

dramatic for the  $[\text{Ni}(\text{N-ethylen})_3](\text{ClO}_4)_2$  complex. For example, the Racah parameters,  $\beta$ , derived from aqueous solution spectra produce a nephelauxetic series where N-ethylen displays the largest nephelauxetic effect and the remaining ligands are essentially equivalent. These data, coupled with the  $Dq$  value, indicate that the inductive character of N-ethylen is more pronounced in water than that of the other ligands, or that species other than the tris complex are present in the aqueous solution. An obvious possibility is  $\text{trans-}[\text{Ni}(\text{N-ethylen})_2(\text{H}_2\text{O})_2]^{2+}$ . In fact, the aqueous spectrum of an authentic sample of this

compound is identical with that observed by dissolving  $[\text{Ni}(\text{N-ethylen})_3](\text{ClO}_4)_2$  in water.

It is apparent that the general shift of the absorption bands in aqueous solution, the visible hydrolysis reactions, and the unexpected changes in  $\epsilon_{\text{max}}$  demonstrate the complexity of aqueous solutions of amine coordination compounds and the subsequent care that must be exercised in interpreting data quantitatively in such solutions.

**Acknowledgment.**—The authors gratefully acknowledge that this research was supported in part by a grant from the Ohio State University Grant-in-Aid Fund.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY  
HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS 02138

## Structural Interconversions of Octahedral, Planar, and Tetrahedral Nickel(II) Complexes

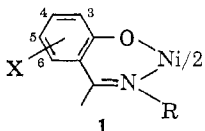
By A. CHAKRAVORTY, J. P. FENNESSEY,<sup>1a</sup> AND R. H. HOLM<sup>1b</sup>

Received July 24, 1964

A series of bis(N-R-salicylaldimine)nickel(II) complexes has been prepared in which the R group contains a site capable of coordination. Complexes with  $\text{R} = \text{CH}_3\text{CHCH}_2\text{OCH}_3$  but differing in the extent and position of chelate ring substitution have been thoroughly studied. For these complexes it has been shown from measurement of ligand field spectra and proton contact shifts that in the temperature range  $-40$  to  $50^\circ$  in chloroform solution discrete octahedral, planar, and tetrahedral stereoisomers are present in equilibrium. At low temperatures the octahedral form predominates; at higher temperatures the equilibrium is displaced toward the planar and tetrahedral forms. For two complexes the temperature dependence of the distribution of stereoisomers has been estimated from spectral data. The spectra of the octahedral complexes were found to be quite similar to those of associated paramagnetic bis(salicylaldimine)nickel(II), suggesting quasi-octahedral coordination in the latter. The spin density distributions in the coordinated ligand systems were shown to be similar in sign in the octahedral and tetrahedral stereoisomers.

### Introduction

Recent and extensive investigations of variously substituted bis(salicylaldimine)nickel(II) complexes (1) have clearly revealed that the particular structure or



structures exhibited in the crystalline, molten, and solution phases is a sensitive function of the nitrogen substituent R and, to a lesser extent, of the ring substituent X. When  $\text{R} = n\text{-alkyl}$  the complexes are diamagnetic in solution at and above room temperature and have a planar structure.<sup>2,3</sup> When  $\text{R} = \text{sec-alkyl}$  or  $t\text{-Bu}$  a square-planar  $\rightleftharpoons$  tetrahedral equilibrium exists in solution which has been thoroughly studied,<sup>4-9</sup>

especially by nuclear magnetic resonance.<sup>4,7,9</sup> A similar equilibrium apparently exists in the molten  $n\text{-alkyl}$  complexes.<sup>10</sup> A more complicated behavior exists in solutions of the methyl,<sup>3</sup>  $n\text{-alkyl}$ ,<sup>11</sup> and  $\text{sec-alkyl}$ <sup>6,12</sup> complexes below room temperature due to the formation of detectable amounts of paramagnetic associated species. When  $\text{R} = \text{aryl}$  associated species are frequently stable in solution below and considerably above room temperature<sup>13,14</sup>; above  $\sim 100^\circ$  associated, planar, and tetrahedral species exist in equilibrium with the latter favored at the higher temperatures.<sup>14</sup>

All nickel(II) salicylaldimine complexes which have been studied in any detail contain as R substituents only simple alkyl and aryl groups, so that in their monomeric forms only planar or tetrahedral structures are

(1) (a) N.I.H. Predoctoral Fellow, 1963-1964; (b) Alfred P. Sloan Foundation Fellow.

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

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

(4) A. Chakravorty and R. H. Holm, *ibid.*, **86**, 3999 (1964).

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

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

(7) R. H. Holm, A. Chakravorty, and G. O. Dudek, *ibid.*, **85**, 821 (1963); **86**, 397 (1964).

(8) L. Sacconi, M. Ciampolini, and N. Nardi, *ibid.*, **86**, 819 (1964).

(9) A. Chakravorty and R. H. Holm, *Inorg. Chem.*, **3**, 1010 (1964).

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

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

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

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

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

TABLE I  
 CHARACTERIZATION, MAGNETIC, AND MOLECULAR WEIGHT DATA FOR SUBSTITUTED BIS(SALICYLALDIMINE)NICKEL(II) COMPLEXES

R <sup>a</sup>	X	M.p., °C.	Calcd. %			Found, %			$\mu_{\text{eff}}$ (B.M.) <sup>g</sup>	Mol. wt. <sup>f</sup>	
			C	H	N	C	H	N		Calcd.	Found
CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	H	197-198	59.62	6.37	6.32	59.85	6.26	6.41	3.23	443	454
CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	3-CH <sub>3</sub>	168-169	61.17	6.85	5.95	61.16	6.93	5.94	3.22		
CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	4-CH <sub>3</sub>	198-199	61.17	6.85	5.95	61.69	6.75	6.11	3.24	471	465
CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	5-CH <sub>3</sub>	193-194	61.17	6.85	5.95	61.22	6.83	6.02	3.27	471	462
CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	4,5-(CH <sub>3</sub> ) <sub>2</sub>	220	62.55	7.27	5.62	62.30	7.17	5.81			
CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	4,6-(CH <sub>3</sub> ) <sub>2</sub>	155-156	62.55	7.27	5.62	62.70	7.20	5.86			
CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	5,6-Benzo	224-225	66.32	5.94	5.16	66.53	6.07	5.13	3.22		
CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	H	147-148	57.86	5.83	6.75	57.86	5.67	6.90		415	395
CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	H	137-138	59.62	6.37	6.32	59.73	6.18	6.25		443	434
CH <sub>3</sub> CHCH <sub>2</sub> OH <sup>b</sup>	H	243-245	57.86	5.83	6.75	57.69	5.54	6.71			
CH <sub>3</sub> CH <sub>2</sub> CHCH <sub>2</sub> OH <sup>b</sup>	H	241-242	59.62	6.37	6.32	59.72	6.40	6.21	3.18		
<i>o</i> -C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> <sup>c</sup>	H	>300	65.78	4.73	5.48	66.45	4.70	5.51	3.22		
CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub> <sup>d</sup>	H	175-177	61.43	7.30	11.94	61.81	7.40	11.75	3.12	469	447

