served for the future. It should be noted that the associations of Ag^+ and CN^- are the strongest which have been measured in molten salt solutions. Values of $-\Delta A_1$ for associations of Ag^+ with various ions in molten nitrates are in the order $CN^- > I^- > Br^- > Cl^- > SO_4^{-2}$.

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Studies on Nickel(II) Complexes. III.[1,2] Bis-(N-arylsalicylaldimine) Complexes

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It has been found that upon alteration of the R substituent in bis-(R-N-salicylaldimine)-nickel(II) complexes from methyl or *n*-alkyl to certain aryl groups, large increases in the solution paramagnetism in inert solvents are produced. The factors affecting this surprising behavior were investigated in an extensive study of the R = aryl complexes. By variation of substituents and their positions on the aryl portion of the molecules, it was found that the spectral and magnetic properties and the extent of molecular association could be consistently controlled. On the basis of this behavior the complexes fall into three categories: (1) those with *o*-substituted aryl groups, which are diamagnetic and monomeric; (2) those with phenyl and *p*-substituted aryl complexes, which are strongly paramagnetic in solution ($\mu_{eff} \geqslant 2.8$ B.M.), associated ($1.5 < \bar{n} < 2.0$), and are either diamagnetic or paramagnetic solids; (3) those with *m*-substituted aryl groups, which have in solution $\mu_{eff} \geqslant 3.2$ B.M., $2 < \bar{n} < 3$, and are always paramagnetic solids. For complexes of the second category the magnetic and molecular weight data at 37° were interpreted in terms of a diamagnetic monomer–paramagnetic dimer equilibrium. The results present further substantiation of the relation between solution paramagnetism and molecular association of apparently quadricoördinate Ni(II) complexes. The nature of the associated forms in no case could be deduced with certainty from the data; however, the presence of axially perturbed *trans*-planar coördination units appears likely.

Introduction

Considerable evidence has been accumulated recently which demonstrates that certain paramagnetic nickel complexes, apparently four-coördinate on the basis of simplest formulation, are in fact additionally coördinated in a fashion such that the triplet state of the metal ion becomes substantially stabilized. The best characterized example of this effect at present is Ni(II) acetylacetonate, which has been shown to contain octahedrally coördinated nickel ions in the discrete trimers[3] present in the fully paramagnetic solid[4] and to be trimeric in benzene,[5] in which it is likewise fully paramagnetic.[4] Only at relatively high temperatures is the association appreciably broken down in inert solvents and spectral evidence indicates that diamagnetic monomers are formed.[6] Further, molecular association of more sterically encumbered β-diketone complexes has been shown to be less complete and the spectral and magnetic features of these complexes in inert media have been successfully though not uniquely interpreted in terms of monomer–trimer equilibria.[4,6] In a preceding part[2] of this series it was demonstrated that the anomalous partial paramagnetism of bis-(N-methylsalicylaldimine)-nickel(II) in solution has its origin in molecular association and a model of the associated species was suggested. All of these results tend to emphasize the relation between paramagnetic behavior and molecular association in both the solid and solution phases.

Previously it had been found that variation of the nature of the group appended to the imine nitrogen in bis-(salicylaldimine)-nickel(II) complexes from *n*-alkyl to certain aryl functions produced in solution a change from essentially complete occupation of a singlet state to predominant

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[1] Part I, R. H. Holm, *J. Am. Chem. Soc.*, **82**, 5632 (1960).

[2] Part II, R. H. Holm, *ibid.*, **83**, 4683 (1961).

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

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

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

[6] J. P. Fackler, Jr., and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 3775 (1961).

TABLE I

CHARACTERIZATION OF BIS-(R-N-SALICYLALDIMINE)-NICKEL(II) COMPLEXES

R	Calcd.				Found			
	Ni	C	H	N	Ni	C	H	N
C_6H_5	13.00	69.22	4.47	6.21	12.9	69.45	4.55	6.14
$C_6H_5(3\text{-}CH_3)$	12.25	70.18	5.05	...	12.3	69.98	4.78	...
$C_6H_5(5\text{-}CH_3)$	12.25	70.18	5.05	...	12.2	69.72	5.07	...
$C_6H_5(3\text{-}i\text{-}C_3H_7)$	10.96	71.80	6.03	...	11.0	71.56	5.90	...
$C_6H_5(5\text{-}i\text{-}C_3H_7)$	10.96	71.80	6.03	...	10.8	71.70	5.89	...
$p\text{-}C_6H_4CH_3$	12.25	70.18	5.05	5.85	12.1	69.67	5.04	5.62
$m\text{-}C_6H_4CH_3$	12.25	70.18	5.05	5.85	12.2	70.34	4.99	5.75
$o\text{-}C_6H_4CH_3$	12.25	70.18	5.05	5.85	12.3	69.82	5.18	5.68
$p\text{-}C_6H_4F$	12.05	64.11	3.73	5.76	11.9	64.21	3.82	5.64
$p\text{-}C_6H_4Cl^a$	11.29	60.05	3.49	5.39	11.2	59.46	3.34	5.22
$m\text{-}C_6H_4Cl^a$	11.29	60.05	3.49	5.39	11.2	59.47	3.44	5.12
$p\text{-}C_6H_4N(CH_3)_2$	10.92	...	...	10.43	10.9	...	...	10.51
$2,4\text{-}C_6H_3(CH_3)_2$	11.57	71.03	5.56	...	11.7	71.15	5.77	...
$2,5\text{-}C_6H_3(CH_3)_2$	11.57	71.03	5.56	5.52	11.6	71.28	5.69	5.52
$3,4\text{-}C_6H_3(CH_3)_2{}^b$	11.57	71.03	5.56	...	11.5	69.97	5.36	...
$3,5\text{-}C_6H_3(CH_3)_2{}^b$	11.57	71.03	5.56	...	11.4	69.81	5.45	...

