

n.m.r. spectrum suggests the presence of only one isomer under our experimental conditions. Unfortunately, the correct stereochemistry cannot be ascertained. For Mo(VI)-EDTA, in addition to the possibility of *cis* and *trans* carboxylate bonding at each molybdenum atom, the two molybdenums also can be *cis* and *trans* relative to one another along the Mo-N-CH<sub>2</sub>-CH<sub>2</sub>-N-Mo linkage. Reference to molecular models (Fisher-Taylor-Hirschfelder type) indicates that the conversion between the *cis* and *trans* configurations is highly hindered due to steric factors. Since the four ethylenic protons are equivalent only in the *trans* configuration and only a single sharp resonance is observed for these hydrogens, it is possible to conclude that the isomer under study is that in which the two molybdenums are *trans* with respect to one another. The chemical shifts of the methylenic hydrogens and the  $|J|$  value between each nonequivalent pair of protons are nearly equal for both the EDTA and MIDA chelates, indicating that the bonding at the molybdenum atoms must be the same in both cases. The simplicity of the methylene multiplet also indicates that the carboxylate groups are bonded to the molybdenum atoms at both ends of the chelates either both *cis* or both *trans*.

Only one isomer is possible for Mo(VI)-NTA with the structure depicted in Fig. 2. Here because of a threefold axis of symmetry through the nitrogen and molybdenum atoms of the chelate, all six methylenic protons become equivalent. This is in accord with the n.m.r. data.

The carboxylate groups are concluded to be coordinated rigidly to the metal ion in these chelates. In both the EDTA and MIDA chelates this strong carboxylate bonding would result in pairs of nonequivalent methylenic protons, as observed. If the carboxylate bonds were weak and ligands were rapidly coordinating with and dissociating from the metal ion, the spin multiplet for the methylene protons would collapse into a single averaged resonance, as was observed for all the other EDTA chelates investigated thus far.<sup>2</sup> Although a single resonance is indeed observed for Mo(VI)-NTA, it seems inconceivable that

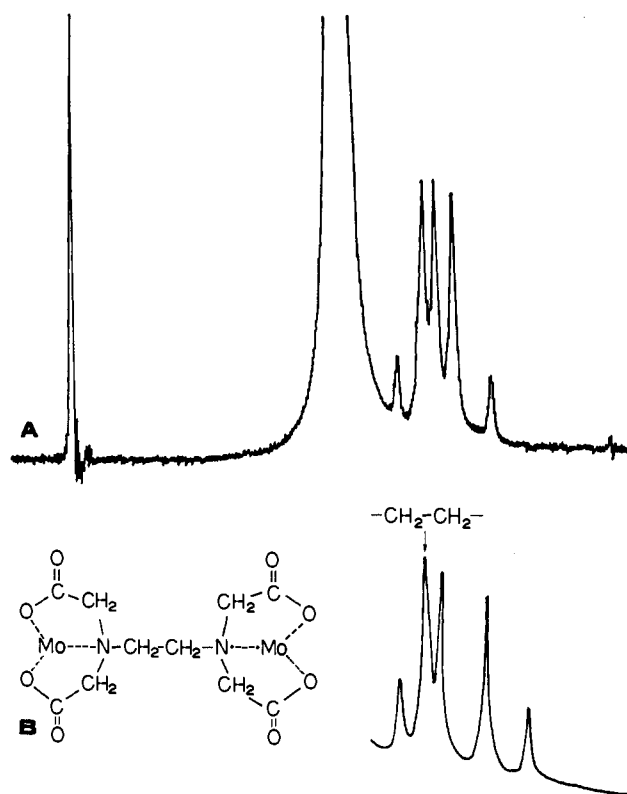


Fig. 4.—A: Spectra of [Mo(VI)]<sub>2</sub>-EDTA at 56.4 Mc. B: Spectra of [Mo(VI)]<sub>2</sub>-EDTA at 100 Mc.

the nature of the coordination should be different for this ligand.

Finally, it is interesting to note that in Mo(VI)-EDTA, the resonance for the ethylenic protons occurs at a lower field than the center of the multiplet for the methylene protons. This is in contrast to all the other EDTA chelates investigated up to now.<sup>2</sup> This result can be understood in terms of deshielding effects arising from the close proximity of the oxygen atoms of the Mo=O bonds to the ethylenic protons.

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## Studies on Nickel(II) Complexes. V.<sup>1</sup> A Nuclear Resonance Study of Conformational Equilibria

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Complexes of the general type bis-(R-N-salicylaldimine)-Ni(II) in which R is a *sec*-alkyl group have previously been shown to exist in a planar  $\rightleftharpoons$  tetrahedral equilibrium in solutions of noncoordinating solvents at and above room temperature.<sup>1</sup> These complexes have now been thoroughly studied by means of proton magnetic resonance and are found to exhibit isotropic proton hyperfine contact shifts. In this respect they are similar to bis-(N,N-disubstituted aminotroponimine)-Ni(II) complexes extensively studied by others.<sup>10</sup> Two sorts of complexes have been examined—those which contain either optically inactive or optically active R groups. For the optically inactive species spin densities on the ligand systems have been evaluated from measurement of contact shifts and magnetic moments. For both the optically inactive and active species analysis of the temperature dependence of the contact shifts has yielded values of  $\Delta F$ ,  $\Delta H$ , and  $\Delta S$  for the solution equilibria. Complexes containing optically active groups consist of diastereoisomeric mixtures when prepared from racemic amines. Each diastereoisomer is shown to possess a separate set of contact shifts. The relation of each such set to a given diastereoisomer is proved and it is shown that the thermodynamic parameters for each isomer can be separately determined. The detection of molecular association in solution is demonstrated from contact shift measurements. Procedures for extensive optical resolution ( $\geq 95\%$ ) of two *sec*-alkylamines are reported.

### Introduction

As a result of investigations of the past several years, there has now emerged a reasonably clear picture of the

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

relation between the magnetic and spectral properties of formally four-coordinate nickel(II) complexes and the immediate coordination environment of the metal ion in these complexes when in solution. Of prime interest have been those complexes which, in solutions of es-

sentially noncoordinating solvents, exhibit magnetic moments intermediate between zero and  $\sim 3$  B.M. Earlier claims, based on the valence bond model, that the paramagnetism arose from the presence of tetrahedral species are almost certainly incorrect in every case considered.<sup>2</sup> It is now well established in these and other cases that the paramagnetism arises from the presence of associated species.<sup>3-5</sup> However, in the absence of important axial interactions, such as apparently are provided by molecular association, four-coordinate nickel(II) complexes may possess a paramagnetic ground state in strictly planar symmetry, and in symmetries which are exactly or approximately tetrahedral.<sup>6-8</sup> There are at present no examples of spin-free planar Ni(II) complexes, but many tetrahedral and pseudo-tetrahedral species have been prepared.<sup>1,9-13</sup>

Recently it has become quite clear that in solution the energy difference between the planar and tetrahedral conformations may be adjusted such that both these conformations are populated at room temperature. Three general groups of Ni(II) complexes have been reported to exist in solution in a conformational equilibrium. The best characterized examples are the bis-(N,N-disubstituted aminotroponimine) complexes, which have been extensively and elegantly studied by Eaton, Phillips, and Caldwell<sup>10</sup> by measurement of proton resonance contact shifts. Complexes of the general type  $[(C_6H_5)_2RP]_2NiX_2$  (X = halide) show similar isomerism in solution,<sup>11,12</sup> and in some cases both stereoisomers of a given complex have been isolated.<sup>12</sup> Finally, earlier work in this series,<sup>1</sup> together with that of others,<sup>13</sup> has demonstrated that bis-(N-sec-alkylsalicylaldehyde)-Ni(II) complexes exist in both the planar and tetrahedral forms in solutions of noncoordinating solvents, and that the proportion of tetrahedral species increases with increasing temperature.<sup>13</sup>

Herein we report the results of a study of proton resonance contact shifts of bis-(N-sec-alkylsalicylaldehyde)-Ni(II) complexes. This study has allowed a determination of spin density distributions on various substituted salicylaldehyde ligands, thermodynamic characterization of the structural interconversion, and has provided a sensitive method for detecting the presence of solute association. In addition, the detection and identification of diastereoisomeric complexes involved in the conformational equilibrium are described. Preliminary results of the study of the diastereoisomers have already appeared.<sup>14</sup>

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## Experimental

**Preparation of Compounds. a. Resolution of Amines.**—2-Aminobutane: The inactive amine was resolved into the (+) and (−) isomers by the method of Thomé<sup>15</sup> as improved by Bruck, *et al.*,<sup>16</sup> using (+)- and (−)-tartaric acid, respectively. The following rotations were obtained:  $[\alpha]^{25}_D + 7.53^\circ$  (lit.<sup>15</sup>  $+ 7.48^\circ$ ),  $-7.50^\circ$  (lit.<sup>16</sup>  $-7.64^\circ$ ).

