

The results of the equilibrium studies are in agreement with the structures assigned the isomers. The free energy change of -0.51 kcal. is much less than the -1.6 kcal. observed for an axial-to-equatorial interconversion of a methyl group on a cyclohexane,¹⁵ but the lower free energy difference observed in this study is in part a result of the lower non-bonded interaction resulting from the somewhat longer B-N bond distance (expected to be about 1.60 Å. as in similar compounds).⁴ The slow rate of methyl group interconversion in the

(15) C. W. Beckett, K. S. Pitzer and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 2488 (1947).

presence of rapid N-H exchange indicates that the energy barrier to interconversion is fairly large even though the energy difference between an axial and an equatorial methyl group is small.

The chemistry of both isomers of 1,3,5-trimethylcycloborazane is being investigated at the present time, and the results will be published in the near future.

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Configurations and Magnetic Properties of the Nickel(II) Aminotroponeimineates

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The magnetic moments, electronic spectra and frequencies of n.m.r. absorption of the bis-nickel(II) chelates of aminotroponeimines are found to depend markedly on temperature, solvent and the structure of the ligand. It is shown that all these chelate characteristics are compatible with an intramolecular diamagnetic \rightleftharpoons paramagnetic equilibrium. The diamagnetic form of these chelates is identified with a square planar configuration about nickel, and the paramagnetic form, with an approximately tetrahedral configuration. Values of ΔG , ΔE and ΔS for the solution equilibria of several of these chelates derived from temperature dependences of n.m.r. contact shifts, magnetic susceptibilities and spectral intensities are presented.

Introduction

The ground electronic state of nickel(II) coordination compounds (singlet, diamagnetic or triplet, paramagnetic) is exceptionally sensitive to geometry and/or strength of the ligand field.¹ While it has been generally accepted that the four-coordinated diamagnetic compounds of nickel(II) have a square planar structure corresponding to an electronic configuration $3d_4s_4p^2$ for the bonding orbitals of the nickel atom, the structures and configurations of the four-coordinated paramagnetic complexes are by no means well established. The earlier theory of Pauling² assigned to these compounds the configuration $4s_4p^3$ corresponding to a structure of tetrahedral symmetry, but more recent applications of ligand field theory¹ suggest that the square planar configuration may be retained in the triplet state. In view of this uncertainty, nickel(II) complexes in which the diamagnetic and paramagnetic forms (or states) are of sufficiently similar energies to permit thermal population of both are of particular interest.

Several examples have been reported³⁻⁸ of formally four-coordinated nickel(II) complexes which in solution exhibit temperature dependent magnetic moments in the range $0 < \mu_{\text{eff}} < 3.3$ B.M. The best characterized of these is the nickel(II) bis-acetylacetonate which X-ray studies have shown⁹ to exist as a discrete trimer in the solid. Here, nickel is surrounded by an octahedron of oxygen atoms and $\mu_{\text{eff}} = 3.2$ B.M.¹⁰ This

(1) (a) C. J. Ballhausen and A. D. Liehr, *J. Am. Chem. Soc.*, **81**, 538 (1959); (b) G. Maki, *J. Chem. Phys.*, **28**, 651 (1958); **29**, 162 (1958); **29**, 1129 (1958).

(2) L. Pauling, "The Nature of the Chemical Bond," 2nd edition, Oxford University Press, 1940.

(3) J. B. Willis and D. P. Mellor, *J. Am. Chem. Soc.*, **69**, 1237 (1947).

(4) H. C. Clark and A. L. Odell, *J. Chem. Soc.*, 3431 (1955).

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

(6) J. P. Fackler, Jr., and F. A. Cotton, *ibid.*, **83**, 3775 (1961).

(7) R. H. Holm, "Advances in the Chemistry of Coordination Compounds," edited by S. Kirschner, The Macmillan Co., New York, N. Y., 1961, pp. 341-349.

(8) R. H. Holm, *J. Am. Chem. Soc.*, **83**, 4683 (1961).

(9) G. J. Bullen, R. Mason and P. Pauling, *Nature*, **189**, 291 (1961).

(10) F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **83**, 2818 (1961).

same moment is observed for the acetylacetonate in benzene solution where it has been established that the chelate also is trimeric.¹¹ Nickel(II) chelates of β -diketones containing bulky substituents are found to exhibit in solution temperature dependent magnetic moments which can be understood on the basis of a

monomeric \rightleftharpoons polymeric
(square planar, diamagnetic) (octahedral, paramagnetic)

equilibrium.⁶ Similarly, Holm and co-workers^{7,8} have established the existence of an associative equilibrium for the nickel(II) bis-salicylaldimines which would appear to account for the anomalous magnetic properties of solutions of this class of chelates.

While it is thus clear that the temperature dependent magnetic moments observed in solutions of certain classes of formally four-coordinated nickel(II) chelates can be attributed to associative equilibria, it is by no means certain that such equilibria are universally the cause of such effects.¹² Recently, new classes of four-coordinated non-chelated nickel(II) complexes have been reported which are paramagnetic and for which tetrahedral or approximately tetrahedral structures have been established.¹³⁻¹⁵

In earlier work,¹⁶ we pointed out the existence of a solution equilibrium for bis-nickel(II) aminotropone-

square planar \rightleftharpoons tetrahedral
(diamagnetic) (paramagnetic)

imineates. In this paper, we will present results of the n.m.r., susceptibility and spectral studies of this phenomenon.

(11) D. P. Graddon and E. C. Watton, *Nature*, **190**, 906 (1961).

(12) Here we are classifying together solute-solute interactions such as occur in the β -diketone⁶ and salicylaldimine⁷ nickel(II) chelates, and solvent-solute interactions of the type postulated by Ballhausen and Liehr¹⁸ and Maki.¹⁵

(13) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(14) D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961), and references therein.

(15) M. C. Browning, R. F. B. Davies, D. J. Morgan, L. E. Sutton and L. M. Venanzi, *J. Chem. Soc.*, 4816 (1961), and references therein.

(16) D. R. Eaton, A. D. Josey, W. D. Phillips and R. E. Benson, *Mol. Phys.*, **5**, 407 (1962); D. R. Eaton, A. D. Josey, W. D. Phillips and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962); D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4100 (1962).

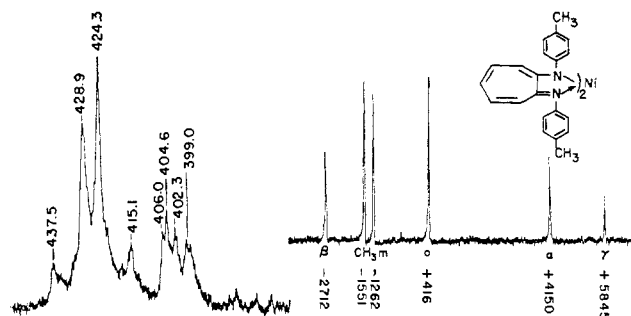
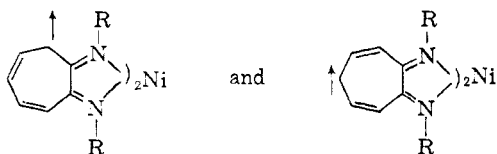


Fig. 1a.— H^1 spectrum of aromatic protons of N,N' -di-(*p*-tolyl)-aminotroponeimine: solvent $CDCl_3$; resonance frequency 60 Mc./sec.

Fig. 1b.— H^1 spectrum of the nickel(II)- N,N' -di-(*p*-tolyl)-aminotroponeimineate: solvent $CDCl_3$; resonance frequency 60 Mc./sec.