[a] Calcd. for $0.5H_2O$: Ni, 11.09; C, 59.03; H, 3.62; N, 5.30. [b] Calcd. for $0.5H_2O$: Ni, 11.37; C, 69.79; H, 5.67.

occupation of a triplet state.[7] The factors underlying this surprising change in magnetic properties have been investigated and the results, in the form of an extensive study of the N-aryl complexes, are presented here. These results serve to demonstrate further the generality of molecular association in Ni(II) complexes, at least in solution, and its concomitant effect on magnetic properties.

Experimental

Preparation of Compounds.—All complexes prepared and characterized in this work are listed in Table I. The phenyl[8] complex and its 3- and 5-substituted derivatives and the *p*-dimethylaminophenyl[9] complex were prepared according to published procedures. The remaining complexes were prepared by refluxing a mixture of bis-(salicylaldehyde)-nickel(II) dihydrate with a threefold excess of amine in ethanol for 4–5 hr. The crude complexes thus obtained were recrystallized or reprecipitated two or three times from chloroform or benzene in combination with petroleum ether and dried *in vacuo* at 80–100° over phosphorus pentoxide. Reactions involving *o*-substituted anilines always gave dark green crystalline products which were easily recrystallized and whose analyses corresponded well with anhydrous forms of the expected complex. Reactions involving *m*-, *p*-, or disubstituted anilines proceeded no less readily but always produced a lighter green microcrystalline product, usually appreciably soluble in benzene, toluene, or chloroform only on prolonged heating. These products were difficult to recrystallize and were purified by reprecipitation as above. In several instances (see Table I) consistently low analyses for carbon were obtained in several different preparations of the same compound. The analytical data are perhaps in better agreement with the presence of $0.5H_2O$ per mole of complex, although repeated hydrogen analyses were always low. The most satisfactory analytical sample of the *m*-tolyl complex was obtained by reaction of bis-(salicylaldehyde)-nickel(II) dihydrate in an excess of the pure amine at 110° for 4 hr. followed by purification as above. Complexes of the tolyl series have been reported previously by Hunter and Marriott,[10] who obtained them by direct reaction of nickel acetate and the Schiff base in solution or by reaction of salicylaldehyde, amine, and nickel acetate in solution.

Magnetic Measurements.—Magnetic measurements were made as previously described using a sensitive Gouy balance.[2] Standards for measurements on solids and solutions were $CoHg(SCN)_4$[11] and distilled and freshly boiled water.[12] For toluene dried over sodium the gram susceptibility was determined as -0.7160×10^{-6} (lit.,[13] -0.7175×10^{-6}); the value for purified chloroform was as previously determined.[2] Solutions were thermostated during measurement by the use of a thin-walled dewar flask of special design in which the sample tube was suspended and through which thermostated water from a constant temperature source was circulated. Solutions were equilibrated 2–3 hr. at a given temperature before measurements; temperature control of the sample was at least $\pm 0.1°$. Freshly prepared solutions were allowed to stand at least 3 hr. before measurement. Where checked the solute susceptibility was not dependent upon the age of the solution. Susceptibilities measured over a temperature range were found to exhibit completely reversible changes over several cycles of heating from 20 to 70° over a period of 1 week. Susceptibility values $\gtrsim 1000 \times 10^{-6}$ were measured with a precision of $< \pm 3\text{–}4\%$ even at the most dilute concentrations. Solute susceptibilities were calculated at all temperatures using solution densities determined pycnometrically in a vessel calibrated

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

(8) F. Basolo and W. R. Matoush, *ibid.*, **75**, 5663 (1953).

(9) P. Pfeiffer and H. Krebs, *J. prakt. Chem.*, **155**, 77 (1939).

(10) L. Hunter and A. Marriott, *J. Chem. Soc.*, 2000 (1937).

(11) B. N. Figgis and R. S. Nyholm, *ibid.*, 4190 (1958).

(12) H. Auer, *Ann. Physik*, **18**, 893 (1933).

(13) G. Foex, "Constantes Selectionees diamagnetisme et paramagnetisme," Masson et Cie, Paris, 1957.

over the necessary temperature range. Diamagnetic corrections were calculated using Pascal's constants as given by Selwood.[14]

Spectral Measurements.—All spectra were obtained in quartz cells on a Cary Model 14 spectrophotometer at temperatures controlled to ±0.1° by circulation of thermostated water through an insulated cell compartment. Solutions were prepared from reagent grade chloroform or toluene dried over sodium. Spectral changes were found to be entirely reversible with temperature and in all cases to be independent of the age of the solution. Extinction coefficients were calculated using solution densities or by correction of the 25° values by a density ratio of pure solvent.

