies carried out over the past several years it has become firmly established that certain bis(*N*-substituted)salicylaldimine Ni(II) complexes exhibit a structural equilibrium in solution involving planar and pseudo-tetrahedral forms.¹⁻³ When the nitrogen substituent R is a secondary or tertiary alkyl group this equilibrium is predominant at room temperature. At sufficiently low temperatures another equilibrium involving paramagnetic associated species sets in. Thus the scheme



represents the general behavior of this group of complexes. In fact, it is becoming increasingly clear that these equilibria occur for most salicylaldimine complexes of nickel(II) in solutions of noncoordinating solvents, and that they are displaced to the right with increasing temperature. The relative importance of the equilibria A and B and the equilibrium concentrations of the three solute forms are primarily dependent on the group R. When R = CH₃ or *n*-alkyl only A is of any importance and lies heavily to the right.^{4,5} When R = aryl A is in general shifted to the left at room temperature,^{6,7} whereas at sufficiently high temperatures ($\gtrsim 100^\circ$) tetrahedral species can be detected⁷ so that process B commences to contribute to the solution composition. Equilibrium B is apparently predominant in the high temperature molten phases of complexes with R = *n*-alkyl.⁸

The particular advantage of complexes with R = *sec*- or *t*-alkyl is that they permit the study of the process

of structural interconversion at room temperature and above with little or no interference from the presence of polymeric forms. Accordingly, the factors affecting the position of equilibrium B have been thoroughly studied by nuclear resonance in an extensive series of complexes.¹ As demonstrated by studies of the bis(*N,N*-disubstituted aminotroponimine)nickel(II) complexes, which exhibit only equilibrium B, an analysis of the proton resonance contact shifts allows a determination of the thermodynamic changes associated with the structural change⁹ and of the distribution of spin densities in the coordinated ligand system.¹⁰ We report here an extension of our previous study on salicylaldimine complexes^{1,2} to include Ni(II) complexes of a series of *o*-hydroxynaphthaldimines. This study has yielded spin density distributions in the naphthalene rings and thermodynamic data for the structural change, and has afforded a comparison with related results obtained from a similar study of salicylaldimine complexes.

Experimental

Preparation of Compounds.—2-Hydroxy-1-naphthaldehyde was obtained from Chemical Procurement Laboratories, College Point, New York.

1-Hydroxy-2-naphthaldehyde was prepared by reducing the corresponding acid with 3% sodium amalgam,¹¹ using *p*-toluidine¹² rather than sodium bisulfite¹³ to bind the aldehyde. The precipitated Schiff base was collected, decomposed with acid, and steam distilled to yield yellow crystals, m.p. 54–55°.

2-Hydroxy-3-naphthaldehyde has been prepared previously by Rosenmund reduction of 2-acetoxy-3-naphthoylchloride.¹³ We reduced this compound using lithium tri-*t*-butoxyaluminumhydride in diglyme at –60° following the general procedure of Brown and Subba Rao.¹⁴ The reaction product was poured onto ice and the precipitated solid hydrolyzed with sodium hydroxide. The sodium salt was collected, decomposed with acid, and steam

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

(2) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 181 (1963).

(3) L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 411 (1963).

(4) R. H. Holm, *ibid.*, **83**, 4683 (1961).

(5) H. C. Clark, K. Macvicar, and R. J. O'Brien, *Can. J. Chem.*, **40**, 822 (1962).

(6) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **1**, 599 (1962).

(7) L. Sacconi and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 1750 (1963).

(8) L. Sacconi, *J. Chem. Soc.*, 4608 (1963).

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

(10) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962).

(11) H. Weil and H. Ostermeier, *Ber.*, **54**, 3217 (1921).

(12) L. N. Lavrishcheva, N. M. Przhivalgovskaya, S. A. Voitkevich, and V. N. Belov, *J. Gen. Chem. USSR*, **27**, 1346 (1957).

(13) M. Calvin and N. C. Melchior, *J. Am. Chem. Soc.*, **70**, 3273 (1948).

(14) H. C. Brown and B. C. Subba Rao, *ibid.*, **80**, 5377 (1958).

distilled. The product was collected as yellow crystals, m.p. 102–103°; yield 30% based on the acid.