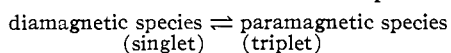
Results

N.m.r. Studies.—Large shifts in the nuclear magnetic resonance (n.m.r.) spectra of the nickel(II) aminotroponeimineates have been attributed^{16,17} to isotropic hyperfine contact interactions. The paramagnetic (triplet) form of a nickel(II) chelate possesses a d^8 configuration containing two unpaired electrons. Suitable overlap of appropriate nickel d-orbitals with nitrogen $p\pi$ -orbitals of the aminotroponeimine ligand results in some delocalization of the unpaired electrons of nickel to the ligand. On the valence bond formulation, this delocalization can be described by structures such as



The presence of unpaired π -electron spin density on the carbon atoms of the seven-membered ring is manifested in the proton magnetic resonance spectrum by large high field (positive spin density) or low field (negative spin density) shifts. Distributions of spin density in a variety of N -substituted nickel(II) aminotroponeimineates have been discussed in earlier publications.^{16,17} For present purposes, it is sufficient to note that the contact shift for a given proton of the chelate depends on the average susceptibility of the nickel aminotroponeimineate and, hence, on the fraction of paramagnetic molecules present.

Observation of hyperfine contact shifts averaged over the diamagnetic and paramagnetic forms of nickel in these chelates demands fulfillment of two conditions: (1) equilibrium between singlet and triplet species must be established in a time which is shorter than the reciprocal of contact shifts (in c.p.s.) and (2) the electron relaxation and/or exchange time must also be small compared to the reciprocal of this shift. Both these conditions appear to be satisfied for nickel(II) aminotroponeimineates in solution. For the equilibrium



we have

$$-RT \ln K = \Delta G = \Delta E - T\Delta S \quad (1)$$

where K is the equilibrium constant. The contact shift of the i^{th} hydrogen atom then will be given by

$$\frac{\Delta H_i}{H} = \frac{\Delta f_i}{f} = -a_i \frac{\gamma_e}{\gamma_H} \frac{g\beta S(S+1)}{2SkT} \left(3 + \exp \frac{\Delta G}{RT} \right)^{-1} \quad (2)$$

(17) W. D. Phillips and R. E. Benson, *J. Chem. Phys.*, **33**, 607 (1960); R. E. Benson, D. R. Eaton, A. D. Josey and W. D. Phillips, *J. Am. Chem. Soc.*, **83**, 3714 (1961).

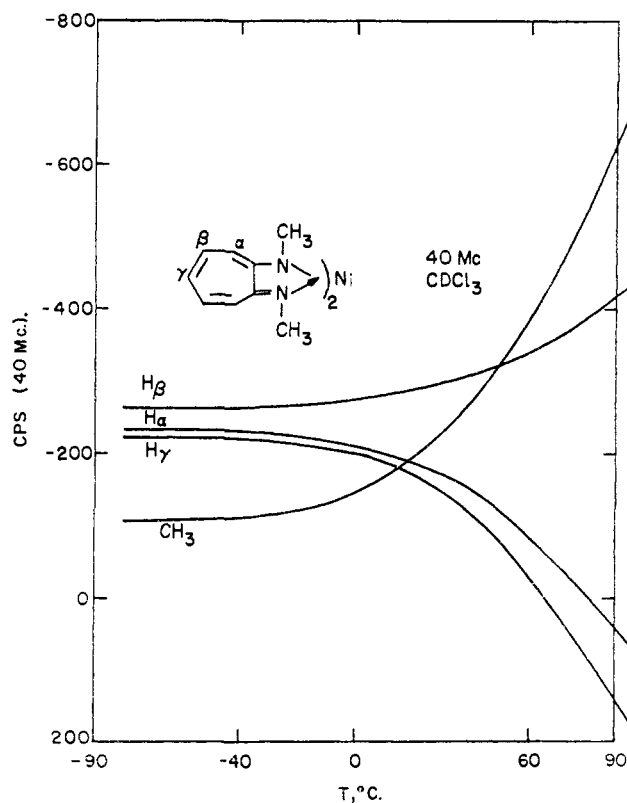


Fig. 2.—Temperature dependences of contact shifts of nickel(II)- N,N' -dimethylaminotroponeimineate: internal reference $(CH_3)_4Si$.

In this equation, H is the resonance field and f the resonance frequency of the n.m.r. experiment, a_i is the hyperfine coupling constant for the i^{th} proton, γ_e and γ_H are the magnetogyric ratios of the electron and proton, respectively, g is the spectroscopic splitting factor for the system and β is the Bohr magneton. The other symbols have their usual significance. Contact shifts were measured relative to the ligand or to the diamagnetic zinc chelate. Chemical shifts for a ligand and its corresponding zinc chelate proved to be almost identical so choice of reference was largely a matter of convenience.

Proton contact shifts of up to 5000 c.p.s. at 40 Mc./sec. have been observed for the nickel(II) aminotroponeimineates. The spectra of a typical ligand and its corresponding nickel chelate are shown in Fig. 1. For all nickel(II) aminotroponeimineates, the equilibrium shifts toward the paramagnetic form with increasing temperatures. Measurements were made over the temperature range 200–350°K. and in several instances the chelates were sufficiently paramagnetic to allow contact constants to be obtained by extrapolation to $T = \infty$. ΔG can then be obtained as a function of temperature from eq. 2. For the more diamagnetic chelates a linear relationship between ΔG and T was assumed and the experimental data were fitted to eq. 2 to give the parameters a_i and ΔG . In all cases where a_i and ΔG were determined independently, the linear relationship between ΔG and T demanded by eq. 1 was found. Very little variation was found for the coupling constants a_i of H_α , H_β , and H_γ among the various chelates. This invariance of spin density on the seven-membered ring to variations in ligand structure indicates that the extent and nature of the nickel–nitrogen π -bonding remains fairly constant throughout this series of N -substituted nickel(II) aminotroponeimineates.

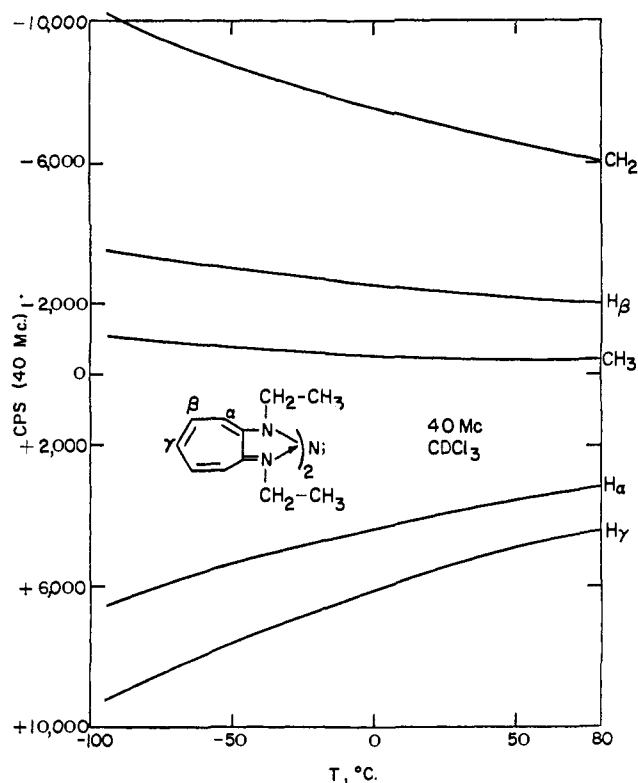


Fig. 3.—Temperature dependences of contact shifts of nickel(II)-*N,N'*-diethylaminotroponeimineate: internal reference $(\text{CH}_3)_4\text{Si}$.

If the above arguments are correct, the proton resonances of a chelate which is only slightly paramagnetic at room temperature should approach those of the ligand or zinc chelate at low temperatures. Such an example is provided by the *N,N'*-dimethyl chelate, the proton resonances of which are plotted against temperature in Fig. 2. The asymptotic approach to the ligand spectrum at low temperatures is clearly seen. Analysis of the temperature dependences of the proton resonances of the *N,N'*-dimethyl chelate in terms of eq. 2 yields a value of 2960 cal./mole for the 23° free energy difference between the two magnetic forms of the chelate. Since the diamagnetic (singlet) form is the more thermodynamically favored over the accessible temperature range, this value of ΔG_{23}^0 corresponds to equilibrium in which at 23° only 0.5% of the molecules are in the paramagnetic (triplet) form.