2-Aminooctane: The (−) isomer was obtained following the procedure of Mann and Porter.<sup>17</sup> The resolved product gave  $[\alpha]^{25}_D - 6.65^\circ$  (lit.<sup>17</sup>  $-6.60^\circ$ ).

1,3-Dimethylbutylamine: This amine was previously resolved by Karrer and Dinkel<sup>18</sup> using the costly dibenzoyl-*d*-tartaric acid as the resolving agent and methanol as the recrystallization medium. They partially resolved the amine, obtaining  $[\alpha]^{19}_D + 4.2^\circ$  (methanol solution). We have more completely resolved the (−)-amine with (+)-tartaric acid: 50 g. of the racemic amine was added to a solution of 84 g. of the tartaric acid in 200 ml. of hot methanol. The resulting solution was left to crystallize overnight. This crop of crystals was then recrystallized nine times from decreasing volumes of methanol (200, 100, 80, 60, 5 × 30 ml.); 20 g. of the *l*-amine-*d*-tartrate then isolated was treated with 30% aqueous sodium hydroxide to liberate the amine, which was extracted with ether. The ether was removed and the fraction boiling at 105–108° collected. This sample gave  $[\alpha]^{25}_D - 10.73^\circ$  ( $d^{25}_D$  0.7416).

2-Amino-3-methylbutane: Partial resolution ( $[\alpha]^{16}_D - 0.84^\circ$ ) has been reported by crystallizing the *d*-tartrate salt from methanol-acetone mixtures.<sup>18</sup> Procedure for a more complete resolution is given here. Starting with 30 g. of inactive amine and 52 g. of (+)-tartaric acid in 200 ml. of methanol, and recrystallizing the product nine times from methanol (200, 200, 150, 80, 5 × 60 ml.), 19 g. of salt was collected. The amine was liberated as above. The first distillate (80–82°) was dried over KOH and redistilled twice, the 82° fractions being collected; 4.6 g. of the amine having  $[\alpha]^{25}_D - 3.45^\circ$  was finally obtained.

In all cases the nickel complexes prepared from the active amines with the specified rotations displayed proton resonances characteristic of the active diastereoisomeric complex only. Therefore, it can be assumed that these amines are  $\geq 95\%$  optically pure.

**b. Substituted salicylaldehydes** were obtained in 20–40% yield by use of the Duff reaction<sup>19</sup> on the appropriate phenols, except for the 5-aryloxy derivative which was obtained by alkaline coupling of salicylaldehyde with diazotized aniline.<sup>20</sup>

**c. Complexes.**—All complexes prepared and characterized in this work are listed in Table I. These were obtained by refluxing a suspension of the appropriate hydrated bis-(salicylaldehyde)-Ni(II) complex with a slight excess of amine in dichloromethane solution for 1 hr. The resulting brown solutions were dried over sodium sulfate, the solvent removed, and the resultant products recrystallized several times from dichloromethane-*n*-hexane or *n*-hexane alone, depending on solubility. All complexes were obtained as green or brown crystalline solids. Analytical data are given in Table I. The several Zn(II) and Pd(II) complexes mentioned in the text were prepared similarly.<sup>21</sup>

**Magnetic Measurements.**—Measurements on solids and solutions were made by the Gouy method as previously described.<sup>14</sup> Solution measurements of solute susceptibilities have a relative accuracy of  $\pm 4\%$  with respect to the calibrant, distilled and degassed water. Sample temperatures were controlled to  $\pm 0.1^\circ$ .

**Spectral Measurements.**—Solution spectra were obtained on a Cary 14 spectrophotometer at temperatures controlled to  $\pm 0.1^\circ$ .

**Proton Resonance Measurements.**—Depending on the magnitude of chemical shifts, spectra were obtained on either a Varian HR-60 or A-60 spectrometer operating at 60 Mc./sec. Spectra at other than room temperature were recorded on the A-60 spectrometer equipped with a variable temperature probe, and were calibrated using an audio oscillator monitored by a frequency counter. The temperature was monitored by measuring the peak separations of methanol and ethylene glycol. Deuterated solvents were supplied by Merck Sharp and Dohme of Canada. Solutions measured were 0.1–0.2 *M* in complex or free ligand and contained  $\sim 4\%$  v./v. of tetramethylsilane as an internal standard.

## Results and Discussion

The complexes which are the subject of this investigation are of the general type I in which R is an optically

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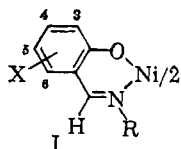
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TABLE I  
 CHARACTERIZATION OF SUBSTITUTED BIS-(SALICYLALDIMINE)-NICKEL(II) COMPLEXES

R	X	M.p., °C.	Calcd., %			Found, %		
			C	H	N	C	H	N
-CH(CH <sub>3</sub> ) <sub>2</sub>	4-CH <sub>3</sub>	218-219	64.26	6.86	6.81	64.07	6.95	6.75
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-CH <sub>3</sub>	205-206	64.26	6.86	6.81	64.49	6.76	6.84
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-C <sub>2</sub> H <sub>5</sub>	138-140	65.63	7.34	6.38	65.58	7.18	6.52
-CH(CH <sub>3</sub> ) <sub>2</sub>	5- <i>n</i> -C <sub>3</sub> H <sub>7</sub>	103-105	66.83	7.77	6.00	67.16	8.02	6.13
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-C <sub>6</sub> H <sub>5</sub>	220-221	71.79	6.03	5.23	71.56	6.16	5.32
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-N <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	214-215	64.99	5.46	14.21	65.19	5.84	13.81
-CH(CH <sub>3</sub> ) <sub>2</sub>	4,5-(CH <sub>3</sub> ) <sub>2</sub>	272-274	65.63	7.34	6.38	65.96	7.58	6.48
-CH(CH <sub>3</sub> ) <sub>2</sub>	4,6-(CH <sub>3</sub> ) <sub>2</sub>	194-195	65.63	7.34	6.38	65.54	7.29	6.45
-CH(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	5-CH <sub>3</sub>	125	66.83	7.77	6.00	67.19	8.01	6.17
-C(CH <sub>3</sub> ) <sub>3</sub>	5-CH <sub>3</sub>	201-202	65.63	7.34	6.38	65.79	7.41	6.78
CH <sub>3</sub> CHCH <sub>2</sub> CH <sub>3</sub>	4-CH <sub>3</sub>	167-168	65.63	7.34	6.38	65.67	7.27	6.39
CH <sub>3</sub> CHCH <sub>2</sub> CH <sub>3</sub>	5-CH <sub>3</sub>	152-153	65.63	7.34	6.38	65.60	7.55	6.47
CH <sub>3</sub> CHCH <sub>2</sub> CH <sub>3</sub>	4,5-(CH <sub>3</sub> ) <sub>2</sub>	228-230	66.83	7.77	6.00	67.00	8.10	5.90
CH <sub>3</sub> CHCH <sub>2</sub> CH <sub>3</sub>	4,6-(CH <sub>3</sub> ) <sub>2</sub>	123-124	66.83	7.77	6.00	66.93	7.89	6.20
CH <sub>3</sub> CH(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	5-CH <sub>3</sub>	123	66.83	7.77	6.00	67.18	7.93	6.03
CH <sub>3</sub> CH(CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	5-CH <sub>3</sub>	122	68.84	8.47	5.35	68.87	8.66	5.40
CH <sub>3</sub> CH(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	5-CH <sub>3</sub>	84-86	69.70	8.77	5.08	69.60	9.06	5.03
CH <sub>3</sub> CHCH(CH <sub>3</sub> ) <sub>2</sub>	5-CH <sub>3</sub>	150-151	66.83	7.77	6.00	67.11	7.82	5.93
CH <sub>3</sub> CHCH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	5-CH <sub>3</sub>	141-142	67.89	8.14	5.66	67.94	8.37	5.37

active or inactive *sec*-alkyl group. Certain of these



complexes have been prepared previously.<sup>1,13</sup> Characterization data for new compounds are presented in Table I. Earlier work<sup>1,13</sup> leaves little doubt that at room temperature and above these complexes exist in a conformational equilibrium in noncoordinating solvents, and that in nearly all cases the planar form is favored at room temperature, with ~60% of the molecules possessing this conformation. Both the planar and tetrahedral forms have been identified in the optical spectra.<sup>1,13</sup> Many of these complexes crystallize in the paramagnetic form. Preliminary X-ray results<sup>22</sup> on the prototype molecule bis-(*N*-isopropylsalicylaldimine)-nickel(II) reveal a gross tetrahedral structure, but with significant distortions from the idealized C<sub>2v</sub> symmetry of the coordination sphere.

