

# The Synthesis and Proton Resonance Study of the Solution Equilibria of Bis( $\beta$ -ketoamino)nickel(II) Complexes

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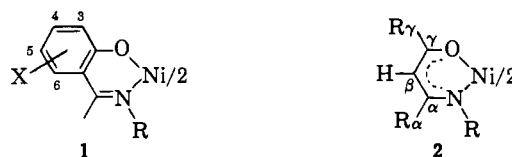
A series of four-coordinate Ni(II) complexes derived from  $\alpha,\beta$ -unsaturated  $\beta$ -ketoamines and of the general formulation  $Ni[R_\gamma COCH(NHR)R_\alpha]_2$  have been synthesized. Two groups of complexes having  $R_\alpha = R_\gamma = CH_3$  and  $R_\alpha = CH_3, R_\gamma = C_6H_5$  were thoroughly investigated by spectral, magnetic, and proton resonance measurements. For both groups it has been demonstrated that a planar  $\rightleftharpoons$  tetrahedral equilibrium exists whose position is strongly dependent on the steric nature of the R group. As in several other systems, the presence of the configurational equilibrium allows favorable relaxation conditions such that well-defined isotropic proton contact shifts have been measured and analyzed. It is concluded that the spin imbalance exists in the lowest filled ligand  $\pi$ -orbital. For both series it was found that when R = sec-alkyl the complexes are  $\sim 100\%$  tetrahedral at room temperature, but when R = aryl in the first series and n-alkyl in the second series the equilibrium is strongly shifted toward the planar form. In these cases  $\Delta F$ ,  $\Delta H$ , and  $\Delta S$  values for the structural change were determined from the contact shifts. The detection of a small amount of molecular association of complexes having R = aryl was demonstrated from contact shift measurement. A brief comparison of solution equilibria and  $\pi$ -bonding in  $\beta$ -ketoamine and salicylaldimine nickel(II) complexes is given.

## Introduction

One of the most interesting and recent fundamental developments in the chemistry of four-coordinate nickel(II) complexes has been the recognition of configurational (planar  $\rightleftharpoons$  tetrahedral) equilibria in solutions of noncoordinating solvents. These equilibria have been definitely established in solutions of bis(N-substituted salicylaldimino),<sup>2-5</sup> bis(N-substituted naphthaldimino),<sup>5d,6</sup> and bis(N,N'-disubstituted aminotroponeimino)<sup>7</sup> complexes. In these groups of complexes the position of equilibrium at a given temperature is predominantly dependent on the steric nature of the nitrogen substituent R, but in all cases R may be varied such that the free energy difference between the planar and tetrahedral configurations is sufficiently

small to allow population of both configurations, frequently at room temperature.

The formation of tetrahedral species is apparently due to steric crowding in the planar form which can be adjusted by variation of R. Because of the obvious structural similarity between bis(salicylaldimino) complexes 1, and bis( $\beta$ -ketoamino) complexes 2, particularly with respect to the steric disposition of the R group, it appeared likely that the latter complexes would also manifest the configurational equilibrium



and thereby provide a comparison of structural and electronic effects on the position of equilibrium and bonding in these two related series of complexes.

Configurational equilibria in nickel(II) complexes have been effectively studied by means of proton magnetic resonance.<sup>3,4,6-9</sup> An analysis of the proton hyperfine contact shifts allows evaluation of the thermodynamic parameters for the structural change and determination of spin density distributions on the coordinated ligand systems.<sup>9</sup> We have previously reported<sup>10</sup> that certain bis( $\beta$ -ketoamino)nickel(II) complexes exhibit isotropic proton contact shifts and, dependent on the nature of R, are involved in the configurational equilibrium. Herein we report the results of our complete study of these complexes, including a general synthetic procedure, characterization of the solution equilibria, and a discussion of electronic structures of the paramagnetic tetrahedral configurations.

## Experimental

**Preparation of Ligands.** The  $\beta$ -ketoamines used in this work were prepared by adding a 50% mole excess of the appropriate primary amine directly to the  $\beta$ -diketone. The mixture was heated at 100° for several hours in the presence of calcium sulfate. The products were purified by vacuum distillation or crystallization and were identified by their proton resonance spectra<sup>11</sup>; they were not further characterized.

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Table I. Characterization of Bis( $\beta$ -ketoamino)nickel(II) Complexes

R <sub>γ</sub>	R <sub>α</sub>	R	M.p., °C. <sup>a</sup>	% C		% H		% N	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	125	50.93	50.88	7.12	7.02	9.90	10.04
CH <sub>3</sub>	CH <sub>3</sub>	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	158	56.67	57.05	8.32	8.36	8.26	8.41
CH <sub>3</sub>	CH <sub>3</sub>	<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	79–80	58.88	58.70	8.78	8.92	7.63	7.38
CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>11</sub>	150–151	63.03	62.65	8.66	8.90	6.68	6.55
CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	152	66.23	66.01	6.48	6.43	6.44	6.64
CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> <sup>b</sup>	163–165	64.90	64.86	5.94	6.11	6.88	6.98
CH <sub>3</sub>	CH <sub>3</sub>	<i>o</i> -C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	137	66.24	66.42	6.49	6.41	6.44	6.43
CH <sub>3</sub>	CH <sub>3</sub>	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	156–157	66.24	66.08	6.49	6.45	6.44	6.56
CH <sub>3</sub>	CH <sub>3</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	183–184	66.24	66.10	6.49	6.47	6.44	6.42
CH <sub>3</sub>	CH <sub>3</sub>	α-C <sub>10</sub> H <sub>7</sub>	244	71.03	70.80	5.56	5.56	5.52	5.35
CH <sub>3</sub>	CH <sub>3</sub>	β-C <sub>10</sub> H <sub>7</sub>	220	71.03	71.03	5.56	5.60	5.52	5.39
CH <sub>3</sub>	H	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	129	54.06	53.83	7.78	7.97	9.01	8.89
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub> <sup>c</sup>	202–203	64.90	64.94	5.94	5.82	6.88	6.77
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> (green)	116		65.78		6.59		6.34
		(brown)	162–164	66.24	66.45	6.49	6.61	6.44	6.64
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	125	67.41	67.32	6.96	6.87	6.05	5.90
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>i</i> -C <sub>3</sub> H <sub>7</sub> <sup>d</sup>	196	67.41	67.16	6.96	6.98	6.05	5.94
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>3</sub> H <sub>5</sub> <sup>e</sup>	151–152	68.00	67.76	6.15	6.10	6.10	6.09
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	92–93	68.45	68.21	7.39	7.42	5.70	5.80
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub>	169–171	68.45	68.70	7.39	7.53	5.70	5.51
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	154	68.45	68.38	7.39	7.20	5.70	5.53
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>11</sub>	179–180	70.73	70.96	7.42	7.61	5.16	4.91
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub> <sup>f</sup>	198–199	64.26	64.28	6.93	7.00	5.35	5.38

<sup>a</sup> Uncorrected. <sup>b</sup> Extracted with dichloromethane and recrystallized from absolute ethanol. <sup>c</sup> Extracted and recrystallized from toluene. <sup>d</sup> Golden-yellow crystals. <sup>e</sup> Extracted with benzene and recrystallized from benzene-*n*-heptane. <sup>f</sup> Mol. wt. calcd. 523; found (osmometric) 514, 527.

The sodium salt of formylacetone was prepared according to Claisen<sup>12</sup> and converted to 4-isopropylaminobut-3-en-2-one by the method of Bernary.<sup>13</sup> 1-Phenyl-2-methylbutane-1,3-dione was prepared by the method of Johnson, *et al.*<sup>14</sup>

**Preparation of Complexes.** The complexes listed in Table I were all prepared by the following general method. Technical *t*-butyl alcohol was dried over calcium sulfate and then refluxed over sodium and distilled. To 300 ml. of dried *t*-butyl alcohol was added 0.1 g.-atom of potassium. After the potassium had dissolved completely, the solution was heated to ~50° and 0.08 mole of  $\beta$ -ketoamine added. The solution was stirred for 15 min. and then allowed to cool to room temperature. Approximately 0.06 mole of tetraethylammonium tetrabromonickelate(II)<sup>15</sup> was added to the solution; the mixture was stirred vigorously at room temperature for several hours and then filtered to yield the crude product as an olive-green solid. This material was extracted with hot *n*-heptane, the dark green solution filtered, and the product induced to crystallize by volume reduction and cooling. In those cases in which the product was somewhat soluble in *t*-butyl alcohol, the filtrate was evaporated *in vacuo* to yield a green oil which was extracted with hot *n*-heptane and combined with the extract of the solid residue. One or two further recrystallizations from *n*-heptane produced analytically pure complexes which were isolated as dark green or olive-green crystals. Exceptions to this general procedure and to the color of the final products are given in footnotes to Table I. Yields of purified complexes ranged from 10 to 70%. The bis( $\beta$ -ketoamino)nickel(II) complexes

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are usually readily soluble in most nonpolar solvents. They are, however, slowly decomposed in solution by small amounts of water or acids. For this reason optimum yields were obtained when atmospheric moisture was excluded and rigorously dry solvents were employed. For a given R group in 2, stability to hydrolytic decomposition appears from qualitative observation to increase in the order R<sub>γ</sub> = C<sub>6</sub>H<sub>5</sub> > CH<sub>3</sub>, while for a given R<sub>γ</sub> group this order appears to be R = aryl > *sec*-alkyl > *n*-alkyl. Because of the solution instability of the *n*-alkyl compounds, certain measurements in solution had to be performed under scrupulously dry conditions as described below.