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.). At least two determinations at each of the specified concentrations in Table V were performed and the average given. Estimated errors are given in the table. Where solubility permitted the monomeric species gave virtually identical results when measured by freezing point depression in benzene. Using this method a number of the associated species gave poorly reproducible results; a preliminary report[15] of the monomerism of the *m*- and *p*-tolyl complexes in freezing benzene now must be regarded as incorrect.

Results

In this study complexes of the general type I have been investigated in which R = aryl and X = CH_3, or *i*-C_3H_7. Previous work in this Laboratory has dealt with complexes derived from the same basic salicylaldimine skeleton but in which R = methyl or *n*-alkyl. Complexes in which R = *s*-alkyl will be discussed in a forthcoming part of this series. Certain preliminary results on these N-aryl complexes already have been reported.[7,15]

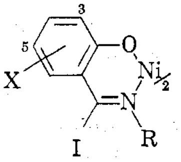

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TABLE II

MAGNETIC DATA FOR SOLID BIS-(R–N–SALICYLALDIMINE)-NICKEL(II) COMPLEXES

R	χ^m_{corr}	T (°K.)	μ_{eff} (B.M.)
C_6H_5[a]	....	297	0
p-$C_6H_4CH_3$	4520	295	3.28
m-$C_6H_4CH_3$	4671	296	3.34
o-$C_6H_4CH_3$[b]	....	297	0
p-C_6H_4F[b]	....	297	0
p-C_6H_4Cl	4659	297	3.34
m-C_6H_4Cl	4765	296	3.39
p-$C_6H_4N(CH_3)_2$[b]	....	297	0
2,4-$C_6H_3(CH_3)_2$[b]	....	298	0
2,5-$C_6H_3(CH_3)_2$[b]	....	297	0
3,4-$C_6H_3(CH_3)_2$	4474	296	3.27
3,5-$C_6H_3(CH_3)_2$	4606	298	3.33

[a] $\chi^g = -0.426 \times 10^{-6}$. [b] Accurate susceptibility not determined.

TABLE III

MAGNETIC DATA FOR BIS-(R-N-SALICYLALDIMINE)-NICKEL(II) COMPLEXES IN CHLOROFORM AT 25.0°

R	Concn. (mmolal)	$10^6\chi^m_{corr}$	μ_{eff} (B.M.)
C_6H_5	23.89	3562	2.93
	32.83	3570	2.93
C_6H_5(3-*i*-C_3H_7)	29.89	95	0.48
	51.15	174	0.65
C_6H_5(5-CH_3)	30.44	3613	2.95
	99.27	3921	3.07
C_6H_5(5-*i*-C_3H_7)	23.98	3330	2.83
p-$C_6H_4CH_3$	27.18	3816	3.03
	60.06	3837	3.05
m-$C_6H_4CH_3$	26.83	4167	3.16
	67.32	4151	3.16
o-$C_6H_4CH_3$	26.37	87	0.46
	59.61	584	1.19
p-C_6H_4F	24.42	3477	2.89
	38.26	3550	2.92
p-C_6H_4Cl	26.61	4094	3.14
m-C_6H_4Cl	24.91	4283	3.20
	48.11	4369	3.23
	76.53	4493	3.28
p-$C_6H_4N(CH_3)_2$	25.65	4036	3.11
2,4-$C_6H_3(CH_3)_2$	25.06–60.99	....	0
2,5-$C_6H_3(CH_3)_2$	25.58–75.00	....	0
3,4-$C_6H_3(CH_3)_2$	25.64	4384	3.24
	72.70	4379	3.24
3,5-$C_6H_3(CH_3)_2$	25.63	4475	3.28
	72.80	4436	3.26
3,5-$C_6H_3(CH_3)_2$ (in C_6H_{12})	26.47	4319	3.23

Magnetic data for the N-aryl complexes in the solid and solution phases are presented in Tables II and III. Results are given in terms of susceptibilities and magnetic moments per nickel ion. It first is to be noted that six of the complexes are fully paramagnetic solids, a behavior which alone is interesting for all other bis-complexes of the salicylaldimine type,[2,16,17] as well as most internal Ni(II) complexes, are diamagnetic solids. Exceptions in the first case are the presumably associated forms of bis-(N-methylsalicyl-

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[14] P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 78.

[15] R. H. Holm in "Advances in the Chemistry of Coordination Compounds," S. Kirschner, ed., The Macmillan Co., New York, N. Y., 1961, pp. 341–349.

[16] Certain N-*s*-alkylsalicylaldemine complexes have been found to be fully paramagnetic and will be discussed in a future part of this series.

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

aldimine)-nickel(II),[18,19] its 5-chloro analog,[20] and certain N-substituted *o*-hydroxyacetophenoneimine complexes, all of which are rendered paramagnetic by thermal treatment of the initially diamagnetic solids. Further, magnetic behavior in the solid and solution phases clearly is dependent on the exact structural nature of the aryl group. Inspection of the solution magnetic data reveals that all complexes except those bearing *o*-substituents on the aryl portion or 3-substituents on the benzene ring are strongly paramagnetic in solution, with moments >2.8 B.M. always being observed. Particularly striking are the phenyl, *p*-fluorophenyl, and *p*-dimethyl aminophenyl complexes which are diamagnetic solids yet give solution moments at room temperature exceeding the spin-only value. This behavior is similar in kind but not in degree to that of bis-(N-methylsalicylaldimine)-nickel(II), which at virtually the same concentrations and temperature in chloroform exhibits moments ≤ 1.3 B.M.[2] Complexes that are paramagnetic as solids usually become slightly less paramagnetic in solution. Where solubility permitted the concentration dependence of the susceptibility was checked and found to be slight. Again, this behavior is to be contrasted with the partially associated N-methyl complex, whose susceptibility in chloroform and benzene is markedly concentration dependent.