**Magnetic Susceptibility Studies.**—Magnetic moments in chloroform solution at 30 and 50° are given in Table II; moments of some of the crystalline solids are listed in Table III. The moments of the solids are seen to be exceedingly sensitive to R and X substituents, this sensitivity very probably being due to the exigencies of crystal packing. To illustrate this effect, it has been possible to grow mixed crystals of the complex R = *i*-Pr, X = 5-Me, diamagnetic in its own pure solid phase, and the corresponding (tetrahedral) zinc complex with the result that the nickel complex becomes paramagnetic and is thus "forced" into the tetrahedral configuration. Except for complexes bearing a substituent in the 6-position, the solution moments fall into the range 1.8–2.4 B.M. As in toluene solution,<sup>1</sup> the planar form of these complexes is favored at and near room temperature in chloroform. The equilibrium distribution between the two conformations is demonstrably solvent dependent and several measurements in CS<sub>2</sub> solution (*cf.* Table II) show that the planar form is much more heavily favored in that sol-

vent. The solvent effect is discussed in greater detail in a subsequent section.

 TABLE II  
 MAGNETIC MOMENTS IN CHLOROFORM SOLUTION

R	X	T, °C.	$\mu_{\text{eff}}$ , B.M. <sup>a,b</sup>
-CH(CH <sub>3</sub> ) <sub>2</sub>	H	30, 50	2.29, 2.33
-CH(CH <sub>3</sub> ) <sub>2</sub>	3-CH <sub>3</sub>	30, 50	2.18, 2.31
-CH(CH <sub>3</sub> ) <sub>2</sub>	4-CH <sub>3</sub>	30, 50	2.35, 2.36, (1.58)
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-CH <sub>3</sub>	30, 50	2.28, 2.33, (1.48)
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-C <sub>2</sub> H <sub>5</sub>	30, 50	2.24, 2.26
-CH(CH <sub>3</sub> ) <sub>2</sub>	5- <i>n</i> -C <sub>3</sub> H <sub>7</sub>	30, 50	2.13, 2.19
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-C <sub>6</sub> H <sub>5</sub>	30, 50	2.29, 2.32
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-N <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	30, 50	2.49, 2.39
-CH(CH <sub>3</sub> ) <sub>2</sub>	4,5-(CH <sub>3</sub> ) <sub>2</sub>	30, 50	2.47, 2.49
-CH(CH <sub>3</sub> ) <sub>2</sub>	4,6-(CH <sub>3</sub> ) <sub>2</sub>	30	0.93
-CH(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	5-CH <sub>3</sub>	30, 50	2.00, 2.09
-C(CH <sub>3</sub> ) <sub>3</sub>	5-CH <sub>3</sub>	30	3.22
CH <sub>3</sub> CHCH <sub>2</sub> CH <sub>3</sub>	H	30	2.11
CH <sub>3</sub> CHCH <sub>2</sub> CH <sub>3</sub>	4-CH <sub>3</sub>	30	2.30, (1.54)
CH <sub>3</sub> CHCH <sub>2</sub> CH <sub>3</sub>	5-CH <sub>3</sub>	30	2.23, (1.50)
CH <sub>3</sub> CHCH <sub>2</sub> CH <sub>3</sub>	4,5-(CH <sub>3</sub> ) <sub>2</sub>	30	2.42
CH <sub>3</sub> CHCH <sub>2</sub> CH <sub>3</sub>	4,6-(CH <sub>3</sub> ) <sub>2</sub>	30	1.06
CH <sub>3</sub> CH(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	5-CH <sub>3</sub>	30	2.18
CH <sub>3</sub> CH(CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	5-CH <sub>3</sub>	30	2.23
CH <sub>3</sub> CH(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	5-CH <sub>3</sub>	30	2.21
CH <sub>3</sub> CHCH(CH <sub>3</sub> ) <sub>2</sub>	5-CH <sub>3</sub>	30	1.81
CH <sub>3</sub> CHCH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	5-CH <sub>3</sub>	30	2.24

<sup>a</sup> Moments in parentheses refer to ~0.1 M solutions in CS<sub>2</sub> at 30°; all moments calculated from the Curie law. <sup>b</sup> Error ±2% when  $\mu_{\text{eff}} \geq 1.8$  B.M., arising from estimated error of ±4% in solute susceptibility measurements.

That the planar form is thermodynamically more stable in chloroform solution near room temperature is readily apparent by calculation of the free energy change for the interconversion planar (diamagnetic,  $S = 0$ ) → tetrahedral (paramagnetic,  $S = 1$ ). The susceptibility of such a system containing singlet and triplet magnetic species is given by

$$\chi^m = \frac{2g^2\beta^2N}{3kT} \left[ \frac{3}{3 + e^{\Delta F/kT}} \right] \quad (1)$$

whence<sup>10</sup>

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

The symbols have their usual meanings;  $\mu_{\text{eff}}$  is the ob-

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TABLE III  
MAGNETIC MOMENTS OF SOLIDS AT ROOM TEMPERATURE

R	X	$\mu_{eff}$ , B.M.
-CH(CH <sub>3</sub> ) <sub>2</sub>	H	3.28 <sup>a</sup>
-CH(CH <sub>3</sub> ) <sub>2</sub>	3-CH <sub>3</sub>	0 <sup>a</sup>
-CH(CH <sub>3</sub> ) <sub>2</sub>	4-CH <sub>3</sub>	3.29
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-CH <sub>3</sub>	0 <sup>b</sup>
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-C <sub>2</sub> H <sub>5</sub>	3.27
-CH(CH <sub>3</sub> ) <sub>2</sub>	5- <i>n</i> -C <sub>3</sub> H <sub>7</sub>	0 <sup>b</sup>
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-C <sub>6</sub> H <sub>5</sub>	0 <sup>b</sup>
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-N <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0 <sup>b</sup>
-CH(CH <sub>3</sub> ) <sub>2</sub>	4,5-(CH <sub>3</sub> ) <sub>2</sub>	3.27
-CH(CH <sub>3</sub> ) <sub>2</sub>	4,6-(CH <sub>3</sub> ) <sub>2</sub>	0 <sup>b</sup>
CH <sub>3</sub> CHCH <sub>2</sub> CH <sub>3</sub>	H	3.36 <sup>a</sup>
CH <sub>3</sub> CHCH <sub>2</sub> CH <sub>3</sub>	4-CH <sub>3</sub>	3.27
CH <sub>3</sub> CHCH <sub>2</sub> CH <sub>3</sub>	5-CH <sub>3</sub>	3.28
CH <sub>3</sub> CHCH <sub>2</sub> CH <sub>3</sub>	4,5-(CH <sub>3</sub> ) <sub>2</sub>	3.30
CH <sub>3</sub> CHCH <sub>2</sub> CH <sub>3</sub>	4,6-(CH <sub>3</sub> ) <sub>2</sub>	0 <sup>b</sup>

<sup>a</sup> Ref. 1. <sup>b</sup> Accurate susceptibility not determined.

served magnetic moment at temperature  $T$  and  $\mu_{\infty} = g[S(S+1)]^{1/2} = g\sqrt{2}$  is the moment of the completely paramagnetic species.<sup>23</sup> Calculation of  $\Delta F$  values from the measured moments gives substantial positive values in all cases except when  $R = t$ -Bu. In agreement with proton contact shift measurements (*vide infra*), the susceptibility measurements of Sacconi, *et al.*,<sup>13</sup> show that the equilibrium shifts toward the tetrahedral form with increasing temperature. For example, in bibenzyl solution at 80°  $\Delta F$  for the  $R = i$ -Pr complex is calculated to be +1100 cal. mole<sup>-1</sup> and at 180° +348 cal. mole<sup>-1</sup>.

**Proton Contact Shift Studies.**—The proton resonance spectra of the bis-(*N*-*sec*-alkylsalicylaldimine) complexes show large shifts to high and low fields relative to the resonance positions of the free Schiff bases. This pattern of behavior is analogous to that exhibited by bis-(*N,N*-disubstituted aminotroponimine)-Ni(II) complexes<sup>26-30</sup> and, as in those cases, these large shifts are attributed to isotropic hyperfine contact interactions. The conditions necessary for the observation of hyperfine contact shifts have been discussed previously.<sup>10,27,30</sup> If the rate of structural interconversion is sufficiently rapid, the observed contact shifts will be averaged over the magnetic singlet and triplet configurations of the complex, and at a temperature  $T$  the contact shifts will depend on the free energy change according to the equation<sup>26-30</sup>

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

(23) In all calculations reported herein  $\mu_{\infty}$  has been taken as 3.3 B.M. ( $g = 2.33$ ). While this moment is considerably below the range (3.9-4.2 B.M.) predicted by theory<sup>24</sup> and occasionally observed<sup>9,25</sup> for tetrahedral Ni(II) complexes, it is not unexpected<sup>1</sup> in view of the distorted tetrahedral structure of the  $R = i$ -Pr complex<sup>22</sup>; this moment is essentially the mean of the moments of a number of crystalline *N-sec*-alkylsalicylaldimine complexes (*cf.* Table III and ref. 1). This same value has been assumed by others and therefore tends to normalize comparisons of free energies and spin densities with those of the *N,N*-disubstituted aminotroponimine complexes.<sup>10</sup>

(24) B. N. Figgis, *Nature*, **182**, 1568 (1958).

