

*Exchange Reactions and Magnetic Susceptibilities of Complex Salts.  
Part II.\* Magnetic Susceptibilities of Some Complex Nickel Salts.*

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Magnetic susceptibilities over a temperature range of 100° have confirmed that bis-salicylaldoximenickel and bis-*N*-methylsalicylaldiminenickel form in pyridine solution complexes which presumably are octahedral and contain two pyridine molecules per nickel atom. Measurements of bis-salicylaldehyde-*o*-phenylenedi-iminenickel and bis-salicylaldiminenickel in pyridine solution show the occurrence of temperature-dependent equilibria between dia- and para-magnetic forms which appear to be respectively planar and octahedral. Equilibria also occurred in solutions of bis-*N*-methylsalicylaldiminenickel in chloroform, benzene, toluene, and *m*-xylene, where the two forms are more probably planar and tetrahedral respectively. Calculations have been made of the equilibrium constants; hence the heats of reaction, free energy, and entropy changes have been obtained and related to the structural changes involved in the equilibria.

THE validity of the distinction made by magnetic measurements between covalent and ionic bonds in metallic complexes has been widely discussed in recent years. It is now generally accepted that covalent bonding, utilising the hybrid-bond systems suggested by Pauling (*J. Amer. Chem. Soc.*, 1931, **53**, 1391), results in increased electron pairing and hence a reduction in the magnetic moment.

The nature of the co-ordinate link in highly paramagnetic salts is less certain and has been variously described as "ionic" and "covalent involving outer *d* orbitals" (Huggins, *J. Chem. Phys.*, 1937, **5**, 527) while Taube (*Chem. Rev.*, 1952, **50**, 69) and others have suggested the use of  $4s4p^34d^2$  hybrid orbitals. Craig, Maccoll, Nyholm, Orgel, and Sutton (*J.*, 1954, 332) have made overlap integral calculations for this type of bonding and have shown that such bonds are highly polar, and not very different in character from "ionic" bonds. Resonance is then possible between covalent and ionic forms, so that the magnetic moment gives no indication of the covalent contribution to the bonding. Magnetic-susceptibility determinations thus divide complexes into (a) a class using inner *d* orbitals which give rise to essentially covalent bonds and (b) a class in which the bonds are highly polar.

Values of the magnetic moment intermediate between the values for the two alternative modes of spin coupling are very rare and hence interest was centred on the values reported by Willis and Mellor (*J. Amer. Chem. Soc.*, 1947, **69**, 1237) for complexes of nickel and derivatives of salicylaldehyde in various solvents. The majority of these complexes were diamagnetic as solids, but solvents such as pyridine, chloroform, benzene, and dioxan caused changes to paramagnetism with values of approximately 2 B.M., these values being independent of concentration. However, the magnetic susceptibilities had been observed at only one temperature. A further investigation of these susceptibilities has therefore been made over a wide temperature range.

*Discussion of Results.*—Attempts to extend the ranges of solvents and concentrations were restricted by the low solubilities; however, certain new results were added to those of Willis and Mellor. All these determinations were made at 298° K.

The results in Table 1 thus confirm the occurrence of these intermediate values of the magnetic moments as well as their concentration independence.

*Temperature dependence.* Eight solutions were investigated over a temperature range, the results being given in Tables 2 and 3.

For the pyridine solutions of bis-salicylaldoximenickel and bis-*N*-methylsalicylaldiminenickel, the plots of  $1/\chi_M(\text{corr.})$  against *T* are straight lines giving values of 30° and 40° respectively for the molecular field constants. For the remaining compounds, all were

\* Part I, *J.*, 1954, 63.

TABLE 1.