The temperature dependence of the solution susceptibilities of the representative complexes is set out in Table IV and Fig. 1. The phenyl and *p*-fluorophenyl complexes clearly show no Curie dependence whereas the *m*-chlorophenyl complex exhibits an apparent Curie–Weiss behavior. Significantly, the moments of the first two complexes decrease well below the spin-only value at the higher temperatures, necessitating the formation of diamagnetic, undoubtedly monomeric, species whose concentration increases with increasing temperature.

Table IV

Temperature Dependence of the Susceptibilities of Some Bis-(R-N-salicylaldimine)-nickel(II) Complexes in Toluene

	R					
	C_6H_5[a]		p-C_6H_4F[b]		m-C_6H_4Cl[c]	
T (°K)	χ^{m}_{corr}	μ_{eff}	χ^{m}_{corr}	μ_{eff}	χ^{m}_{corr}	μ_{eff}
293.0	4077	3.10	3968	3.06	4697	3.33
303.0	3761	3.03	3473	2.93	4350	3.26
313.0	3435	2.95	3026	2.76	4122	3.23
323.0	3050	2.82	2631	2.62	3891	3.19
333.0	2579	2.64	2169	2.43	3650	3.13
343.0	1978	2.34	1890	2.29	3397	3.07

[a] 29.96 mmolal, 0.02573 *M* (20°). [b] 29.54 mmolal, 0.02538 *M* (20°). [c] 50.01 mmolal, 0.04270 *M* (20°).

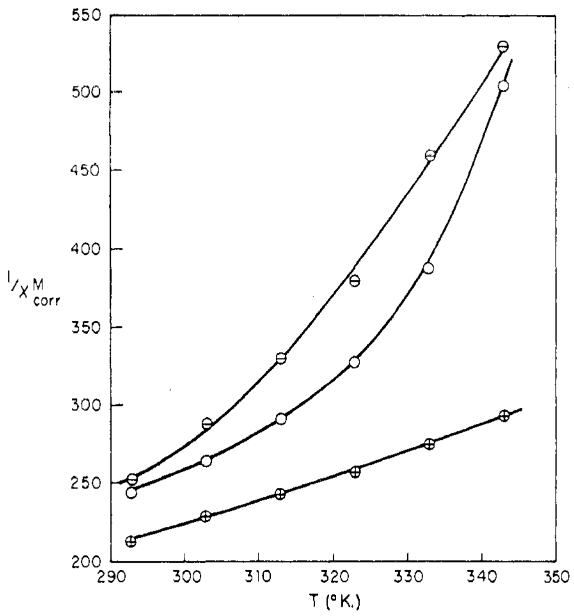

Fig. 1.—Plot of the reciprocal of corrected molar susceptibility *vs.* temperature in toluene solution: O, R = C_6H_5, 29.96 mmolal; ⊖, R = p-C_6H_4F, 29.54 mmolal; ⊕, R = m-C_6H_4Cl, 50.01 mmolal.

Substantial clarification of the magnetic results is afforded by a consideration of the molecular weight data for complexes in toluene at 37°. The results, expressed in terms of the average degree of association $\bar{n}$, serve to buttress earlier conclusions[2,4,7] that paramagnetic behavior of apparently quadricoördinate nickel complexes in solutions of non-coördinating solvents is accompanied by molecular association, whereas monomeric species are diamagnetic. Solubilities permitted the measurement of a representative number of complexes. As is inferred from the magnetic data, *o*-substituted complexes are monomeric and all others associated. Again, the structural nature of the aryl group affects the properties of the complexes such that the phenyl and *p*-substituted species have $1.5 < \bar{n} < 2$ and *m*-substituted species have $2 < \bar{n} < 3$. These complexes are without exception strongly paramagnetic in solution. Direct comparison of magnetic

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(18) 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).

(19) C. M. Harris, S. L. Lenzer, and R. L. Martin, *Australian J. Chem.*, **14**, 420 (1961).

(20) H. C. Clark and R. J. O'Brien, *Can. J. Chem.*, **39**, 1030 (1961).

TABLE V

MOLECULAR WEIGHT DATA FOR BIS-(R-N-SALICYLALDIMINE)-NICKEL(II) COMPLEXES IN TOLUENE AT 37.0°

R	Concn. (moles/l., 25°)	$\bar{n}^a$
C_6H_5	0.02139, 0.02557, 0.02982	1.78, 1.81, 1.83
p-C_6H_4F	.02200, .03023, .03529	1.59, 1.65, 1.70
p-$C_6H_4CH_3$	.01853, .02086	1.70, 1.73
m-$C_6H_4CH_3$	.02609, .04141	2.69, 2.69
m-C_6H_4Cl	.02526, .04188, .07020	2.44, 2.56, 2.60
3,4-$C_6H_3(CH_3)_2$	.02642, .05328, .07496	2.37, 2.48, 2.45
3,5-$C_6H_3(CH_3)_2$	.02713, .05096, .07684	2.82, 2.85, 2.84
2,4-$C_6H_3(CH_3)_2$	.02635, .04921, .05480	1.01, 1.00, 0.98
2,5-$C_6H_3(CH_3)_2$	.02270, .04380, .07490	0.99, 0.99, 1.01
CH_3	.01920, .03011,	1.03, 1.07
i-C_3H_7	.02244, .04344, .06356	1.06, 1.04, 1.04

[a] Estimated error ≤ ±6% except for the last four complexes, where it is ±2%.

and molecular weight data obtained under identical conditions is given in Table VI.