<sup>a</sup> All complexes isolated as bright green crystals except where noted otherwise. <sup>b</sup> Light green crystals. <sup>c</sup> Black crystals. <sup>d</sup> Brown crystals. <sup>e</sup> Measurements made at 22-25°, corrected for diamagnetism. <sup>f</sup> Each sample measured at three concentrations in the range 0.02-0.08 M; no systematic variation of mol. wt. with concentration observed; results are the mean of three measurements.

possible. Quasi-octahedral structures have been proposed for the paramagnetic polymeric modification of the R = CH<sub>3</sub> complex in the solid<sup>15</sup> and in solution<sup>8</sup> and for the associated R = aryl complexes.<sup>13</sup> We wish to report the results of an investigation of complexes in which the R substituent contains an additional donor site, thus permitting the formation of discrete monomeric octahedral species. This work represents the first part of an investigation of Schiff base complexes containing potential coordinating functions on the side chain attached to the donor nitrogen atom. The results of studies of complexes formed from amino acids will be reported subsequently. There has been very little prior investigation of salicylaldimine nickel(II) complexes in which R carries a potential donor site. Pfeiffer, *et al.*,<sup>16</sup> prepared 1 with R = CH<sub>2</sub>COOC<sub>2</sub>H<sub>5</sub> and nickel(II)-salicylaldehyde-glycine complexes have been studied in aqueous solution.<sup>17</sup> Ray and Mukherjee<sup>18</sup> have reported complexes obtained from the condensation of salicylaldehyde and amino acids, but their proposed structures are highly questionable and will be discussed in a later communication. A complex of salicylidene-*o*-hydroxybenzene has been prepared<sup>19</sup> but its structure is uncertain. Schrauzer<sup>20</sup> has briefly mentioned complexes with R = (CH<sub>2</sub>)<sub>n</sub>OH, *n* = 2-6, but no definite indications of structures were given.

The new complexes prepared in this work contain an R substituent bearing an -OH, -OCH<sub>3</sub>, or -N(CH<sub>3</sub>)<sub>2</sub> functional group. The evidence presented below shows that, depending on the structure of the alkyl portion of R, the ring substituent X, and the temperature, intramolecular ring closure may occur to produce discrete monomeric octahedral complexes. Optical spectral, magnetic, and proton resonance measurements reveal that in many cases structural equilibria exist

involving octahedral, planar, and tetrahedral complexes.

### Experimental

**Preparation of Compounds.**—The complexes were prepared by refluxing the appropriate salicylaldehyde compound and amine in 2:1 mole ratio in dichloromethane for 1 hr. Complexes containing methoxyl groups were recrystallized from dichloromethane-hexane and those containing hydroxyl groups from ethanol containing a small amount of diethylamine. Characterization data are presented in Table I.

**Magnetic Measurements.**—Measurements on solids were made using the Gouy method with HgCo(NCS)<sub>4</sub> as the calibrant. Temperature-dependent solution measurements were made by an n.m.r. method.<sup>21</sup>

**Spectral Measurements.**—All measurements were made on a Cary Model 14 spectrometer. Solids were examined in finely dispersed hydrocarbon mulls sandwiched between quartz plates. Solution spectra were obtained at temperatures controlled to ±0.1°.

**Proton Resonance Measurements.**—These measurements were made as previously described<sup>7</sup> using tetramethylsilane as an internal standard.

**Molecular Weight Measurements.**—Molecular weights were obtained in chloroform solution at 37° using a Mechrolab osmometer. The calibrant was bis(*N-n*-butylsalicylaldimine)nickel(II) whose molecular weight was checked using a benzil solution standard.

### Results and Discussion

The complexes characterized in this work are set out in Table I. All but one contain an oxygen atom as a potential donor site in the R substituent. For purposes of discussion the complexes can be considered of three types—those with a branched chain alkyl portion and a terminal methoxy (A) or hydroxyl group (B) and those with a straight-chain alkyl portion and a terminal methoxyl group (C). Unlike the planar and tetrahedral forms of complexes with R = *sec*-alkyl groups, which are obtained as dark green or brown solids, type A and type B complexes are isolated as brilliant green crystals and light green microcrystals, respectively. Without exception type A and B complexes are paramagnetic and type C complexes are diamagnetic solids. Some representative results for the paramagnetic complexes are given in Table I.

(15) C. M. Harris, S. L. Lenzer, and R. L. Martin, *Australian J. Chem.*, **11**, 331 (1958); L. Sacconi, P. Paoletti, and R. Cini, *J. Am. Chem. Soc.*, **80**, 3583 (1958); H. C. Clark and R. J. O'Brien, *Can. J. Chem.*, **39**, 1030 (1961).

(16) P. Pfeiffer, W. Offermann, and H. Werner, *J. prakt. Chem.*, **159**, 313 (1941).

(17) L. J. Nunez and G. L. Eichhorn, *J. Am. Chem. Soc.*, **84**, 901 (1962).

(18) P. Ray and A. K. Mukherjee, *J. Indian Chem. Soc.*, **27**, 707 (1950).

(19) P. Pfeiffer, T. Hesse, H. Pfitzner, W. Scholl, and H. Thielert, *J. prakt. Chem.*, **149**, 217 (1937).

(20) G. N. Schrauzer, *Angew. Chem. Intern. Ed. Engl.*, **3**, 185 (1964).