Compound	Solvent	Concn.		B.M.	Solvent	Concn.		B.M.	
		$\times 10^5$	$\chi_M(\text{corr.}) \times 10^6$			$\times 10^5$	$\chi_M(\text{corr.}) \times 10^6$		
Bis-salicylaldoxime-nickel	$C_6H_5N$	1558	4004	3.10	$CHCl_3$	313	1203	1.70	
		869	3890	3.05					
Bis-salicylaldiminenickel	$C_6H_5N$	718	1921	2.15	$C_6H_5N$	511	1984	2.18	
		4690	3934	3.07					
Bis- <i>N</i> -methylsalicylaldiminenickel	$C_6H_5N$	2365	3999	3.10	Dioxan	1891	1944	2.16	
		1145	4061	3.12					
		2158	1587	1.95					
	$CHCl_3$	EtOH	1025	1532	1.92	$C_6H_5Me$	1852	1359	1.81
			520	1596	1.96				
			206	2729	2.56				
Bis-salicylaldehyde-ethylenedi-iminenickel	$C_6H_5N$	841	0	Diamag.	$m-C_6H_4Me_2$	855	300	0.85	
Bis-salicylaldehyde- <i>o</i> -phenylenedi-iminenickel	$C_6H_5N$	795	2293	2.35	$CHCl_3$	193	0	Diamag.	
		629	2308	2.35					

TABLE 2. Corrected molar susceptibilities (c.g.s. units  $\times 10^6$ ). Solvent: pyridine.

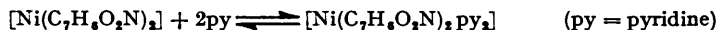
Temperature ( $^{\circ}K$ )	198 $^{\circ}$	257 $^{\circ}$	273 $^{\circ}$	298 $^{\circ}$	316 $^{\circ}$
Bis-salicylaldoximenickel .....	5686	4370	4204	3953	3714
Bis- <i>N</i> -methylsalicylaldiminenickel .....	5552	4266	4111	3922	3720
Bis-salicylaldiminenickel .....	5473	3708	3151	1954	1151
Bis-salicylaldehyde- <i>o</i> -phenylenedi-iminenickel .....	6289	3327	2911	2312	1477

TABLE 3. Corrected molar susceptibilities of bis-*N*-methylsalicylaldiminenickel in various solvents.

Solvent	198 $^{\circ}$	250 $^{\circ}$	273 $^{\circ}$	298 $^{\circ}$	323 $^{\circ}K$
Chloroform .....	5767	3922	3037	1546	860
Benzene .....	—	—	3050	1358	503
Toluene .....	5615	4173	1900	811	—
<i>m</i> -Xylene .....	—	2839	1176	300	—

fully paramagnetic with moments of 2.95—3.20 B.M. at 198 $^{\circ}K$ , but above this temperature the Curie-Weiss law was not obeyed and apparent equilibria were observed between dia- and para-magnetic forms, the former predominating at the higher temperatures.

Willis and Mellor suggested that in pyridine solutions, the change to paramagnetism is due to the formation of octahedral complexes as follows:



They were unable to isolate the pyridine addition derivatives of any of the above compounds, but Basolo and Matoush (*J. Amer. Chem. Soc.*, 1953, 75, 5663) have since obtained certain of these derivatives by slow crystallisation from pyridine solutions. We were able to isolate pyridine adducts of bis-salicylaldoximenickel and bis-*N*-methylsalicylaldiminenickel by the addition of excess of water to the pyridine solutions. The precipitates so obtained could be dried without decomposition over calcium chloride and the loss of weight on heating at 110 $^{\circ}C$  for several hours was then determined. For the adduct of bis-salicylaldoximenickel, the fraction of weight lost was 0.348 (Calc. for loss of two molecules of pyridine from  $[Ni(C_7H_6O_2N)_2(py)_2]$ : 0.325). Similarly for the adduct of bis-*N*-methylsalicylaldiminenickel, the observed fraction of weight lost was 0.327, compared with a calculated loss of 0.328.

Hence, in the pyridine solutions of the above two compounds there is complete formation of paramagnetic pyridine adducts which contain two pyridine molecules per nickel atom and presumably utilise the highly polar outer  $sp^3d^2$  octahedral configuration.

For the remaining pyridine solutions, the magnetic measurements show the occurrence of temperature-dependent equilibria between dia- and para-magnetic forms. These equilibria also probably occur between diamagnetic planar forms and octahedral pyridine adducts, the latter being less stable at higher temperatures, so that their formation is incomplete. The lower stability of the pyridine adducts of bis-salicylaldiminenickel and bis-salicylaldehyde-*o*-phenylenedi-iminenickel is not unexpected since Basolo and Matoush

were unable to isolate them. In view of the strong co-ordinating power of pyridine it is unlikely that the equilibrium would be between planar and tetrahedral forms.