*Bis(3-ethylamino-1-phenyl-but-2-en-1-ono)palladium(II)*. This complex was prepared by the preceding method and recrystallized from *n*-heptane to yield yellow crystals, m.p. 213°.

*Anal.* Calcd. for C<sub>24</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>Pd: C, 59.69; H, 5.84; N, 5.80. Found: C, 59.45; H, 5.68; N, 5.62.

*Bis(4-aminopent-3-en-2-ono)nickel(II)* was prepared as previously described,<sup>16</sup> m.p. 247–248°; lit.<sup>16</sup> m.p. 247–248°.

*Bis(N-2,6-dimethylphenyl-4-aminopent-3-en-2-ono)nickel(II)* was obtained by the above procedure, m.p. 223–224°. Previous synthesis<sup>16</sup> by a ligand-exchange reaction yielded a product with m.p. 219–220°.

**Magnetic Susceptibility Measurements.** Measurements on solids and solutions were made by the Gouy method using standard nickel chloride solution and distilled water as the calibrants, respectively. Solutions were freshly prepared before measurement. Reproducible results on solutions of complexes with R = *n*-alkyl and with R<sub>α</sub> = R<sub>γ</sub> = CH<sub>3</sub>, R = C<sub>6</sub>H<sub>11</sub> could not be obtained using solutions prepared in the

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**Table II.** Magnetic Moments in Solid and Solution Phases<sup>a</sup>

R <sub>γ</sub>	R <sub>α</sub>	R	Solid		Solution	
			μ <sub>eff</sub> , B.M. <sup>b</sup>		Solvent	μ <sub>eff</sub> , B.M.
CH <sub>3</sub>	CH <sub>3</sub>	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	3.37		CCl <sub>4</sub>	3.36 ± 0.05
CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>11</sub>	3.35		CHCl <sub>3</sub>	3.28 ± 0.05
CH <sub>3</sub>	CH <sub>3</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	Dia. <sup>c</sup>		CHCl <sub>3</sub>	1.23 ± 0.22
CH <sub>3</sub>	CH <sub>3</sub>	β-C <sub>10</sub> H <sub>7</sub>	Dia. <sup>c</sup>		CHCl <sub>3</sub>	1.07 ± 0.43
CH <sub>3</sub>	H	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	3.21		CCl <sub>4</sub>	2.48 ± 0.06
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	Dia. (green) <sup>c</sup>		CHCl <sub>3</sub>	1.83 ± 0.13
			3.18 (brown)			
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	Dia. <sup>c</sup>		CHCl <sub>3</sub>	1.58 ± 0.14
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	3.35		CS <sub>2</sub>	3.33 ± 0.05
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	~1.0		CHCl <sub>3</sub>	2.67 ± 0.06
					CH <sub>2</sub> Cl <sub>2</sub>	2.82 ± 0.06
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	Dia. <sup>c</sup>		CCl <sub>4</sub>	1.40 ± 0.18
					C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	1.57 ± 0.14
					CHCl <sub>3</sub>	1.65 ± 0.14
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	3.34		CS <sub>2</sub>	3.32 ± 0.05
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>11</sub>	3.28		CS <sub>2</sub>	3.26 ± 0.05
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	3.19		CHCl <sub>3</sub>	3.18 ± 0.05

<sup>a</sup> All values obtained at ambient room temperature (20–26°) and corrected for diamagnetism. <sup>b</sup> Estimated error ± 1% except for μ<sub>eff</sub> ~ 1.0 B.M. <sup>c</sup> Accurate susceptibility not measured.

**Table III.** Optical Spectral Data<sup>a</sup>

R <sub>γ</sub>	R <sub>α</sub>	R	Medium <sup>b</sup>	λ <sub>max</sub> , cm. <sup>-1</sup> (ε <sub>molar</sub> )					
CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CCl <sub>4</sub>	20,200 (60)	17,100 (50)				
CH <sub>3</sub>	CH <sub>3</sub>	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	CCl <sub>4</sub>	19,200 (14)	16,800 (20)	14,800 (11)	11,000 (<1)	6060 (19)	
CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>11</sub>	CCl <sub>4</sub>	19,200 (16)	16,800 (20)	14,800 (7)	11,000 (<1)	6060 (18)	
CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	CHCl <sub>3</sub>	20,800 (58)	16,450 (44)				<sup>c</sup>
CH <sub>3</sub>	CH <sub>3</sub>	<i>o</i> -C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	CHCl <sub>3</sub>	20,500 (60)	16,450 (49)				
CH <sub>3</sub>	CH <sub>3</sub>	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	CHCl <sub>3</sub>	20,400 (42)	16,550 (46)		10,800 (<1)	6350 (4.5)	
CH <sub>3</sub>	CH <sub>3</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	CHCl <sub>3</sub>	20,400 (37)	16,550 (45)		10,800 (<1)	6350 (4.5)	
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	Toluene		17,100 (20)		11,000 (<1)	6660 (8)	
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> (green)	Mull	<sup>d</sup>	16,200				
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> (brown)	Mull		17,100	14,800	10,900	6550	
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	CS <sub>2</sub>	<sup>d</sup>	16,800 (20)	14,500 (10)	10,900 (<1)	6060 (20)	
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	CS <sub>2</sub>	<sup>d</sup>	17,250 (26)		10,900 (<1)	6350 (15)	
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	CS <sub>2</sub>		16,700 (18)	14,800 (9)	10,900 (<1)	6060 (20)	
			Mull	<sup>d</sup>	16,500	14,800	10,900	6450	
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>11</sub>	CS <sub>2</sub>	<sup>d</sup>	16,700 (15)	14,800 (7)	10,900 (<1)	6060 (18)	
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	CHCl <sub>3</sub>		16,100 (19)		9750 (20)		
			Mull	<sup>d</sup>	16,400		10,000		

<sup>a</sup> All data obtained at room temperature. <sup>b</sup> Mull spectra taken in Kaydol. <sup>c</sup> Weak broad band at 6000–7000 cm.<sup>-1</sup>. <sup>d</sup> Ligand-field band obscured by more intense absorptions in this region.

air from reagent quality solvents; such solutions slowly deposited light green solids during measurement. Reproducible results were obtained by first drying the solvents employed (*cf.* Table II) over phosphorus pentoxide (CCl<sub>4</sub>, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>) or sodium (toluene) followed by distillation under dry nitrogen using a 60-cm. column packed with glass helices. A small central cut of distillate (~10 ml.) was admitted to a previously evacuated and flamed-out Gouy sample tube containing the requisite amount of dried complex. The tube was then sealed *in vacuo*. Solutions prepared *in situ* by this method showed no evident decomposition over periods of several days.

**Proton Resonance Measurements.** Proton chemical shifts were measured as previously described<sup>3</sup> using tetramethylsilane as an internal reference in order to eliminate bulk susceptibility corrections. Proton contact shifts were measured relative to the free ligand in the same solvent and calculated from the relation Δ*f*<sub>i</sub> = Δ*f*<sub>i</sub>(complex) - Δ*f*<sub>i</sub>(ligand). Chemical shifts were found to be unaffected by traces of water in the solution and the age of the solution and were completely reversible with temperature. No significant

dependence on concentration was detected in those cases checked.

**Molecular Weight Measurements.** Owing to slow decomposition of a number of the complexes except under rigorously dry conditions, attempts to obtain reliable molecular weights by an osmometric method were usually unsatisfactory. Evidence bearing on the question of molecular association of the complexes is discussed in the text.

**Spectral Measurements.** The data shown in Table III were obtained using a Cary Model 14 recording spectrophotometer. The tabulated extinction coefficients are approximate because of estimated corrections of overlapping bands. The intensities of the near-infrared bands were corrected for the absorbance of a weak vibrational overtone at ~5900 cm.<sup>-1</sup>.