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

TABLE II  
 SPECTRAL DATA FOR Ni(II) COMPLEXES IN CHLOROFORM SOLUTION<sup>a</sup>

R	X	$\epsilon_{\max}, \text{cm.}^{-1}$			$f_o$	$f_t$	$f_p$
		16,100	9800	6800			
CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	H	29.1	22.8	8.2	0.85	0.06	0.09
CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	3-CH <sub>3</sub>	38.9	19.1	17.2	0.71	0.17	0.12
CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	4-CH <sub>3</sub>	32.4	24.1	10.2	0.90	0.08	0.02
CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	4,5-(CH <sub>3</sub> ) <sub>2</sub>	36.9	21.5	12.4	0.80	0.12	0.08
CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	4,6-(CH <sub>3</sub> ) <sub>2</sub>	66.1	41.2	6.7	0.42	0.06	0.52
CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	5,6-Benzo	56.2	21.1	9.4	0.79	0.08	0.13
CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	5-CH <sub>3</sub>	36.8	22.7	12.4	0.85	0.12	0.03
		29.7	23.1		Chloroform, 25°		
		24.1	22.8		Ethanol, 25°		
		12.9 <sup>b</sup>	13.4 <sup>c</sup>	~0	Pyridine, 25°		
CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	H	65.1	4.6	~0	Chloroform, 25°		
CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	H	70.7	0	0			
CH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	H	67.0	0	0			

<sup>a</sup> All results in chloroform solution at 50° unless otherwise stated. <sup>b</sup>  $\lambda_{\max}$  16,900 cm.<sup>-1</sup>. <sup>c</sup>  $\lambda_{\max}$  10,000 cm.<sup>-1</sup>.

The structure of type A and B complexes in the solid and the predominant structure in solution is readily deduced from the ligand-field spectra. The spectra of the solids are all essentially the same; the solution spectra of type B complexes could not be obtained because of their very low solubility in noncoordinating solvents. When the complexes A are dissolved in chloroform bright green solutions, which are similar to the color of aqueous nickel ion, are formed. The spectra of these solutions below room temperature and the spectra of the solids are practically the same, and the spectra of a typical complex are shown in Figure 1.

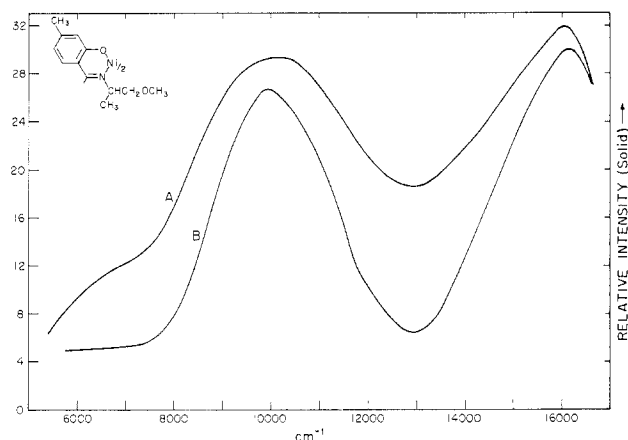
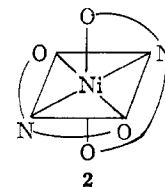


Figure 1.—Absorption spectrum of bis(4-methyl-N-2-(1-methoxy)propylsalicylaldimine)nickel(II): A, transmittance spectrum in Nujol mull; B, chloroform solution (0.0237 M) at -25°.

Pertinent spectral data, to be referred to subsequently, are set out in Table II. The intensities and frequencies of the two principal features (9800 and 16,100 cm.<sup>-1</sup>) are inconsistent with either planar<sup>2,3</sup> or tetrahedral<sup>5,6,8,9</sup> structures, but do closely resemble those of certain associated species.<sup>13</sup> However, the results of molecular weight measurements given in Table I demonstrate negligible association at 37°, at which temperature the solution spectra show the same principal features observed in the solid, although certain spectral

changes are evident and are discussed below. It is concluded that the paramagnetism and principal spectral features are attributable to octahedral complexes of structure 2 which are formed by intramolecular ring closure with two methoxyl (or hydroxyl) oxygens completing the coordination sphere.



Assuming effective octahedral symmetry the bands at 9800 and 16,100 cm.<sup>-1</sup> are assigned to the <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub> (ν<sub>1</sub>), <sup>3</sup>T<sub>1g</sub>(F) (ν<sub>2</sub>) transitions, respectively. Taking  $Dq = 980 \text{ cm.}^{-1}$  the remaining ligand field transition, <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub>(P), is predicted from the Liehr-Ballhausen nomograph<sup>22</sup> ( $\lambda - 275 \text{ cm.}^{-1}$ ,  $F_2 = 14F_4 = 1260 \text{ cm.}^{-1}$ ) to be at 27,000 cm.<sup>-1</sup>. This band is obscured by more intense absorption in this region. The energies of the ligand-field transitions are within a few per cent of those observed for other Ni-N<sub>2</sub>O<sub>4</sub> complexes, aqueous [Ni(EDTA)]<sup>-1,-2</sup>, for which  $Dq \cong 1000 \text{ cm.}^{-1}$ .<sup>23</sup>

The solutions of type A complexes when heated above room temperature are perceptibly thermochromic to the eye, changing from bright green to a darker brownish green. The latter color is characteristic of tetrahedral bis(salicylaldimine)nickel(II) complexes. The following results serve to demonstrate the simultaneous existence of octahedral, planar, and tetrahedral stereoisomers in solution and the increase in the proportion of the latter two isomers with increasing temperature.

**Proton Resonance Results.**—Bis(salicylaldimine)-nickel(II) complexes in the octahedral configuration, like those existing in the tetrahedral configuration,<sup>4,7,9</sup> have been found to manifest isotropic proton contact

(22) A. D. Liehr and C. J. Ballhausen, *Ann. Phys. (N. Y.)*, **6**, 134 (1959).

(23) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley, Inc., Reading, Mass., 1962, p. 296.