Spectral data are summarized in Table VII. All diamagnetic complexes exhibit only one observable ligand field band (615 mμ) of essentially constant energy and intensity. The red-shifts of this band produced by alkyl substitution on the benzene ring are similar to those previously observed in the N-alkyl series.[2] All complexes paramagnetic in solution show essentially the same spectra regardless of the magnetism of the solid phase from which they were derived. A single band appears in the 600–620 mμ region and is much reduced in intensity compared to the transition of similar energy in diamagnetic complexes. A second very weak band occurs in the range 770–800 mμ and a very broad and diffuse band at ~1000 mμ with occasional indication of structure at 900–950 mμ. Solutions of the paramagnetic complexes in inert solvents have visible thermochromic behavior. At room temperature and below the solutions are clear green but upon warming the color intensifies to a brownish green, the effect being more pronounced for the phenyl and p-substituted species than for those with m-substituents. The temperature dependence of the spectra for some representative complexes was examined at 10° intervals in the range 20–70° and some of those results are given in Fig. 2. Comparison with the magnetic data of Table IV shows that for the phenyl and p-fluorophenyl complexes the intensity of the 615 mμ band bears a qualitative inverse, and that of the 1000 mμ band, a direct relation to the susceptibility. Further, just as the magnetic moment of the m-chlorophenyl complex has a relatively small temperature dependence, so do the spectral intensities. The magnetic moment of the 3,5-dimethylphenyl complex presumably also would show a small temperature dependence.

TABLE VI

COMPARISON OF MOLECULAR WEIGHT AND MAGNETIC DATA IN TOLUENE AT 37.0°

R	Concn. (mmolal)		$10^6\chi^g_{solute}$	μ_{eff} (B.M.)
C_6H_5	29.91	1.81	7.49	3.00
	35.03	1.83	7.28	2.97
p-C_6H_4F	35.60	1.65	6.69	2.96
	41.28	1.70	6.63	2.95
p-$C_6H_4CH_3$	24.43	1.73	7.30	3.06
i-C_3H_7	26.33	1.06	3.54	1.98
	51.16	1.04	3.60	1.99
	74.89	1.04	3.54	1.98

TABLE VII

SPECTRAL DATA FOR BIS-(R-N-SALICYLALDIMINE)-NICKEL(II) COMPLEXES IN CHLOROFORM AT 25.0°

R	Concn. (moles/l., 25°)	λ_{max} (mμ)	ε (l. mole^{-1} cm.$^{-1}$)
C_6H_5	0.0300	615, 780, 1005	23.8, <1, 8.5
C_6H_4(3-CH_3)	.0050	633	75.7
C_6H_4(5-CH_3)	.0300	618, 785, 1005	28.6, <1, 8.3
C_6H_4(3-i-C_3H_7)	.0050	640	83.9
C_6H_4(5-i-C_3H_7)	.0300	622, 785, 1010	35.2, <1, 6.0
p-$C_6H_4CH_3$	.0300	610, 780, 1005	21.5, <1, 9.2
m-$C_6H_4CH_3$	.0300	610, 780, 1005	17.7, <1, 10.1
o-$C_6H_4CH_3$	.0100	616	88.7
p-C_6H_4F	.0300	619, 785, 1005	25.5, <1, 8.5
p-C_6H_4Cl	.0300	617, 770, 1000	22.1, <1, 9.9
m-C_6H_4Cl	.0300	615, 790, 1005	16.5, <1, 11.4
p-$C_6H_4N(CH_3)_2$	.0300	~605(sh), ~780(sh), ~1000	........[a]
2,4-$C_6H_3(CH_3)_2$	.0100	615	90.7
2,5-$C_6H_3(CH_3)_2$	.0100	615	88.7
3,4-$C_6H_3(CH_3)_2$	.0300	605, 775, 1010	17.0, <1, 10.3
3,5-$C_6H_3(CH_3)_2$	.0300	602, 790, 1005	14.0, <1, 10.0

[a] Band feature at 605 mμ obscured by intense tail-off from the ultraviolet, feature at ~1000 mμ has no well defined maximum.

