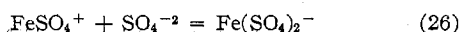When a second anion is added to the activated complex as in eq. 25 the free energy change for SO_4^{-2} is more
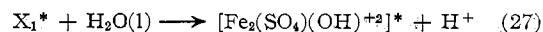
$$X_1^* + Z^{-n} = X_2^* \qquad (25)$$

negative than is the free energy of reaction 26 since $k_2 > k_1$, whereas the two free energy changes are approximately equal for the other ions where data have been obtained. A repetition of the argument given in the preceding paragraph suggests that SO_4^{-2} may exert its stabilizing influence in the activated complex, as compared to the reactants, by a bridging role rather than as just an inner-shell ligand in a reactant in an outer-sphere activated complex.

$$FeSO_4^+ + SO_4^{-2} = Fe(SO_4)_2^- \qquad (26)$$

Reaction 13 contains a type of activated complex which, to date, has not been observed in the Fe(II) + Fe(III) exchange catalyzed by the ions already mentioned. A possible reason for this is that the precision obtained is too poor in the case of the other anions. If a SO_4^{-2}-bridged activated complex is formed then

several alternatives are possible for the disposal of the OH^- ion. Some of these possibilities are that it may form an additional bridge between Fe(II) and Fe(III) or it may simply replace a water molecule in the inner coördination shell of either Fe(II) or Fe(III). Some evidence as to which possibility is most probable can be obtained from the free energy level diagram in Fig. 4. It is seen that the free energy change in reaction 27 is only slightly less than that in reaction 28 and considerably less than that in reaction 29. Hence it seems

$$X_1^* + H_2O(1) \longrightarrow [Fe_2(SO_4)(OH)^{+2}]^* + H^+ \qquad (27)$$

ably less than that in reaction 29. Hence it seems

$$Fe^{+3} + H_2O(1) \longrightarrow FeOH^{+2} + H^+ \qquad (28)$$

$$Fe^{+2} + H_2O(1) \longrightarrow FeOH^+ + H^+ \qquad (29)$$
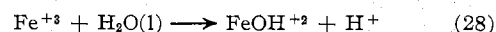
probable that OH^- ion replaces a water ligand in the first coördination shell of Fe^{+3} in X_1^* and that the Fe(II) coördination shell is not disturbed.

Contribution from the Department of Chemistry, Harvard University, Cambridge 38, Massachusetts

Studies on Nickel(II) Complexes. IV.[1] Bis-(N-*sec*-alkylsalicylaldimine) Complexes: Conformational Equilibria in Solution

By R. H. HOLM and K. SWAMINATHAN

Evidence is presented that the partial paramagnetism exhibited by bis-(N-*sec*-alkylsalicylaldimine)–Ni(II) complexes in toluene solutions at and above 37° is not a result of molecular association. In inert solvents these complexes have a fundamentally different behavior than their N-methyl, -*n*-alkyl, and -aryl counterparts, whose solution paramagnetism can be accounted for by a model involving molecular association as the sole means of obtaining paramagnetic behavior.[1,6] Evidence is presented in the form of X-ray, molecular weight, spectral, and magnetic data as well as steric considerations to show that a conformational equilibrium exists in solution between planar (diamagnetic) and tetrahedral (paramagnetic) forms.

Introduction

It is now well recognized that an assembly of complexes of bivalent nickel which are four-coördinate on the basis of simplest formulation can achieve partial or complete occupancy of a triplet spin state by one, or a combination of several, basic effects. These are: (1) the presence of an in-plane ligand field whose intrinsic strength, in the absence of any axial interactions, is insufficient to pair spins; (2) the imposition, through the agency of solvent or solute, of an axial component on a given in-plane field so as to reduce the tetragonality of the field and produce a triplet ground state; (3) the presence of tetrahedral or pseudo-tetrahedral species. No well authenticated examples of (1), *i.e.*, of a rigorously planar triplet complex, are yet known.

Paramagnetic behavior arising from effect (2), especially through solvent–solute interaction, is well established.[2,3] More recently, it has been shown that solute–solute interaction, manifested by molecular association in solutions of inert solvents, has a profound effect on the magnetic behavior in these media. Examples of this effect are found in nickel complexes of β-diketones[4] and certain N-substituted salicylaldimines. Earlier work in this series,[5] as well as that by others,[6] leaves little doubt that the paramagnetic behavior of bis-(N-methyl- and -*n*-alkylsalicylaldimine)–Ni(II) complexes in inert solvents arises solely from an

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

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

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

(4) F. A. Cotton and J. P. Fackler, Jr., *ibid.*, **83**, 2818 (1961); J. P. Fackler, Jr., and F. A. Cotton, *ibid.*, **83**, 3775 (1961).

(5) R. H. Holm, *ibid.*, **83**, 4683 (1961); part II.