The remaining solutions contain bis-*N*-methylsalicylaldiminickel dissolved in typical non-polar solvents such as benzene, chloroform, toluene, and *m*-xylene, where normal co-ordination of solvent molecules is improbable.

Nyholm recently suggested (*Chem. Rev.*, 1953, 53, 263) that for some complexes the planar arrangement of the solid may be partly due to the effect of intermolecular forces, which may be reduced in solution, allowing the isolated molecule to assume the shape of lowest potential energy. For nickel complexes this would apparently be the tetrahedral configuration. The energy difference between the planar and tetrahedral structures may therefore be small, allowing the natural occurrence of a thermal equilibrium.

That the equilibrium in these non-co-ordinating solvents is between planar and tetrahedral forms has already been suggested by Willis and Mellor and later by Basolo and Matoush. The latter workers observed intermediate values of the magnetic moment of bisformylcamphorethylenedi-iminenickel in methylbenzene solvents and it is probable that here also a temperature-dependent equilibrium occurs. They conclude that the effect is not due to solvation since no correlation can be drawn between the base strength of the solvent and the amount of paramagnetism.

The results obtained for bis-*N*-methylsalicylaldiminickel in methylbenzene solvents show considerable similarity to those for bisformylcamphorethylenediaminenickel, although the susceptibility at 25° shows a more marked decrease with change of solvent. Again no correlation can be drawn between the base strength, as given by McCaulay and Lien (*J. Amer. Chem. Soc.*, 1951, 73, 2013), and the amount of paramagnetism; indeed, it seems probable that the decrease in paramagnetism as the solvent is changed from benzene to toluene to *m*-xylene is rather an effect of the increasing asymmetry of the solvent molecules. Although not conclusively proved, it thus seems probable that in these solvents the equilibrium is between planar and tetrahedral forms.

Susceptibility determinations over a temperature range for ethyl alcohol and dioxan solutions of bis-*N*-methylsalicylaldiminickel were not made owing to the low solubility and hence the large errors in alcohol, and to the high freezing point (11° c) of dioxan. However, in these solvents, co-ordination of the solvent molecules is possible, so the paramagnetic form may be either octahedral or tetrahedral.

Where applicable, it is obviously possible to define the equilibrium constant as  $K = [\text{Diamagnetic}]/[\text{Paramagnetic}]$ . From purely paramagnetic susceptibilities at 198° K, the susceptibilities of the pure paramagnetic form at 316°, 298°, 273°, and 250° K could be calculated, the molecular field constants being assumed to be zero. Values of  $K$  thus obtained are given in Table 4.

TABLE 4.

Compound	Solvent	257°	273°	298°	316°
(1) Bis-salicylaldiminickel .....	Pyridine	0.17	0.27	0.87	1.97
(2) Bis-salicylaldehyde- <i>o</i> -phenylenedi-iminenickel	Pyridine	0.46	0.57	0.81	1.67
(3) Bis- <i>N</i> -methylsalicylaldiminickel .....	Chloroform	0.25	0.38	1.48	2.69
		250°	273°	298°	323°
(4) Bis- <i>N</i> -methylsalicylaldiminickel .....	Benzene	—	0.35	1.79	5.94
(5) " " " "	Toluene	0.08	1.18	3.65	—
(6) " " " "	<i>m</i> -Xylene	0.59	2.51	11.6	—

The plots of  $\log_{10} K$  against  $1/T$  were straight lines within experimental error, and hence approximate values for the heats of reaction were calculated. The free-energy change could also be calculated from the relation  $\Delta G = RT \log_e K$ . The entropy changes were obtained by using the equation  $\Delta G = \Delta H - T\Delta S$ .