shifts.<sup>24,25</sup> The spectrum of a typical octahedral complex is shown in Figure 2. The assignment of the ring proton signals was made by examination of a series of methylated complexes at the same temperature. The contact shifts of four type A complexes, those with X = 3-, 4-, 5-CH<sub>3</sub>, and 4,6-(CH<sub>3</sub>)<sub>2</sub>, were studied over the range -40 to 100°. The temperature dependencies of the ring methyl signals are shown in Figure 3. From Figures 2 and 3 it is observed that these signals occur in pairs and that each member of a pair has a similar temperature dependence but not necessarily equal intensity. These paired features, which are also occasionally observed in the ring proton signals, arise from the presence of an optically active center in each R group. Complexes prepared from racemic 1-methoxy-2-aminopropane consist of a mixture of diastereoisomers, (+,+), (-,-), and (+,-); the optically active and *meso* forms have observably different contact shifts. The existence of geometrical isomers is rejected since it is impossible for the Schiff base ligand to dispose itself at the corners of an octahedral face without unreasonable strain. Observations of separate sets of contact shifts for diastereoisomeric complexes involved in the planar  $\rightleftharpoons$  tetrahedral equilibrium have been reported previously, and the observed contact shift differences were explained in terms of different free energy changes associated with the structural change of each isomer.<sup>7</sup> However, at -40° nearly all the complexes, particularly that with X = 4-CH<sub>3</sub>, exist in ~100% octahedral form (*vide infra*). In this case the contact shifts  $\Delta f_i$  have no explicit free energy dependence and are given by<sup>24</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 the symbols have their usual meanings.<sup>24</sup> We interpret the separate signals of the two isomers to be due principally to sufficiently large differences in the nuclear-electron coupling constants  $a_{CH_3}$  and  $a_H$ . These results furnish other examples of the great sensitivity of contact shifts to subtle differences in molecular structure. Thus, in the 4-CH<sub>3</sub> complex the  $a_{4-CH_3}$  values need differ by only ~2% to produce the observed 10 c.p.s. separation at -40°. It was generally found that the intensities of components of paired signals were not equal. Evidently the octahedral diastereoisomers are not isolated in statistical amounts after preparation and purification. McDonald and Phillips<sup>29</sup> have found that diastereoisomeric octahedral

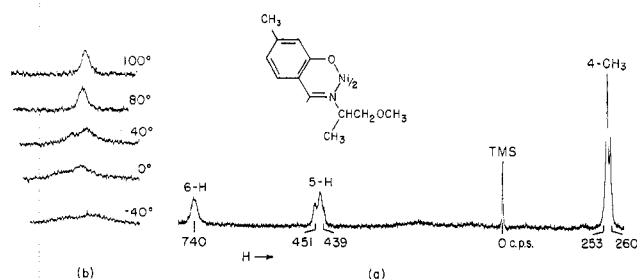


Figure 2.—(a) Proton resonance spectrum of bis(4-methyl-N-2-(1-methoxy)propylsalicylaldimine)nickel(II) at -40° in CDCl<sub>3</sub> solution; the 3-H signal has a larger positive contact shift than 4-CH<sub>3</sub> and is not shown. (b) Spectrum of the methoxyl group as a function of temperature.

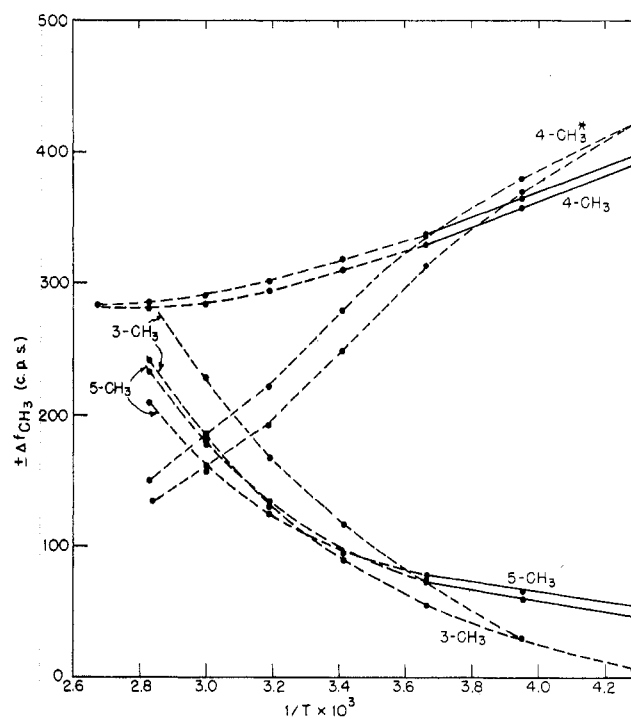


Figure 3.—Plot of the contact shifts of ring methyl groups in four bis(N-2-(1-methoxy)propylsalicylaldimine)nickel(II) complexes as a function of temperature in CDCl<sub>3</sub> solution. Solid lines refer to linear, dashed lines to nonlinear dependence of  $\Delta f$  on  $T^{-1}$ ; 4-CH<sub>3</sub>\* refers to the 4,6-(CH<sub>3</sub>)<sub>2</sub> complex. Signs of contact shifts are: +, 4-CH<sub>3</sub>, 4-CH<sub>3</sub>\*; -, 3-CH<sub>3</sub>, 5-CH<sub>3</sub>.

bis(histidino)cobalt(II) complexes exhibit separate sets of contact shifts and are not formed in statistical amounts in aqueous solution.

The temperature dependence of the contact shifts can be utilized in a qualitative fashion to demonstrate the formation of other than octahedral stereoisomers as the temperature is varied. For an assembly of paramagnetic complexes with the same ground state eq. 1 applies. The contact shifts should possess a linear dependence on  $1/T$  so long as no new species are formed. The temperature dependencies of the ring methyl signals of four type A complexes are shown in Figure 3. It is clear that only for the X = 4-CH<sub>3</sub> and 5-CH<sub>3</sub> complexes is there a region of linear behavior, and that this region is quite limited (-40 to 0°). The corresponding Curie dependence of the magnetic moments

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

(25) Some contribution to the total contact shifts from pseudo-contact interactions<sup>26</sup> cannot be excluded. These interactions are strongly dependent on the anisotropy of the  $g$ -tensor,  $|g_{||} - g_{\perp}|$ . While some anisotropy must exist due to the pseudo-tetragonal nature of the ligand field, it is assumed to be small. Essentially isotropic behavior has been found in various Ni(H<sub>2</sub>O)<sub>6</sub><sup>+2</sup> salts<sup>27</sup> and in a tris-chelate Ni(II) complex.<sup>28</sup>

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

(27) B. Bleaney and K. W. H. Stevens, *Rept. Progr. Phys.*, **16**, 108 (1953); K. D. Bowers and J. Owen, *ibid.*, **18**, 304 (1955).

(28) M. Peter, *Phys. Rev.*, **116**, 1432 (1959).

(29) C. C. McDonald and W. D. Phillips, *J. Am. Chem. Soc.*, **85**, 3736 (1963).