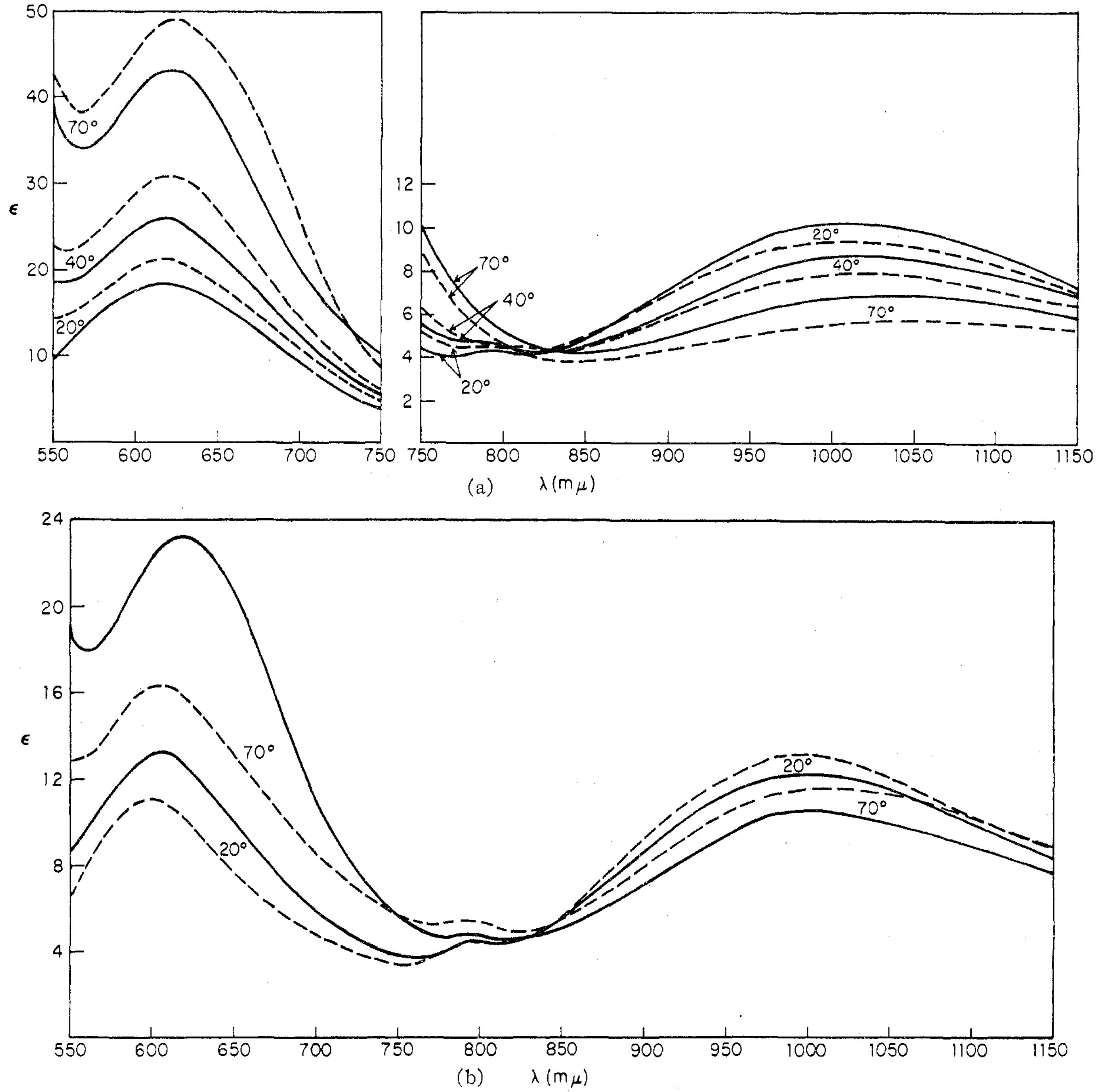

Fig. 2.—Temperature dependence of the ligand field spectra of some representative bis-(R-N-salicylaldimine)-nickel(II) complexes in toluene: (a) —— R = C_6H_5, ---- R = p-C_6H_4F; (b) —— R = m-C_6H_4Cl, ---- R = 3,5-$C_6H_3(CH_3)_2$ (0.03008 *M*, 20°) (for other concentrations see Table IV).

Discussion

From a consideration of tetragonal Ni(II) complexes using either the strong[21] or weak[22] field models, it is quite well substantiated theoretically and abundantly verified experimentally that imposition of an axial component on a fixed planar ligand field can result only in a decrease of the singlet–triplet separation Δ. This effect was put on a nearly quantitative basis by Maki,[22] who postulated that in complexes with sufficiently weak in-plane fields paramagnetism in ostensibly inert solvents such as chloroform and benzene could arise due to a decrease in Δ effected through the agency of solvent interaction. Previous work in this series, however, has shown that insofar as the solution magnetic properties of bis-(N-methylsalicylaldimine)-nickel(II) are concerned, this mechanism for the reduction of Δ is of little if any consequence.[2] The axial component required to effect a sufficient reduction in Δ so as to bring the first excited triplet state within thermal range, or to make Δ negative whereby the triplet lies lowest, almost certainly is furnished exclusively by solute–solute interaction. The

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

[22] G. Maki, *J. Chem. Phys.*, **28**, 651 (1958); *ibid.*, **29**, 1129 (1959).

role of such solvents thus is predominantly one of controlling the degree of association rather than direct interaction with the complex. Accordingly, in this work with closely related molecules we discard substantial solvent effects on Δ and assume throughout that the only important source of the axial component stabilizing the triplet state arises from solute–solute interaction.

Consideration of the experimental results outlined in the previous section permits a division of the complexes studied into three general categories which are now discussed.