Solution	$\Delta H$ (cal.)	$\Delta G$ (at 25°)	$\Delta S$ (e.u.)	Solution	$\Delta H$ (cal.)	$\Delta G$ (at 25°)	$\Delta S$ (e.u.)
(1)	7960	30	27	(4)	9990	— 380	35
(2)	3740	—125	13	(5)	10,700	— 980	39
(3)	7210	—360	25	(6)	9060	—1500	35

The errors in these values are higher than for results obtained by other methods, the values for  $\Delta S$  having an error of approximately  $\pm 15$ —20%. For solutions (2) and (5) the

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error may be slightly larger, and it is therefore possible to obtain only an indication of the meaning of the entropy changes.

For solutions (1) and (2) solvation appears to be involved and the equilibrium can be represented as



The entropy increase is probably due to the large increase in the number of free particles. The results may be compared with the work of Calvin and Bailes (*J. Amer. Chem. Soc.*, 1946, **68**, 958) who obtained for the reaction



where there is an increase of three in the number of particles, the value  $\Delta S = 24$  e.u.

For the remaining solutions, the equilibrium is more probably between planar and tetrahedral forms. The fact that the conversion from the paramagnetic into the diamagnetic configuration is an endothermic reaction supports Nyholm's suggestion that for certain complexes in solution the tetrahedral form is the state of lowest energy. Nor is the entropy change inconsistent with this suggestion. It is probable that the electric dipole moment of the tetrahedral form is responsible for the association of a number of solvent molecules. On conversion into the planar *trans*-form, this dipole disappears, with the liberation of excess of associated solvent molecules, accompanied by an increase in entropy (cf. Chatt and Wilkins, *J.*, 1952, 273). However, it is doubtful whether this effect would be great enough fully to account for the comparatively large entropy change.

#### EXPERIMENTAL

*Preparation and Analysis of Compounds.*—The compounds investigated were prepared by the general methods of Pfeiffer (*Annalen*, 1933, **503**, 84). Each compound was analysed for nickel and nitrogen content, the nitrogen being determined by the standard Kjeldahl method and the nickel by precipitation with dimethylglyoxime.

Ni complex with	Formula	Found (%)		Calc. (%)	
		N	Ni	N	Ni
Salicylaldoxime .....	$\text{Ni}(\text{C}_7\text{H}_5\text{O}_2\text{N})_2$	8.49	17.63	8.47	17.75
Salicylaldimine .....	$\text{Ni}(\text{C}_7\text{H}_5\text{ON})_2$	9.47	19.61	9.37	19.65
<i>N</i> -Methylsalicylaldimine .....	$\text{Ni}(\text{C}_8\text{H}_6\text{ON})_2$	8.43	17.72	8.56	17.95
Salicylaldehyde-ethylenedi-imine .....	$\text{Ni}(\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_2)$	8.52	17.93	8.63	18.05
Salicylaldehyde- <i>o</i> -phenylenedi-imine ...	$\text{Ni}(\text{C}_{20}\text{H}_{14}\text{O}_2\text{N}_2)$	7.41	15.68	7.52	15.75

The solvents used in the magnetic measurements were of "AnalaR" grade or were carefully dried and purified by standard methods.

*Magnetic Measurements.*—Magnetic susceptibilities were determined with the use of a Gouy-type magnetic balance, the current through the electromagnet being regulated within 0.002%.

Susceptibilities were determined at 316°, 298°, 273°, 257° (or 250°), and 198° K. The two highest temperatures were maintained by the use of a water thermostat, and at 273° by ice-water. A solid carbon dioxide-acetone freezing mixture was used at 198° K. For measurements at 257°, use was made of ice-salt freezing mixtures, and at 250° melting carbon tetrachloride was used, although both these cases probably involved a slightly larger error in temperature.

The apparatus was calibrated with acetone, benzene, and freshly-boiled, distilled water, French and Trew's susceptibility values (*Trans. Faraday Soc.*, 1945, **41**, 439) being used.

The susceptibilities of the complexes were determined from the differences between those of the pure solvents and the solutions, according to the formula

$$\chi_{g(\text{complex})} = [\chi_{g(\text{solvent})}(1-x) - \chi_{g(\text{solution})}]/x$$

where  $x$  = fraction by weight of complex in solution. After calculation of the molar susceptibilities, corrections for the diamagnetism of the ligands were made by using Pascal's constants (Selwood, "Magnetochemistry," Interscience Publishers Inc., New York, 1943, pp. 51-55).