TABLE III  
MAGNETIC MOMENTS OF Ni(II) COMPLEXES IN  
CHLOROFORM SOLUTION<sup>a</sup>

<i>t</i> , °C.	$\mu_{\text{eff}}$ , B.M. <sup>b</sup>			
	R = (CH <sub>3</sub> ) <sub>2</sub> N- (CH <sub>3</sub> ) <sub>2</sub> X = H	R = CH <sub>3</sub> CHCH <sub>2</sub> - OCH <sub>3</sub> X = 4-CH <sub>3</sub>	R = CH <sub>3</sub> CH- CH <sub>2</sub> OCH <sub>3</sub> X = 5-CH <sub>3</sub>	R = CH <sub>3</sub> CHCH <sub>2</sub> - OCH <sub>3</sub> X = 4,6-(CH <sub>3</sub> ) <sub>2</sub>
-40	3.22	3.24	3.30	3.26
-20	3.23	3.25	3.28	3.22
0	3.24	3.25	3.30	3.15
20	3.25	3.25	3.25	2.97
40	3.20	3.23	3.15	2.69
60	3.17	3.20	3.09	2.31
80		3.15	3.03	2.12

<sup>a</sup> Solutions 0.055–0.059 *M* in complex. <sup>b</sup> Estimated error  $\pm 0.05$  B.M.; results calculated from Curie law.

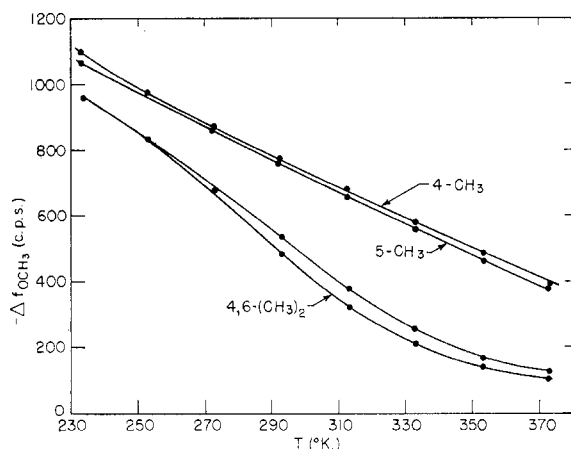


Figure 4.—Plot of the contact shifts of the  $-\text{OCH}_3$  group in three bis(*N*-2-(1-methoxy)propylsalicylaldehyde)nickel(II) complexes ( $\text{X} = 4\text{-CH}_3$ ,  $5\text{-CH}_3$ ,  $4,6\text{-(CH}_3)_2$ ) as a function of temperature in  $\text{CDCl}_3$  solution.

(*cf.* Table III) of these complexes in this temperature region are observed, and deviations from this behavior, as sensed by the less accurate susceptibility measurements, are not large even at the higher temperatures. The  $4,6\text{-(CH}_3)_2$  complex shows a more pronounced departure of its magnetic moment from a Curie dependence, in agreement with the contact shift results. Departures of the contact shifts and magnetic moments from a strict Curie dependence are interpreted to arise from the presence of planar and tetrahedral stereoisomers with the equilibria octahedral  $\rightleftharpoons$  planar  $\rightleftharpoons$  tetrahedral being shifted to the right with increasing temperature. This direction of displacement is in agreement with the observed rapid increase in the  $3\text{-CH}_3$  and  $5\text{-CH}_3$  contact shifts (*cf.* Figure 3) in their respective complexes. The ratios of the coupling constants of these substituents in the tetrahedral (with  $\text{R} = i\text{-C}_3\text{H}_7$ ) and octahedral forms are  $\sim 230:1$  and  $30:1$ , respectively, indicating that the formation of tetrahedral complexes will rapidly increase the contact shifts. The corresponding ratio for  $4\text{-CH}_3$  is  $3:1$  so that a much less rapid change is expected in the contact shifts. A decrease with gradual leveling off is observed over the accessible temperature range of measurement. The contact shifts are averaged over the three stereoisomers, and up to  $100^\circ$  the proportion

of tetrahedral form is not yet sufficient to cause an increase in the shifts, while the proportion of diamagnetic planar form, which does not contribute to the contact shifts, is increasing. The rapid decrease of the  $4\text{-CH}_3$  shift in the  $4,6\text{-(CH}_3)_2$  complex has a similar explanation. Susceptibility measurements on the  $\text{R} = i\text{-C}_3\text{H}_7$ ,  $\text{X} = 4,6\text{-(CH}_3)_2$ , complex have shown only one-sixth as much tetrahedral form as for the  $4\text{-CH}_3$  complex at  $30^\circ$ .<sup>7</sup>

The decrease in the proportion of octahedral form with increasing temperature is demonstrated additionally by the temperature dependence of the shifts of the methoxyl protons. Representative results are shown in Figures 2b and 4. In the octahedral form 2 the methoxyl group is coordinated and negative contact shifts are observed, presumably because of a  $\sigma$ -transmission of spin density. At low temperatures the signals are broadened because of electron-nuclear dipole-dipole relaxation involving the paramagnetic metal ion. As the temperature is raised the line widths and contact shifts decrease. This is just the behavior to be expected from a rightward shift of the above equilibrium since the methoxyl group is not bound to the metal in the planar and tetrahedral forms in which zero and very small contact shifts, respectively, will occur.

**Optical Spectral Results.**—Temperature-dependent spectral measurements of type A complexes in chloroform solution from  $-25$  to  $50^\circ$  demonstrate that as the temperature is raised, the octahedral form is diminished and planar and tetrahedral isomers are formed. The  $9800\text{ cm.}^{-1}$  band decreases while at  $16,100\text{ cm.}^{-1}$ , where the planar form has an absorption maximum,<sup>2,3</sup> there is a net increase in intensity; a feature emerges at  $\sim 6800\text{ cm.}^{-1}$  which has been assigned<sup>5</sup> as  $\nu_2$  in tetrahedral complexes. The qualitative conclusions from the temperature-dependent proton resonance and spectral results are thus in accord.