## Results and Discussion

In this investigation bis(β-ketoamino)nickel(II) complexes of the general structural type **2** have been studied. These may be divided into two principal groups containing complexes with R<sub>α</sub> = R<sub>γ</sub> = CH<sub>3</sub> and R<sub>α</sub> =

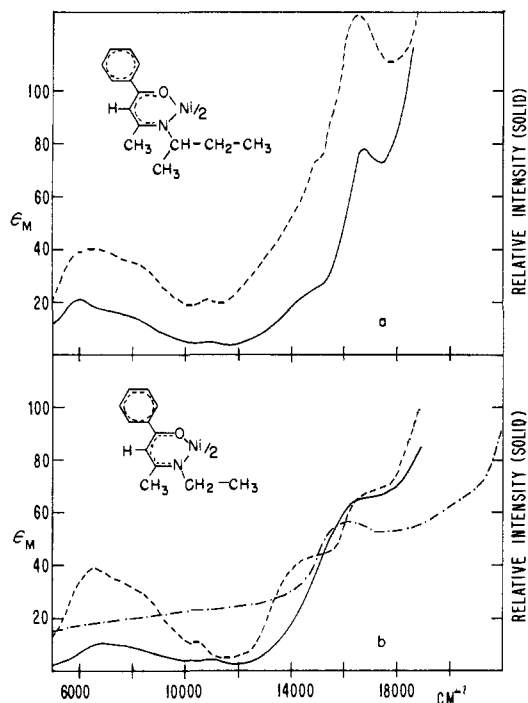


Figure 1. (a) Ligand-field spectra of bis(1-phenyl-3-*sec*-butylamino-but-2-en-1-ono)nickel(II) (B-*s*-Bu): -----, solid; ———, 0.0137 *M* solution in carbon disulfide. (b) Ligand-field spectra of bis(1-phenyl-3-ethylamino-but-2-en-1-ono)nickel(II) (B-Et): -----, solid (green form); -----, solid (brown form); ———, 0.020 *M* solution in dry toluene.

$\text{CH}_3$ ,  $R_\gamma = \text{C}_6\text{H}_5$ . Those of the first group are derived from the parent  $\beta$ -diketone acetylacetone while those of the second group are derived from benzoylacetone. Members of these two groups are designated hereafter as A-R and B-R, respectively, in which R is the nitrogen substituent, rather than by the cumbersome systematic nomenclature.

**Synthetic Method.** The existence and considerable stability of metal complexes, including those of Ni(II), derived from tetradentate ligands prepared by condensation of  $\beta$ -diketones and primary diamines have long been recognized.<sup>17</sup> However, only a relatively small number of bis complexes obtained from  $\alpha,\beta$ -unsaturated  $\beta$ -ketoamines have been reported and are principally those of Cu(II).<sup>16, 18, 19</sup> These complexes have been prepared from the metal salt and ligand in aqueous solution in the presence of strong base,<sup>18</sup> or by ligand-exchange reactions.<sup>16, 19</sup> Of the bis( $\beta$ -ketoamino)nickel(II) complexes prepared prior to this work, only A-H has been obtained by reaction in solution.<sup>16, 20</sup> Of the remaining complexes, *viz.*, A- $\text{C}_6\text{H}_5$ , A-2,6- $\text{C}_6\text{H}_3(\text{CH}_3)_2$ , B- $\text{C}_6\text{H}_5$ , and that with  $R_\alpha = R_\gamma = R = \text{C}_6\text{H}_5$ , the last three have been prepared

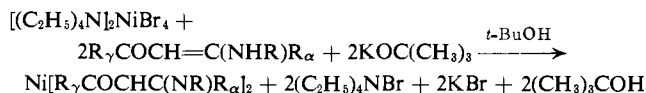
(17) A. Combes and C. Combes, *Bull. soc. chim. France*, [3] 7, 778 (1892); G. T. Morgan and J. D. Main-Smith, *J. Chem. Soc.*, 912 (1926); P. J. McCarthy, R. J. Hovey, K. Ueno, and A. E. Martell, *J. Am. Chem. Soc.*, 77, 5820 (1955); M. Honda and G. Schwarzenbach, *Helv. Chim. Acta*, 40, 27 (1957); A. E. Martell, R. L. Belford, and M. Calvin, *J. Inorg. Nucl. Chem.*, 5, 170 (1958); R. J. Hovey, J. J. O'Connell, and A. E. Martell, *J. Am. Chem. Soc.*, 81, 3189 (1959).

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(19) D. F. Martin, *Advances in Chemistry Series*, No. 37, American Chemical Society, Washington, D. C., 1963, p. 192; A. W. Struss and D. F. Martin, *J. Inorg. Nucl. Chem.*, 25, 1409 (1963).

(20) R. D. Archer, *Inorg. Chem.*, 2, 292 (1963).

by ligand-exchange reactions with A-H.<sup>16</sup> Neither of these procedures appears to be of general utility. In particular, attempted synthesis of complexes with  $R = \text{alkyl}$  in aqueous or aqueous alcohol solutions usually produced bis(acetylacetonato)nickel(II) hydrate as the principal product owing to the hydrolytic instability of the  $\beta$ -ketoamine complexes. The following reaction carried out under anhydrous conditions affords a rather general synthetic route to bis( $\beta$ -ketoamino)nickel(II) complexes. Use of the complex



nickel salt offers a convenient method of introducing the metal in an anhydrous and reactive form. A strong base such as *t*-butoxide is required to remove the weakly acidic proton of the ligand which, it should be noted, has been proven to exist in general as the ketoamine rather than the enol-imine tautomer.<sup>11, 21</sup> This method, or variations thereof, appears to be generally useful in preparing hydrolytically unstable complexes derived from weakly acidic ligands and has been successfully applied to the synthesis of bis- and tris(pyrrole-2-aldimino) complexes<sup>22</sup> and tris( $\beta$ -ketoamino)chromium(III) complexes.<sup>23</sup> The present scope of the method is indicated by the variety of complexes prepared; these are set out in Table I.

**Existence of the Tetrahedral Configuration.** Prior to a consideration of the proton resonance results, it is first necessary to establish the existence of the tetrahedral or pseudo-tetrahedral form in the solid and solution phases. This may be done by reference to the representative magnetic and spectral data in Tables II and III. It is noted that all complexes with  $R = \alpha$ -branched-chain alkyl (except B- $\text{C}_3\text{H}_7$ ) are paramagnetic in the solid with magnetic moments in the range 3.21–3.37 B.M., which is that found for solid tetrahedral bis(salicylaldimino)nickel(II) complexes.<sup>2, 5, 6</sup> However, certain polymerized quasi-octahedral<sup>5c</sup> salicylaldimine complexes also have moments in the solid in this range.<sup>24</sup> Strong evidence for the tetrahedral structure can be obtained from the ligand-field spectra. For those paramagnetic complexes which have essentially the same magnetic moments in the solid and in solution, the spectra in these two phases are the same, as is shown for a typical case in Figure 1a. These spectra bear a strong resemblance to those of a group of fully paramagnetic branched chain salicylaldimine complexes, one member of which has been shown by an X-ray determination<sup>25</sup> to have a pseudo-tetrahedral structure. The spectra consist of a very broad feature with maxima in the range 6000–6700  $\text{cm}^{-1}$  ( $\nu_2$ ), a very weak band at  $\sim 11,000 \text{ cm}^{-1}$ , and two or three discernible bands at 14,500–19,200  $\text{cm}^{-1}$  ( $\nu_3$ ). The spectra are also similar to those of the tetrahedral tetrahalonickel(II) species<sup>26a</sup> and, as in the

(21) G. O. Dudek and E. P. Dudek, *J. Am. Chem. Soc.*, 86, 4283 (1964).

(22) A. Chakravorty and R. H. Holm, *Inorg. Chem.*, 3, 1521 (1964); R. H. Holm, A. Chakravorty, and L. J. Theriot, to be published.

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(26) (a) G. P. Smith, C. H. Liu, and T. R. Griffiths, *J. Am. Chem. Soc.*, 86, 4796 (1964), and references cited therein. (b) It should be noted that

case of the salicylaldimine complexes, the following assignments in idealized tetrahedral symmetry appear reasonable<sup>26b</sup>:  ${}^3T_1 \rightarrow {}^3A_2(\nu_2) \rightarrow {}^3T_1(P)(\nu_3) \rightarrow {}^1D$  ( $\sim 11,000 \text{ cm.}^{-1}$ ). A convincing dissimilarity is observed between these spectra and those of polymerized salicylaldimine complexes.<sup>5e,24</sup> In the salicylaldimine series complex **1** ( $R = \text{CH}_3\text{CHCH}_2\text{OCH}_3$ ) has been shown<sup>27</sup> to have the *trans*-octahedral structure and to have spectral properties extremely similar to the polymeric quasi-octahedral salicylaldimine complexes. The complex  $\text{B-CH}_3\text{CHCH}_2\text{OCH}_3$  is assigned this same structure and its spectrum, with the following assignments, is unrelated to those of the remaining fully paramagnetic complexes:  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  ( $16,100 \text{ cm.}^{-1}$ ),  $\rightarrow {}^3T_{2g}$  ( $9750 \text{ cm.}^{-1}$ ).

Further evidence for the lack of molecular association in solution has been obtained from a Beer's law study of *A-i-Pr* in  $\text{CCl}_4$  solution at room temperature. In the concentration range  $0.0057\text{--}0.200 \text{ M}$  an excellent Beer's law dependence was observed for the absorbances at  $6060, 11,000, 16,800,$  and  $19,200 \text{ cm.}^{-1}$ .