The paramagnetic (triplet) form of the *N,N'*-diethyl chelate is, on the other hand, much lower in energy than the diamagnetic form over the accessible temperature range, and the contact shifts consequently exhibit a temperature dependence closely proportional to $1/T$ (Fig. 3). A temperature dependence similar to that of the *N,N'*-diethyl chelate is exhibited by the *N,N'*-di(*n*-propyl) chelate. Free energy differences between the paramagnetic and diamagnetic species of the *N,N'*-diaryl nickel(II) aminotroponeimineates generally are smaller than for the *N,N'*-dialkyl chelates and the contact shifts have temperature dependences such as shown in Fig. 4. At low temperatures where the diamagnetic form of an *N*-aryl chelate is favored, proton contact shifts approach the chemical shifts of the ligand or zinc chelate; at higher temperatures, contact shifts approach a $1/T$ temperature dependence signifying that the equilibrium has shifted almost entirely to the paramagnetic form of the chelate.

Values of the parameters ΔE and ΔS obtained from analysis of the temperature dependences of the contact shifts of the β -hydrogen (H_β) of the seven-membered

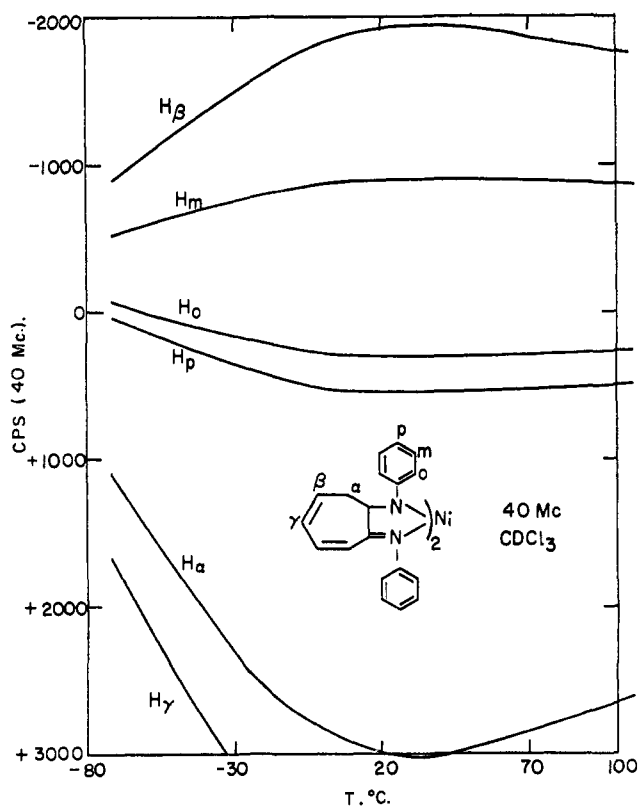


Fig. 4.—Temperature dependences of contact shifts of nickel(II)-*N,N'*-diphenylaminotroponeimineate: internal reference $(\text{CH}_3)_4\text{Si}$.

ring are presented in Table I where results for twenty-eight nickel(II) aminotroponeimineates are given. The H_β resonance was chosen for the temperature studies since this proton is present in all the compounds examined and it is sufficiently far removed from the nickel atom to make unlikely complications arising from possible pseudocontact interactions. It is apparent from eq. 2 that the ratios $\Delta f_i/\Delta f_j$, where i and j are different protons, should be independent of temperature. In Table II, temperature dependences of contact shifts for the eight non-equivalent sets of protons of the *N,N'*-di(*p*-phenylazophenyl) derivative and their ratios relative to the H_β shift (at the same temperature) are shown. It is seen that there is a variation in these ratios of up to 5–6% over the temperature range considered; the thermodynamic results given in Table I must, therefore, be regarded as uncertain in absolute value to this extent. Results for the *N,N'*-di(*p*-tolyl) chelate (based on the contact shifts of the CH_3 resonance) in sixteen different solvents are tabulated in Table III. A number of other nickel(II) aminotroponeimineates have been studied in different solvents and in general their behaviors with respect to solvent dependences of magnetic properties parallel that of the *N,N'*-di(*p*-tolyl) derivative very closely.

Susceptibility Studies.—The susceptibility of a system in which there exists an equilibrium between diamagnetic (singlet) and paramagnetic (triplet) species will be given by

$$\chi_m = \frac{2g^2N\beta^2}{3kT} \left(1 + \frac{1}{3} \exp \frac{\Delta G}{RT} \right)^{-1} \quad (3)$$

From this it follows that

$$\Delta G = RT \ln \left[3 \left(\frac{\mu_{\text{eff}}^2}{\mu^2} - 1 \right) \right] \quad (4)$$

where μ_{eff} is the measured magnetic moment at temperature T and μ is the moment of the fully para-

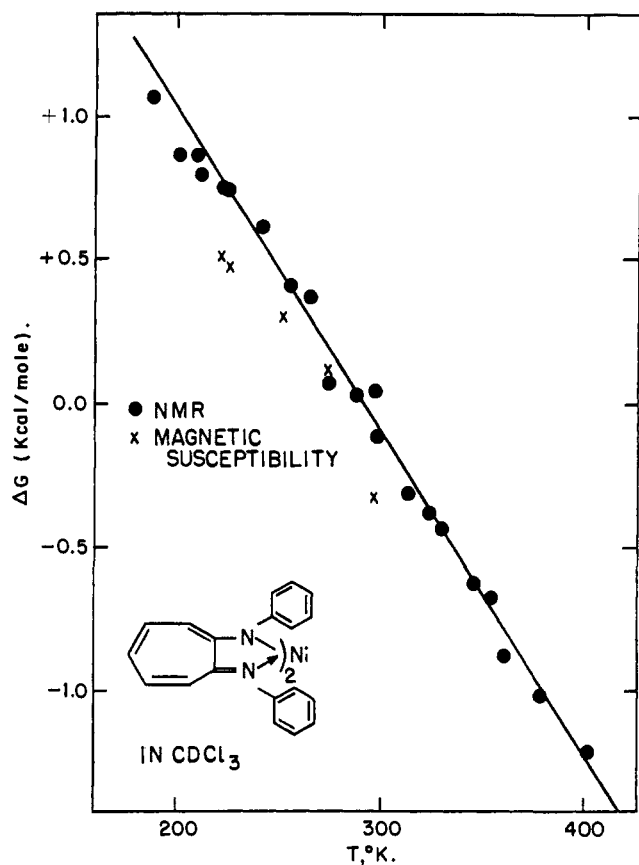


Fig. 5.—Temperature variation of the free energy of the diamagnetic \rightleftharpoons paramagnetic equilibrium in nickel(II)-N,N'-diphenylaminotroponimineate.





















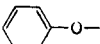
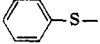
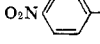
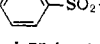
magnetic species. The magnetic moments of a number of the more paramagnetic nickel(II) aminotroponimineates all approach 3.3 B.M. at high temperatures and this value was therefore taken for μ_{∞} . This value for μ_{∞} is fairly typical for octahedral nickel(II) chelates¹⁸ and close to magnetic moments found recently for some approximately tetrahedral nickel chelates.¹⁹ Values of ΔG obtained from eq. 4 are plotted against temperature in Fig. 5. This figure also contains results obtained by the n.m.r. method. The agreement between the two sets of data is seen to be satisfactory. Susceptibility data for the N,N'-di-(*p*-tolyl) chelate are given in Table IV.

Electronic Spectra.—The aminotroponimine ligands are intensely colored and nickel(II) aminotroponimineates exhibit ligand and charge-transfer bands extending up to 6500 Å. However, a band appears in the spectrum of the N,N'-dimethyl chelate at 7900 Å. ($\epsilon = 600$) which is absent in the ligand and zinc chelate. Since this chelate is 99.5% in the diamagnetic form at 23°, this band is attributed to a singlet-singlet transition centered on nickel. The 7900 Å. band is missing in the spectrum of the N,N'-diethyl chelate (~100% paramagnetic) but instead bands appear at 11,400 Å. ($\epsilon \approx 150$) and 13,250 Å. ($\epsilon \approx 85$) which are assigned to triplet-triplet electronic transitions centered on nickel.