The fractions of the various stereoisomers as a function of temperature can be estimated from the spectra. In only two cases,  $\text{X} = 3\text{-CH}_3$  and  $4,6\text{-(CH}_3)_2$ , was the decrease in octahedral concentration sufficient to permit determination with fair accuracy of the fractions of planar and tetrahedral forms from  $-25$  to  $50^\circ$ . The procedure was as follows. The fraction  $f_o$  of octahedral form was given by  $f_o = \epsilon_{\text{obsd}}/\epsilon_o$  at  $9800\text{ cm.}^{-1}$  since only the octahedral form absorbs at this frequency.  $\epsilon_o$  is the limiting extinction coefficient of the octahedral complex and was obtained by extrapolating measured values of the  $\text{X} = 4\text{-CH}_3$  and  $5\text{-CH}_3$  complexes to  $-40^\circ$ . The average value obtained, 26.8, was used for the octahedral form of all complexes. The fraction  $f_t$  of tetrahedral form was obtained from the relation

$$f_t = \frac{\epsilon_{\text{obsd}} - f_o a}{\epsilon_t} \quad (2)$$

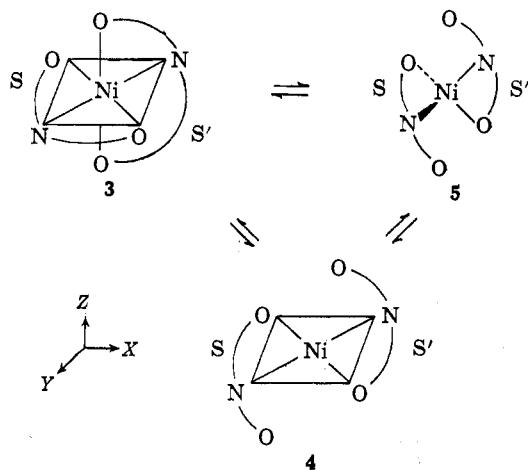
using values obtained at  $6900\text{ cm.}^{-1}$ . The observed absorbance  $\epsilon_{\text{obsd}}$  was corrected by an amount  $f_o a$  in which  $a$  is the residual intensity of the pure octahedral form at this frequency. That the octahedral form does

have nonzero absorbance in this region can be seen from Figure 1.  $\epsilon_t$  is the limiting extinction coefficient of the tetrahedral form and was obtained from the relation

$$\epsilon_t = \epsilon_{\text{obsd}} \left( \frac{\mu_{\text{obsd}}}{\mu_t} \right)^{-2} \quad (3)$$

in which the observed quantities refer to the  $R = i\text{-C}_3\text{H}_7$  complexes at  $50^\circ$  in chloroform solution. Under these conditions only planar and tetrahedral isomers exist.<sup>7</sup> In eq. 3 the limiting moment of the tetrahedral form  $\mu_t$  and  $\mu_{\text{obsd}}$  were taken from previous work<sup>7</sup> and  $\epsilon_{\text{obsd}}$  ( $6900 \text{ cm.}^{-1}$ ) measured in this study.<sup>30</sup> The fractions  $f_p$  of planar form could not be assessed directly and were obtained by difference. The temperature-dependent distributions of the stereoisomeric forms for two complexes are given in Figure 5 and the fractions at  $50^\circ$  for all type A complexes are given in Table II. While the  $f_o$  values are believed accurate to  $<5\%$  in all cases, it is to be emphasized that the  $f_t$  and  $f_p$  results can be regarded as fair estimates only and are not suitable for the calculation of thermodynamic quantities.

**Interconversion and Distribution of Stereoisomers.**—The interconversion of the stereoisomeric forms of type A complexes has been found to be reversible with temperature. The structural equilibrium is depicted in the following in which S and S' represent the salicyaldimine chelate rings. A very important observa-



tion is that, of type A and C complexes, only the former readily adopt the octahedral form. At  $25^\circ$  in chloroform solution the 2-methoxyethyl complex shows small contact shifts (4-H,  $-208$ ; 5-H,  $+36$ ; 6-H,  $-49$  c.p.s.), indicating a small concentration of octahedral form, and the 3-methoxypropyl complex has no contact shifts and is thus completely in the planar form. The  $R = \text{CH}_2\text{COOC}_2\text{H}_5$  complex, although too insoluble for n.m.r. measurements, exists only in the planar form since no absorptions (*cf.* Table II) characteristic of the other two forms were observed. Therefore, in the salicyaldimine series that steric requirement necessary to the formation of tetrahedral complexes at ordinary

(30) The values of  $\epsilon_t$  obtained in this way were found to be somewhat dependent upon X; thus  $\epsilon_t = 58(\text{H})$ ,  $78(3\text{-CH}_3)$ ,  $63(4\text{-CH}_3)$ ,  $63(5\text{-CH}_3)$ ,  $61[4,5\text{-(CH}_3)_2]$ .  $\epsilon_t$  values for 4,6-( $\text{CH}_3$ )<sub>2</sub> and 5,6-benzo could not be accurately evaluated due to the low fraction of tetrahedral form<sup>7,9</sup> and were taken to be 61.

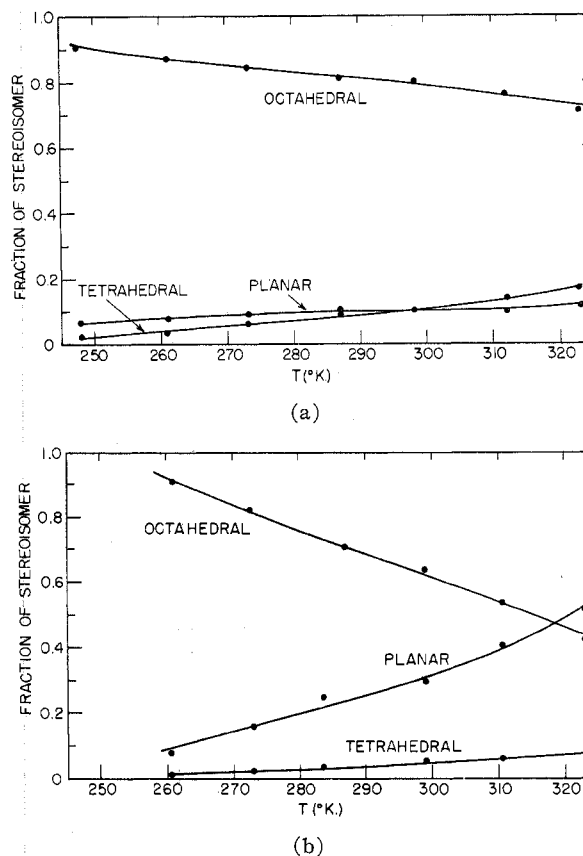


Figure 5.—The temperature dependence of the fractions of octahedral, planar, and tetrahedral stereoisomers in chloroform solution for (a) bis(3-methyl-N-2-(1-methoxy)propylsalicyaldimine)nickel(II), (b) bis(4,6-dimethyl-N-2-(1-methoxy)propylsalicyaldimine)nickel(II).

temperatures, *viz.*, the presence of the local  $\text{N}-\text{C} \begin{smallmatrix} \text{C} \\ \diagup \end{smallmatrix}$  rather than the  $\text{N}-\text{C}-\text{C}$  structure, is also critical to the formation of octahedral complexes when a weakly basic donor atom completes the coordination sphere.