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

equilibrium between diamagnetic monomeric and associated paramagnetic species in which the triplet state of some or all of the nickel ions in the aggregates is stabilized by axial interactions. A very similar situation is found in the bis-(N-aryl-salicylaldimine)-Ni(II) complexes.[1]

We first reported several years ago that alteration of the N-substituent from *n*-alkyl to *sec*-alkyl groups in bis-(salicylaldimine)-Ni(II) complexes resulted in a change from essentially diamagnetic behavior to an intermediate paramagnetism of ~2–2.5 B.M. in inert solvents at room temperature.[7] These complexes possess magnetic and spectral properties markedly different from their *n*-alkyl or aryl counterparts and, as will become evident, constitute some of the few examples of the often postulated[8] but seldom authenticated conformational equilibrium in solution between square planar diamagnetic and tetrahedral paramagnetic forms. In an independent and apparently parallel investigation Sacconi, *et al.*,[9] briefly report similar conclusions.

Experimental[10]

Preparation of Compounds.—All complexes were readily prepared in yields ≥ 60% by refluxing in ethanol 0.1 mole of the appropriate nickel (or zinc) salicylaldehyde complex with a 10% mole excess of the primary amine. The substituted nickel salicylaldehyde complexes were prepared previously.[5] The crude products, obtained from the hot reaction mixture by slow addition of water, were purified by two or three recrystallizations from the solvents indicated.

Bis-(N-cyclopropylsalicylaldimine)-Ni(II) was recrystallized from benzene–petroleum ether; m.p. 183–184°.

Anal. Calcd. for $C_{20}H_{20}N_2O_2Ni$: C, 63.57; H, 5.32; N, 7.39; Ni, 15.48. Found: C, 63.45; H, 5.38; N, 7.35; Ni, 15.41.

Bis-(N-isopropylsalicylaldimine)-Ni(II) was recrystallized from chloroform–isopropyl alcohol; m.p. 203–204°.

Anal. Calcd. for $C_{20}H_{24}N_2O_2Ni$: C, 62.70; H, 6.31; N, 7.32; Ni, 15.32. Found: C, 62.49; H, 6.15; N, 7.44; Ni, 15.30.

Bis-(N-*sec*-butylsalicylaldimine)-Ni(II) was recrystallized from ligroin; m.p. 146–147°.

Anal. Calcd. for $C_{22}H_{28}N_2O_2Ni$: C, 64.27; H, 6.86; N, 6.81; Ni, 14.27. Found: C, 64.10; H, 6.90; N, 6.83; Ni, 14.20.

Bis-(N-isobutylsalicylaldimine)-Ni(II) was recrystallized from chloroform–petroleum ether; m.p. 157–158°.

Anal. Found: N, 6.81; Ni, 14.25.

Bis-(N-cyclopentylsalicylaldimine)-Ni(II) was recrystallized from toluene; m.p. 161–162°.

Anal. Calcd. for $C_{24}H_{28}N_2O_2Ni$: N, 6.44; Ni, 13.49. Found: N, 6.46; Ni, 13.40.

Bis-(N-cyclohexylsalicylaldimine)-Ni(II) was recrystallized from chloroform; m.p. 211–212°.

Anal. Calcd. for $C_{26}H_{32}N_2O_2Ni$: C, 67.41; H, 6.98; N, 6.05; Ni, 12.67. Found: C, 67.31; H, 6.73; N, 6.02; Ni, 12.50.

Bis-(3-methyl-N-isopropylsalicylaldimine)-Ni(II) was recrystallized from ligroin; m.p. 132–133°.

Anal. Calcd. for $C_{22}H_{28}N_2O_2Ni$: N, 6.81; Ni, 14.27. Found: N, 6.59; Ni, 14.35.

Bis-(3-ethyl-N-isopropylsalicylaldimine)-Ni(II) was recrystallized from ligroin; m.p. 143–144°.

Anal. Calcd. for $C_{24}H_{32}N_2O_2Ni$: N, 6.38; Ni, 13.36. Found: N, 6.25; Ni, 13.20.

Bis-(3-isopropyl-N-isopropylsalicylaldimine-Ni(II) was recrystallized from ligroin; m.p. 165–167°.

Anal. Calcd. for $C_{26}H_{36}N_2O_2Ni$: N, 6.00; Ni, 12.56. Found: N, 5.96; Ni, 12.62.

Bis-(5-isopropyl-N-isopropylsalicylaldimine)-Ni(II) was recrystallized from ligroin; m.p. 149–150°.

Anal. Found: N, 6.05; Ni, 12.70.

Bis-(3-*t*-butyl-N-isopropylsalicylaldimine)-Ni(II) was recrystallized from ligroin; m.p. 191–193°.