Fully paramagnetic or diamagnetic complexes which in solution have moments much less than  $3.2\text{--}3.3 \text{ B.M.}$  also exhibit spectral features indicative of tetrahedral species; some representative data are given in Table III. The intensities of  $\nu_2$  are reduced compared to the fully paramagnetic complexes (*cf.* Figures 1a and b). In addition, features at  $\sim 16,500\text{--}17,100 \text{ cm.}^{-1}$  and  $20,400\text{--}20,800 \text{ cm.}^{-1}$  are evident. These are assigned to the singlet-singlet transitions of the planar form. The intensity of the lower energy feature is augmented by partial overlap with  $\nu_3$  of the tetrahedral form. A similar pattern of singlet-singlet absorptions has also been observed in planar bis(salicylaldimino)nickel(II) complexes<sup>28</sup> and in *A-H*.<sup>20</sup>

It is concluded that the spectral and magnetic susceptibility results are consistent with the existence of planar or tetrahedral forms in the solid and either or both of these forms in solution. Associated paramagnetic species could not be detected by spectral measurements. However, in a few cases such species have been detected by the more sensitive proton resonance technique (*vide infra*). In no case do they make a substantial contribution to the solution composition.

**Structural Interconversion in the Solid Phase.** As the spectral, magnetic, and proton resonance results (*vide infra*) demonstrate, a planar  $\rightleftharpoons$  tetrahedral equilibrium exists for a number of bis( $\beta$ -ketoamino)nickel(II) complexes in solution. In one case it has been possible to effect the planar  $\rightarrow$  tetrahedral structural conversion in the solid phase. When prepared by the general synthetic method followed by recrystallization from *n*-heptane, *B-Et* is obtained as a crystalline green diamagnetic solid. Heating this form at  $100^\circ$  *in vacuo* for 0.5 hr. results in the formation of a brown crystalline paramagnetic ( $3.18 \text{ B.M.}$ ) form with the

these spectra exhibit certain features not readily accounted for at present. The origin of the broad shoulder on the high energy side of  $\nu_2$  in these and related bis-chelate tetrahedral nickel(II) complexes<sup>2,5,6</sup> is obscure. Likewise, the splitting of components of  ${}^3T_1(P)$  in  $\nu_3$  is  $\sim 4400 \text{ cm.}^{-1}$  in the *A-R* series; in  $\text{NiX}_4^{2-}$  this splitting is  $\leq 2500 \text{ cm.}^{-1}$ . The origin of this relatively large splitting is unknown. A possible cause is a pronounced pseudo- $C_{2v}$  component to the ligand field.

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

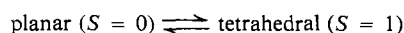
(28) G. Maki, *J. Chem. Phys.*, **29**, 1129 (1958).

same elemental composition (*cf.* Table I). The ligand-field spectra in Figure 1b show that the green form is planar whereas the brown form is tetrahedral. Spectral, magnetic, and proton resonance properties of solutions prepared from either form are identical. The moment of the brown form is  $0.1\text{--}0.2 \text{ B.M.}$  less than those for other solid tetrahedral complexes, but it could not be increased by heating for an additional 5 hr. The small moment of solid  $\text{B-C}_3\text{H}_5$  may also be due to some tetrahedral form, but because of decomposition it was not possible to effect any structural conversion by heating the solid. These results indicate that, as in solution, the energy difference between stereoisomers in the solid may not be large. This has been demonstrated for certain planar bis(salicylaldimino)nickel(II) complexes which may be forced into the tetrahedral form by cocrystallization with the analogous zinc complexes.<sup>29</sup> Structural conversion of solid Ni(II) complexes has been observed in only one other case,  $\text{NiBr}_2(\text{PEtPh}_2)_2$ , the planar form of which may be converted to the tetrahedral form on heating or standing.<sup>30</sup>

**Proton Resonance Results.** Bis( $\beta$ -ketoamino)nickel(II) complexes exhibit large proton resonance contact shifts in their tetrahedral configurations, as have been found for the Ni(II) complexes of aminotroponeimines,<sup>7,9</sup> salicylaldimines,<sup>3,4,8</sup> naphthalaldimines,<sup>6</sup> and for  $\text{Ni}(\text{PPh}_3)_2\text{X}_2$ .<sup>31</sup> The spectrum of a representative complex, *A-i-Pr*, is shown in Figure 2. Shifts of substituents at the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -positions of the chelate rings are of primary concern. Contact shifts and coupling constants are collected in Table IV. For the fully paramagnetic species the coupling constants were obtained from the measured contact shifts using the relation<sup>9,32</sup>

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

in which  $\Delta f_i$  is the observed contact shift of the *i*th proton in c.p.s., *f* the spectrometer frequency,  $a_i$  the electron nuclear coupling constant in gauss for the *i*th proton, and  $\gamma_e$  and  $\gamma_H$  the gyromagnetic ratios of the electron and proton, respectively. The *g*-value of the triplet *S*-state was obtained from the magnetic moment of the solid. For those cases in which the rapid configurational equilibrium



occurs and lies sufficiently to the left that the contact shifts do not possess a Curie behavior, these shifts are dependent on the free energy of the structural change and are given by<sup>9</sup>

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

Values of  $\Delta F$  used to calculate coupling constants in the *B-R* series were obtained from the measured magnetic moments  $\mu_{\text{eff}}$  in the same solvent using eq. 3 where

(29) A. Chakravorty, *Inorg. Chem.*, **4**, 127 (1965).

(30) R. G. Hayter and F. S. Humiec, *J. Am. Chem. Soc.*, **84**, 2004 (1962).

(31) (a) G. N. LaMar, W. D. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, **41**, 2126 (1964); (b) E. A. LaLancette and D. R. Eaton, *J. Am. Chem. Soc.*, **86**, 5145 (1964).

(32) H. M. McConnell and C. H. Holm, *J. Chem. Phys.*, **27**, 314 (1957).

**Table IV.** Contact Shifts<sup>a</sup> and Coupling Constants

R <sub>γ</sub>	R <sub>α</sub>	R	Position	Solvent	Δf <sub>i</sub> , c.p.s.	a <sub>i</sub> , gauss	ρ <sub>β</sub>
CH <sub>3</sub>	CH <sub>3</sub>	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	α	CCl <sub>4</sub>	2135	-0.301 ± 0.019	0.0366
			β		5838	-0.823 ± 0.053	
			γ		1456	-0.205 ± 0.013	
CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>11</sub>	α	CDCl <sub>3</sub>	1873	-0.281 ± 0.017	0.0368
			β		5509	-0.827 ± 0.050	
			γ		1235	-0.185 ± 0.011	
CH <sub>3</sub>	H	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	α	CCl <sub>4</sub>	-7464	1.84 ± 0.016	0.0388
			β		3533	-0.872 ± 0.073	
			γ		1051	-0.259 ± 0.022	
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	α	CDCl <sub>3</sub>	681	-0.326 ± 0.059	0.0353
			β		1660	-0.795 ± 0.140	
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	α	CDCl <sub>3</sub>	507	-0.330 ± 0.070	0.0355
			β		1225	-0.798 ± 0.170	
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	α	CS <sub>2</sub>	2243	-0.318 ± 0.020	0.0384
			β		6093	-0.865 ± 0.055	
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>3</sub> H <sub>5</sub>	α	CDCl <sub>3</sub>	1497	-0.337 ± 0.027	0.0401
			β		4013	-0.903 ± 0.072	
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	α	CH <sub>2</sub> Cl <sub>2</sub>	1678	-0.339 ± 0.026	0.0415
			β		4630	-0.934 ± 0.072	
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	α	CCl <sub>4</sub>	380	-0.311 ± 0.093	0.0332
			β		913	-0.748 ± 0.220	
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	α	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	468	-0.305 ± 0.064	0.0325
			β		1125	-0.732 ± 0.150	
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	α	CDCl <sub>3</sub>	586	-0.345 ± 0.072	0.0372
			β		1421	-0.838 ± 0.180	
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	α	CS <sub>2</sub>	2199	-0.312 ± 0.020	0.0379
			β		2223	-0.316 ± 0.020	
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>11</sub>	α	CS <sub>2</sub>	5988	-0.850 ± 0.055	0.0385
			β		6008	-0.853 ± 0.055	
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>11</sub>	α	CS <sub>2</sub>	2170	-0.313 ± 0.020	0.0385
			β		6003	-0.867 ± 0.055	
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	α	CDCl <sub>3</sub>	820	-0.123 ± 0.011	0.0385
			β		1231	-0.184 ± 0.016	

<sup>a</sup> All data refer to room temperature; contact shifts measured at 60 Mc./sec.

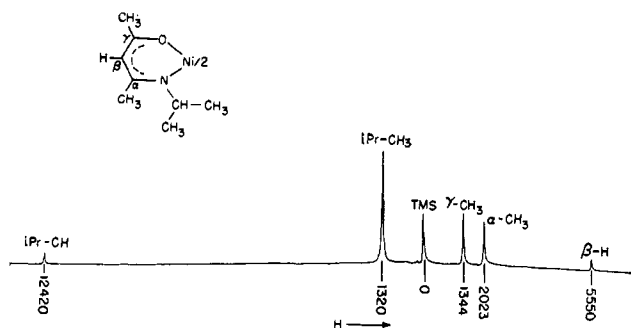


Figure 2. Proton resonance spectrum of bis(4-isopropylamino-3-en-2-ono)nickel(II) (A-*i*-Pr) in CDCl<sub>3</sub> solution at 25°. Frequencies are the chemical shifts.