The pronounced relative ease of formation of octahedral type A complexes can be rationalized. It is not possible to convert the planar form 4 to the *trans-trans* octahedral form 3 without proceeding through a quasi-tetrahedral intermediate. This conversion can occur by the following simple displacements of ring S' relative to ring S: (1) rotation about  $x$  by  $90^\circ$  to give the tetrahedral form 5; (2) clockwise rotation by  $\sim 45^\circ$  about  $y$ ; (3) counterclockwise rotation by  $45^\circ$  about  $z$  with the formation of  $\text{Ni}-\text{OCH}_3$  bonds to give the octahedral form 3. This simple rearrangement involves intramolecular displacements, and an intermolecular process, such as that which produces ligand exchange between tetrahedral complexes,<sup>4</sup> cannot be excluded, however.

The temperature-dependent n.m.r. and spectral studies have shown that the octahedral form is the most stable at the lower temperatures. From previous work<sup>7,9</sup> it may be inferred that the complete stability order with decreasing temperature is octahedral  $>$  planar  $>$  tetrahedral. This is another manifestation of the tendency of Ni(II) complexes to achieve octahedral coordination,

TABLE IV  
CONTACT SHIFTS AND SPIN DENSITIES IN OCTAHEDRAL AND  
ASSOCIATED COMPLEXES

R	X	Position	Contact shift, c.p.s. <sup>a</sup>	Spin density
CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>	H	3	+647 <sup>b</sup>	+0.0036
		4	-1381 <sup>b</sup>	-0.0076
		5	+131 <sup>b</sup>	+0.0007
CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	H	6	-266 <sup>b</sup>	-0.0015
		3	+810 <sup>c</sup>	+0.0052
		4	-1700 <sup>b</sup>	-0.0094
CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	4-CH <sub>3</sub>	5	+75 <sup>b</sup>	+0.0004
		6	-298 <sup>b</sup>	-0.0017
		3	+831 <sup>c</sup>	+0.0050
CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	5-CH <sub>3</sub>	4	+396 <sup>d</sup>	-0.0002
		5	-43 <sup>d</sup>	-0.0016
		6	-314 <sup>d</sup>	-0.0016
CH <sub>3</sub> CHCH <sub>2</sub> OCH <sub>3</sub>	5-CH <sub>3</sub>	3	+874 <sup>e</sup>	+0.0056
		4	-1688 <sup>b</sup>	-0.0093
		5	-53 <sup>d</sup>	-0.0017
<i>m</i> -C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> <sup>f</sup>	H	6	-338 <sup>d</sup>	-0.0017
		4	-1468	-0.0098
		5	+695	+0.0046
		6	-871	-0.0058

<sup>a</sup> When separate signals from the two diastereoisomers were resolved, the average shift is given. <sup>b</sup> -20°. <sup>c</sup> 0°. <sup>d</sup> -40°. <sup>e</sup> 20°. <sup>f</sup> All data from ref. 35.

steric effects permitting, and it is concluded that at least part of the stabilization of this configuration is the crystal field stabilization energy, which is estimated to be  $\sim 12,000$  cm.<sup>-1</sup>. The actual distribution of stereoisomers at any temperature will depend on their relative free energies, and these will in turn be a function of the detailed molecular structure, as has been clearly shown to be the case for systems containing only planar and tetrahedral Ni(II) complexes.<sup>4,7,9,31</sup> It is noted that 3- and 6- substituents, which tend to stabilize the tetrahedral and planar forms, respectively, also tend to destabilize the octahedral form relative to these two configurations. It appears that if the donor atom in the R group is sufficiently strong, an octahedral configuration can be produced in the absence of significant stabilization of the tetrahedral form. Thus when R = (CH<sub>2</sub>)<sub>3</sub>N(CH<sub>3</sub>)<sub>2</sub> a monomeric octahedral complex is formed whose magnetic moment (Table III) and contact shifts do not significantly deviate from a Curie behavior in the range -40 to 40°.<sup>32</sup>

Other examples of complexes formed by potential tridentate Schiff base ligands have been summarized by Goodwin.<sup>33</sup> These ligands contain more strongly coordinating sites than ether oxygen atoms and, as inferred from magnetic moments of solids, apparently utilize their tridentate functionality. Of the very few nickel complexes referred to, it appears especially likely that the green paramagnetic bis(N-acylhydrazone-

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

(32) Above  $\sim 40^\circ$  the contact shifts of the ring protons rapidly decrease, indicating the formation of some planar species. It is assumed that the octahedral form of this complex has a structure analogous to **3**. The possibility that in this case the longer alkyl chain might allow the formation of more than one geometrical isomer was investigated by preparing the X = 4- and 5-CH<sub>3</sub> complexes. No splitting of the sharp methyl signals was observed in chloroform at 25°.

(33) H. A. Goodwin in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, pp. 144-153.

salicylaldimine) complexes prepared by Sacconi<sup>34</sup> are octahedral with a structure related to **2**, rather than tetrahedral as inferred from the paramagnetism.<sup>34</sup>

**Model for Associated Species.**—A now well-recognized complication in the solution chemistry of ostensibly four-coordinate Ni(II) complexes in relatively inert solvents is the tendency to form associated species. This behavior has been well documented in bis(salicylaldimine) complexes,<sup>9,11-14</sup> and it has been postulated<sup>3,13</sup> that the oligomers contain some or all of the nickel ions in quasi-octahedral coordination of the type Ni-N<sub>2</sub>O<sub>4</sub>, thereby accounting for the paramagnetism of these species. The octahedral complexes studied in this work might serve as useful models in which the coordination environment of nickel is related to that in the oligomers. Recently Sacconi and Ciampolini<sup>14</sup> have concluded that the spectra of the paramagnetic modification of the R = CH<sub>3</sub> complex and of the solid R = aryl complexes are indicative of the octahedral coordination. This conclusion is substantiated inasmuch as the two main features of those spectra (at 11,000, 18,000 and 10,000, 16,800 cm.<sup>-1</sup>, respectively) compare rather closely with those at 9800 and 16,100 cm.<sup>-1</sup> observed for the octahedral complexes and are best assigned as the octahedral  $\nu_1$  and  $\nu_2$  absorptions. The spectral similarities include the presence of a shoulder (unassigned) at  $\sim 7500$  cm.<sup>-1</sup> (cf. Figure 1).