Anal. Calcd. for $C_{28}H_{40}N_2O_2Ni$: C, 67.89; H, 8.14; N, 5.66; Ni, 11.85. Found: C, 67.85; H, 8.33; N, 5.73; Ni, 11.60.

Bis-(N-isopropylsalicylaldimine)-Zn(II) was recrystallized from chloroform–ligroin to give very light yellow plate-like crystals; m.p. 225–227°.

Anal. Calcd. for $C_{20}H_{24}N_2O_2Zn$: C, 61.62; H, 6.21; N, 7.19. Found: C, 61.82; H, 6.15; N, 6.99.

Bis-(N-*sec*-butylsalicylaldimine)-Zn(II) was recrystallized from chloroform–ligroin to give white needles; m.p. 171–172°.

Anal. Calcd. for $C_{22}H_{28}N_2O_2Zn$: C, 63.24; H, 6.75; N, 6.71. Found: C, 63.07; H, 6.60; N, 6.88.

Magnetic Measurements.—Magnetic measurements were made as previously described[1,5] using a sensitive Gouy balance. Calibrants for solids and solutions were $CoHg(SCN)_4$ and distilled and freshly boiled water, respectively. The gram susceptibility for solvent toluene dried over sodium was as previously determined.[1] Measurements were made on freshly prepared solutions; in no case was the solute susceptibility dependent upon the age of the solution, indicating rapid establishment of equilibrium. Susceptibilities measured over a temperature range were found to be completely reversible in behavior. The data in Tables II and III are believed accurate to ±4%.

Spectral Measurements.—All solution spectra were obtained on a Cary Model 14 spectrophotometer at temperatures controlled to ±0.1°. Spectral changes were found to be entirely reversible with temperature and independent of the age of the solutions. Extinction coefficients were calculated using solution densities or by correction of the 25° values by a density ratio of pure solvent. Transmittance spectra of solids in the 1000–1600 mμ range were obtained using mull suspensions as previously described.[11] Spectra of solids in the 500–1000 mμ range were obtained as diffuse reflectance spectra using a Beckman DU spectrophotometer with standard reflectance accessory.

Molecular Weight Measurements.—Molecular weights were measured at 37.00° on solutions prepared from toluene dried over sodium using a Mechrolab osmometer (Mechrolab, Inc., Mountain View, Calif.). Estimated error is stated in the table. At least two determinations at each of the specified concentrations in Table IV were performed and the average is given.

X-Ray Powder Measurements.—Powder data were obtained on a Philips Norelco X-Ray Diffractometer using CuKα radiation (Ni filter). We are indebted to M. C. Babineau of A. D. Little, Inc., Cambridge, Mass., for these results.

Results and Discussion

Complexes examined in this investigation are of the general type I in which R is a *sec*-alkyl group, isopropyl, *sec*-butyl, cyclopropyl, cyclopentyl, and cyclohexyl; and X is methyl, ethyl, isopropyl, and *t*-butyl.
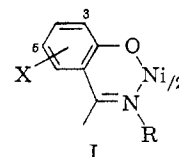
(7) R. H. Holm and T. M. McKinney, *J. Am. Chem. Soc.*, **82**, 5506 (1960).

(8) H. S. French, M. Z. Magee, and E. Sheffield, *ibid.*, **64**, 1924 (1942); S. Fujii and M. Sumitani, *Sci. Rept. Tohoku Univ., First Ser.*, **37**, 49 (1953); J. B. Willis and D. P. Mellor, *J. Am. Chem. Soc.*, **69**, 1237 (1947); H. C. Clark and A. L. Odell, *J. Chem. Soc.*, 520 (1956).

(9) L. Sacconi, P. L. Orioli, P. Paoletti, and M. Ciampolini, *Proc. Chem. Soc.*, 255 (1962).

(10) All melting points are uncorrected.

I

TABLE I

MAGNETIC DATA FOR SOLID BIS-(N-sec-ALKYLSALICYLALDIMINE)–
NICKEL(II) COMPLEXES

R^a	x^m_{corr}	T (°K.)	μ_{eff} (B.M.)
$C_3H_5{}^b$	...	297	0
i-C_3H_7	4476	298	3.28
i-$C_3H_7(3$-$CH_3)^b$	...	297	0
i-$C_3H_7(3$-$C_2H_5)$	4557	297	3.30
i-$C_3H_7(3$-i-$C_3H_7)$	4611	298	3.33
i-$C_3H_7(3$-t-$C_4H_9)$	4531	298	3.30
i-$C_4H_9{}^b$	...	296	0
s-C_4H_9	4713	297	3.36
$C_5H_9{}^b$	...	296	0
$C_6H_{11}{}^b$	...	298	0

^{a} Ring substituent in parentheses. ^{b} Accurate susceptibility not determined.