The nickel complexes of the hydroxyaldehydes were prepared by standard methods.¹⁸ The Schiff base complexes were prepared, unless otherwise noted, by refluxing the amine and the starting nickel complex in 2:1 mole ratio in ethanol or dichloromethane for 1 hr.

Bis(N-isopropyl-2-hydroxy-1-naphthaldimine)nickel(II) (1) was prepared in dichloromethane and recrystallized from hexane-dichloromethane to yield greenish black crystals, m.p. 204–207°.

Anal. Calcd. for C₂₃H₂₃N₂O₂Ni: C, 69.60; H, 5.84; N, 5.80. Found: C, 69.25; H, 5.76; N, 5.90.

Bis(N-*t*-butyl-2-hydroxy-1-naphthaldimine)nickel(II) (2) was obtained by repeated evaporation of a solution of *t*-butylamine in dichloromethane in which the starting nickel complex was suspended. The evaporations were carried out until the entire residue was brown. The thoroughly dry residue was recrystallized from dry toluene to give brown crystals, m.p. 263–265°.

Anal. Calcd. for C₃₀H₃₂N₂O₂Ni: C, 70.47; H, 6.31; N, 5.48. Found: C, 70.74; H, 6.16; N, 5.67.

Bis(N-isopropyl-1-hydroxy-2-naphthaldimine)nickel(II) (3) was prepared in ethanol and purified by recrystallization from hexane-dichloromethane to give brown-black crystals, m.p. 228°.

Anal. Found: C, 69.93; H, 5.98; N, 5.99.

Bis(N-3-pentyl-1-hydroxy-2-naphthaldimine)nickel(II) (4) was prepared and purified as was **3**; brownish crystals, m.p. 152–154°.

Anal. Calcd. for C₃₂H₃₆N₂O₂Ni: C, 71.26; H, 6.73; N, 5.20. Found: C, 71.63; H, 7.02; N, 5.48.

Bis(N-isopropyl-2-hydroxy-3-naphthaldimine)nickel(II) (5) was prepared in dichloromethane and recrystallized from chloroform; brown needles, m.p. 252–256°.

Anal. Found: C, 69.20; H, 5.75; N, 5.96.

Bis(N-3-pentyl-2-hydroxy-3-naphthaldimine)nickel(II) (6) was prepared and purified as was **5**; brown needles, m.p. 220–222°.

Anal. Found: C, 71.44; H, 7.00; N, 5.58.

Bis(N-*t*-butyl-2-hydroxy-3-naphthaldimine)nickel(II) (7) was prepared by heating the starting nickel complex with *t*-butylamine in dry toluene in an open flask. The red solution which first formed gradually turned brown on continued heating (1 hr.). The hot brown solution was filtered and allowed to crystallize. The first crop of brown-black crystals was collected, m.p. >280°.

Anal. Found: C, 70.14; H, 6.31; N, 5.83.

Complexes with R = *t*-C₄H₉ are exceedingly sensitive to moisture, being readily hydrolyzed to the amine and the nickel complex of the hydroxynaphthaldehyde. Stable solutions could be prepared in solvents dried over molecular sieves. With a given R group the solubilities of hydroxynaphthaldehyde complexes in nonpolar solvents are 2,3 ≪ 2,1 < 1,2. Within a given group the solubilities are isopropyl < 3-pentyl < *t*-butyl. Of the complexes of the 2,3 group, only the *t*-butyl derivative was sufficiently soluble to allow accurate magnetic and proton resonance measurements.

Magnetic Measurements.—Measurements on solids and solutions were made by the Gouy method. Solute susceptibilities in a number of cases were also determined by the nuclear resonance method of Evans.¹⁵ The agreement between the two methods was in every case < 0.05 B.M.

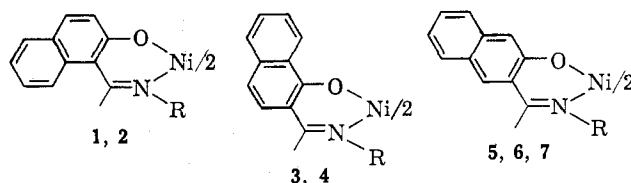
Spectral Measurements.—Solution and mull spectra were obtained on a Cary Model 14 spectrophotometer.