Proton contact shifts have been observed for a series of ring-substituted R = aryl complexes in carbon disulfide solution.<sup>35</sup> It has been shown that these complexes are highly associated and fully paramagnetic in solution.<sup>13</sup> In Table IV a comparison of contact shifts and apparent spin densities is given for one such associated complex and several octahedral complexes. The spin densities have been calculated assuming that pseudocontact contributions<sup>25</sup> to the total contact shifts and  $\sigma$ -transmission of spin density are unimportant. These assumptions, which appear reasonable, cannot be fully justified. It is evident that in the associated and octahedral complexes the spin density distributions are similar only with respect to sign. The manner and extent of delocalization of unpaired spin are evidently dependent in detail on structure. It is perhaps significant that the spin densities have the same sign but generally smaller values than those observed<sup>7</sup> in tetrahedral bis(salicylaldimine) complexes in which spin is transferred to the ligand by  $\pi$ -bonding. If the complexes in Table IV are weakly tetragonal, as their electronic spectra imply, the unpaired spins are in the  $\sigma$ -orbitals  $d_{x^2-y^2}$  and  $d_{z^2}$ . Since spin density transmission by polarization of  $\sigma$ -electrons would be expected to attenuate rapidly from bond to bond, it is felt that spin is transferred mainly by a mechanism involving the ligand  $\pi$ -orbitals. Two possibilities are (1) exchange polarization of the pair  $t_{2g}$  electrons by the unpaired  $e_g$  electrons followed by  $\pi$ -delocalization, and (2) a "reverse"  $\pi$ - $\sigma$  polarization whereby the unpaired  $e_g$  electrons polarize the paired electrons in the  $\pi$ -orbitals of

(34) L. Sacconi, *J. Am. Chem. Soc.*, **74**, 4503 (1952).

(35) E. A. LaLancette, D. R. Eaton, R. E. Benson, and W. D. Phillips *ibid.*, **84**, 3968 (1962).

the donor atom. The net unpaired spin in both cases can then be distributed according to a simple valence bond description.<sup>4</sup> A mechanism for spin transfer in other octahedral nickel complexes has been given elsewhere.<sup>3f</sup>

Finally, we mention briefly the type B complexes. These species are highly insoluble in inert solvents such as chloroform or benzene, but dissolve readily upon the addition of a small amount of an aliphatic amine to give a greenish brown solution. Solubility is very

(36) R. S. Milner and L. Pratt, *Discussions Faraday Soc.*, **34**, 88 (1962).

probably effected by hydrogen bonding between the amine and the hydroxyl group. The insolubility of these complexes in nonhydrogen-bonding solvents appears to be due to intermolecular hydrogen bonding such as has been found in crystalline bis(N-2-hydroxyethylsalicylaldehyde)copper(II).<sup>37</sup>

**Acknowledgment.**—Financial support by the National Science Foundation (Grant GP-590) and the Milton Fund of Harvard University is gratefully acknowledged.

(37) E. R. Boyko, Abstracts, Intern. Union of Crystallography, Sixth Intern. Congress, Rome, Italy, Sept., 1963.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN

## Semiempirical Molecular Orbital Theory for Transition Metal Complexes

By RICHARD F. FENSKE

Received July 3, 1964

Although the modified Wolfsberg and Helmholz approach to molecular orbital theory for transition metal complexes has had apparent success in recent applications, evaluation of the technique indicates that not only are the results strongly dependent upon the initial assumptions but also agreement between theory and experiment obtained in previous calculations may not be valid. Specifically, consideration is given to the use of hybridized ligand orbitals for  $\sigma$ -bonding, estimation of  $H_{ij}$  terms in the secular determinant, and approximation of the ligand diagonal term,  $H_{jj}$ , by the hydride method with respect to the determination of the energy levels in  $\text{TiF}_6^{-3}$ . The results show that among other things appreciable covalent character and the importance of  $\pi$ -bonding are automatic consequences of rather arbitrary assumptions. In general the method can lead to erroneous values and interpretations and should not be accepted without strong reservations.

### Introduction

In recent months there has been renewed interest in a semiempirical molecular orbital method for the determination of the electronic energy levels of transition metal complexes. The method, originally suggested by Wolfsberg and Helmholz<sup>1</sup> and modified by Ballhausen and Gray,<sup>2</sup> has been applied to the vanadyl,<sup>2</sup> hexafluorotitanate(III),<sup>3</sup> and permanganate<sup>4,5</sup> ions. However, closer examination of these and similar calculations brings to light certain ambiguities which tend to undermine one's trust in the validity of the method.

This discussion deals essentially with the estimation of electronic energy levels. Although not explicitly treated here, we also have reservations concerning the compatibility of the results with other experimental evidence such as n.m.r. hyperfine splittings. However, proponents of the method have never claimed the approach to be necessarily useful in this regard, its principal application being to the interpretation of absorption spectra. It will be shown that discrepancies arise even in this limited application. It is the purpose of this report to call attention to these discrepancies and to examine their causes.

Because of the simplicity of the system, particular attention will be given to the evaluation of the energy levels of the  $\text{TiF}_6^{-3}$  complex. In the original calculation for this complex by Bedon, Horner, and Tyree,<sup>3</sup> the excellent agreement between the theoretical and experimental value of  $10Dq$  was cited as indicative of the usefulness of the semiempirical approach. It should be noted that neither the transition assignment,  ${}^2T_{2g} \rightarrow {}^2E_g$ , nor the  $10Dq$  value of  $17,500 \text{ cm.}^{-1}$  proposed by Bedon, *et al.*, is being questioned here. What is in doubt is that the agreement obtained between the calculated and experimental result substantiates the validity of the theoretical method.

### The Method of Calculation

The secular determinant,  $|H_{ij} - EG_{ij}| = 0$ , which arises from the adoption of the LCAO approach to molecular orbital theory, is conveniently factored by application of group theory. In the secular determinant the  $G_{ij}$  are group overlap integrals which can be expressed in terms of two center overlap integrals multiplied by suitable coefficients.

In the modified method<sup>2-5</sup> the diagonal terms for the central metal orbitals,  $H_{ii}$ , are estimated as the negative of the valence state ionization energies (VSIE) of the atoms or ions. The VSIE values are dependent upon the assumed electron configuration of the valence state and the assumed charge on the metal. In general, the

(1) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

(2) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

(3) H. D. Bedon, S. M. Horner, and S. Y. Tyree, Jr., *ibid.*, **3**, 647 (1964).

(4) R. F. Fenske and C. C. Sweeney, *ibid.*, **3**, 1105 (1964).

(5) A. Viste and H. B. Gray, *ibid.*, **3**, 1113 (1964).