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

$\mu_{\infty} = g\sqrt{2}$ . The contact shifts and coupling constants obtained are set out in Table IV. The main source of experimental error in the  $a_i$  quantities obtained from eq. 1 and 2 is the error in magnetic moment measurements (*cf.* Table II).

All complexes show a consistent pattern of shifts in which  $\alpha$ - and  $\gamma$ -CH<sub>3</sub> and  $\beta$ -H are shifted upfield; R-alkyl groups are shifted downfield. Assignment of the two methyl signals in the A-R series follows from substitution of  $\gamma$ -CH<sub>3</sub> by phenyl.<sup>33</sup> The more

(33) Nuclear resonance studies<sup>21</sup> have demonstrated that condensation of benzoylacetone and primary amines occurs at the acetyl ( $\alpha$ ) rather than the benzoyl ( $\gamma$ ) carbon. Preliminary X-ray results have been re-

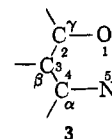
upfield methyl signal persists in the B-R series and is due to  $\alpha$ -CH<sub>3</sub>. The coupling constants at the  $\alpha$ -position in these two series are quite similar, thus strengthening the assignment.

*Delocalization of Spin.* There appears little doubt that in these and similar complexes<sup>3, 4, 6-9, 31</sup> spin is predominantly placed on the ligand system as a result of  $\pi$ -bonding with the nickel ion.<sup>3, 7</sup> It is, however, necessary to determine whether the spin imbalance in the ligand  $\pi$ -system occurs principally in (a) the lowest unfilled  $\pi$ -MO ( $\psi_1$ ) as a result of net spin transfer from nickel to the ligand, or in (b) the highest filled  $\pi$ -MO ( $\psi_3$ ) as a result of net spin transfer from the ligand to nickel. A simple Hückel calculation of spin densities suffices to distinguish between these possibilities. Using  $\beta_{\text{CO}} = 1.5\beta$ ,  $\beta_{\text{CN}} = 1.2\beta$ ,  $\alpha_{\text{O}} = \alpha + 1.5\beta$ , and  $\alpha_{\text{N}} = \alpha + \beta$ , the following MO's are obtained.

$$\psi_3(0.580\beta) = -0.384\phi_1 + 0.235\phi_2 + 0.713\phi_3 + 0.178\phi_4 - 0.508\phi_5$$

$$\psi_4(-0.860\beta) = 0.363\phi_1 - 0.571\phi_2 + 0.053\phi_3 + 0.617\phi_4 - 0.398\phi_5$$

The orbitals are numbered as shown in 3. The spin



ported for Ni(II) and Cu(II) complexes said to be derived from 3-amino-1-phenyl-2-buten-1-one (G. E. Gurr, *Inorg. Chem.*, **3**, 614 (1964)), indicating R<sub>α</sub> = CH<sub>3</sub> and R<sub>γ</sub> = C<sub>6</sub>H<sub>5</sub>.

**Table V.** Comparison of Calculated and Observed Spin Densities

Ligand $\pi$ -electron configuration	Method		$\rho_\alpha$	$\rho_\beta$	$\rho_\gamma$
$\psi_1^2 \psi_2^2 \psi_3^2 \psi_4^1$	HMO	Calcd.	+0.381	+0.003	+0.326
$\psi_1^2 \psi_2^2 \psi_3^1$	HMO	Calcd.	+0.032	+0.508	+0.055
	VB <sup>a</sup>	Calcd.	-0.2824	+0.6972	-0.2489
A- <i>i</i> -Pr ( $Q_{\alpha,\gamma} = +27$ , $Q_\beta = -22.5$ )		Obsd.	-0.0111	+0.0366	-0.00759
$\rho_{\text{calcd}}/\rho_{\text{obsd}}$			25.4	19.0	32.8
A- <i>i</i> -Pr ( $Q_\alpha = +20.3$ , $Q_\gamma = +15.6$ , $Q_\beta = -22.5$ )		Obsd.	-0.0148	+0.0366	-0.0131
$\rho_{\text{calcd}}/\rho_{\text{obsd}}$			19.0	19.0	19.0

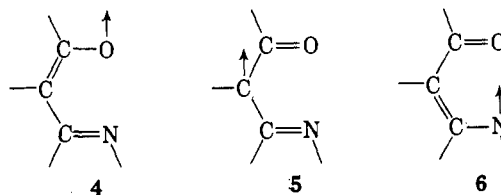
<sup>a</sup>  $\rho_o = +0.3745$ ,  $\rho_N = +0.4614$ .

densities calculated from these functions are given in Table V and are compared with the spin densities observed for one typical fully paramagnetic complex, A-*i*-Pr. The observed spin densities are obtained from the measured coupling constants in Table IV using the relation  $a_i = Q\rho_{Ci}$ . It is clear that placement of the odd spin in the lowest empty ligand MO,  $\psi_4$ , predicts the wrong pattern of spin density distribution, *viz.*,  $\rho_{\alpha,\gamma} \gg \rho_\beta$ . Indeed,  $\rho_\beta$  is essentially zero, and in a MO model including electron correlation<sup>34</sup> would become negative, contrary to observation. Existence of the odd spin in  $\psi_3$ , however, is in much better agreement with experiment. A large positive spin density is predicted for  $\rho_\beta$  whereas  $\rho_\alpha$  and  $\rho_\gamma$  are much smaller. Although it is obvious that no great reliance can be placed on Hückel spin densities, which of necessity must be positive, the above comparison is believed of reliable predictive value and provides fairly good evidence that in the  $\beta$ -ketoamines, as in the aminotroponeiminates and salicylaldimines, the odd spin in the complex is delocalized in the lowest filled MO of the ligand anion. It is noted that this is not always the case for in several nickel(II) pyromethenes the observed spin densities have been successfully interpreted assuming spin delocalization in the lowest empty ligand  $\pi$ -MO.<sup>35</sup>

Further evidence for spin delocalization in  $\psi_3$  derives from the observed identity of coupling constants and, hence, spin densities in the two chelate rings of a given complex. For reasons previously given,<sup>4</sup> this observation strongly suggests that the nickel has the  $(xz)^1(yz)^1$  configuration in the pseudo- $C_{2v}$  symmetry of the tetrahedral form.  $\psi_3$  has  $\pi$ -symmetry with respect to these metal orbitals, thereby allowing symmetric spin density distribution over both rings.

The existence of the net spin in the lowest filled  $\pi$ -MO of this odd-alternant ligand system permits a valence bond calculation of spin densities. It is noted that such calculations have had exceptional success in reproducing observed spin densities in the aminotroponeiminates when scaled down by a constant factor.<sup>9</sup> The ground-state wave function was taken as a combination of the following bond eigenfunctions **4**, **5**, and **6** in which one full spin is present on the ligand. Exchange integrals except those between contiguous atoms were neglected and the values  $\gamma_{12} = 1.4\gamma^3$ ,  $\gamma_{4,5} = 1.2\gamma^9$ , and  $\gamma_{23} = \gamma_{34} = \gamma$  used. Eigenvectors and eigenvalues were evaluated by standard proce-

dures<sup>36</sup> and the ground-state energy  $E = Q + 2.669\alpha$  obtained. The calculated spin densities, which are not too sensitive to the relations between exchange



integrals, are given in Table V and compared with experiment. The quality of agreement between experiment and theory is seriously dependent on  $Q_{CCH_3}$  at the  $\alpha$ - and  $\gamma$ -positions, a quantity which is variable in value<sup>3,9,31a,37</sup> (usually between 5 and 30 gauss) but always positive.  $Q_{CH}$  is, however, much less variable<sup>38</sup>; a value of -22.5 gauss has been used to obtain  $\rho_\beta$ . When  $Q_{CCH_3} = 27$  gauss<sup>39</sup> is employed, the ratios of calculated and observed spin densities are in tolerable agreement for calculations at this level of approximation. The agreement may in fact be somewhat better, for if it is assumed that  $\rho_\beta$  obtained from experiment is correct (*i.e.*, all of the spin in the  $\beta$ -position is in the  $\rho\pi$  orbital), then reasonable values of  $Q_{CCH_3}$  at the  $\alpha$ - and  $\gamma$ -positions bring the calculated and observed ratios of  $\rho_\alpha$  and  $\rho_\gamma$  into agreement with the corresponding ratio of  $\rho_\beta$ , as is shown in Table V. Because of the uncertainty in  $Q_{CCH_3}$  values, coupling constants rather than spin densities are given in Table IV. Experimental spin densities have been calculated only for the  $\beta$ -position.