(25) J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **1**, 866 (1962); **2**, 572 (1963).

(26) 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).

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

(28) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Mol. Phys.*, **5**, 407 (1962).

(29) D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4100 (1962).

(30) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Discussions Faraday Soc.*, **34**, 77 (1962).

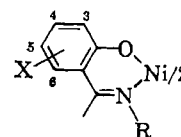
in which  $\Delta f_i$  is the observed contact shift in c.p.s. of the  $i$ th proton,  $f$  is the spectrometer frequency,  $a_i$  is the hyperfine interaction constant in gauss for the  $i$ th proton in the fully paramagnetic species, and  $\gamma_e$  and  $\gamma_H$  are the gyromagnetic ratios of the electron and proton, respectively.<sup>31a</sup> All contact shifts were measured at 60 Mc./sec. relative to the uncomplexed ligand.

Contact shift data at 50° for eleven complexes bearing an optically inactive R substituent are set out in Table IV. Only the shifts of the protons and groups attached to the benzene ring are to be considered.<sup>31b</sup> The spectrum in two solvents of the representative complex bis-(5-methyl-*N*-isopropylsalicylaldimine)-nickel(II) is shown in Fig. 1. The assignment of signals given

TABLE IV  
CONTACT SHIFTS AND SPIN DENSITIES

R	X	$\Delta F^{50^\circ}$ , cal. <sup>a</sup>	Position	Contact shift $\Delta f_i$ , c.p.s. <sup>b</sup>	Spin density <sup>d</sup>
-CH(CH <sub>3</sub> ) <sub>2</sub>	H	711	3	+736	+0.0103
			4	-604	-0.0848
			5	+731	+0.0103
-CH(CH <sub>3</sub> ) <sub>2</sub>	3-CH <sub>3</sub>	730	6	-114	-0.0016
			3	+835	<sup>e</sup>
			4	-762	-0.0109
-CH(CH <sub>3</sub> ) <sub>2</sub>	4-CH <sub>3</sub>	677	5	+853	+0.0122
			6	-111	-0.0016
			3	+842	+0.0122
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-CH <sub>3</sub>	711	4	+416	<sup>f</sup>
			5	+767	+0.0111
			6	-104	-0.0015
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-CH <sub>3</sub>	711	3	+796	+0.0112
			4	-610	-0.00855
			5	-581	<sup>g</sup>
-CH(CH <sub>3</sub> ) <sub>2</sub>	$\alpha$ $\beta$ 5-CH <sub>2</sub> CH <sub>3</sub>	783	6	-137	-0.0019
			3	+766	+0.0114
			4	-578	-0.00857
-CH(CH <sub>3</sub> ) <sub>2</sub>	$\alpha$ $\beta$ $\gamma$ 5-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	858	5	-417( $\alpha$ )	
			5	+79( $\beta$ )	
			5	+58( $\gamma$ )	-0.0019
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-C <sub>6</sub> H <sub>5</sub>	718	3	+731	+0.0115
			4	-546	-0.00858
			5	-345( $\alpha$ )	
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-C <sub>6</sub> H <sub>5</sub>	718	5	+94( $\beta$ )	
			5	+58( $\gamma$ )	
			6	-116	-0.0018
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-N <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	645	3	+732	+0.0103
			4	-582	-0.00820
			5 <sup>o</sup>	+167	+0.0024
-CH(CH <sub>3</sub> ) <sub>2</sub>	4,5-(CH <sub>3</sub> ) <sub>2</sub>	529	5 <sup>p</sup>	+133	+0.0019
			6	-141	-0.0020
			3	+640	+0.00849
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-CH <sub>3</sub>	962	4	-632	-0.00840
			5 <sup>o</sup>	+112	+0.0015
			5 <sup>p</sup>	+122	+0.0016
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-CH <sub>3</sub>	529	6	-188	-0.0025
			3	+818	+0.0100
			4	+463	<sup>h</sup>
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-CH <sub>3</sub>	962	5	-648	<sup>i</sup>
			6	-127	-0.0016
			3	+574	+0.0100
-C(CH <sub>3</sub> ) <sub>3</sub>	5-CH <sub>3</sub>	-1140	4	-447	-0.00775
			5	-405	<sup>j</sup>
			6	-76	+0.0013
-C(CH <sub>3</sub> ) <sub>3</sub>	5-CH <sub>3</sub>	-1140	3	+1751	+0.0120
			4	-1379	-0.00947
			5	-1099	
-C(CH <sub>3</sub> ) <sub>3</sub>	5-CH <sub>3</sub>	-1140	6	-73	-0.0005

<sup>a</sup> Calculated from susceptibility measurements at 50° (*cf.* Table II); estimated error,  $\pm 7\%$ . <sup>b</sup>  $\Delta f = f_{\text{complex}} - f_{\text{true ligand}}$  at 50° and 60 Mc. in CDCl<sub>3</sub> solution; both complex and ligand referenced internally to tetramethylsilane. <sup>c</sup> Contact shifts at  $m$ -position  $\sim 0$  c.p.s. <sup>d</sup> Estimated error  $\pm 5\%$ . <sup>e</sup>  $+Q_{\text{CCH}_3}$  values: <sup>e</sup> 26.9, <sup>f</sup> 16.0, <sup>g</sup> 18.3, <sup>h</sup> 15.1, <sup>i</sup> 17.4, <sup>j</sup> 17.8.



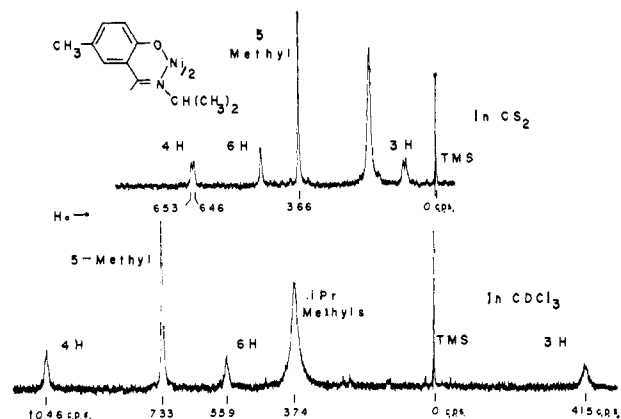
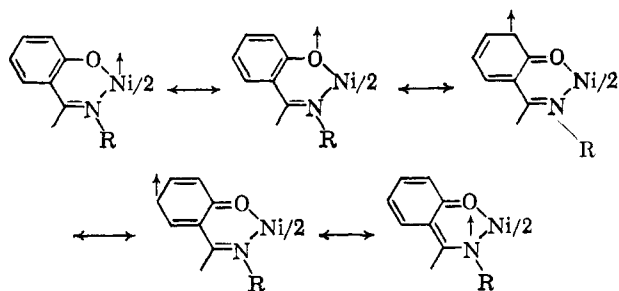


Fig. 1.—Proton resonance spectra of bis-(5-methyl-N-isopropylsalicylaldimine)-Ni(II) in carbon disulfide and chloroform at 30°. Frequencies are the chemical shifts.

in the table is readily verified from the spectrum in carbon disulfide and the expected signs of the contact shifts based on valence bond considerations. Assuming that the predominant mechanism for effecting paramagnetic spin densities of carbons 3–6 of the aromatic ring is metal-ligand  $d\pi-p\pi$  bonding in the tetrahedral form,<sup>27</sup> the following valence bond structures (neglecting formal charges) are of importance.



For this odd-alternant chelate ring system these structures predict positive spin densities at 3-C and 5-C, whereas 4-C and 6-C acquire negative spin densities through electron correlation effects.<sup>27,32</sup> Because spin is transferred to the aromatic protons by an indirect  $\pi-\sigma$  spin polarization mechanism,<sup>33</sup> 3-H and 5-H will possess positive and 4-H and 6-H negative contact shifts. In  $\text{CS}_2$  solution, in which the planar form is heavily favored, first-order proton spin-spin splittings of less than 10 c.p.s. are resolvable. In Fig. 1, the high- and low-field doublets are unambiguously assigned to 3-H and 4-H, respectively, leaving the low-field singlet of the same intensity assignable to 6-H.