Reference to Table I shows that certain of these complexes are fully paramagnetic solids and that certain regularities are evident. The three complexes bearing a closed chain nitrogen substituent are diamagnetic whereas those complexes with open chain sec-alkyl substituents are, with one exception, paramagnetic. However, as the data of Table II show, all sec-alkyl com-

TABLE II

MAGNETIC DATA FOR BIS-(N-sec-ALKYLSALICYLALDIMINE)–Ni(II)
COMPLEXES IN TOLUENE AT 37.0°

	Concn. (mmolal)	$10^6 x^m_{corr}$	μ_{eff} (B.M.)
C_3H_5	26.85, 51.37, 65.74	1628, 2160, 2476	2.02, 2.32, 2.49
i-C_3H_7	26.33, 51.16, 74.89	1567, 1583, 1571	1.98, 1.99, 1.98
i-$C_3H_7(3$-$CH_3)$	25.45, 49.20, 73.45	1941, 2047, 2067	2.20, 2.26, 2.27
i-$C_3H_7(3$-$C_2H_5)$	25.55, 50.45, 74.74	2461, 2457, 2521	2.48, 2.48, 2.51
i-$C_3H_7(3$-i-$C_3H_7)$	26.88, 49.30, 85.20	2971, 2893, 2871	2.73, 2.71, 2.70
i-$C_3H_7(3$-t-$C_4H_9)$	25.01, 50.05, 80.85	3987, 3897, 3959	3.16, 3.12, 3.15
i-$C_3H_7(5$-i-$C_3H_7)$	24.75	1412	1.88
i-C_4H_9	79.14	<0	0
s-C_4H_9	25.86, 50.58, 71.66	1783, 1717, 1744	2.11, 2.07, 2.09
C_5H_9	25.49	2065	2.27

plexes, regardless of the nature of their solid phase, become strongly paramagnetic in toluene. All but one assume intermediate magnetic moments per nickel, i.e., $0 < \mu_{eff} < 2.8$ B.M. Examples of this type of magnetic behavior are now quite well known in nickel chemistry and occur particularly frequently in the salicylaldimine series in the presence[1-3,5,6] and absence[12] of non-interacting solvents. In this series, excepting the molten N-n-alkyl complexes[12] where the origin of the observed weak paramagnetism is not yet clarified, such magnetic behavior almost certainly is due to a temperature, solvent, and concentration dependent equilibrium between diamagnetic planar monomers and paramagnetic aggregates.

Inspection of Table IV reveals the exceedingly important distinction between the solution behavior of the N-sec-alkyl complexes studied in this work and that of the analogous methyl, n-alkyl, and aryl species examined previously. It is clear that with the exception of the cyclopropyl derivative all sec-alkyl complexes are essentially or exactly monomeric *under the same condi-*

(11) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Am. Chem. Soc.*, **83**, 4157 (1961).

(12) L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *ibid.*, **82**, 3487 (1960).

tions of solvent, concentration, and temperature where they are found to be appreciably paramagnetic (*cf.* Table II).

A similar comparison of degrees of association and solution susceptibilities of certain N-aryl complexes revealed that all of the paramagnetism could be accounted for by the observed association, although the presence of paramagnetic monomers could not be definitely eliminated.[1] Earlier cryoscopic measurements of the molecular weights of the isopropyl, sec-butyl, and cyclopentyl complexes in benzene yielded $\bar{n} = 1.4$, 1.2, and 1.5, respectively.[7] Evidently the degrees of association are observably temperature dependent, as little difference is anticipated in the solvent properties of benzene and toluene. We had earlier pointed out[7] that associa-

TABLE III

TEMPERATURE DEPENDENCE OF THE SUSCEPTIBILITY OF
BIS-(N-ISOPROPYLSALICYLALDIMINE)-Ni(II)^a IN TOLUENE

T (°K.)	x^m_{corr}	μ_{eff} (B.M.)
272.2	1588	1.87
282.3	1545	1.88
293.4	1522	1.90
303.4	1492	1.91
313.2	1471	1.93
323.1	1459	1.95
333.3	1415	1.95
343.5	1400	1.97

^{a} Concentration 0.04357 M (25°), 51.18 mmolal.

TABLE IV

MOLECULAR WEIGHT DATA FOR BIS-(N-sec-ALKYLSALICYL-
ALDIMINE)–Ni(II) COMPLEXES IN TOLUENE AT 37.0°

R^a	Concn. (mmolal)^b	$\bar{n}^c$
C_3H_5	26.86, 51.34, 81.80	1.11, 1.20, 1.30
i-C_3H_7	26.33, 51.16, 74.89	1.06, 1.04, 1.04
i-$C_3H_7(3$-$CH_3)$	25.40, 49.60, 73.18	1.02, 1.00, 1.00
i-$C_3H_7(3$-$C_2H_5)$	26.26, 50.11, 73.30	0.97, 0.98, 0.97
i-$C_3H_7(3$-i-$C_3H_7)$	27.05, 49.94, 84.66	.99, 1.00, .97
i-$C_3H_7(3$-t-$C_4H_9)$	25.19, 48.59, 80.02	.98, 1.00, .98
i-C_4H_9	25.93, 51.30, 79.22	.98, 0.98, 1.00
s-C_4H_9	25.75, 48.66, 71.82	.99, 0.98, 0.98
$C_5H_9{}^d$	25.67	1.02