Proton Resonance Measurements.—These measurements were made as previously described.¹

Results and Discussion

The complexes studied fall into the three groups shown below, and are specified by reference to the Experimental section. None of these complexes has been previously prepared. From a combined study

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



of the magnetic susceptibilities, electronic spectra, and proton resonance spectra, the existence of a planar ⇌ tetrahedral equilibrium in solution has been established. The evidence for this equilibrium is summarized below.

Magnetic Susceptibility Studies.—The pure crystalline complexes are either diamagnetic (**1**, **5**, **6**) or paramagnetic (**2**, **3**, **4**, **7**) with magnetic moments of 3.30 ± 0.03 B.M. at 25°. Thus in the crystalline phase the complexes are either wholly planar or wholly pseudo-tetrahedral.¹⁶ In solution, however, the moments fall in the range $0 < \mu_{\text{eff}} < 3.3$ B.M. (*cf.* Table I), indicating

TABLE I
MAGNETIC MOMENTS IN CHLOROFORM SOLUTION

Complex ^a	μ_{eff} , B.M. ^b
1	0.86 (30°)
2	3.23 (25°)
3	2.78 (20°), 2.83 (50°)
4	2.93 (20°), 2.96 (50°)
6	1.80° (50°)
7	3.23 (25°)

^a Concentration of solutions ~ 0.1 M. ^b Moments calculated from Curie law; estimated error $\pm 2\%$ when $\mu_{\text{eff}} \geq 1.8$ B.M. ^c Estimated error $\pm 10\%$ due to low solubility.

the existence of diamagnetic planar species, the proportion of which is obviously dependent on the gross structure of the complex and the specific R group. As will be seen from the proton resonance results, the contribution to the magnetic moments at room temperature and above from associated paramagnetic species is negligible. The free energy change for the planar → tetrahedral conversion can then be calculated from the relation⁹

$$\Delta F = RT \ln \left[3 \left(\frac{\mu_{\infty}^2}{\mu_{\text{eff}}^2} - 1 \right) \right] \quad (1)$$

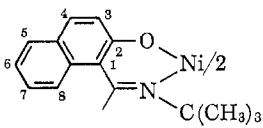
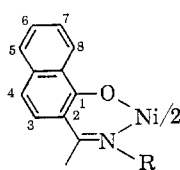

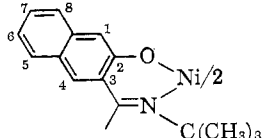
in which the moment of the tetrahedral form, μ_{∞} , is taken to be 3.30 B.M. The results are given in Table II.

Spectral Studies.—The existence of tetrahedral molecules in solution is readily established from comparison of solution and solid state spectra in cases where the solid is paramagnetic. One such comparison, that of **3**, is seen in Fig. 1. The spectra rather closely resemble those of related salicylaldimine complexes and can be assigned similarly. The Liehr-Ballhausen nomograph,¹⁷ while calculated for rigorous tetrahedral symmetry, is still useful in cases of gross tetrahedral symmetry. Accordingly, we make the following assignments: ${}^3T_1 \rightarrow {}^3A_2(F)$, 6900 cm.⁻¹

(16) The structure of one such paramagnetic pseudo-tetrahedral complex has been determined; *cf.* M. R. Fox, E. C. Lingafelter, P. L. Orioli, and L. Sacconi, *Nature*, **197**, 1104 (1963).

(17) A. D. Liehr and C. J. Ballhausen, *Ann. Phys. (N. Y.)*, **6**, 1341 (1959).

TABLE II
FREE ENERGY CHANGES, CONTACT SHIFTS, AND SPIN DENSITIES FOR
BIS(N-SUBSTITUTED *o*-HYDROXYNAPHTHALDIMINE)-Ni(II) COMPLEXES^a

Complex	ΔF , cal.	Position	Contact shift, c.p.s. ^b	Spin density ^c		
	-1200 (25°)	3	+1250	+0.0084		
		4	-1950	-0.0131		
		5	-101	-0.0007		
		6	+818	+0.0055		
		7	-148	-0.0010		
		8	+1046	+0.0070		
		 R = CH(CH ₃) ₂	+14 (50°)	3	-114	-0.0011
				4	+1530	+0.0143
5	+125			+0.0012		
6	-251			-0.0023		
7	+105			+0.0010		
8	-638			-0.0060		
 R = CH(CH ₂ CH ₃) ₂	-203 (50°)			3	-73	-0.0006
				4	+1580	+0.0137
		5	+105	+0.0009		
		6	-248	-0.0022		
		7	+96	+0.0008		
		8	-690	-0.0060		
			-1200 (25°)	1	+2138	+0.0144
				4	-190	-0.0013
5	-84			-0.0006		
6	+854			+0.0057		
7	-317			-0.0021		
8	+566			+0.0038		

^a All measurements made in chloroform solution. ^b Measured at the temperatures indicated for ΔF . ^c Calculated using $Q = -22.5$ G.