Considered first are complexes containing optically inactive *sec*-alkyl groups. Contact shifts for several of the more soluble complexes in Table IV were obtained over the range  $-40$  to  $120^\circ$ . Typical are the results for the  $\text{R} = 3\text{-pentyl}$  complex shown in Fig. 2. Above  $\sim 40^\circ$  the contact shifts appear to be approaching a maximum which is required by eq. 3, but below this temperature the shifts increase, a situation clearly in-

(31) (a) To maintain consistency with previous work (ref. 26–30), a factor of 2S has been included in the denominator of eq. 3. This factor implies a definition of spin density such that the sum of the individual spin densities is 2S and not unity, the original definition (cf. H. M. McConnell and D. B. Chestnut, *J. Chem. Phys.*, **28**, 107 (1958)). (b) The remaining proton resonances have been located and all show negative contact shifts. For example, the following shifts were obtained at  $31^\circ$  for the  $\text{R} = i\text{-Pr}$ ,  $\text{X} = 5\text{-Me}$  complex in chloroform:  $-298$  (*i-Pr*, Me's),  $-6059$  (C-H, *i-Pr*),  $-11,570$  c.p.s. (HC=N, verified by deuteration).

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

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

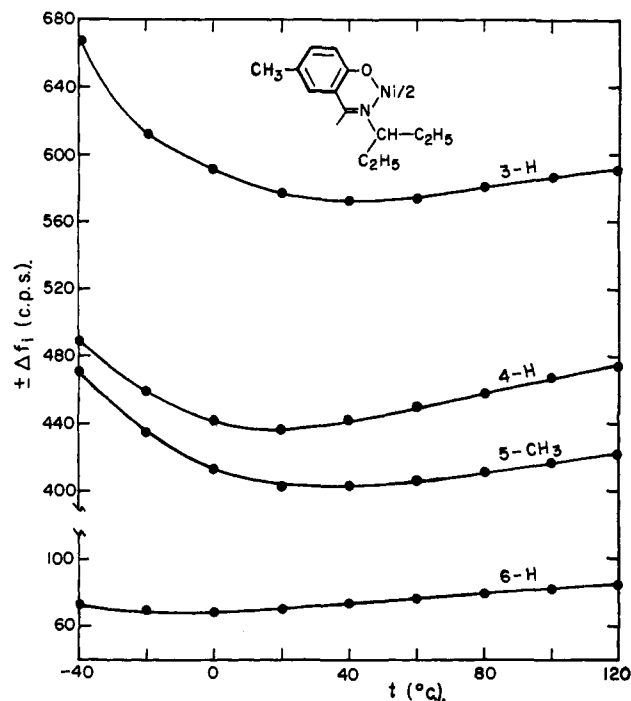


Fig. 2.—Temperature dependence of the contact shifts of bis-(5-methyl-N-3-pentylsalicylaldimine)-Ni(II) in chloroform; 3-H shifts are positive, all others negative.

compatible with (3) when  $\Delta F$  is a positive quantity decreasing with increasing temperature. The peculiar temperature dependence of the contact shifts below  $\sim 40^\circ$  is attributed to solute association (*vide infra*). In all cases it has been assumed that at  $50^\circ$  associated species make a negligible contribution to the measured susceptibilities from which  $\Delta F^{50^\circ}$  values in Table IV are calculated. Values of  $a_i$  can then be obtained from (3) using the measured contact shifts.<sup>34</sup> For the various complexes, temperature dependences of  $\Delta F$  were calculated from contact shifts of the narrow 5-methyl resonance. Results for the 3-pentyl complex are given in Fig. 6. Only above  $50^\circ$  was the linear variation required by eq. 4 satisfied. In this region the experimental

$$\Delta F = \Delta H - T\Delta S \quad (4)$$

points were fitted to a least mean squares plot (cf. Fig. 6) and  $\Delta H$  and  $\Delta S$  for the structural interconversion evaluated. Results for three of the inactive complexes are given in Table VI.

**Spin Density Distributions.**—Elegant utilization of contact shift measurements for mapping spin densities in variously substituted aminotroponimine ligands has been made by Phillips, *et al.*<sup>26–30</sup> For aromatic C–H fragments the spin density on the  $i$ th carbon atom is given by<sup>33</sup>

$$a_i = Q_{\text{CH}\rho\text{C}} \quad (5)$$

Taking  $Q_{\text{CH}} = -22.5$  the spin densities in a series of related salicylaldimine ligands<sup>5</sup> have been calculated and are given in Table IV. The alternating signs of the spin densities agree with expectation for a nonalternant system. The use of eq. 5 to calculate spin densities requires that the spin is placed on the ligand by a  $\pi$ -bonding mechanism, as distinct from a spin-polarization mechanism operating in the  $\sigma$ -system.<sup>35</sup> Applying the

(34) Unlike the majority of aminotroponimine complexes,  $\Delta F$  values for the *N-sec*-alkylsalicylaldimine complexes remain positive over the entire temperature range of measurement. Therefore, determination of  $a_i$  values by extrapolation of contact shifts to limiting values as  $1/T \rightarrow 0$  is not possible.

(35) Contact shifts due to this effect have been observed in octahedral complexes; cf. R. S. Milner and L. Pratt, *Discussions Faraday Soc.*, **34**, 88

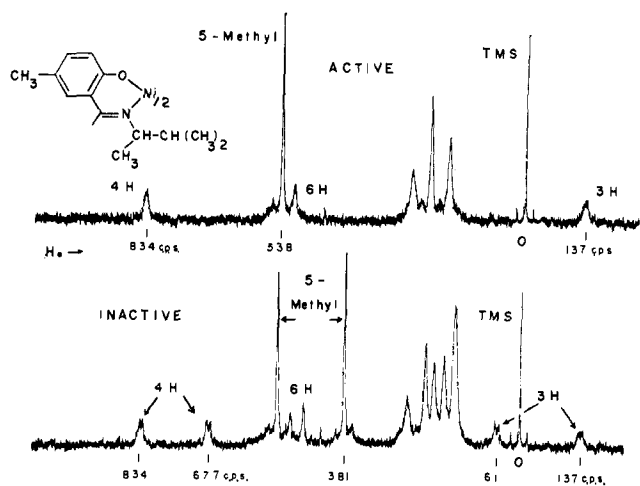


Fig. 3.—Proton resonance spectrum of bis-(5-methyl-N-2-(3-methyl)-butylsalicylaldehyde)-Ni(II) in chloroform at 30°: (a) *meso* and racemic forms (inactive), (b) (-, -) form (active).

previously developed criterion for  $\pi$ -delocalization,<sup>27-30</sup> a comparison of experimental spin densities and those calculated by the method of McConnell and Dearman<sup>36</sup> assuming one electron transferred to the  $\pi$ -system of the ligand is given in Table V. Taking the calculated positive spin densities as the more reliable results,<sup>27-30</sup> it is seen that for the R = *i*-Pr complex a factor of 36 brings the calculated and observed values in agreement. On this basis approximately  $1/36$  of an electron is transferred to the  $\pi$ -system of each ligand in this complex. A similar amount of electron spin transfer is found in the 5-phenyl and 5-azophenyl complexes. Observed spin densities at 6-C are in poor agreement with theory ( $\rho_{6C} = -0.2190$  for X = H) in all cases; other than the observed tendency<sup>29</sup> of valence bond calculations to overestimate negative spin densities, the reason for the disagreement is unknown.

TABLE V

COMPARISON OF CALCULATED AND OBSERVED SPIN DENSITIES<sup>a</sup>

Compound		Position	$\rho_{\text{calcd}}$	$\rho_{\text{calcd}}/\rho_{\text{exptl}}^b$
R	X			
<i>i</i> -Pr	H	3	+0.3477	33.8
		4	- .1972	23.2
		5	+ .3897	37.8
<i>i</i> -Pr	5-C <sub>6</sub> H <sub>5</sub>	3	+ .3246	31.5
		4	- .1950	23.8
		<i>o</i>	+ .1289	54
		<i>m</i>	- .0657	<sup>c</sup>
		<i>p</i>	+ .1118	59
<i>i</i> -Pr	5-N=NC <sub>6</sub> H <sub>5</sub>	3	+ .2944	34.6
		4	- .1851	22.0
		<i>o</i>	+ .1025	68
		<i>m</i>	- .0512	<sup>c</sup>
		<i>p</i>	+ .0852	53

<sup>a</sup> The results of these calculations were kindly made available by Drs. W. D. Phillips and D. R. Eaton and were obtained using  $\beta_{\text{CN}} = 1.2\beta_{\text{CC}}$ ;  $\beta_{\text{CO}} = \beta_{\text{NN}} = 1.4\beta_{\text{CC}}$ . <sup>b</sup> For  $\rho_{\text{exptl}}$  see Table IV. <sup>c</sup> Experimental values too small to be measured accurately.

Further evidence that spin density is delocalized mainly by  $\pi$ -bonding is afforded by substitution at 5-C with phenyl and azophenyl groups. Spin densities are observed to alternate in sign in the attached rings.