It is estimated that the spin imbalance on each ligand amounts to  $\sim 1/20$  of a full spin. The  $\beta$ -ketoamino group is then apparently more strongly  $\pi$ -bonding to tetrahedral Ni(II) by a factor of  $\sim 3/2$  than is a salicylaldimino group<sup>3</sup> but less strongly  $\pi$ -bonding by  $\sim 1/2$  than is an aminotroponeimino group, these factors referring to the relative fractions of spin lost to the nickel. Whether or not an  $N_4$  donor atom set is intrinsically capable of greater  $\pi$ -bonding to Ni(II) than is an  $O_2N_2$  set is currently being investigated in these laboratories.

*Contributions to Contact Shifts.* The preceding con-

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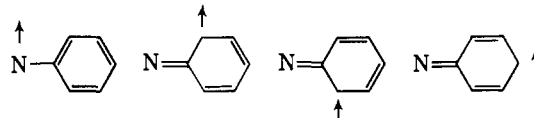
siderations are based on  $\pi$ -delocalization of spin density and the attendant validity of the relation  $a_i = Q\rho_{Ci}$ . Contributions to the isotropic contact shifts other than from  $\pi$ - $\sigma$  spin polarization are considered briefly at this point.

(1) *Pseudo-Contact Interactions.*<sup>40</sup> These interactions, which constitute another isotropic shift mechanism, are generally considered to be of negligible effect in tetrahedral Ni(II) complexes due to the near cubic symmetry of the  $g$ -tensor. In chelated Ni-O<sub>2</sub>N<sub>2</sub> complexes the pseudo-symmetry of the ligand field is only C<sub>2v</sub>, requiring rhombic symmetry of  $g$ .<sup>31a</sup> If, however, the  $(xz)^1(yz)^1$  configuration (<sup>3</sup>A<sub>2</sub> ground state) is correct, these complexes possess effective axial symmetry. Using the expression for the pseudo-contact shifts appropriate to axial symmetry,<sup>40</sup> it is found that only ~13% of the observed absolute shift of  $\beta$ -H in A-*i*-Pr, for example, could be due to pseudo-contact effects if  $|g_{||} - g_{\perp}|$  were as large as 1. Inasmuch as principal  $g$ -values are unknown for any tetrahedral Ni(II) complex, a more meaningful estimate of pseudo-contact contributions cannot be made. The assumption of  $|\Delta g^1| = 1$  appears too large for the <sup>3</sup>A<sub>2</sub> ground state; it is concluded that pseudo-contact contributions to the total contact shifts may be neglected. In this connection it is noted that the observed shifts in Ni(PPh<sub>3</sub>)<sub>2</sub>X<sub>2</sub> complexes, which clearly have a pronounced C<sub>2v</sub> component to the ligand-field symmetry, have been successfully interpreted assuming negligible pseudo-contact effects.<sup>31a</sup>

(2)  *$\sigma$ -Transmission of Spin Density.* This effect operates *via* spin polarization in the  $\sigma$ -system, produces negative contact shifts, and attenuates rapidly from bond to bond.<sup>41</sup> There is some evidence for its existence in the chelate rings of the  $\beta$ -ketoamine complexes. Replacement of  $\alpha$ -CH<sub>3</sub> by H in A-*i*-Pr results in  $\Delta f_{\alpha-H} = -7464$  c.p.s. at 25°. The opposite signs of the proton and methyl shifts at this position are indicative of some  $\pi$ -spin density, but the proton shift is larger than expected. Assuming that  $\rho_{\alpha-C^{\pi}}$  is unchanged upon replacing CH<sub>3</sub> by H<sup>9</sup> and taking  $Q_{CCH_3} = +20$  and  $Q_{CH} = -22.5$  at this position (*cf.* Table V), the expected proton coupling constant is  $\sim 1/5$  of that observed. The enhancement of the negative contact shift is believed due to a  $\sigma$ -effect. The unique proton of the isopropyl group in this complex will be shifted strongly by  $\sigma$ -spin transmission and has a contact shift of  $-14,450$  c.p.s. This proton is separated from the metal by the same number of bonds as is  $\alpha$ -H, so that a substantial  $\sigma$ -contribution to the shift of  $\alpha$ -H is very likely. There is no strong evidence that  $\gamma$ -CH<sub>3</sub> shifts are affected by a  $\sigma$ -contribution. Attenuation effects would be expected to make  $\sigma$ -effects at  $\beta$ -H very small.

It is concluded that pseudo-contact interactions and  $\sigma$ -transmission of spin density are of minor importance in effecting contact shifts, which are dominated by  $\pi$ -delocalization of spin. Remaining evidence bearing on this point is summarized as follows: (i) observed spin densities alternate in sign as required by theory and do not attenuate as the distance from the metal increases; (ii) replacement of  $\beta$ -H by CH<sub>3</sub> in A-*i*-Pr

produces a negative contact shift for the methyl group<sup>42</sup>; (iii) shifts of aromatic protons in aryl groups of the A-aryl series alternate in sign, in agreement with the valence bond structures. In A-C<sub>6</sub>H<sub>5</sub> the relative spin



densities on the phenyl ring ( $\rho_o/\rho_p = 0.63$ ,  $\rho_m/\rho_p = -0.73$  at 80°) are in most satisfactory agreement with those recently cited<sup>31b</sup> for cases in which the spin is known to be in the  $\pi$ -system of the ligand.

*Complexes of the A-R Series.* All complexes prepared in this series exhibited contact shifts except A-H, which remained completely diamagnetic in chloroform solution up to 85°. The solid form is also diamagnetic.<sup>20</sup> Of the remaining complexes, all those with R = aryl are diamagnetic and become only weakly paramagnetic in solution, whereas the fully paramagnetic solids dissolved with essentially unchanged magnetic moments. Complexes with R = methyl and benzyl gave small contact shifts in carbon tetrachloride at room temperature,  $\Delta f_{\alpha-CH_3}$  being 47 and 35 c.p.s., respectively, and were not studied in detail. Complexes with R = aryl in general gave larger contact shifts whose temperature dependence was studied over the range  $-30$  to  $100^\circ$ .

The temperature dependences of the contact shifts of the R = aryl complexes differed to a degree such that the complexes can be divided in two groups. In both groups the contact shifts increased with temperature as predicted by eq. 2 for a positive  $\Delta F$  of the planar  $\rightarrow$  tetrahedral conversion. In one group (R = phenyl, *m*- and *p*-tolyl,  $\beta$ -naphthyl) the contact shifts increased more rapidly than in the other (R = *o*-tolyl, 2,6-dimethylphenyl,  $\alpha$ -naphthyl), and the calculated free energies displayed, over a limited temperature range, the linear dependence required by

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

Complexes of the latter group showed no linearity of calculated  $\Delta F$  with temperature over the range of measurement. Temperature dependencies of the contact shifts and free energies for several of the complexes are given in Figures 3 and 4. The coupling constants used in calculating  $\Delta F$  values were taken from A-*i*-Pr inasmuch as no A-aryl complex could be prepared having a sufficiently large solution magnetic moment to permit an independent accurate determination of  $a_i$  values. Thermodynamic data characterizing the structural change obtained from a least-mean-squares fit of  $\Delta F$  vs.  $T$  are given in Table VI. Because of instrumental limitations the temperature dependence of chemical shifts  $>+500$  c.p.s. could not be followed. Shifts of  $\alpha$ - and  $\gamma$ -CH<sub>3</sub>, but not those of  $\beta$ -H, could be followed up to  $100^\circ$  and were used for calculation of  $\Delta F$ . The values obtained from these separate shifts differ by about 6 or 7% and, for uniform comparison with the B-R series, the thermodynamic

(42) The complex A-*i*-Pr ( $\beta$ -CH<sub>3</sub>) could not be isolated in a pure condition; the spectrum was observed in the presence of unreacted ligand so that the sign but not the magnitude of the contact shifts could be determined. Several attempts to prepare the  $\beta$ -phenyl complex yielded none of the desired product.

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(41) J. A. Happe and R. L. Ward, *ibid.*, **38**, 1211 (1963).