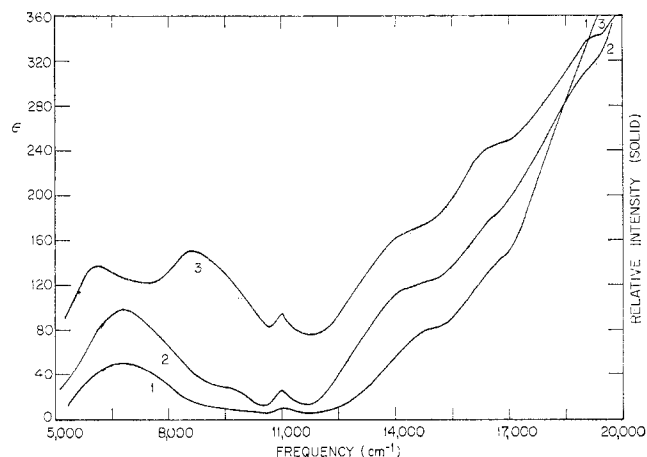


Fig. 1.—Ligand field spectra of bis(N-isopropyl-1-hydroxy-2-naphthalaldimine)nickel(II) in chloroform (1), solid Nujol mull (2), and bis(N-*t*-butylsalicylaldimine-1-hydroxy-2-naphthalaldimine)nickel(II) in solid Nujol mull (3).

(ν_2); \rightarrow 1D , 11,000 cm^{-1} ; \rightarrow ${}^3T_2(P)$, 14,800, 16,400 cm^{-1} (ν_3). The doublet structure of ν_3 is reasonably attributed to splitting of the excited state by the approximate C_{2v} component of the ligand field. Spectral examination in carbon tetrachloride solution to 4000 cm^{-1} failed to detect ν_1 (${}^3T_1 \rightarrow {}^3T_2(F)$). Planar salicylaldimine Ni(II) complexes show a ligand field band near 16,000 cm^{-1} ($\epsilon \sim 70$)^{3,4,18} and no other absorptions at lower energies. The band at 16,400 cm^{-1}

cannot be attributed to the planar form on the basis of its intensity and its occurrence at nearly the same energy in the spectrum of the solid. Therefore, due to the overlap of the ν_3 region of the tetrahedral form with the spin-allowed transitions in the planar form, it has not been possible to establish from the optical spectra the presence of planar molecules in solutions of 2, 3, 4, 6, and 7. Their presence is established with certainty for 1, 3, and 4 from magnetic data. The proportion of planar molecules in solutions of 2 and 7 cannot be accurately determined but from the magnetic data can be calculated to be less than 5%.

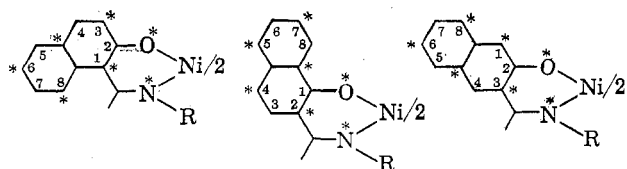
One feature of the spectra which also occurs in the salicylaldimine complexes³ cannot be explained at present. In the solid complexes with $R = i\text{-C}_3\text{H}_7$ a shoulder is evident at ~ 9200 cm^{-1} . Complexes with $R = t\text{-C}_4\text{H}_9$ show in the solid and in solution a well-defined feature at ~ 8600 cm^{-1} in addition to the band assigned as ν_2 at 6000 cm^{-1} . These two features cannot be components of ν_2 since the 3A_2 state cannot be decomposed by low symmetry components of the ligand field. Assignment of the lower energy feature as ν_1 gives extremely poor agreement with theory, whereas the Dq obtained from the proposed assignment of ν_2 allows a fit to within 10% of the remaining transition energies.¹⁷ While we are unable to offer a satisfactory interpretation, it is noted that two band maxima in the ν_2 region have been observed in at least one other pseudo-tetrahedral nickel complex.¹⁹

(18) L. Sacconi, P. Paoletti, and G. Del Re, *J. Am. Chem. Soc.*, **79**, 4062 (1957).