1. **_o_-Substituted Aryl and 3-Substituted Complexes.**—Examples of these types that were examined are the 2,4- and 2,5-dimethylphenyl, *o*-tolyl, and 3-methyl- and 3-isopropyl-N-phenyl complexes. The first three are diamagnetic solids and the first two monomeric and completely diamagnetic in solution. The *o*-tolyl and 3-isopropyl species are weakly paramagnetic in solution. The dominant behavior, then, is one of a diamagnetic non-associative type which parallels quite closely that of the N-*n*-alkyl complexes. Further similarities are found in the spectra where aryl and alkyl complexes both show one ligand field band, at 615 mμ and assigned as ^1A_g–$^1B_{3g}$.[22] This indicates that the in-plane field strength is virtually unaffected by altering the nitrogen substituent from alkyl to aryl in these monomeric species. This group of aryl complexes is the only one in which association and substantial solution paramagnetism at 25° are lacking, and this behavior must be related to a structural effect produced by substituents. Examination of metal chelate scale models reveals that the effects of *o*- and 3-substituents are similar in that they tend to constrain rotation of the aryl group about the N–C bond, thereby tending to keep the group more nearly, but not exactly, normal to the rest of the molecule which is taken as essentially planar. This configuration certainly would prevent any kind of lateral association, as is postulated to occur in the solution aggregates of the N-methyl complex, by increasing the effective van der Waals thickness of the molecule. The results also show that this structure presumably is sufficiently inflexible to allow formation of the associated models discussed below.

2. **Phenyl and _p_-Substituted Aryl Complexes.**—Within this category complexes have been isolated which are either diamagnetic (phenyl, *p*-fluorophenyl, *p*-dimethylaminophenyl) or fully paramagnetic solids (*p*-tolyl, *p*-chlorophenyl). The only other report of paramagnetic N-aryl nickel complexes of this general type is that by Zelentsov, *et al.*,[23] who found the bis-complexes of 5-bromo-N-phenylsalicyaldimine and N-*p*-iodophenyl-2-hydroxy-1-naphthaldimine to have moments of 3.04 and 3.02 B.M., respectively. Regardless of the nature of the solid phase the above complexes give moments of 2.9–3.1 B.M. in chloroform and, solubility permitting, were found to be associated in toluene to roughly the same degree with $\bar{n} < 2$.

The relationship between solution paramagnetism and molecular association now has been firmly established in this and previous work. However, on no system has a quantitative comparison been made between a non-integral degree of association and the extent of paramagnetism. In nickel complexes such a comparison can be meaningful only when $\bar{n} < 2$, assuring the presence of some monomers. An obvious difficulty in dealing with the solution equilibria is that, unlike the β-diketone nickel complexes,[3,4,6] one does not have prior knowledge of either the most likely degree of association or of the structure of the associated molecule. However, the $\bar{n}$ values are at least suggestive of the existence of dimers in which it may be reasonably assumed that the mode of association is such that both nickels, which are not necessarily magnetically equivalent, are in triplet states. The likelihood of such a monomer–dimer equilibrium is made apparent from a consideration of the magnetic and molecular weight data (Table VI) obtained under the same conditions. With this equilibrium

$$\bar{n} = f_1 + 2(1 - f_1)$$

where f_1 is the weight fraction of monomer. Further

$$\chi^g_{\text{solute}} = f_1\chi_1^g + (1 - f_1)\chi_2^g$$

where χ_1^g and χ_2^g are the gram susceptibilities of monomer and dimer, respectively. The plausibility of the equilibrium involving diamagnetic monomers and paramagnetic dimers then can be tested by calculating χ_2^M, the corrected molar susceptibility of dimer, which from the data of Table II is reasonably expected in the range 4100–4600 × 10^{-6} per nickel at 37°. Average values obtained for the phenyl and *p*-fluorophenyl complexes are 4300 and 5100, respectively, and for the *p*-tolyl complex, 5100 × 10^{-6}. The

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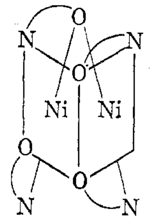
(23) V. V. Zelentsov, I. A. Savich, and V. B. Evdokimov, *Nauchn. Dokl. Vysshei Shkoly, khim. i khim. Tekhnol.*, 672 (1958); *Chem. Abstr.*, **53**, 5789e (1959).

agreement with expectation is reasonable in view of the sensitivity of χ_2^g to $\bar{n}$. With equilibria involving higher aggregates the agreement can only be worsened under the same assumptions, and $(1/n)\chi_n^M$ becomes impossibly large in, *e.g.*, a monomer–trimer case where an average value of $\sim 8600 \times 10^{-6}$ is calculated for the phenyl complex. Otherwise, the magnetic–molecular weight relations of Table VI are most simply accounted for by assuming that paramagnetism is not restricted solely to the associated species, a situation without established precedent in previous studies of associated nickel complexes.[2,4] Several such cases now have been found in N-*s*-alkyl complexes, which are associated in freezing benzene.[7] Representative data for the prototype N-isopropyl complex are given in Table VI. The degree of association is very slight at 37° and clearly cannot account for all of the paramagnetism. The ligand field spectrum, with bands at 580, 690, 905, and 1470 mμ, bears little resemblance to that of any paramagnetic N-aryl complex. Further, the spectra of complexes in this category indicate some residual intensity of the singlet–singlet band in diamagnetic complexes, and reveal no bands in addition to those found in the spectra of complexes of the third category ($\bar{n} > 2$) in which the postulation of these species is not required.[24] Despite the likelihood of a diamagnetic monomer–paramagnetic dimer equilibrium, attempts to fit the concentration and temperature dependent spectral data of the phenyl complex in chloroform to this equilibrium, and to several others involving higher species, yielded unconvincing results.