^{a} Ring substituent in parentheses. ^{b} Corresponds to the range 0.02–0.07 M (25°). ^{c} Estimated error ±3%. ^{d} Insufficiently soluble for measurements at higher concentrations.

tion need not necessarily account for all the paramagnetism observed in benzene solutions of these complexes at 25°. Measurement of the susceptibility of the representative isopropyl complex in toluene from 0 to 70° (Table III) shows only a slight variation in the magnetic moment and a small increase in the moment at and above 40°, where the only important contribution to the paramagnetic susceptibility must arise from monomeric species.

It is evident from the foregoing discussion that a model involving molecular association, with its concomitant rationalization of magnetic behavior, does not apply to systems of the bis-(N-sec-alkylsalicylaldimine) complexes in toluene solution at and above 37° and within the concentration ranges specified in Table IV. We have, therefore, conducted our magnetic and

spectral measurements under these conditions so as to eliminate associated species from consideration. Only the cyclopropyl complex is appreciably associated under these conditions. We defer discussion of this complex until later and confine our remarks to systems containing monomers.

Because under the above experimental conditions solute paramagnetism must arise from monomeric species, two situations must be considered[13]: (1) the presence of some or all of the solute molecules in a non-planar configuration whereby the distortion is small enough to preserve a singlet ground state but large enough to bring a triplet state within thermal range; and (2) the presence of species possessing a triplet ground state and hence described as tetrahedral or pseudo-tetrahedral. The latter is clearly the limiting case of large distortions from planarity. It should be noted that with nearly all complexes studied, (2) and (1), in which all solute molecules are distorted, cannot be readily distinguished by the data presented herein.[14] On the basis of the evidence described below, (2), *viz.*, an equilibrium between planar and tetrahedral species, is concluded to be the correct explanation. This conclusion is drawn from the following evidence.

1. X-Ray Results.—In Table VI a comparison of the more prominent lines in the X-ray powder patterns of the N-isopropyl and N-*sec*-butyl nickel and zinc complexes is given. These selected data from the two sets of essentially superimposable diffractometer tracings reveal the isomorphism of the two pairs of complexes. Earlier it was concluded in a preliminary study that the analogous N-*n*-butyl zinc complex is tetrahedral and that the Co(II) complex is isomorphous with it.[17] It is then very reasonable to assume that the *sec*-alkyl zinc complexes and, hence, the nickel complexes, are tetrahedral. Sacconi, *et al.*,[9] report that the zinc and cobalt complexes are also isomorphous. There is some recent spectral evidence suggesting that these *sec*-alkyl Co(II) complexes are pseudo-tetrahedral.[18] From X-ray evidence there seems little doubt that the crystalline *sec*-alkyl zinc and nickel complexes are isostructural and thus tetrahedral or nearly so.

(13) On the basis of previous work[5] we eliminate solvation as a cause of paramagnetism but take note that the extent of paramagnetism as regulated by a solution equilibrium may well have a solvent dependence.

(14) These two situations are in principle distinguishable, most convincingly by a careful and extensive study of the temperature dependence of the susceptibility. In (1) the susceptibility is governed by a simple energy difference between states.[15] Systems of this type should manifest a Boltzmann temperature dependence of susceptibility, in which case the average moment per nickel approaches $g\beta\sqrt{6/2}$ (g is the g-factor of the lowest triplet state) as $T \rightarrow \infty$, and very small entropy changes for the magnetic interconversion. In (2) the susceptibility depends on free energy changes[16] so that average moments may approach the pure triplet state moment, $g\beta\sqrt{S(S+1)}$ as a limit; further, with conformational equilibria appreciable entropy changes are anticipated and have been found.[16] Extensive temperature dependent susceptibility measurements are being performed in connection with studies of the contact shifts observed in the proton resonance spectra of these compounds (R. H. Holm, G. O. Dudek, and A. S. Chakravorty, to be published).

(15) C. J. Ballhausen and A. D. Liehr, *J. Am. Chem. Soc.*, **81**, 538 (1959).

(16) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *ibid.*, in press.

(17) E. Frasson and C. Panattoni, *Z. Krist.*, **116**, 154 (1961).

(18) H. Nishikawa, S. Yamada, and R. Tsuchida, *Z. Naturforsch.*, **17b** 78 (1962).