(19) F. A. Cotton, O. D. Faut, and D. M. L. Goodgame, *ibid.*, **83**, 344 (1961).

Nuclear Resonance Studies.—It is now well recognized due to the original work of Eaton, Phillips, *et al.*,^{9,10,20,21} that Ni(II) complexes involved in a dynamic planar-tetrahedral equilibrium satisfy one or both of those relaxation conditions²² required for the observation of reasonably narrow proton resonance signals in paramagnetic molecules. Isotropic hyperfine contact shifts of ligand protons are readily detected and their temperature dependences analyzed to yield a thermodynamic description of the structural change and spin density distribution in the ligand system. Using this approach extensive studies of bis(N,N-disubstituted aminotroponimine)^{9,10,20,21} and bis-(N-*sec*- and -*t*-alkylsalicylaldimine)-Ni(II)¹ complexes have been carried out.

The naphthalaldimine complexes exhibit large proton resonance shifts to high and low fields relative to the free ligands or zinc complexes. These contact shifts presumably result from metal-ligand π -bonding in the paramagnetic (tetrahedral) form whereby a fraction of unpaired spin is transferred to the ligand π -system and delocalized. The chelate ring systems in the three groups of complexes are odd-alternant and for each the valence bond structures expected to contribute to spin delocalization can be represented as shown below.



The starred positions are those at which the unpaired electron can be placed in at least one valence bond structure. Structures involving long bonds are neglected. At these carbon atoms the valence bond model predicts positive spin densities, whereas the remaining carbon atoms acquire negative spin densities through electron correlation effects.^{22,23} Because spin is transferred to the aromatic protons by an indirect π - σ spin polarization mechanism,²² the protons attached to the starred carbons will acquire a positive contact shift. All other protons will exhibit negative contact shifts. In this study we are concerned only with those protons attached to the naphthalene ring.

Two predictions of a qualitative nature follow from the valence bond model and arise as a necessary consequence of the structural isomerism of the three groups of complexes. Complexes of the 2,1 and 1,2 groups should display resonance patterns in which the signs of the contact shifts for given numbered protons are opposite. On the other hand, complexes of the 2,1 and 2,3 groups should give contact shifts of the same sign for given numbered protons. No predictions can be made of the relative magnitude of the contact shifts among the three isomeric groups of complexes.

(20) D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4100 (1962); D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Discussions Faraday Soc.*, **34**, 77 (1962).

(21) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **39**, 3513 (1963).

(22) H. M. McConnell and D. B. Chesnut, *ibid.*, **28**, 107 (1958).

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

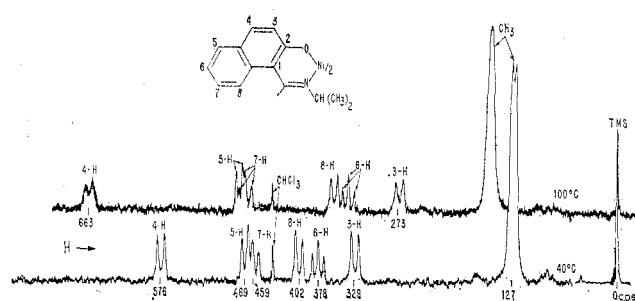


Fig. 2.—Proton resonance spectrum of bis(N-isopropyl-2-hydroxy-1-naphthalaldimine)nickel(II) in CDCl_3 at 40 and 100°. Frequencies (c.p.s.) are the chemical shifts.

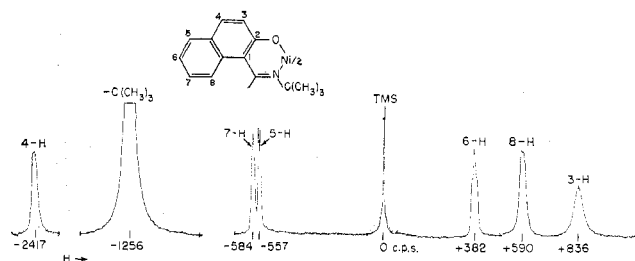


Fig. 3.—Proton resonance spectrum of bis(N-*t*-butyl-2-hydroxy-1-naphthalaldimine)nickel(II) in CDCl_3 at 25°. Frequencies (c.p.s.) are the chemical shifts. (The 7-H and 5-H signals were recorded at a faster sweep rate than were the other signals.)