(1962); in a tetrahedral complex spin density could be introduced into the  $\sigma$ -system of the ligand since the set  $d_{xz}$ ,  $d_{yz}$ ,  $d_{xy}$  has  $\sigma$  as well as  $\pi$  symmetry in this case.

(36) H. M. McConnell and H. H. Dearman, *J. Chem. Phys.*, **28**, 51 (1958).

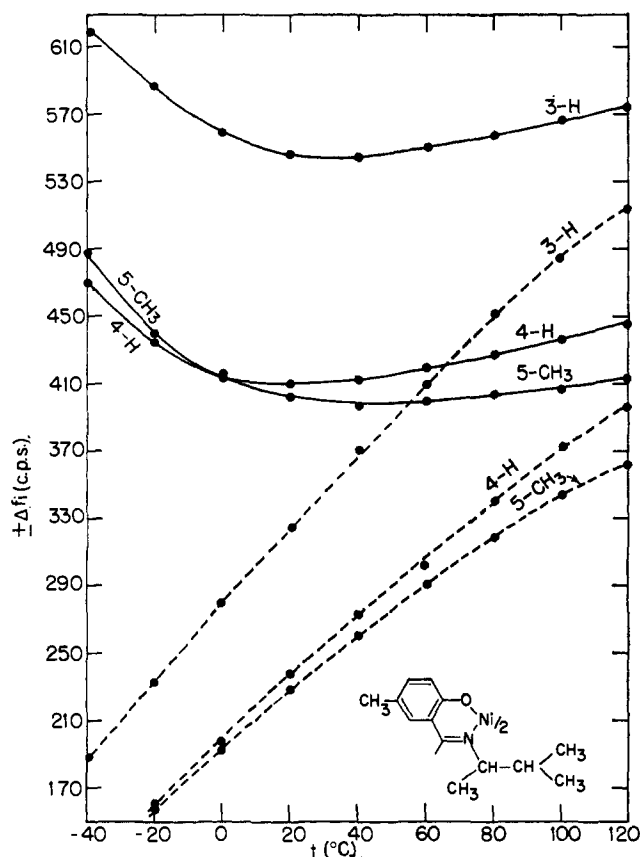


Fig. 4.—Temperature dependence of the contact shifts of bis-(5-methyl-N-2-(3-methyl)-butylsalicylaldehyde)-Ni(II) in chloroform: —, (-, -) form; ----, *meso* form; 3-H shifts are positive, others negative.

Further, the attenuation factors  $\rho(5-C)/\rho(\text{para-C})$  for spin density transmission, 5.4 for 5-C<sub>6</sub>H<sub>5</sub> and 6.4 for 5-N<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, are comparable to those (8.2 for N-phenyl-*p*-azophenyl, 6.8 for  $\gamma$ -azophenyl) found<sup>29</sup> in the aminotroponeimines, in which spin density is predominantly transferred by metal-ligand  $\pi$ -bonding. The contact shifts of the methyl protons are opposite in sign for those of a proton at the same position, and this tends to confirm the theory that hyperfine splitting of methyl groups bonded to an aromatic carbon has the same sign as the spin density at that carbon.<sup>37</sup> Values of  $Q_{\text{CCH}_3}$  are then positive, this sign being in agreement with a theoretical valence bond description of hyperconjugation as a mechanism for the electron-nucleus hyperfine splitting.<sup>37</sup> Assuming that spin densities at 3-, 4-, and 5-C are unaffected by methyl substitution,<sup>27</sup> values of  $Q_{\text{CCH}_3}$  have been calculated and are given in Table IV. Only at 3-C is there a value in good agreement with the best experimental value, 27.1, observed in the ethyl radical.<sup>39</sup> However, the lower values at 4-C and 5-C do not necessarily constitute evidence against a  $\pi$ - $\sigma$  spin polarization mechanism<sup>37</sup> and, thereby, against spin transfer by  $d\pi$ - $p\pi$  bonding at the outset, inasmuch as  $Q_{\text{CCH}_3}$  values appear to be sensitive to the position of substitution in related molecules.<sup>29,38</sup>

The extent of spin density transfer in these salicylaldehyde complexes ( $\sim 1/30$ ) of an unpaired spin is considerably less than that ( $\sim 1/10$ ) in the aminotroponeimine complexes. Moreover,  $\rho_{5C}$  (R = *i*-Pr)/ $\rho_{7C}$  (N-Et) is only  $\sim 0.2$ . While the extent of transfer undoubtedly

(37) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958); but see also ref. 38.

(38) J. R. Bolton, A. Carrington, and A. D. McLachlan, *Mol. Phys.*, **5**, 31 (1962).

(39) R. W. Fessenden and R. Schuler, *J. Chem. Phys.*, **33**, 935 (1960).

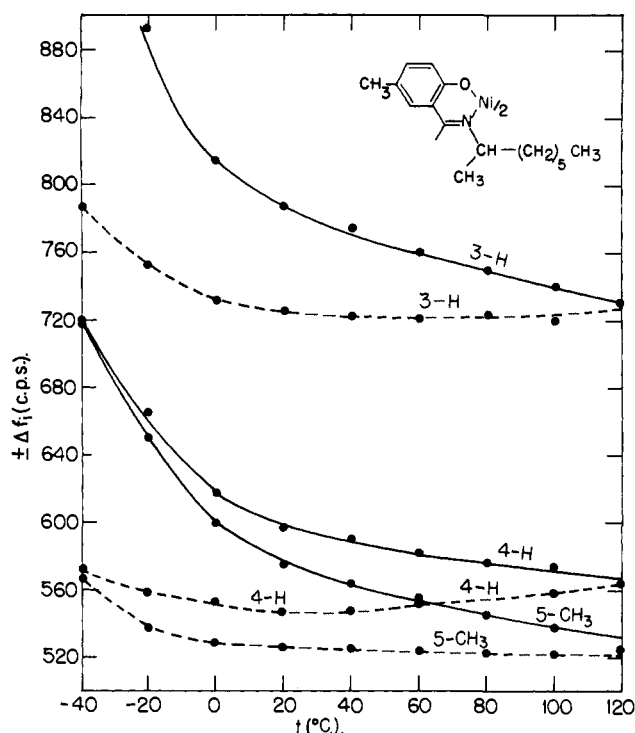


Fig. 5.—Temperature dependence of the contact shifts of bis-(5-methyl-N-2-octylsalicylaldimine)-Ni(II) in chloroform: —, (+,+) form; ---, (−,−) form; 3-H shifts are positive, others negative.

depends on bond angles and distances in the chelate ring of the tetrahedral form, the decrease in the salicylaldimines may also be due to the fact that one path of transfer involves oxygen. It has been demonstrated that oxygen is relatively ineffective as a linking group for transmitting spin density<sup>27,30</sup> and the reasons for this have been discussed.<sup>27</sup> Ethylenic and azo groups are much more effective and it is expected that the isosteric CH=N group would act similarly. Apparently —CH=N— and —O— in combination are, on the basis of intrinsic spin transmissivities, less effective than —RC=N— and the demonstrably efficient —NR— linkage,<sup>30</sup> both of which are formally present in the aminotroponimine chelate ring. Another contributing factor to the lower spin densities on the salicylaldimine ligands is that, in a valence bond sense, spin can be transferred only at the expense of interfering with benzenoid resonance. No such resonance inhibition to spin density transfer is present in the aminotroponimines. Finally, the spin density distribution found for the N-sec-alkylsalicylaldimines is similar in sign to but different in magnitude from those recently measured in some bis-(N-arylsalicylaldimine)-Ni(II) complexes.<sup>40</sup> However, this is not unexpected because these compounds achieve paramagnetism through molecular association<sup>4</sup> and probably contain quasi-octahedrally coordinated Ni(II).

**Diastereoisomeric Complexes.**—Proton resonance spectra of complexes having an optically active substituent R are quite similar to those of closely related complexes bearing an optically inactive group R in terms of magnitudes of contact shifts. Five complexes with optically active R groups have been examined over a  $-40$  to  $120^\circ$  range. In all cases a striking result is evident upon spectral comparison with complexes having inactive R groups; *viz.*, that all signals related to a given proton or methyl group attached to the ben-

(40) E. A. LaLancette, D. R. Eaton, R. E. Benson, and W. D. Phillips, *J. Am. Chem. Soc.*, **84**, 3968 (1962).