The above assignment is borne out in the electronic spectrum of the N,N'-dibenzyl nickel(II) aminotroponimineate. From the thermodynamic quantities listed in Table I, it can be calculated that an equilibrium composition for this chelate in CDCl_3 at 23° is 17% of the diamagnetic species and 83% of the paramagnetic

(18) B. N. Figgis and J. Lewis, "Modern Coördination Chemistry," edited by J. Lewis and R. G. Wilkins, Interscience Publishers, Inc., 1960, p. 407.

TABLE I
SINGLET-TRIPLET EQUILIBRIUM OF NICKEL(II) AMINOTROPONE-
IMINEATES IN CDCl_3 SOLUTION

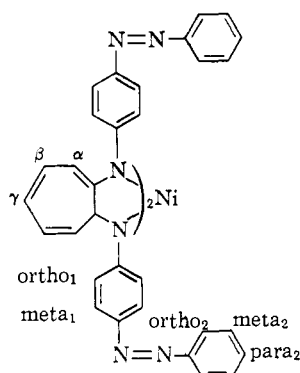
	X ^b	R ^b	ΔE , kcal./mole	ΔS , e.u.
1	H	CH ₃	6.16	10.3
2	H	C ₂ H ₅	1.25	9.1
3	H	C ₃ H ₇	1.22	9.9
4	H	CH ₂ CH=CH ₂	3.02	13.1
5	H	-CH ₂ - 	4.68	16.8
6	H		3.08	10.3
7	H		4.51	12.7
8	H		2.92	10.0
9	H		3.20	10.2
10	H		3.56	9.6
11	H		4.92	13.3
12	H		3.90	10.3
13	H		4.01	11.8
14	H		4.10	13.0
15	H		4.18	13.5
16	H		4.21	11.9
17	H		2.66	9.8
18	H		3.75	10.6
19 ^a	H		3.24	9.3
20	H		4.07	11.4
21	H		4.54	11.4
22	Br		4.49	11.6
23	Br		3.44	10.1
24	Br		4.48	10.8
25		C ₂ H ₅	1.14	8.2
26		C ₂ H ₅	1.99	9.6
27		C ₂ H ₅	1.63	9.2
28		C ₂ H ₅	1.92	9.8

^a In CS₂. ^b X is the substituent at the γ -position and R is the substituent on N.

species. An 8000 Å. band is attributed to a singlet-singlet transition of a diamagnetic species and 12,000 Å. bands are assigned to triplet-triplet transitions of a paramagnetic species.

This identification is confirmed by the temperature dependence exhibited by the component bands of the spectrum. With decreasing temperature, the intensity

TABLE II
N.M.R. DATA ON NICKEL(II) N,N'-DIAZOBENZENE AMINOTROPONEIMINEATE IN CDCl₃



40 Mc./sec. referenced to corresponding ligand

Temp., °C.	Δf_{HB} , c.p.s.	Δf_{meta_1} , c.p.s.	Δf_{meta_2} , c.p.s.	Δf_{ortho_1} , c.p.s.	Δf_{ortho_2} , c.p.s.	Δf_{para_2} , c.p.s.	Δf_{ortho_1} , c.p.s.	Δf_{HD} , c.p.s.	$\Delta f_{H\gamma}$, c.p.s.
23	-1718	-776	-80	+64	+108	+631	+631	+3313	+4646
10	-1742	-785	-76	+62	+105	+637	+637	+3343	+4701
-5	-1732	-783	-80	+67	+107	+631	+631	+3343	+4704
-20	-1657	-762	-80	+65	+107	+608	+608	+3279	+4625
-35	-1556	-716	-67	+66	+107	+552	+552	+3031	+4306
-50	-1424	-652	-67	+50	+89	+501	+501	+2798	+4009
-65	-1201	...	-56	+38	+81	+417	+417	+2384	+3362
	$\frac{\Delta f}{\Delta f_{HB}}$	$\frac{\Delta f}{\Delta f_{HB}}$	$\frac{\Delta f}{\Delta f_{HB}}$	$\frac{\Delta f}{\Delta f_{HB}}$	$\frac{\Delta f}{\Delta f_{HB}}$	$\frac{\Delta f}{\Delta f_{HB}}$	$\frac{\Delta f}{\Delta f_{HB}}$	$\frac{\Delta f}{\Delta f_{HB}}$	$\frac{\Delta f}{\Delta f_{HB}}$
23	1.000	0.452	0.047	0.037	0.063	0.367	0.367	1.928	2.704
10	1.000	.451	.044	.036	.060	.366	.366	1.919	2.699
-5	1.000	.452	.046	.039	.062	.364	.364	1.930	2.716
-20	1.000	.460	.048	.039	.065	.367	.367	1.979	2.791
-35	1.000	.460	.043	.042	.069	.355	.355	1.948	2.767
-50	1.000	.457	.047	.035	.063	.352	.352	1.965	2.815
-65	1.000		.047	.032	.067	.347	.347	1.985	2.799

TABLE III

SINGLET-TRIPLET EQUILIBRIUM OF NICKEL-N,N'-DI-(*p*-TOLYL)-AMINOTROPONEIMINEATE IN DIFFERENT SOLVENTS

Solvent	ΔE , kcal./mole	ΔS , e.u.
Cyclohexane	3.77	11.4
Cyclohexene	3.67	11.4
1,4-Cyclohexadiene	3.46	11.1
CCl ₂ F ₂	3.39	10.7
Cyclohexyl chloride	3.31	10.5
1,3-Cyclohexadiene	3.30	10.4
Carbon tetrachloride	3.28	10.9
Toluene	3.16	10.3
Diethylamine	3.15	10.3
Chloroform	3.06	10.4
Chlorotoluene	2.96	9.7
Cyclohexylamine	2.96	9.0
Anisole	2.95	9.8
<i>cis</i> -Dichloroethylene	2.92	9.4
CCl ₂ FCCl ₂ F	2.91	8.7
Benzene	2.89	9.0
<i>p</i> -Xylene	2.78	8.4
<i>o</i> -Bromotoluene	2.73	8.4
1-Chlorobutane	2.65	8.4
Pyridine	2.64	9.3
<i>m</i> -Xylene	2.62	8.1
Cyclohexanone	2.61	8.9
1-Bromobutane	2.60	8.2
Mesitylene	2.56	7.9
Methylene chloride	2.55	9.2
Methylene bromide	2.46	9.2
<i>o</i> -Xylene	2.39	7.4
Carbon disulfide	2.34	8.8
Methyl iodide	2.05	8.3

TABLE IV

TEMPERATURE DEPENDENCE OF THE MAGNETIC MOMENT OF NICKEL(II)-N,N'-DI-(*p*-TOLYL)-AMINOTROPONEIMINEATE (IN CHCl₃)

Temp., °C.	μ , B.M.	Temp., °C.	μ , B.M.
70	3.17	-5	2.81
55	3.11	-20	2.61
40	3.07	-35	2.47
24	3.05	-50	2.27
10	2.95	-65	2.00

of the 8000 Å. band increases and that of the 12,000 Å. bands decrease, consistent with the above analysis and the previously discussed reduction of magnetic moment of the chelate with temperature decrease. The extinction coefficients for bands arising from either 100% triplet molecules or 100% singlet molecules can, therefore, be obtained with fair accuracy by extrapolation to high temperature or to low temperature, respectively. The fractions of singlet (N_S) and triplet (N_T) molecules at any temperature are then determined readily from measured optical densities at that temperature. It is then shown easily that

$$\Delta G = RT \ln 3 \left(\frac{1}{N_T} - 1 \right)$$

or

$$\Delta G = RT \ln 1/3 \left(\frac{1}{N_S} - 1 \right) \quad (5)$$

The difficulty encountered in measuring extinction coefficients limits the accuracy of this method, but, as shown in Fig. 6, agreement between the values of ΔG obtained at different temperatures from optical measure-