The spectra of complexes of the 2,1 group are considered first. The spectrum of 1 at two temperatures is given in Fig. 2. Assignments are readily made from the predicted signs of the contact shifts and the first-order spin-spin couplings, which in this case are well resolved because of the small proportion of paramagnetic species. The two doublets of equal intensity at high and low field are components of an AB pair with $J = 9.0$ c.p.s. (*vide infra*) and are assigned to 3-H and 4-H, respectively, rather than 8-H and 5-H. The only assignments which are uncertain in the 40° spectrum are those for 5-H and 7-H, whose signals overlap due to extremely small contact shifts. At 100° the contact shifts are increased as the equilibrium is slightly but detectably displaced toward the paramagnetic form. The triplet and doublet structures of 7-H and 5-H, respectively, then become distinguishable. The spectrum of 2 is shown in Fig. 3. Broader signals and much larger contact shifts result from the displacement of the equilibrium to >95% of the tetrahedral form. The relative broadness of the 3-H signal tends to confirm its assignment. The broadening is probably due to dipolar nuclear-electron relaxation¹⁰ and should be most pronounced for that proton nearest the paramagnetic metal.

The spectra of complexes of the 1,2 and 2,3 groups can be assigned on a similar basis. The spectra and assignments are presented in Fig. 4 and 5.

For a system of singlet and triplet molecules rapidly interconverted by structural change, the temperature dependence of the contact shifts is given by¹⁰

$$\frac{\Delta f_i}{f} = -a_i \left(\frac{\gamma_e}{\gamma_H} \right) \frac{g\beta S(S+1)}{2SkT} \left[\frac{1}{3 + e^{\Delta F/kT}} \right] \quad (2)$$

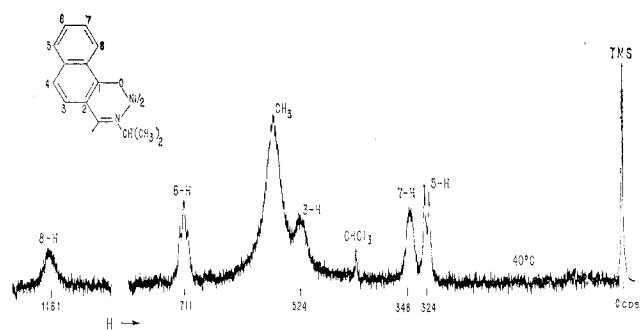


Fig. 4.—Proton resonance spectrum of bis(*N*-isopropyl-1-hydroxy-2-naphthaldimine)nickel(II) in CDCl_3 at 40° . Frequencies (c.p.s.) are the chemical shifts.

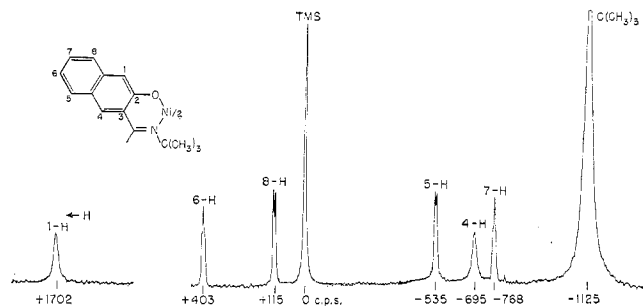


Fig. 5.—Proton resonance spectrum of bis(*N*-*t*-butyl-2-hydroxy-3-naphthaldimine)nickel(II) in CDCl_3 at 25° . Frequencies (c.p.s.) are the chemical shifts.

in which Δf_i is the observed contact shift of the proton i in c.p.s.,²⁴ f is the spectrometer frequency, a_i is the hyperfine contact interaction constant in gauss for proton i in the triplet form, and γ_e and γ_H are the gyromagnetic ratios of the electron and proton, respectively. Measurement of μ_{eff} and Δf_i at a given temperature determines a_i . Measurement at other temperatures allows an evaluation of ΔF as a function of temperature. This procedure is practical only for cases in which the equilibrium is measurably displaced with temperature, *i.e.*, for complexes **3** and **4**. The results obtained by using the large shifts Δf_{8H} are plotted in Fig. 6, in which the linearity required by

$$\Delta F = \Delta H - T\Delta S \quad (3)$$

is obeyed over significantly wider temperature ranges than those for the analogous salicylaldimine complexes. Deviations from linearity have been attributed to the onset of equilibrium A.¹ Thus, for **3** and **4** there is no appreciable molecular association at -20 and 20° , respectively. In view of these results and previous molecular weight studies,³ the measured moments and contact shifts of the $R = t\text{-C}_4\text{H}_9$ complexes at 25° are ascribed entirely to the tetrahedral form. Contact shifts and spin densities calculated from them using the relation²²