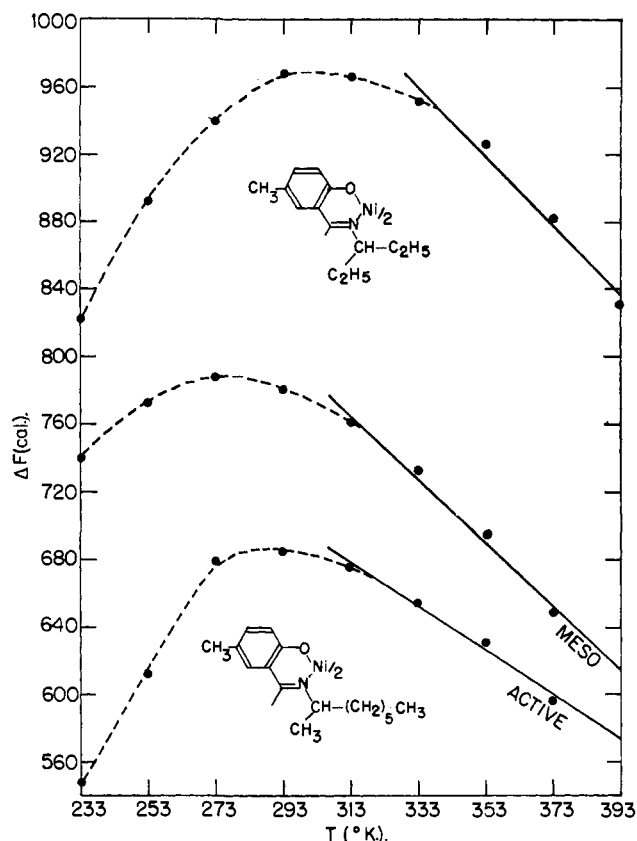


Fig. 6.—Temperature dependence of the free energy changes for the planar  $\rightleftharpoons$  tetrahedral interconversions of bis-(5-methyl-N-3-pentylsalicylaldimine)-Ni(II) and bis-(5-methyl-N-2-octylsalicylaldimine)-Ni(II) in chloroform. Dashed lines represent regions of nonlinearity.

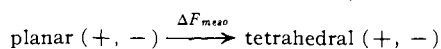
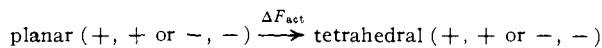
zene ring occur in pairs. The spectrum of the R = 2-(3-methyl)-butyl complex is given in Fig. 3a as an example; the spectrum of the R = 2-butyl complex has been presented earlier.<sup>14</sup> The effect is particularly evident from the doubled signal of the 5-Me group. The large separations between the components of the doublets require a chemical shift mechanism. The two signals arising from a given proton or methyl group have been shown by proton double resonance to be independent.<sup>14</sup> These signals are then due to distinct molecular species.

The origin of the doubled sets of resonances is readily detected when it is observed that only those complexes with optically active R groups show this effect. Such complexes were originally prepared from the racemic amines and therefore contain essentially equimolar proportions of a racemic [(+, +) and (−, −)] and a *meso* [(+, −)] form. The complexes so obtained are mixtures of diastereoisomers, each of which is responsible for one set of resonances. This contention has been proved in four cases (R = 2-butyl, 2-octyl, 2-(3-methyl)-butyl, 2-(4-methyl)-pentyl) by resolution of the parent amines and preparation of optically active complexes. These complexes show only one set of resonances and in every case the inner set of resonances disappears (*cf.* Fig. 3b), thus proving that the *meso* isomers have the smaller set of contact shifts. The doubled features imply two distinct averages of chemical shift over the planar and tetrahedral forms. Because the contact shifts are exponentially dependent upon the free energy difference between the two conformers, the results for a given diastereoisomeric pair indicate that the changes

TABLE VI  
THERMODYNAMIC VALUES FOR THE PLANAR  $\rightleftharpoons$  TETRAHEDRAL INTERCONVERSION OF DIASTEREOISOMERIC AND OPTICALLY INACTIVE COMPLEXES<sup>a</sup>

R	X	Active			meso			$\Delta F^{60^\circ}$ , cal. <sup>c</sup>	
		$\Delta H$ , cal.	$\Delta S$ , e.u.	Temp. range, <sup>b</sup> °C.	$\Delta H$ , cal.	$\Delta S$ , e.u.	Temp. range, <sup>b</sup> °C.	Active	meso
CH <sub>3</sub> CH(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	5-CH <sub>3</sub>	1240	1.58	60-120	1590	2.41	40-120	709	789
CH <sub>3</sub> CH(CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	5-CH <sub>3</sub>	1080	1.28	40-100	1440	2.12	40-100	656	733
CH <sub>3</sub> CH(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	5-CH <sub>3</sub>	1090	1.32	40-100	1350	1.87	40-100	652	727
CH <sub>3</sub> CHCH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	5-CH <sub>3</sub>	1030	1.02	60-130	1310	1.84	40-120	689	701
					$\Delta F^{60^\circ}$				
-CH(CH <sub>3</sub> ) <sub>2</sub>	4-CH <sub>3</sub>	841	0.53	60-100	665				
-CH(CH <sub>3</sub> ) <sub>2</sub>	5-CH <sub>3</sub>	1090	1.15	60-120	700				
-CH(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	5-CH <sub>3</sub>	1630	2.02	60-120	958				

<sup>a</sup> Values obtained in CDCl<sub>3</sub> solution. <sup>b</sup> Temperature range over which least mean squares plot of  $\Delta F$  vs.  $T$  was constructed. <sup>c</sup> Estimated maximum error  $\pm 10\%$ .



result in  $\Delta F_{\text{act}} \neq \Delta F_{\text{meso}}$ . It is proposed that this distinction arises because the *paramagnetic* states have somewhat different free energies. Unresolvable chemical shift differences have been found between the diastereoisomeric pairs of diamagnetic bis-(5-methyl-*N*-sec-butylsalicylalimine) Pd (planar) and Zn (tetrahedral) complexes.

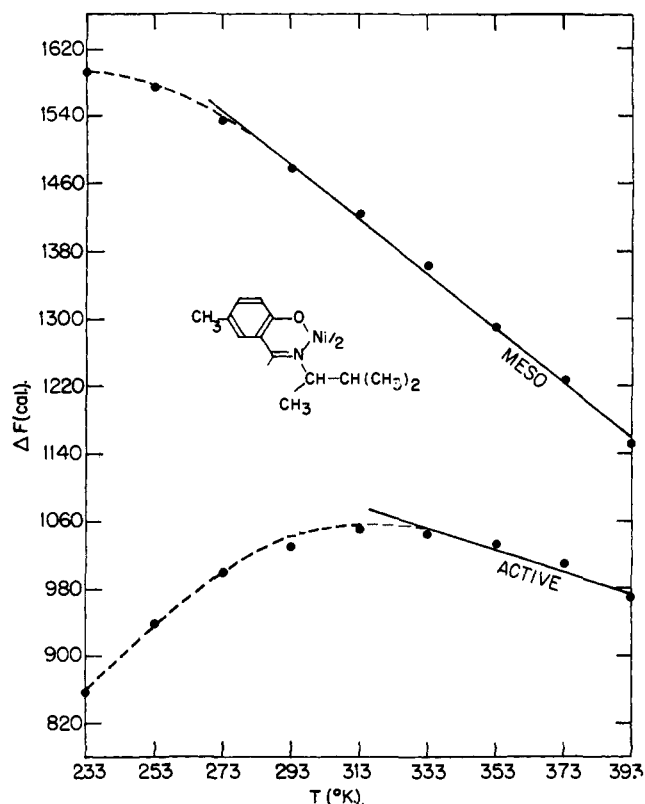


Fig. 7.—Temperature dependence of the free energy changes for the planar  $\rightleftharpoons$  tetrahedral interconversion of bis-(5-methyl-*N*-2-(3-methyl)-butylsalicylalimine)-Ni(II) in chloroform. Dashed lines represent regions of nonlinearity.

A thermodynamic description of the conformational changes of the diastereoisomeric complexes can be obtained from an analysis of the temperature dependence of the contact shifts. Some representative contact shifts are given in Fig. 4 and 5. The data have been treated as follows. Measurements on complexes containing inactive R groups show that the values of the electron-nucleus coupling constants in the paramagnetic form are insensitive within experimental error to the

nature of R. Using the well-defined 5-Me signal as a convenient probe, the mean value  $a_{5\text{Me}} = +0.170 \pm 0.010$  gauss, obtained from measurement on complexes with R = *i*-Pr, 3-pentyl, and *t*-Bu, has been used to calculate  $\Delta F$  at various temperatures from measurement of contact shifts. Reference to Fig. 6 and 7 shows that in the higher temperature regions the expected  $\Delta F$  vs.  $T$  linearity holds. The exception is the *meso* form of the R = 2-(3-methyl)-butyl complex which manifests linearity in the 0-120° range. From a least mean squares fit the enthalpy and entropy changes were evaluated and are set out in Tables VI and VII.