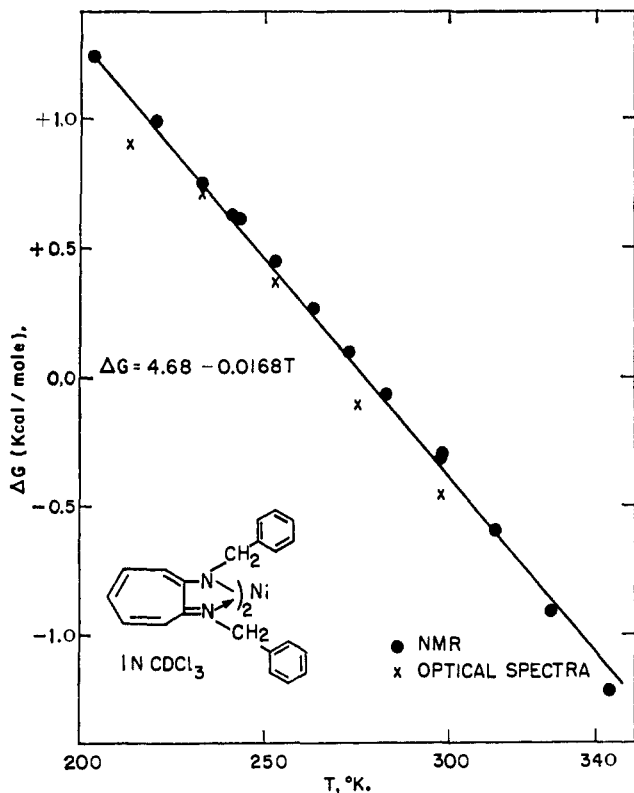


Fig. 6.—Temperature variation of the free energy of the diamagnetic \rightleftharpoons paramagnetic equilibrium in nickel(II)-N,N'-di-benzylaminotroponeimineate.

ments and those obtained from contact shifts is quite satisfactory.

Configurations of the Nickel(II) Aminotroponeimineates.—It is considered that the above experimental results on the nickel(II) aminotroponeimineates indicate that for this class of chelates there is an equilibrium between two magnetic species in solution. On the basis of arguments to be presented below, it is concluded that in one of these forms the nickel atom has a square planar configuration and the molecule is diamagnetic (ground singlet). In the other form the nickel atom has a tetrahedral (or approximately tetrahedral) configuration and the molecule is paramagnetic (ground triplet). Interconversion of these forms occurs by means of a torsional motion. The rate of interconversion is such that in the n.m.r. experiment only a single resonance averaged over the two forms is observed (lifetime less than $\sim 10^{-4}$ sec.) but absorption from both species can be observed in the electronic spectra at 8000 and 12,000 Å (lifetime greater than $\sim 10^{-13}$ sec.). These conclusions are based on the following considerations.

1. Molecular Weight Determinations.—Molecular weight determinations (by freezing point depression) made on several of these chelates have given values corresponding to the monomer to within $\pm 5\%$. It would thus seem that any chelate-chelate association can be ruled out. This conclusion is supported by the observation that there is no dependence of n.m.r. contact shifts on dilution through a range of concentrations exceeding a factor of twenty. Holm's work⁷ on the nickel(II) Schiff bases and Fackler and Cotton's¹⁰ on the nickel(II) acetylacetonates indicates that association and paramagnetism run parallel for these chelate systems. For the nickel(II) aminotroponeimineates, the magnetic moments increase with temperature whereas the degree of association, if present, would be expected to decrease. This temperature dependence of

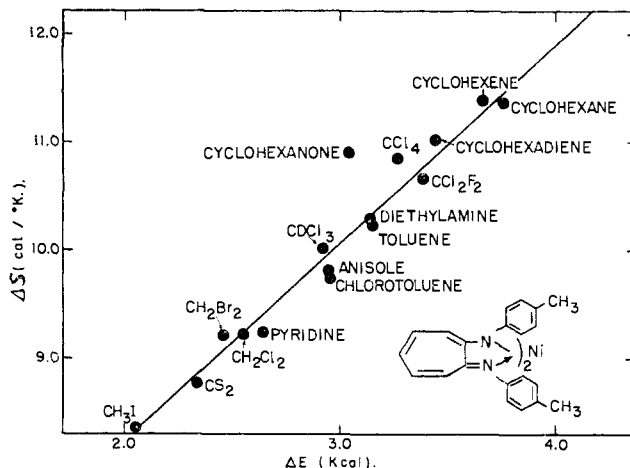
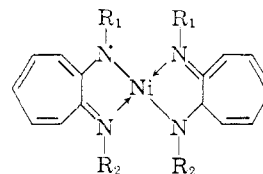


Fig. 7.—Entropies and energies for the diamagnetic \rightleftharpoons paramagnetic equilibrium of nickel(II)-N,N'-di-(p-tolyl)-aminotroponeimineate in various solvents.

the susceptibility in solution is markedly different from that of previously reported nickel chelates and indicates a new type of magnetic behavior.

2. Steric Considerations.—If a model is built of the molecule



it is readily seen that steric difficulties will arise as soon as the groups R_1 and R_2 become bulky, *i.e.*, larger than H atoms or CH_3 groups. The crowding can, however, be relieved by twisting the molecule so that the nickel atom is in an approximately tetrahedral configuration. Steric factors probably are largely responsible for the tetrahedral configuration of nickel chelates with $(C_6H_5)_3P$ ligands.^{19,20} The following qualitative dependences of magnetic properties of the nickel aminotroponeimineates on the sizes of the N-substituents are observed.

Nitrogen substituent	Magnetic character of chelate (at 23° in $CDCl_3$)
$R_1 = R_2 = H$	Diamagnetic
$R_1 = H, R_2 = \text{alkyl}$	Diamagnetic
$R_1 = R_2 = CH_3$	Slightly paramagnetic (<1%)
$R_1 = R_2 = \text{aryl}$	25–75% paramagnetic
$R_1 = R_2 = C_2H_5$ or higher alkyl	Almost completely paramagnetic (>99%)

Models indicate that twisting the N-substituted aryl groups 90° out of the plane of the seven-membered ring provides a reasonable steric configuration for the diamagnetic square planar form. On the other hand, the N-substituents C_2H_5 and larger alkyl groups which lack a plane of symmetry cannot be accommodated in a square planar configuration without distortion. In contrast to N-substitution, however, substitution at the γ position of the seven-membered ring causes only minor changes in the magnetic properties. The above results are, therefore, consistent with a square planar diamagnetic configuration for small N-substituents. As the size of the N-substituent increases, steric repulsion increases and the paramagnetic tetrahedral (D_{2d}) or distorted tetrahedral configuration becomes relatively

(19) F. A. Cotton and R. Francis, *J. Inorg. Nuclear Chem.*, **17**, 62 (1961); F. A. Cotton, O. D. Faut and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **83**, 344 (1961).

(20) L. M. Venanzi, *J. Chem. Soc.*, 719 (1958).

more stable. The observed free energy rather than energy form of the temperature dependence of the magnetic properties of these chelates indicates a thermodynamic equilibrium between two different types of molecules. Temperature dependent populations of the two different electronic states (singlet and triplet) of the same molecular configuration as suggested by Maki^{1b} and Ballhausen and Liehr^{1a} would result in a Boltzmann type of distribution involving only a simple energy term. The presence of the entropy term suggests a configuration or solvation difference between the two magnetic states.

3. Solvent Effects.—The nickel(II) aminotroponeimineates are most soluble (0.1–0.2 molar) in non-polar, non-hydrogen bonding solvents. For a given chelate dissolved in a variety of relatively non-polar solvents, profound effects on the position of the diamagnetic \rightleftharpoons paramagnetic equilibrium are observed. The effect of pyridine on this equilibrium falls between that of CS_2 and CCl_4 . The absence of an anomalous pyridine solvent dependence indicates the absence of direct interaction between the basic pyridine and nickel to form a distorted octahedral complex. The entropy differences between the singlet and triplet forms of the chelates correlate fairly well with the energy differences (Fig. 7). The implication is that these are essentially entropies of solvation with the square planar (singlet, diamagnetic) being more highly solvated than the tetrahedral (triplet, paramagnetic) forms. The entropies are of the right magnitude to arise from this source. This solvation of the square planar form may well be analogous to the microcrystalline ordering of solvent molecules about square planar copper complexes postulated by McConnell²¹ and by Kivelson²² to account for their results on the unequal broadening of the hyperfine components of e.p.r. spectra. Similar e.p.r. line shapes have been observed with copper(II) aminotroponeimineates which are probably planar.²³

There is a rough correlation between the ΔE 's in different solvents and Hildebrand's solvent cohesive energy densities²⁴

$$\delta \equiv (\Delta E^v/V)^{1/2}$$

The smaller diamagnetic-paramagnetic energy differences are associated with the higher solvent cohesive energies (solvents of greater cohesive energy here stabilize the paramagnetic form relative to the diamagnetic form). This effect could arise from competition between solvent-solvent and solvent-solute interactions. These results probably are related to those of McCrae²⁵ as discussed in his analysis of effects of solute-solvent dipole and induced dipole interactions on the frequency of electronic transitions. It appears clear, however, that chemical or coordinate bonding is not involved in the solvation of the nickel(II) aminotroponeimineates.