(24) $\Delta f = f_{\text{obsd}} - f_{\text{lib}}$ where f_{lib} refers to the free ligand or zinc complex. All frequencies were measured relative to tetramethylsilane as an internal standard. The proton resonance spectra of related hydroxynaphthaldimines²⁵ and the parent naphthaldehydes²⁶ have been reported and discussed previously. Our partial assignment of the aromatic protons in the free ligands follows Dudek.²⁶ In cases where a complex resonance pattern was observed, the center of gravity of the band was taken as the reference frequency for the protons involved.

(25) G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 3914 (1961); G. O. Dudek, *ibid.*, **85**, 694 (1963).

(26) G. O. Dudek, *Spectrochim. Acta*, **19**, 691 (1963).

$$a_i = Q_{\text{CH}}\rho_i \quad (4)$$

are given in Table II for four representative complexes.

Certain of the proton resonance results deserve comment. Comparison of Fig. 3, 4, and 5 and reference to Table II demonstrates that the qualitative predictions of the valence bond model concerning the signs of the contact shifts and spin densities in the three isomeric groups of complexes are fulfilled. Previously, it has been demonstrated that the signs of the spin densities in simple α - and β -naphthyl groups agree with valence bond predictions.^{10,20} While the signs of the spin densities in the naphthaldimine complexes and appropriate naphthyl groups are the same at equivalent positions, the magnitudes of the spin densities are largely different. This is not unexpected in view of the perturbing effects of the chelate ring and the proximity of the metal in the naphthaldimine complexes. In **7** 1-H and in **3** 4-H exhibit large contact shifts relative to other protons in the same molecule (*e.g.*, compare with **2**). This situation is consistent with the valence bond model, for in both cases two contributing structures can be written placing an odd electron at 1-C or 4-C, respectively, whereas only one structure can be written placing the odd electron at

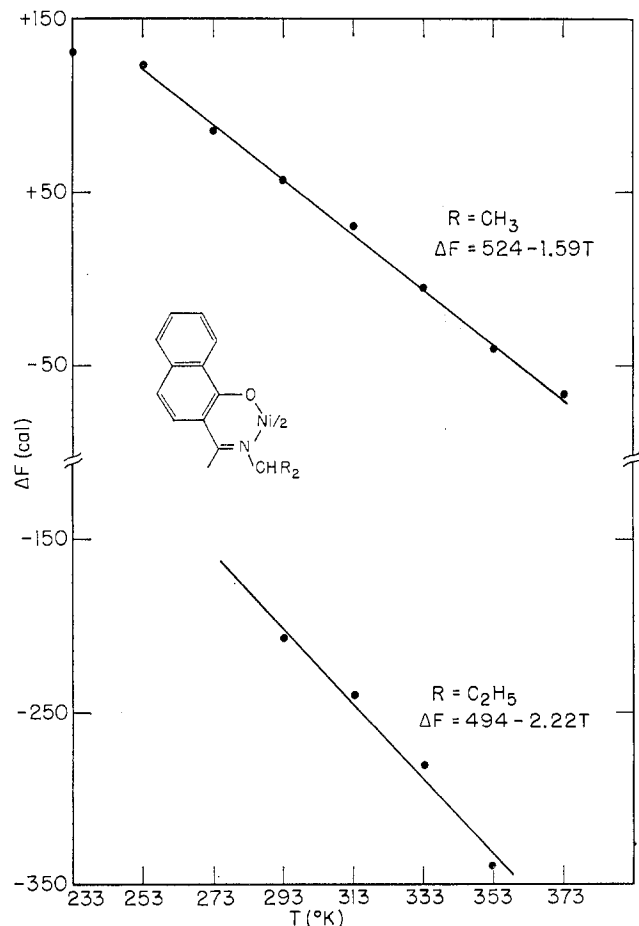


Fig. 6.—Temperature dependences of the free energy changes for the planar \rightarrow tetrahedral interconversion of bis(*N*-isopropyl- and -3-pentyl-1-hydroxy-2-naphthaldimine)nickel(II) complexes in CDCl_3 . The equations shown result from a least mean squares fit.