TABLE V

SPECTRAL DATA FOR BIS-(N-*sec*-ALKYLSALICYLALDIMINE)–Ni(II) COMPLEXES IN TOLUENE AT 37.0°[a]

R^b	λ_{max} (cm.$^{-1}$)	ϵ (1. mole^{-1} cm.$^{-1}$)
C_3H_5	16300, 10000	47.7, ...
	6700	8.4
i-C_3H_7	16900 (sh), 14300 (sh)	... ...
	11000, 6850	2, 22.2
i-C_3H_7(3-CH_3)	16700 (sh), 15100 (sh)	... ...
	11000, 6870	3, 39.7
i-C_3H_7(3-C_2H_5)	c 15000	64.0
	11000, 6850	3, 46.6
i-C_3H_7(3-i-C_3H_7)	c 14600	67.3
	11000, 6830	4, 50.0
i-C_3H_7(3-t-C_4H_9)	c 14100	81.9
	10900, 6580	4, 66.8
i-C_3H_7(5-i-C_3H_7)	16700 (sh) c	...
	11000, 6880	2, 25.6
i-C_4H_9	16100	74.1
s-C_4H_9	16600, 14300 (sh)	72.2, ...
	11000, 6870	1, 20.0
C_5H_9	16900 (sh), 14300 (sh)	... ...
	11000, 6830	2, 28.6

[a] Concentrations 0.0197–0.0200 M (37°). [b] Ring substituents in parentheses. [c] Component not clearly observed.

TABLE VI

X-RAY POWDER DATA FOR SOME BIS-(N-*sec*-ALKYLSALICYLALDIMINE) COMPLEXES[a]

R = i-C_3H_7		R = s-C_4H_9	
Zn	Ni	Zn	Ni
9.80 vs	9.90 vs	10.5 vs	10.5 vs
8.95 m	8.82 m	8.55 w	8.41 w
8.25 m	8.30 m	8.20 w	8.20 w
7.00 m	7.02 m	6.65 m	6.60 m
6.65 w	6.60 w	6.45 m	6.45 m
6.25 s	6.20 s	5.90 w	5.95 w
6.05 w	6.00 w	4.95 s	4.94 s
5.46 s	5.46 s	4.68 w	4.67 w
4.84 m	4.80 w	4.40 m	4.40 w
4.65 m	4.62 m	4.24 vw	4.24 vw
4.48 ms	4.48 m	4.10 w	4.08 w
3.94 m	3.94 m	3.59 w	3.59 w
3.80 m	3.83 w	3.21 w	3.23 w
3.72 w	3.72 w	2.91 w	2.91 w
3.58 w	3.56 w	2.71 w	2.70 vw
3.52 w	3.54 w		
3.36 m	3.37 w		
3.20 m	3.20 m		
3.11 m	3.11 m		

[a] Data are interplanar spacings calculated from the more prominent lines in the ranges: isopropyl, $8° \leqslant 2\theta \leqslant 29°$; *sec*-butyl, $8° \leqslant 2\theta \leqslant 34°$. Relative intensities are listed.

2. Molecular Weights.—As emphasized above, the complexes are monomeric under conditions where appreciable paramagnetism is found and where the spectral features are distinctly different from those observed in systems containing associated species.[1,5]

3. Steric Factors.—Examination of accurate metal chelate scale models reveals a strongly enhanced difficulty in maintaining a planar structure of the bis-complexes when the nitrogen substituent is *sec*-alkyl rather than *n*-alkyl. In particular, interaction with the 3-substituent of the adjacent benzene ring appears unfavorable and can be alleviated by distortion to a non-planar, or best to a tetrahedral, conformation. It is to be noted

that this steric effect is specific to a *sec-* or *t*-alkyl substituent or at least the only important consequences from this effect thus far found have been with complexes bearing these groups. The N-*t*-butyl complex is claimed to be tetrahedral.[9] Branching of the alkyl chain at the β-carbon of the substituent, as in the iso-butyl complex, largely eliminates steric crowding. As the spectrum and diamagnetism of this compound show, it behaves as the *n*-alkyl species and is therefore planar.[3,5] Although the *n*- and *sec*-alkyl groups differ slightly in their inductive capacities, the evidence at hand is taken to support a steric, rather than an electronic, origin for the non-planar structures of these complexes. In other cases, however, both steric[16] and electronic[16,19] factors have been claimed responsible for the relative proportions of tetrahedral species in solutions of two different groups of nickel complexes.

4. Magnetic Data.—The moments of the paramagnetic solids fall into the narrow range 3.28–3.36 B.M. and are then comparable with those for other pseudo-tetrahedral species such as the $[Ni(P(C_6H_5)_3)_2-X_2]$ complexes recently studied.[20,21] These values fall far short of the 3.9–4.2 B.M. range predicted by theory[22] for perfect T_d symmetry and observed experimentally in certain $[NiX_4]^{-2}$ salts.[23] The low orbital contributions arise from a pronounced C_{2v} ligand field component which has the effect of removing degeneracy of some of the levels arising from spin-orbit coupling on the orbitally degenerate $(^3T_1)$ ground state.[24] This situation could be brought about in several ways; a particularly effective means is a distortion from gross tetrahedrality of the $Ni-O_2N_2$ grouping. A better assessment of this effect must await a detailed structural study.