4. $d\pi$ - $p\pi$ Bonding.—Earlier studies^{16,17} on the nickel(II) aminotroponeimineates established the existence of spin density in the $p\pi$ -system of the ligand. It is most likely that this ligand spin density results from nickel-nitrogen $d\pi$ - $p\pi$ bonding which gives rise to spin transfer from the nickel atom to the π -systems of the ligands. The metal d-orbitals appropriate for π -bonding in a square planar configuration are d_{xz} and d_{yz} . For nickel (d^8) in the square planar configuration, these two orbitals are doubly occupied and π -bonding involving them would not result in spin density transfer from metal to ligand. In the tetrahedral configuration, however, overlap occurs between the $p\pi$ -orbitals cen-

(21) H. M. McConnell, *J. Chem. Phys.*, **25**, 709 (1956).

(22) D. Kivelson, *ibid.*, **33**, 1094 (1960).

(23) Unpublished results.

(24) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed., Reinhold Publishing Co., New York, N. Y., 1950.

(25) E. G. McCrae, *J. Phys. Chem.*, **61**, 562 (1957).

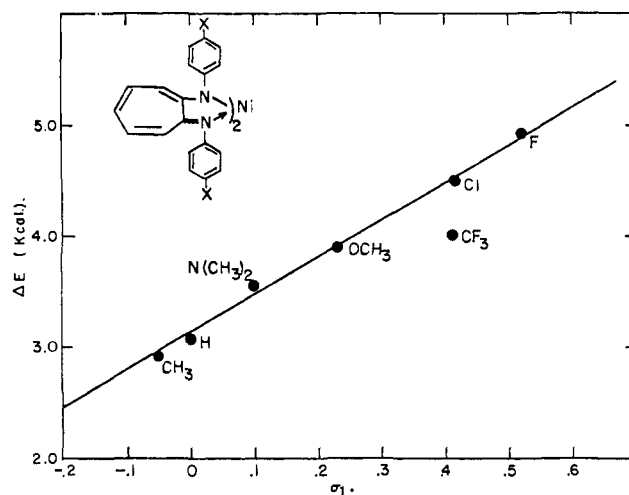


Fig. 8.—Correlation of diamagnetic/paramagnetic energy separation and Taft's σ_1 for some *para* substituted phenyl aminotroponeimineates.

tered on the nitrogen atoms and any of the five d-orbitals of nickel. Thus, π -bonding resulting in transfer of spin density from metal to ligand is expected for a tetrahedral configuration for the nickel(II) aminotroponeimineates, but not for a square planar configuration.

5. Conjugation with the N-Aryl Group.—Even if it is assumed that the square planar configuration is paramagnetic, it is difficult to see how with this geometry appreciable spin densities are placed on the N-aryl substituents. Models show that in the square planar configuration, the planes of the N-aryl groups and the seven-membered rings must be approximately perpendicular. However, comparison between experimental and calculated (valence bond) spin densities shows that there is about the same spin density (0.015 to 0.020) on the nitrogen atom no matter whether nitrogen is considered attached to the seven-membered ring or the N-aryl system. This argues strongly for an approximately coplanar configuration for the seven-membered ring and aryl systems, a condition which could not obtain for a planar configuration of nitrogen about nickel but a probable condition for the tetrahedral arrangement of nitrogen atoms about nickel.

6. Absence of Pseudocontact Interactions and Isotropic g -Values.—There appears to be little if any contribution of pseudocontact interactions²⁶ to the n.m.r. shifts.¹⁶ This implies a rather isotropic g -tensor for nickel in these chelates, a situation to be expected for a paramagnetic tetrahedral configuration but not for a paramagnetic square-planar configuration.

7. Optical Spectra.—The electronic spectra of the diamagnetic N,N' -dimethyl and paramagnetic N,N' -diethyl nickel(II) aminotroponeimineates were discussed briefly in an earlier section. It was shown there that the spectral characteristics for N-substituted nickel(II) aminotroponeimineates which are known from contact shifts or susceptibility studies to be only partially paramagnetic ($0 < \mu_{\text{eff}} < 3.3$ B.M.) are different from the above two. As an additional example of this behavior, the 25° spectrum of the N,N' -ditolyl aminotroponeimineate dissolved in CHCl_3 exhibit its absorption at 8300 ($\epsilon \approx 55$), 11,400 ($\epsilon \approx 115$) and 13,250 Å. ($\epsilon \approx 65$). As the temperature is lowered, the intensity of the 8300 Å. band increases while that of the 13,250 and 11,400 Å. bands decreases. The 8300 Å. band, therefore, is analogous to the 7900 Å., singlet-singlet

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

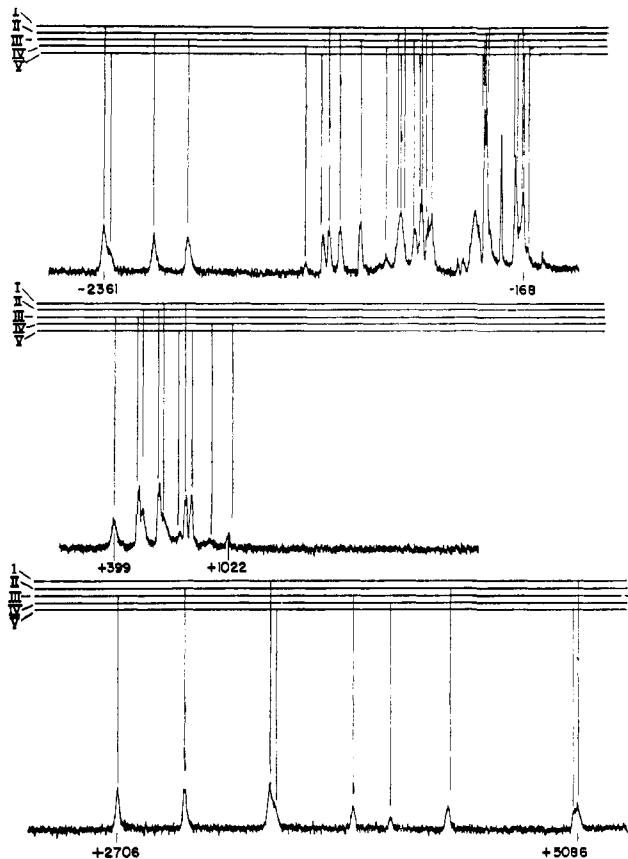


Fig. 9a.— H^1 spectrum of the nickel(II)- N,N' -di-(α -naphthyl)-aminotroponeimineate: solvent $CDCl_3$; resonance frequency 60 Mc./sec.; temperature 23° .

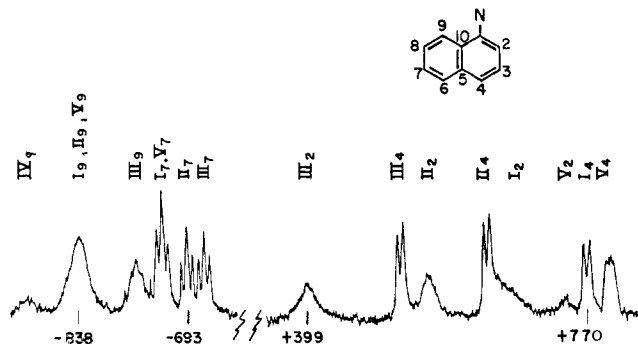


Fig. 9b.—Expansion of central portion of H^1 spectrum of nickel(II)- N,N' -di-(α -naphthyl) aminotroponeimineate.

band observed in the diamagnetic N,N' -dimethyl chelate and the 11,400 and 13,250 Å. bands are the triplet-triplet transitions observed in the paramagnetic N,N' -diethyl chelate. The singlet-singlet and triplet-triplet bands of the N,N' -ditolyl chelate exhibit temperature dependences of intensities which are consistent with observed temperature dependences of contact shifts and susceptibilities and the postulated diamagnetic-paramagnetic equilibrium.