If, however, it is assumed that the monomer–dimer equilibrium above is correct, the structure of the associated form should be such as to provide an additional component to the ligand fields acting on each nickel, thereby stabilizing the triplet state. The spectra are in accord with axially perturbed *trans*-planar Ni(II) species. Using Maki's weak field model[22] the bands at 1000 and 775–800 mμ can be assigned as $^3B_{3g} \rightarrow {}^3B_{1g}$, $\rightarrow {}^1B_{3g}$ or ^1A_g, respectively. The band at ~615 mμ probably is due to the other expected spin-allowed transition, $^3B_{3g} \rightarrow {}^3B_{2g}$ plus some contribution from the singlet–singlet transition in the monomer. The sensitivity of the magnetic and spectral properties of the phenyl and *p*-fluorophenyl complexes to temperature are suggestive of a labile equilibrium such as occurs in the N-methyl complex.[2,26-28] In the absence of any X-ray structural evidence on these complexes, a prolonged discussion of the structure of the associated species is unwarranted. However, certain difficulties in formulating conventional associated structures should be pointed out. First, a lateral type of association between planar molecules, as postulated previously,[2] is difficult, if not impossible, because of the steric requirements of the aryl groups which cannot be nearly coplanar with the chelate rings.[29] Second, a mode of association involving a condensed octahedral structure as in the trimeric acetylacetonate[3] appears sterically possible. If the donor nitrogens retain their imine function, an analogous trimer is not possible since at least two of the six bridging atoms would have to be nitrogens. A condensed dimeric structure is possible but would involve unusual coördination of one nickel if a *cis*-planar configuration is discounted on steric grounds. One such dimer is shown in II. However, such a dimer would not readily dissociate if the strengths of the Ni–O bridge bonds are roughly comparable to those in the acetylacetonate.[6] Further, the apparent dipole moment of the phenyl complex in benzene (2.88 D. at 20°),[30] although measured in a concentration range somewhat below that used in the $\bar{n}$ determinations, is on the basis of rough calculation much too small to be compatible with the extrapolated concentrations of the dimer II.



II

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(24) If paramagnetic monomers were to exist in any of these systems, the triplet state seemingly could be stabilized only by distortion to a non-planar conformation and not as a result of the intrinsic field strength in a planar structure. The former effect, however, is not necessarily without precedent as it appears likely that the paramagnetic behavior of certain bis-(aminotroponeimine)-nickel(II) complexes[25] may be achieved in this way.

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

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

(27) S. Fujii and M. Sumitani, *Sci. Rept. Tohoku Univ., First Ser.*, **37**, 49 (1953).

(28) H. C. Clark and R. J. O'Brien, *Can. J. Chem.*, **37**, 436 (1959).

(29) The possibility of a similar kind of association, effected by a distortion from planarity so as to facilitate intermolecular Ni. . .O (or N) interactions, is recognized but is difficult to assess using molecular models.

(30) G. H. Newman, Ph.D. Thesis, Pennsylvania State University, 1961. This value was uncorrected for atom polarization and was obtained in the concentration range 0.0085–0.0185 *M*.

3. *m*-Substituted Aryl.—This category includes the *m*-tolyl, *m*-chlorophenyl, 3,4-, and 3,5-dimethylphenyl complexes, all of which are fully paramagnetic solids, strongly paramagnetic in solution, and more strongly associated in solution ($2 < \bar{n} < 3$) than the complexes of the second class. The spectra are quite similar to those of the second class and again are consistent with the presence of axially perturbed *trans* planar species. The small difference between the solution and solid phase moments and the degree of association in solution require that the monomer concentration be small.

Because these paramagnetic, presumably associated solids give strongly paramagnetic solutes with a non-integral degree of association, the solution species very likely consist of fragments of the associated solid form and some of this form itself, provided the solid is not infinitely polymerized. Within this group of complexes the much reduced dependence of the spectra and magnetism on temperature indicates a larger positive enthalpy of dissociation than that in the phenyl complex, for example. While this fact may lend support to a condensed octahedral structure for the aggregates, we have been unable to deduce a satisfactory structure based on this model. Such a structure must satisfactorily account for the larger degree of association found with these complexes than with those of the second class and at the same time must not change appreciably the strength and symmetries of the ligand fields in the two classes of complexes, as the spectral similarities would seem to require.[31]

The results presented here further increase the generality of the relation between solution paramagnetism and molecular association on the one hand, and the lack of association and diamagnetism on the other. The same relation undoubtedly exists in the solid. The detailed nature of the associated species in the solid and solution phases could not be deduced from the data and must await X-ray investigation of one or more of the paramagnetic complexes of the second and third categories. Nevertheless, it may be confidently stated from the results of this study that in Ni(II) complexes potentially capable of a monomeric planar structure, the triplet state of the metal ion is stabilized only by additional, presumably axial, coördination.

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[31] Individual molecules and condensed octahedral species also could be associated by means of oxygen bridges furnished by water. In this way the association of individual molecules into dimers would require $1H_2O/2Ni$; association of form II or a related species into a tetramer would necessitate only $1H_2O/4Ni$. In nearly all cases the analytical results tend to support the anhydrous nature of the complexes studied to the extent that $H_2O/Ni < {}^1/_2$. However, a ratio of ${}^1/_4$ cannot be distinguished by the analyses of Table I.