Table VI. Thermodynamic Values for the Planar  $\rightarrow$  Tetrahedral Interconversion<sup>a</sup>

R <sub>γ</sub>	R <sub>α</sub>	R	Solvent	Temp. range, °K. <sup>b</sup>	ΔF <sup>323</sup> , cal./mole <sup>c</sup>	ΔH, cal./mole <sup>c</sup>	ΔS, e. u. <sup>c</sup>
CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	CDCl <sub>3</sub>	310–380	2010 ± 60	3550 ± 30	4.76 ± 0.12
CH <sub>3</sub>	CH <sub>3</sub>	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	CDCl <sub>3</sub>	310–380	1760 ± 60	3230 ± 30	4.55 ± 0.12
CH <sub>3</sub>	CH <sub>3</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	CDCl <sub>3</sub>	310–380	1810 ± 60	3320 ± 30	4.68 ± 0.12
CH <sub>3</sub>	CH <sub>3</sub>	β-C <sub>10</sub> H <sub>7</sub>	CDCl <sub>3</sub>	310–380	1810 ± 60	3170 ± 30	4.20 ± 0.12
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	CDCl <sub>3</sub>	230–280	1030 ± 110 <sup>d,e</sup>	2670 ± 10	5.10 ± 0.35
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	CDCl <sub>3</sub>	230–310	1260 ± 140 <sup>d</sup>	3050 ± 12	5.54 ± 0.40
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	CDCl <sub>3</sub>	230–300	1120 ± 130 <sup>d</sup>	3130 ± 10	6.21 ± 0.40
			CCl <sub>4</sub>	250–320	1460 ± 190 <sup>d</sup>	4060 ± 100	8.04 ± 0.30
			C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	230–310	1320 ± 130 <sup>d</sup>	3610 ± 10	7.10 ± 0.40

<sup>a</sup> All values obtained from contact shifts of α-CH<sub>3</sub>. <sup>b</sup> Range of observation in which ΔF is a linear function of temperature. <sup>c</sup> Larger errors in the B-R than in the A-R series are predominantly due to errors in coupling constants obtained from magnetic moments (cf. Table II); in A-R series coupling constants used in calculations are assumed to be the same as in A-*i*-Pr. (cf. Table IV). <sup>d</sup> Extrapolated values. <sup>e</sup> Value at 0.26 M; ΔF = 2690 - 5.17T (0.16 M), 2570 - 4.74T (0.082 M).

values obtained from the Δf<sub>α-CH<sub>3</sub></sub> temperature dependence are presented in Table VI.

The deviation from a linear temperature dependence of ΔF values calculated from contact shifts has been

The contact shifts of the *o*-tolyl (cf. Figure 3) and α-naphthyl complexes show definite indication of leveling off at or slightly below -30° and would presumably begin to increase at even lower temperatures. How-

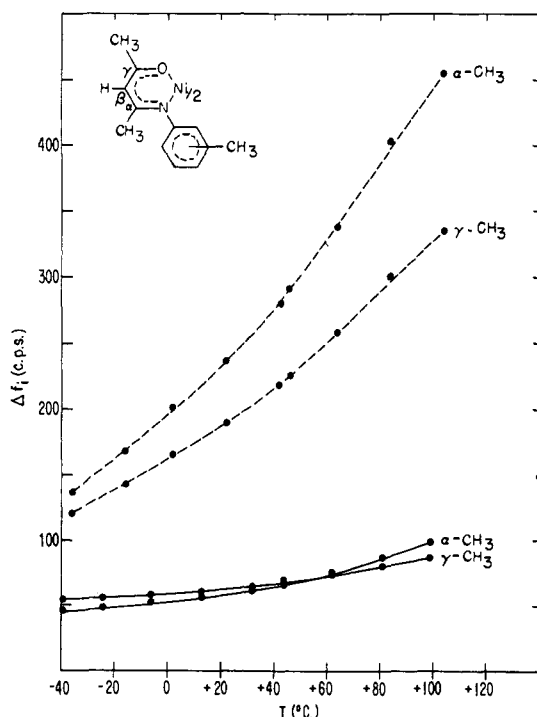


Figure 3. Temperature dependence of the contact shifts of bis(4-*o*-tolylaminopent-3-en-2-ono)nickel(II) (A-*o*-tolyl), —, and bis(4-*p*-tolylaminopent-3-en-2-ono)nickel(II) (A-*p*-tolyl), ----, in chloroform solution.

previously observed for some bis(*N*-*sec*-alkylsalicylaldimino)nickel(II) complexes.<sup>3</sup> The direction of deviation is such as to show that the contact shifts in the nonlinear range are too large, as in previous cases.<sup>3</sup> The additional contribution to the contact shifts arises from averaging over another paramagnetic component (in addition to the tetrahedral form) the associated species, which contains fully paramagnetic nickel ions. At those sufficiently low temperatures at which the associated species become dominant, the contact shifts would commence to increase and finally show a Curie behavior with decreasing temperature.

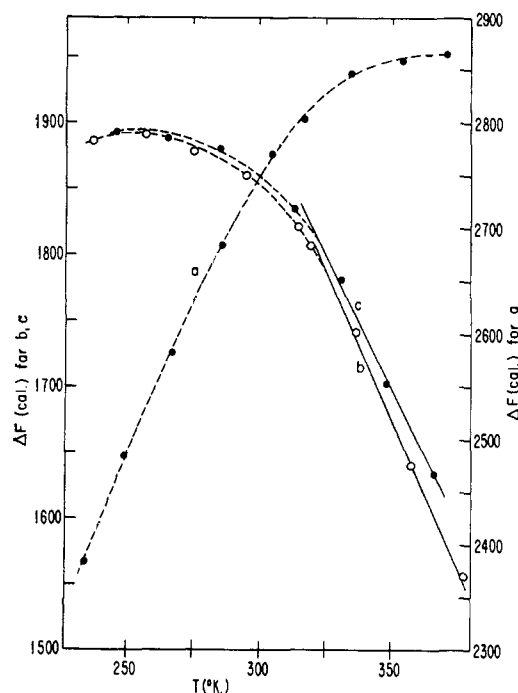


Figure 4. Temperature dependence of the free energy change for the planar  $\rightarrow$  tetrahedral conversion of (a) bis(4-*o*-tolylaminopent-3-en-2-ono)nickel(II) (A-*o*-tolyl), (b) bis(4-*p*-tolylaminopent-3-en-2-ono)nickel(II) (A-*p*-tolyl), (c) bis(4-β-naphthylaminopent-3-en-2-ono)nickel(II) (A-β-naphthyl) in chloroform solution. The dashed lines indicate temperature ranges of nonlinearity.

ever, over the range of observation the decrease of contact shift with temperature, as required by eq. 2, indicates that the principal paramagnetic component in that range is the tetrahedral form. It is readily calculated that this form is present to the extent of only 9–13% at 40° in the four complexes which can be fit to eq. 4. Accordingly, ligand-field spectra revealed only a broad band in the 5000–7000 cm.<sup>-1</sup> range, assigned as ν<sub>2</sub>, and no features which might be indicative of associated species.<sup>3,5c,24</sup>

The p.m.r. spectrum of A-α-naphthyl is different

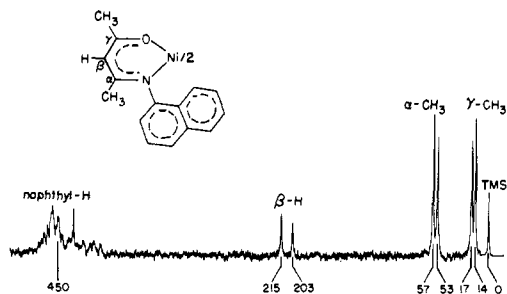


Figure 5. Proton resonance spectrum of bis(4- $\alpha$ -naphthylamino)nickel(II) (A- $\alpha$ -naphthyl) in chloroform at 25°. Frequencies are the chemical shifts.

from other members of the series in that each ring substituent gives rise to a pair of signals, as is shown in Figure 5. The splittings of the  $\beta$ - and  $\alpha$ -signals persist up to 80° at which point the calculated  $\Delta F$  values appear to commence a linear variation with  $T$ . Therefore, the splittings at this temperature can be associated with the structural change.<sup>43</sup> Similar splittings have been observed in diastereoisomeric salicylaldehyde complexes<sup>3,8</sup> and in bis(N,N'-di- $\alpha$ -naphthylaminotroponimine)nickel(II).<sup>7</sup> The three cases are related in that the contact shift differentiation appears to arise mainly from averaging of shifts over two (or more<sup>7</sup>) isomeric tetrahedral (paramagnetic) configurations which have different free energies.<sup>3</sup> In the A-R series the complexes with unsymmetrical R groups (*o*-tolyl, *m*-tolyl,  $\beta$ -naphthyl) do not show doubled signals which, from a previous argument,<sup>7</sup> strongly implies that the diamagnetic forms do not contribute appreciably to the splittings. Stuart-Briegleb metal chelate scale models show that in the tetrahedral form of A- $\alpha$ -naphthyl the R groups cannot rotate completely about the N-C bond owing to steric hindrance, thereby producing two stereoisomers which cannot interconvert freely with the two possible isomers of the planar form. The situation is then quite analogous to that of the aminotroponimine complex above, and, as in that case, the observation of split signals implies an upper limit rate of  $\sim 10^2$  sec.<sup>-1</sup> for the isomeric interconversion.

**Complexes of the B-R Series.** In this series all complexes prepared have R = *n*- or *sec*-alkyl. The *sec*-alkyl complexes are fully paramagnetic in the solid and in solution with the exception of the cyclopropyl derivative. The *n*-alkyl complexes are diamagnetic solids and become moderately paramagnetic in solution. The R = CH<sub>3</sub> and *i*-Bu complexes are weakly paramagnetic and exhibit small contact shifts in solution ( $\Delta f_{\alpha\text{-CH}_3} = +54$  in CDCl<sub>3</sub> and +153 c.p.s. in CS<sub>2</sub>, respectively, at 25°); these complexes were not studied further.