Upon dissolution in toluene the solid paramagnetic complexes undergo decreases in paramagnetism whereas the diamagnetic complexes become appreciably paramagnetic. An indication that the proportion of paramagnetic species is sterically controlled may be taken from the data on the 3-substituted species. The order of increasing proportions of tetrahedral species is $H < CH_3 < C_2H_5 < i\text{-}C_3H_7 < t\text{-}C_4H_9$, which is nicely in accord with the steric considerations mentioned above. Further, substitution in one instance at the 5-position, which should have no important steric consequences, produces no significant change in paramagnetism. Additionally, in the N-*n*-propyl series 3-methyl and 3-isopropyl substituents still preserve diamagnetism in solution.[5] With no ring substituents, the size of the group appended to nitrogen also affects the extent of solution paramagnetism, the order from this and other work[9] being $i\text{-}C_3H_7 < sec\text{-}C_4H_9 < C_5H_9 << t\text{-}C_4H_9$.

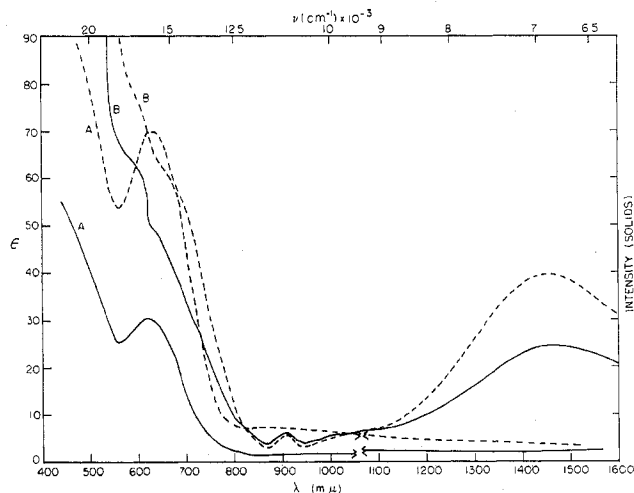The proportion of paramagnetic species in solution can be approximated by comparison with solid state

Fig. 1.————— Bis-(N-cyclopentylsalicylaldimine)-Ni(II): A, solid; B, 0.0197 *M* solution. — — — — Bis-(3-methyl-N-iso-propylsalicylaldimine)-Ni(II): A, solid; B, 0.0200 *M* solution.

susceptibilities, which may be taken as reasonable limits for solution values in the absence of diamagnetic forms. In this way it is seen, for example, that systematic substitution at the 3-position increases this proportion from $\sim$37% (3-H) to $\sim$90% (3-*t*-C_4H_9). The latter complex definitely has a triplet ground state since the maximum average moment expected for a singlet state lowest is 2.9 B.M. We suggest, although we cannot yet prove from available data, that the other complexes also have a triplet ground state. The temperature dependence of the susceptibility of the isopropyl complex in toluene solution (Table III) shows a small increase in magnetic moment with increasing temperature. Over a higher temperature range in xylene and bibenzyl, an increase in the percentage of paramagnetic species is reported.[9] These results reflect the expected positive enthalpy changes for the planar $\rightleftharpoons$ tetrahedral interconversion. A similar situation is met in the bis-(aminotroponeimine) nickel complexes, which presumably owe their tetrahedral structures in solution to steric factors.[16]

5. Spectral Data.—When the *sec*-alkyl complexes are dissolved the solutions take on a characteristic brown color.[25] In Fig. 1 are shown two examples of the spectral changes which take place when a diamagnetic solid is dissolved in toluene. The crystalline isopropyl (3-methyl) and cyclopentyl complexes have no absorption in the near-infrared and show only the single spin-allowed transition in the visible which is always observed for planar nickel complexes of this type.[1,3,5,26] The solution spectra of these complexes are extremely similar to those obtained by dissolving solid paramagnetic species such as the unsubstituted isopropyl complex, the spectra of which are given in Fig. 2. This result is quite representative for the

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(25) Similar brown colors have been noted on heating toluene solutions of certain bis-(N-arylsalicylaldimine) nickel complexes.[1] In these cases, however, the moments decrease up to 70°, indicating that dissociation of solution aggregates predominantly controls the paramagnetic behavior. Above this temperature tetrahedral species may exist, but as yet no investigations have been carried out.