Recently Browning and co-workers¹⁵ have obtained evidence from magnetic susceptibility measurements that a diamagnetic \rightleftharpoons paramagnetic equilibrium exists in benzene solution between two forms of $(n\text{-BuPh}_2\text{P})_2\text{-NiX}_2$, where X is halogen. For this system, the configuration about nickel, at least in the paramagnetic form, is thought to be tetrahedral. Here they too find an absorption band around 6000 Å. which appears to arise principally from the diamagnetic form and a band around 9000 Å. which arises from the paramagnetic form.

Another factor that favors our assignment of the tetrahedral configuration to the paramagnetic form of the nickel(II) aminotroponeimineates is the intensities of the 11,400 ($\epsilon \approx 150$) and 13,250 Å. ($\epsilon \approx 100$) bands. For an octahedral or pseudo-octahedral nickel(II) configuration, triplet-triplet intensities should be of the order of $\epsilon = 2-20$.²⁷ However, our results are consistent with those of Goodgame, Goodgame and Cotton,¹⁴ who noted an increase by a factor of about 10^2 in oscillator strengths of triplet-triplet transitions in tetrahedral nickel(II) complexes over those of the octahedral complexes.

8. Isomerism in the Ni(II) Aminotroponeimineates.—Of the 40-50 nickel(II) aminotroponeimineates so far examined, evidence for isomerism has been found only in one case. The compound in question is the N,N' -di-(α -naphthyl) chelate. The n.m.r. spectrum of this compound is shown in Fig. 9a and the central part of the spectrum is reproduced in expanded form in Fig. 9b. In every other nickel aminotroponeimineate examined there has been a simple one-to-one relation between the number of non-equivalent protons and the number of resonances observed. It is apparent that in the present case there is a considerable excess of resonances. There are ten non-equivalent protons in this molecule, three on the seven-membered ring and seven on the naphthyl group. The observed spectra can be analyzed into five sets, each with the required ten resonances, indicating the presence of five isomers.²⁸ Assignments of resonances to specific hydrogen atoms are based on the direction of the contact shifts (high field or low field) and the observed nuclear spin-spin coupling constants in a manner described more fully elsewhere.¹⁶ Thus the group of lines to extreme low field arises from the β -protons (negative spin densities) and the two groups to extreme high field originate from the α and γ protons (positive spin densities). The central part of the spectrum shown in Fig. 9b is associated with protons of the α -naphthyl groups. Three low field shifts (negative carbon spin densities) and four high field shifts (positive carbon spin densities) are expected from this fragment of the chelate. Of the low field resonances, the five doublets between -1000 and -1250 c.p.s. are assigned to the H_3 position, and the triplets and doublets from -650 to -880 arise from H_7 and H_9 , respectively. On the high field side larger shifts are expected for the positions on the first ring with H_2 giving rise to the series of broad resonances (owing to its proximity to nickel and attendant relaxation effects) and H_4 to the neighboring sharp doublets. H_6 (doublets) and H_8 (triplets) can be disentangled from the close group of lines near the center of the spectrum. The observed frequencies of the lines relative to that of tetramethylsilane, the shifts from the ligand position, the shifts relative to the H_β shifts, and the carbon $p\pi$ spin densities are tabulated in Table V. It may be noted that spin densities at analogous positions on the five isomers are quite similar, indicating that the n.m.r. spectral differences at a given temperature arise mainly from variations of average magnetic moments of electronically similar compounds, in this case stereoisomers. This conclusion is substantiated by examination of the temperature dependence of the spectrum. Figure 10 shows the temperature dependences of the H_β lines. Resonances from the other protons follow this pattern closely. Figure 11 shows the free energy-temperature plots for four of the five isomers. The numerical results are collected in Table V.

(27) W. Manch and W. C. Fernelius, *J. Chem. Educ.*, **38**, 192 (1961).

(28) By five isomers, we mean five distinguishable sets of resonances. Each set of resonances may derive from two or more rapidly interconverting isomers of the α -naphthyl chelate.

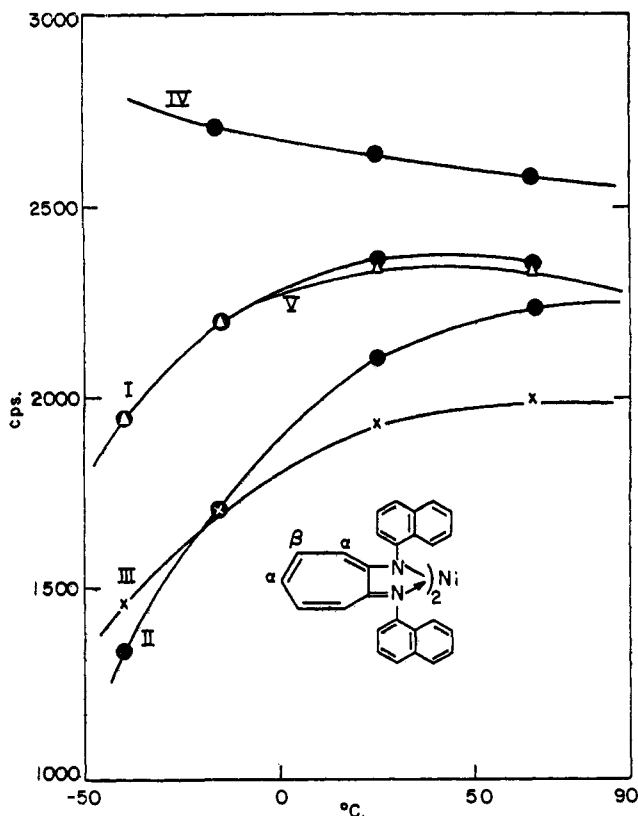


Fig. 10.—Temperature dependences of H_β shifts of the distinguishable isomers of nickel(II) N,N' -di-(α -naphthyl)-aminotroponeimineate: solvent $CDCl_3$; frequency 60 Mc./sec.

Some conclusions can be drawn concerning the rate of isomeric interconversion for the stereoisomers of the α -naphthyl chelate. In an n.m.r. experiment, separate resonances for two non-equivalent nuclei are only observable if there does not exist some chemical or environmental exchange process involving these nuclei with a characteristic frequency exceeding that of the chemical shift between the nuclei. A lower limit on the rate of isomeric interconversion of about 10^2 sec.^{-1} , therefore, is demanded by the observation of separate resonances for the different isomers. If the rate of interconversion among the five isomers²⁸ exceeded about 10^2 sec.^{-1} , only a single, averaged set of ten resonances would be observed. Fast interconversion between two or more but not all five isomers might occur and the spectrum would be modified by reduction in numbers of observed sets of resonances.

TABLE V
SPIN DENSITIES AND DIAMAGNETIC-PARAMAGNETIC PARAMETERS FOR THE NICKEL(II)- N,N' -DI- α -NAPHTHYL)-AMINOTROPONEIMINEATE (IN $CDCl_3$)

	I ^a	II ^a	III ^a	IV ^a	V ^a
ρH_α	+0.0424	+0.0431	+0.0433	+0.0432
ρH_β	-.0210	-.0210	-.0210	-.0210	-.0210
ρH_α	+.0594	+.0601	+.0603	+.0600
ρH_2	+.0120	+.0123	+.0118	+.0129	+.0130
ρH_3	-.00833	-.00869	-.00823	-.00838	-.00874
ρH_4	+.0132	+.0134	+.0135	+.0139	+.0138
ρH_5	+.00065	+.00076	-.00084	-.00084	-.00067
ρH_6	-.00302	-.00300	-.00309	-.00307
ρH_7	+.00275	-.00271	+.00305	+.00267	+.00277
ρH_8	-.00418	-.00481	-.00435	-.00403	-.00424
ΔE , kcal./mole	1.98	2.81	2.01	1.77	~ 2.0
ΔS , e. u.	5.40	7.46	4.46	6.40	

^a Isomeric forms of the chelate; see text.