Further evidence for the proposal that the separate set of signals for each diastereoisomer arises predominantly from the inequality of free energy changes can be obtained from the temperature dependences of the contact shifts. An alternative explanation could be that  $a_i$  and/or  $g$  for the paramagnetic forms of the two isomers are sufficiently different such that the observed separations are realized. First, unreasonably large changes in these quantities are required in view of their direct proportionality to  $\Delta f_i$ . Second, such an effect would result in parallel  $\Delta f_i(T)$  behaviors for each isomer of a given complex. In no case has this been observed. In Fig. 4 and 5  $\Delta f_i(T)$  behavior for each isomer is clearly different in that temperature range in which eq. 4 is obeyed (*cf.* Tables VI and VII). Finally, it is not possible to fit the observed contact shifts of a pair of isomers to a generalized temperature dependence of the form  $\Delta F = a - bT$  so as to yield a reasonably constant value of  $a_i$  for each isomer. Therefore, a direct comparison at a given temperature of the energetics of structural interconversion as a function of the group R can be obtained from the  $\Delta F$  values. For this purpose  $\Delta F$  values at 60° are given in Tables VI and VII.  $\Delta F_{\text{act}} - \Delta F_{\text{meso}}$  is believed to be composed mainly of the free energy differences between the tetrahedral forms in a given solvent. Below 120° the tetrahedral configuration of the active isomer is usually more stable. However, in the R = 2-(4-methyl)-pentyl complex the derived  $\Delta F(T)$  dependences predict at 70° equal free energy changes and, thereby, essentially equal stabilities of the tetrahedral form of each isomer. This situation is observable, for in the 65-80° range the narrow (<6 c.p.s.) 5-Me signals broaden, coalesce, and then become distinct again at higher temperatures.

No satisfactory interpretation of the thermodynamic changes appears possible at present. However, it is to be noted that the entropy changes in CDCl<sub>3</sub> are quite small compared to those (8-16 e.u.) found for the aminotroponeimine complexes in the same solvent.<sup>10</sup> Significant contributions to  $\Delta S$  are expected from (i) the electronic entropy change  $R \ln 3 = 2.2$  e.u., (ii) changes in rotational and vibrational motions of the R group, (iii) changes in solvation of the two conformers.



TABLE VII

SOLVENT EFFECTS ON THE PLANAR  $\rightleftharpoons$  TETRAHEDRAL INTERCONVERSION OF THE R = CH<sub>3</sub>CHCH(CH<sub>3</sub>)<sub>2</sub>, X = 5-CH<sub>3</sub> Ni(II) COMPLEX

Solvent	Active			meso			$\Delta F^{80^\circ}$ , cal.	
	$\Delta H$ , cal.	$\Delta S$ , e.u.	Temp. range, °C.	$\Delta H$ , cal.	$\Delta S$ , e.u.	Temp. range, °C.	Active	meso
CDCl <sub>3</sub>	1480	1.28	60-120	2420	3.19	0-120	1050	1350
Toluene- <i>d</i> <sub>3</sub>	2230	2.73	40-140	3050	4.43	20-140	1320	1580
CS <sub>2</sub>	2600	2.96	20-80	3770	5.69	0-80	1610	1790

The first contribution must be positive and the second expected to be so as judged from molecular models. Analogy to the troponiminates<sup>10</sup> and the known effects of more polar solvents on other salicylaldimine complexes<sup>3</sup> suggest a positive contribution from (iii) also. It is possible, however, that hydrogen bonding of the type O...D-CCl<sub>3</sub> between solvent and the donor oxygens, relatively unhindered in the tetrahedral form, may decrease or make negative an otherwise positive contribution from (iii). It is well established that chloroform forms hydrogen bonds with oxygen functional groups.<sup>41</sup> For one complex (*cf.* Table VII) the presence of non-hydrogen-bonding solvents results in substantial increases in  $\Delta S$ .

**Molecular Association.**—It is now well established that *N-n*-alkyl- and *N*-arylsalicylaldiminickel(II) complexes become paramagnetic in solution and in the solid as a result of molecular association.<sup>3-5,42</sup> Cryoscopic measurements in benzene<sup>13,43</sup> have demonstrated that certain *N-sec*-alkyl complexes also associate. This interaction makes some or all of the nickel ions in a given aggregate paramagnetic and can be sensitively detected by contact shift measurements. Figures 4 and 5 show that as the temperature is lowered the contact shifts increase rapidly and do not follow eq. 3. The signals also broaden quickly as the temperature decreases. These lower temperature regions are those in which the calculated  $\Delta F$  values cannot be fit to eq. 4 and are represented by dashed lines in Fig. 6 and 7. The added contributions to the contact shifts arise from averaging the chemical shifts over another paramagnetic component, the associated species, which contain fully paramagnetic nickel ions. Contact shift measurements<sup>40</sup> on the fully paramagnetic bis-(*N*-arylsalicylaldimine) complexes, which at room temperature and below achieve paramagnetic behavior exclusively by molecular association,<sup>4</sup> reveal much larger contact shifts than any measured in this work down to  $-40^\circ$ . Correction of published shifts to  $-40^\circ$  indicates that, if  $a_i$  values in the associated *N*-aryl and *N-sec*-alkyl complexes are comparable,<sup>44</sup> the 4-H, 5-Me, and 6-H contact shifts will approach *ca.*  $-1900$ ,  $-1000$ , and  $-1100$  c.p.s., respectively, in the limit of full paramagnetism. Consistent with this prediction is the rapid increase of shifts with decreasing temperature. The active diastereoisomer of all complexes associates more readily than does the *meso* isomer. This is particularly evident for the R = 2-(3-methyl)-butyl complex (Fig. 4 and 7).

The presence of associated species can also be detected in the optical spectra. Solutions of the *N-sec*-alkyl complexes are brown to brownish green in color at room temperature and become more intensely brown as the temperature is raised. As the solutions are cooled, however, the intensity lessens and a green color de-

velops. The spectrum of the R = 2-heptyl complex at three temperatures is shown in Fig. 8. At  $-30^\circ$  a shoulder at  $\sim 9700$  cm.<sup>-1</sup> is quite evident which decreases at the higher temperatures, but is still observable at  $50^\circ$ . This feature is correlated with the bands which occur at 10,000 cm.<sup>-1</sup> in solutions<sup>4</sup> and solid phases<sup>42</sup> of the associated *N*-aryl complexes and is reasonably assigned as the lowest energy spin-allowed transition in a weakly tetragonal nickel(II) complex (*i.e.*,  ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$  in an octahedral complex). The related complex with R = cyclopropyl is significantly associated at  $37^\circ$ ; at  $-30^\circ$  in chloroform the complex has a moment of 2.64 B.M., and a well-defined band at 9700 cm.<sup>-1</sup> appears in the bright green solution. No tetrahedral bands are observable. Above  $0^\circ$  optical spectra demonstrate the coexistence in solution of

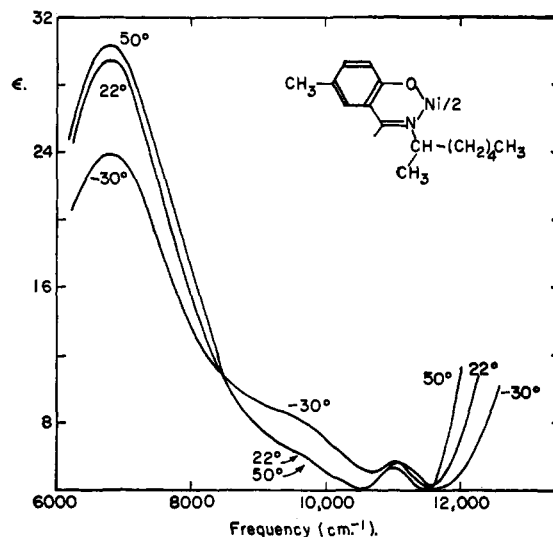


Fig. 8.—Optical spectrum of bis-(5-methyl-N-2-heptylsalicylaldimine)-Ni(II) in chloroform, 0.05 *M*.

planar, tetrahedral, and associated species. Accordingly, the observed contact shifts from 0 to  $100^\circ$  cannot be fit to eq. 3. This complex represents the extreme case of molecular association in *N-sec*-alkyl complexes, and its behavior substantiates the effect of molecular association on contact shifts and optical spectra. The lower limits of the temperature ranges given in Tables VI and VII represent those temperatures above which molecular association makes no observable contribution to the contact shifts. For the R = *i*-Pr complexes this temperature is somewhat higher than that anticipated from direct molecular weight measurements,<sup>1</sup> thereby tending to emphasize the considerable sensitivity of contact shifts as a probe of inter- as well as intramolecular effects in paramagnetic nickel(II) complexes.

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(44) The lack of reliable  $a_i$  values for the paramagnetic associated *N-sec*-alkyl complexes precludes meaningful evaluation of  $\Delta F$ ,  $\Delta H$ , and  $\Delta S$  for the association process.