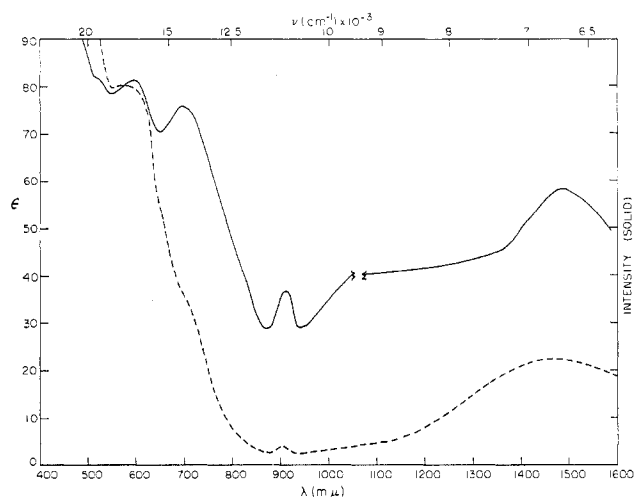(26) G. Maki, *J. Chem. Phys.*, **29**, 1129 (1958).

Fig. 2.—Bis-(N-isopropylsalicylaldimine)-Ni(II):   ———
solid; — — — — 0.0197 M solution. Spectra of solids taken as
transmittance spectra in mulls above 1000 mμ, diffuse reflectance
spectra below 1000 mμ. ϵ values refer to solutions only.

solid paramagnetic complexes and suffices to illustrate
that their spectra are similar in both the solid and solu-
tion phases, particularly with respect to the 6300–
12,000 cm.$^{-1}$ range. In the visible region there is,
however, a noticeable decrease in band resolution upon
passing into the solution phase. This is attributed
to the presence of diamagnetic species which, like
their n-alkyl analogs, should possess a band in the
15,700–16,700 cm.$^{-1}$ range.[3,5] Although we have never
resolved this band in any such case, its presence would
account for the diffuseness of spectral features in the
visible. The solution spectral features of the sec-alkyl
complexes are all rather similar and the data are set
out in Table V.

Comparison of the spectra of the sec-alkyl complexes
with those of other tetrahedral[27] or pseudo-tetra-
hedral[21,28] species reveals definite similarities. The
spectra of the latter complexes have been shown to
be satisfactorily interpreted by the Liehr–Ballhausen
complete treatment of nickel(II) in rigorously tetra-
hedral ligand fields.[24] Using the energy monograph
calculated for $\lambda = -275$ cm.$^{-1}$ and $B = 810$ cm.$^{-1}$
and taking the spectrum of the solid isopropyl complex
($cf.$ Fig. 2) as representative, the following assignments

are made: $^3T_1 \rightarrow {}^3A_2(F)$ (6700 cm.$^{-1}$, ν_2); $\rightarrow {}^1D$ (11,000
cm.$^{-1}$); $\rightarrow {}^3T_2(P)$ (14,400, 16,900 cm.$^{-1}$, ν_3); $\rightarrow {}^1G$
(19,600 cm.$^{-1}$). Taking the ν_2 assignment as most cer-
tain and thereby obtaining $D_q \approx 310$ cm.$^{-1}$, it is found
that the observed energies for remaining transitions
fit the calculated energy scheme to $\pm 10\%$. Agreement
for the solution spectra of other complexes is the same.
These reasonable fits are similar to those found for the
$[Ni(P(C_6H_5)_3)_2X_2]$ complexes[21] in that the low symmetry
component of the ligand field, whatever its origin, has
an observable effect on the magnetism but no pro-
nounced effect on the spectra.

We suggest that the weight of the above evidence
favors the existence of planar $\rightleftharpoons$ tetrahedral conforma-
tional equilibria in solutions of these sec-alkyl complexes
and that the existence of tetrahedral species is due to the
particular steric requirements of the sec-alkyl groups
in these bis-complexes. The bis-(N-sec-alkylsalicylaldi-
mine) species therefore constitute the third general class
of nickel complex in which this conformational effect is
found. Eaton, Phillips, and Caldwell[16] have very re-
cently presented very strong evidence for this effect
in solutions of bis-(aminotroponeimine) complexes.
The same effect is claimed for solutions of bis-(phos-
phine)-dihalo complexes in benzene.[19,29]

Finally, we mention the cyclopropyl complex, which
is the only sec-alkyl derivative appreciably associated
at 37° in toluene solution. Like the other complexes,
however, all of the observed paramagnetism cannot be
due to molecular association. A proportion of the
molecules must exist as tetrahedral species and, there-
fore, solutions of this complex resemble those of, $e.g.$,
the isopropyl and sec-butyl complexes at lower tempera-
tures in that they contain solute in three forms, as
planar diamagnetic, associated paramagnetic, and
tetrahedral species. The existence of associated species
is likely connected with the smaller size of the cyclo-
propyl group; interestingly, the complex is more asso-
ciated than the N-methyl complex under the same condi-
tions.

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