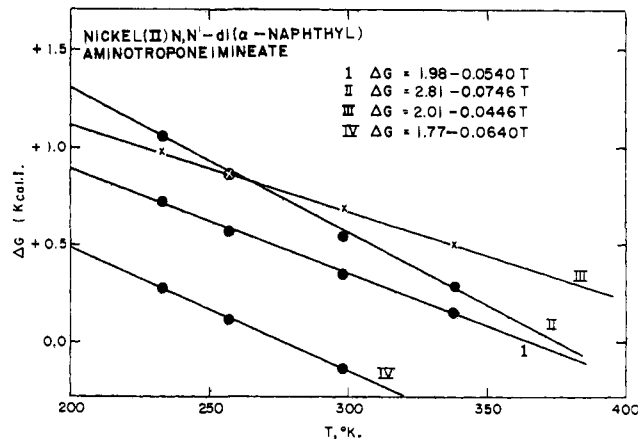
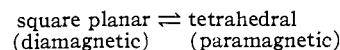


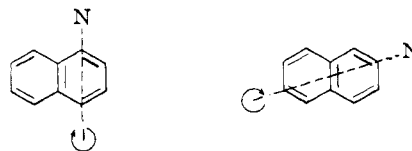
Fig. 11.—Temperature dependences of diamagnetic-paramagnetic free energy differences for four of the five distinguishable isomers of the nickel(II)- N,N' -di-(α -naphthyl)-aminotroponeimineate. Solvent $CDCl_3$.

As discussed earlier, model studies indicate that N -aryl substituted nickel(II) aminotroponeimineates can be accommodated in the square planar configuration only if the planes of the N -aryl groups are oriented approximately perpendicular to that of the seven-membered rings. One would expect then that any unsymmetrical N -aryl substituent (N - m -fluorophenyl, N - m -biphenyl, N -2-phenanthryl, N - β -naphthyl as well as N - α -naphthyl) would exhibit isomers if the paramagnetic state had the square planar configuration. This follows since models show that isomeric interconversion in the square planar configuration by rotation about the $C-N$ bond would be impossible.

The situation, however, is quite different if an equilibrium exists for the nickel(II) aminotroponeimineates.



In the tetrahedral configuration the opportunity for isomeric interconversion *via* rotation about the $C-N$ bond obviously is much greater than for the square planar configuration where rotation about the $C-N$ bond for N -aryl substituents appears to be impossible. However, models again indicate that if the N -substituent is sufficiently asymmetric with respect to rotation about the $C-N$ bond axis, steric interactions could occur even in the tetrahedral configuration which would make isomer interconversion impossible. It is suggested here that such is the case for the N,N' -di-(α -naphthyl) chelate since on rotation about the $C-N$ bond the α -naphthyl group sweeps out a much larger volume than any other N -substituent studied in this series. The α -naphthyl chelate (five isomers observed) may be compared with the β -naphthyl chelate (one isomer observed) where in the latter the $C-N$ bond represents an at least approximate axis of symmetry.



Electronic Effects.—The dominating factors determining the magnetic properties of these chelates appear to be steric in nature. However, it would seem that electronic effects are not entirely absent. This is perhaps most clearly suggested from examination of the energy differences between diamagnetic and paramagnetic forms for a series of *para* substituted N -phenyl nickel(II) aminotroponeimineates. In Fig. 8 these

energy differences are plotted against Taft's inductive parameter σ_I .²⁹ A good correlation is apparent. The original Pauling theory of the stereochemistry of nickel(II) associated the tetrahedral paramagnetic state with ionic bonding and the square planar diamagnetic state with covalent bonding.³ Thus the extreme of ionic bonding leads to a triplet ground state for the Ni^{++} ion. The above $\Delta E/\sigma_I$ correlation is consistent with this picture since the ionic character of the N-Ni bond might reasonably be expected to depend to some extent on the electron withdrawing or releasing powers of the group attached to the nitrogen. The dependence on σ_I suggests that the effect is transmitted through σ -bonds. The greatest negative charge is placed on nitrogen by the *p*-tolyl derivative giving, as a result, the largest contribution from N^- , Ni^+ to the electronic structure, and the least from the *p*-fluorophenyl derivative. A similar trend appears to hold for other substituents, e.g., ΔE for the β -naphthyl derivative (4,070 cal.) is smaller than for the corresponding quinolyl derivative (4,540 cal.).

Too great emphasis should not, of course, be placed on the possible bearing of the $\Delta E/\sigma_I$ correlation on the ionic characters of the Ni-N bonds. It is entirely possible that the correlation simply reflects the dependence of solvation stabilization of one magnetic form over the other on the nature of the *para* substituent of the phenyl ring. Further work will be necessary to distinguish between these two possibilities.

Conclusion.—Several theories have been proposed to account for the existence of both diamagnetic and paramagnetic four-coordinated nickel(II) chelates. The earlier valence bond theory considered the paramagnetic complexes to have sp^3 hybridization, a tetrahedral configuration and to be ionic in character, whereas the diamagnetic complexes were assigned dsp^2 hybridization, a square planar configuration and covalent bonds. In fact the magnetic properties were used as a diagnostic test of bond type. However, the application of ligand field theory by Maki^{1b} and Ballhausen and Liehr^{1a} showed that the square planar configuration about nickel could give rise to either singlet or triplet ground states. It has also been shown that a formally square planar nickel(II) chelate could become paramagnetic by assuming an at least approximately octahedral configuration either by attachment of solvent molecules or by polymerization.

Our interpretation of the present results represents in a sense reversion to the Pauling valence bond picture. Evidence has been produced by a variety of physical approaches which, in the authors opinion, leaves little room for doubt with respect to the principal conclusion of this paper, namely, of the presence of a square

planar-tetrahedral equilibrium in the nickel(II) aminotroponimineates. However, it also appears established that in other nickel(II) chelates the solvation and association mechanisms for achieving paramagnetism are operative. In fact the magnetic properties of nickel(II) coordination compounds in general seem to be determined by a rather delicate balance of steric, electronic, association and solvation factors.

As pointed out by Venanzi²⁰ simple crystal field considerations predict that a square planar configuration will be in general energetically favored over a tetrahedral configuration. This advantage can be overridden by either extreme ionicity as in the tetrahalides or by extreme steric restrictions as in the triphenyl phosphine compounds. When the conditions are less extreme there may be either an equilibrium between square planar and tetrahedral configurations or the molecule may seek to attain the extra exchange energy of a triplet state by assuming an octahedral configuration by solvation or association. The choice among these possibilities would again seem to depend largely on steric considerations. The observation of n.m.r. contact shifts and the synthetic flexibility of the aminotroponimineate system present a particularly favorable situation for studying the case of a square planar-tetrahedral equilibrium. This type of equilibrium is probably by no means unique to these nickel(II) complexes, and the insight obtained by considering the interplay of the different factors in the aminotroponimines should be of general applicability.

Experimental

The general synthesis of the nickel(II) aminotroponimineates has been described elsewhere.³⁰ Magnetic resonance measurements were carried out at 40 and 60 Mc./sec. employing a Varian high resolution n.m.r. spectrometer. The contact shifts were taken as the difference of the frequencies of corresponding lines in the nickel chelate spectra and the ligand (or zinc chelate) spectra. Chelate resonance frequencies were measured relative to tetramethylsilane as an internal standard. Temperature control was achieved by enclosing the sample in a dewar placed between the magnet pole pieces and through which flowed a stream of nitrogen. The nitrogen was cooled by liquid air and then reheated to the desired temperature by means of a small electrical resistance. For temperatures above room temperature the pre-cooling was omitted. Susceptibility measurements were carried out by an n.m.r. method.³¹ The electronic spectra were recorded on a Cary Model 14 spectrophotometer.

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