any other position. In **2** no such double-weighted structures can be written. Lastly, in **3**, **4**, and **7** the proton adjacent to the carbon bonded to the imino group shows very small contact shifts. This effect was encountered in the salicylaldimine complexes when theoretical and experimental spin densities were compared.¹ We are unable to explain this effect.

The proton resonance spectra of naphthalene and substituted naphthalenes are in general quite complex because the chemical shift differences δ_{ij} between two protons are of the same magnitude as the nuclear spin-spin coupling constants J_{ij} . Due to the spectral complexity the coupling constants are not readily obtainable. As Fig. 2 clearly shows, the presence of a small amount of spin density on the ligand reduces the spectra to first-order simplicity. Utilizing measurements of **1** and **2** such that $\delta_{ij}/J_{ij} > 10$ the coupling constants can be determined directly from the spectra. We have determined the following coupling constants (± 0.2 c.p.s.) in the 2-hydroxy-1-naphthaldimines:

$J_{34} = 9.0$, $J_{56} = 7.9$, $J_{67} = 6.8$, and $J_{78} = 8.3$ c.p.s. From a study of the free ligand J_{34} has been found to be 9.1 ± 0.2 c.p.s. The remaining results compare very favorably with those obtained for the β -naphthyl group by a similar procedure²¹: $J_{56} = 8.2$, $J_{67} = 6.5$, $J_{78} = 8.1 \pm 0.2$ c.p.s. Both sets of values are in close agreement with the J_{ij} determined from the most recent analysis of the naphthalene spectrum.²⁷ If the correlation²¹ between bond length and *cis* spin-spin coupling constants is meaningful, the C₃-C₄ bond should be ~ 0.01 Å. shorter than the C₅-C₆ and C₇-C₈ bonds and ~ 0.02 Å. shorter than the C₆-C₇ bond in **1**.

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Complexes of the Rare Earths. VII. 2-Picolyliminodiacetic Acid and 6-Methyl-2-picolyliminodiacetic Acid¹

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The solution stabilities of the rare earth chelates of 2-picolyliminodiacetic and 6-methyl-2-picolyliminodiacetic acids have been measured at 25° and $\mu = 0.1$ (KNO₃). The former ligand apparently functions as a quadridentate ligand in both the 1:1 and 2:1 complexes, whereas the 6-methyl group apparently hinders the coordination of the pyridine nitrogen in the second ligand. The affinity of the rare earth ion for the heterocyclic nitrogen atom appears to be approximately the same as for the hydroxyl group in the analogous compound N-hydroxyethyliminodiacetic acid.

It has been observed quite generally that the rare earth ions form complexes predominantly with molecules which utilize oxygen as the donor atom.² In fact, the solution stabilities of rare earth complexes of organic ligands have been measured only for those ligands in which at least one oxygen atom acts as a donor atom.³ Although this is the case, most workers are of the opinion that in molecules such as the aminopolycarboxylic acids in which the geometry requires the close proximity of the aliphatic nitrogen atoms to the rare earth ion, there is some interaction between the nitrogen atom and the rare earth. In a recent publication Grenthe and Fernelius⁴ suggest that such may not be the case and, furthermore, that the heterocyclic nitrogen atom in the rare earth complexes of

dipicolinic acid is consequently not coordinated. This then leads to the conclusion that in the 3:1 dipicolinic acid-rare earth chelates the coordination number is six.

Our earlier studies have led us to believe that the coordinating tendencies of the rare earths are somewhat broader than have been thought previously and we considered it worthwhile to investigate this problem in more detail. In particular, it was of interest to study the interaction between the pyridine ring and the rare earth ions.

In order to carry out this objective it was necessary to synthesize a compound in which the pyridine ring is suitably located so that the nitrogen atom could reasonably be expected to bond to the metal ion. The recent publication by Irving and da Silva⁵ prompted us to use the iminodiacetate residue as the basic chelating structure and we report herein on the solution stabilities of the rare earth complexes of 2-picolyl-

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