The R = *sec*-Bu complex prepared from the racemic amine showed small splittings ( $\sim 20$  c.p.s.) of the  $\alpha$ - and  $\beta$ -signals. The cause of these splittings is undoubtedly due to the presence of diastereoisomeric complexes as in the case of bis(N-*sec*-butylsalicylaldehyde)nickel(II).<sup>8</sup> Because no diamagnetic form of this complex was detected, the principal cause of the

(43) The  $\gamma$ -CH<sub>3</sub> signal is also split (by 12 c.p.s.) at -45° at which temperature some associated form exists. Possibly the structure of the associated form also contributes to the splitting of this signal. The  $\beta$ -H and  $\alpha$ -CH<sub>3</sub> signals are not resolvably split at this temperature.

splittings is due to slightly different coupling constants of the two paramagnetic isomers. It is perhaps significant to note that in salicylaldehyde complexes the splittings of a given proton or methyl group are frequently larger by factors of 2-5 when free energy inequalities dominate the cause of the splittings.<sup>3,8</sup>

Analysis of the temperature dependence of the contact shifts of the R = *n*-alkyl complexes is straightforward. Calculation of  $\Delta F$  values using coupling constants obtained from measured magnetic moments and the contact shifts of  $\alpha$ -CH<sub>3</sub> yields in each case a linear dependence on temperature in the ranges shown in Table VI and Figure 6. Enthalpy and entropy changes obtained from a least-mean-squares fit of  $\Delta F$  vs.  $T$  are also given in Table VI. No molecular association in solution could be detected by contact shift measurements down to -40°.

Because the contact shifts of several complexes appeared slightly solvent dependent (*cf.* Table IV), the contact shifts of one of these, *viz.*, R = *n*-Bu, were examined in three different solvents. The thermodynamic data in Table VI do reflect a small solvent dependence. In particular, it is noted that the entropy changes are larger in the two nonhydrogen-bonding solvents than in chloroform, and that  $\Delta S$  values for all complexes are considerably greater than those found for the salicylaldehydes (0.5-3.2 e.u.) but less than those (8-16 e.u.) found for the aminotroponimines in chloroform. Contributions to the entropy changes for the salicylaldehydes have been considered previously<sup>3</sup> and should also be operative for the  $\beta$ -ketoamines. Of these contributions the solvation effect appears to be different in degree for the two groups of complexes. The larger entropy changes for the  $\beta$ -ketoamines appear to be due to reduced hydrogen-bonding of the type O  $\cdots$  D-CCl<sub>3</sub> with the donor oxygen in the tetrahedral form, which is more sterically shielded in the  $\beta$ -ketoamines, according to molecular models, when R = *n*- or *sec*-alkyl. The increased  $\Delta S$  values on passing from chloroform to nonhydrogen-bonding solvents have also been observed for the salicylaldehydes and are in accord with the view that hydrogen-bonded solvation of the tetrahedral form tends to decrease or make negative an otherwise positive solvation contribution to  $\Delta S$ ,<sup>3</sup> such as is presumably operative in the aminotroponimines.<sup>7</sup>

Finally, it is observed that the coupling constants in the fully paramagnetic octahedral complex B-CH<sub>3</sub>-CHCH<sub>2</sub>OCH<sub>3</sub> are much reduced compared to B-*i*-Pr, for example. This result is expected inasmuch as the unpaired spins occupy the  $z^2$  and  $x^2 - y^2$  orbitals, which in octahedral symmetry are not  $\pi$ -bonding. Possible mechanisms for spin delocalization have been considered in connection with the analogous salicylaldehyde complex.<sup>22</sup> As in that case and as in the associated quasi-octahedral bis(N-arylsalicylaldehyde)nickel(II) complexes<sup>44</sup> the coupling constants have the same signs as in the tetrahedral form, thereby providing evidence that the spin imbalance is principally in the ligand  $\pi$ -system.

**Comparison of Salicylaldehyde and  $\beta$ -Ketoamino Complexes.** Because of the similarity of the general types 1 and 2 and their participation in the planar  $\rightleftharpoons$  tetra-

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

hedral equilibrium, comparison of certain properties derived from this and a previous study<sup>3</sup> are in order.

(1) *Position of Configurational Equilibrium.* Due to the complications of molecular association in the salicylaldimine series, only a few quantitative comparisons are presently available and are made for identical R groups. These comparisons are among 1 (R = *i*-Pr, X = H), A-*i*-Pr, B-*i*-Pr, and the complex having R<sub>γ</sub> = CH<sub>3</sub>, R<sub>α</sub> = H, and R = *i*-Pr. For the salicylaldimine complex ΔF<sup>60</sup> = 700 cal./mole,<sup>3</sup> indicating 51% tetrahedral form. A-*i*-Pr and B-*i*-Pr exist as ~100% tetrahedral at 25°. A more structurally related comparison can be made with the salicylaldimines using the R<sub>α</sub> = H complex for which ΔF<sup>25</sup> = 413 cal./mole (60% tetrahedral). The tendency of the β-ketoamine ligand system to stabilize tetrahedral Ni(II) is then quite dependent on R<sub>α</sub>. For R<sub>α</sub> = R<sub>γ</sub> = CH<sub>3</sub> this tendency is much greater than, and for R<sub>α</sub> = H, R<sub>γ</sub> = CH<sub>3</sub> is closely comparable with, that of the basic (X = H) salicylaldimine system.

(2) *π-Bonding Effects.* Comparison of calculated and the more reliable experimental spin densities reveals that in the tetrahedral form the β-ketoamine group loses ~<sup>3</sup>/<sub>2</sub> times as much spin to nickel as does the salicylaldimine group. The β-ketoamine group appears to be inherently more strongly π-bonding with respect to tetrahedral Ni(II) if it is assumed that the geometry of the two "tetrahedral" forms is quite similar.

(3) *Molecular Association.* The formation of paramagnetic polymeric species in solution has been detected for salicylaldimine complexes having R = CH<sub>3</sub><sup>45</sup> and *n*-alkyl,<sup>46</sup> *meta*- and *para*-substituted aryl,<sup>5c, 25</sup> and *sec*-alkyl.<sup>3, 47</sup> Of the β-ketoamine complexes studied in detail, only those of the A-aryl series gave evidence of association. Of all salicylaldimine complexes those with R = aryl are the most strongly associated, and aggregates have been shown to exist up to 100° or higher.<sup>5c</sup> In the A-aryl complexes the degree of association is clearly a great deal less, and the *meta*- and *para*-substituted complexes have no detectable aggregates above ~40°. However, the *N-ortho*-substituted arylsalicylaldimines have given little

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

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

(47) R. H. Holm and T. M. McKinney, *J. Am. Chem. Soc.*, **82**, 5506 (1960).

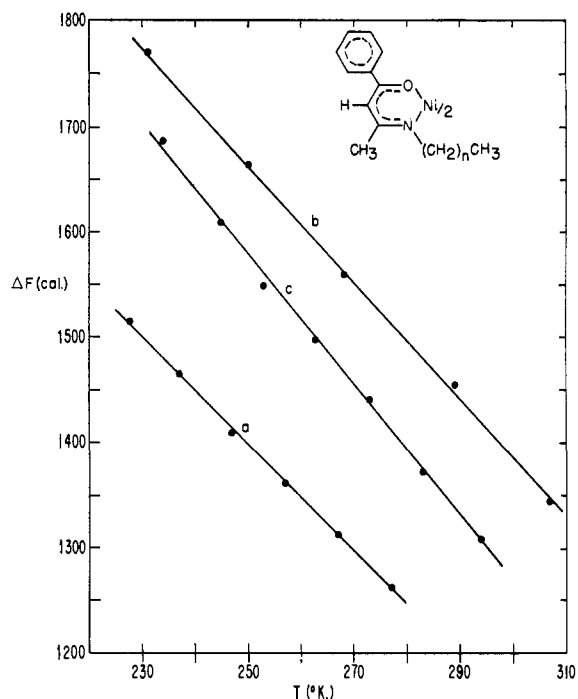


Figure 6. Temperature dependence of the free energy change for the planar → tetrahedral conversion of (a) bis(1-phenyl-3-ethylamino-but-2-en-1-ono)nickel(II) (B-Et), (b) bis(1-phenyl-3-*n*-propylamino-but-2-en-1-ono)nickel(II) (B-*n*-Pr), (c) bis(1-phenyl-3-*n*-butylamino-but-2-en-1-ono)nickel(II) in chloroform solution.

evidence of association compared to the *meta*- and *para*-substituted derivatives. The tendency toward association in the *N*-arylsalicylaldimines is *meta* ~ *para* >> *ortho*, whereas the reverse is true for the β-ketoamines. The cause of this difference is unknown.

In the absence of any detailed X-ray structural information on bis(β-ketoamino)nickel(II) complexes, it appears at present unprofitable to speculate on the differences, cited in (1) and (3), between these and the salicylaldimine complexes which are almost certainly dominated by specific steric effects.

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