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The Magnetic Susceptibility of Some Nickel Complexes in Solution

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In previous communications[1,2] from this Laboratory a correlation has been drawn between the magnetic moments and absorption spectra of tetra-coördinated complexes of Ni^{II}. It was found that the absorption spectrum of a diamagnetic complex, in which the nickel is bound[3] by square (dsp^2) bonds, exhibits, in the neighborhood of 400 mμ, a broad band of considerable intensity (ϵ = 10^3–10^5) which does not occur in the absorption spectrum of the chelate, and which can be attributed to the presence of the nickel atom. On the other hand, a paramagnetic complex, in which nickel is bound by tetrahedral (sp^3) or ionic bonds, possesses a spectrum very similar to that of the chelate, without the appearance of any new band.

The fact that during the examination of several dozen nickel complexes in this Laboratory one or two exceptions to the above rule were found, led us to measure the magnetic susceptibilities of some of them in solution as well as in the solid state. An isolated observation by French, Magee and Sheffield[4] has shown that bis-formylcamphor-ethylenediamine nickel, which is diamagnetic in the solid state, is paramagnetic (μ = 1.9 Bohr magnetons) in methanol solution. Nevertheless the methanol solution shows the nickel band at 385 mμ. Solid paramagnetic nickel complexes (coördination number 4 or 6) have a moment of 2.9–3.2 Bohr magnetons (B.M.), which corresponds to two unpaired electron spins in the nickel atom.

The present paper deals with a survey of the magnetic moments of internal nickel complexes in solution, and reveals the surprising fact that a number of nickel complexes which are diamagnetic in the solid state show, in solution, a magnetic moment of up to 3.2 B.M. The solvents selected for this study were dioxane, benzene, chloroform, pyridine, ethanol and methanol; these solvents, which range in dielectric constant from 2 to 34, are among the best solvents for internal metal complexes. The limited solubility of most of the complexes in the solvents available was the chief factor determining the choice of substances to be studied, since to obtain a reasonably accurate value for the magnetic susceptibility, solutions not weaker than about 0.01 g./ml. were required.

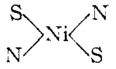
Following the work of Mellor and Craig[5] the complexes are classified according to the electronegativity of the atoms to which the central nickel atom is linked.

Class I

Class II

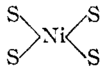
Class III

Class IV



Class V

Class VI



Experimental

A Curie–Chêneveau torsion balance, very similar to that described by Gray and co-workers[6,7] and improved by Rawlinson[8] was used. The volume of solution for each measurement was about 0.4 ml., and the instrument was calibrated at frequent intervals with distilled water (χ = -0.72×10^{-6}) which gave a total deflection of about −40 cm. on a ground-glass scale at a distance of 2 meters from the instrument. Solutions of metal complexes were made up on a weight/weight basis, and the deflection caused by the solvent measured separately and subtracted from that of the solution. Measurements on solids were made with a Gouy balance.

The compounds were mainly those used in previous

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[1] Mills and Mellor, THIS JOURNAL, **64**, 181 (1942).

[2] McKenzie, Mellor, Mills and Short, *J. Proc. Roy. Soc. N. S. Wales*, **78**, 70 (1944).

[3] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 118.

[4] French, Magee and Sheffield, THIS JOURNAL, **64**, 1924 (1942).

[5] Mellor and Craig, *J. Proc. Roy. Soc. N. S. Wales*, **74**, 475 (1941).

[6] Gray and Farquharson, *J. Sci. Instruments*, **9**, 1 (1932).

[7] Gray, Clow and Cruickshank, *ibid.*, **13**, 13 (1936).

[8] Rawlinson, *Australian J. Exp. Biol.*, **18**, 185 (1940).

studies[1,2,5] in this Laboratory; others which were specially prepared for this investigation are referred to individually below.

The dioxane was purified by the method of Eigenberger[9] and the pyridine by drying over solid potassium hydroxide followed by two fractional distillations. The other solvents were of C. P. grade.

Results

These are tabulated below: χ_A is the gram-atomic susceptibility of the central nickel atom, obtained by correcting the gram-molecular susceptibility for the diamagnetism of the chelate groups, and μ is the effective moment of the metal atom. The diamagnetic corrections used are those given by Stoner.[10] The superscripts against the magnetic moments refer to the section entitled "Notes on Individual Compounds."

Notes on Individual Compounds

(*a*) The paramagnetic complexes bis-salicylaldehyde nickel and bis-8-hydroxyquinoline nickel have practically the same moment in pyridine solution as they have in the solid state. Efforts to isolate from these solutions pyridine-addition compounds of definite formula were fruitless.

(*b*) The behavior of bis-formylcamphor-ethylenediamine nickel with pyridine is interesting. In freshly prepared solution the complex was diamagnetic and green in color, with an absorption band (ϵ = 150) at 620 mμ. Over a period of two weeks, the complex became more and more strongly paramagnetic, finally reaching a moment of 3.15 B.M. At the same time the color became deep brown, and the band at 620 mμ disappeared. It was clear that some chemical interaction had taken place, and the formation might be expected of bis-pyridine-bis-formylcamphor-ethylenediamine nickel. In this compound all six coördination positions of the nickel atom would be filled; and the d^2sp^3 bonds would give rise to two unpaired electron spins. The brown pyridine solution, when evaporated to dryness at room temperature, gave a glassy brown mass smelling strongly of pyridine. All attempts to obtain it in a crystalline form by recrystallization from various solvents were fruitless. After drying *in vacuo* it still smelt somewhat of pyridine. Different preparations gave discrepant analyses (N, 7.70, N, 6.90, whereas the bis-pyridine compound referred to above requires N, 9.35).

(*c*) The addition of pyridine to bis-salicylaldoxime nickel, a green diamagnetic compound, produced an almost colorless solution in which the nickel atom had a moment of 3.10 B.M. On adding water to the solution a white precipitate was formed which, however, on filtration and washing with water, turned green once more. A similar transformation occurred when the pyridine solution was evaporated in air; the white compound is apparently only stable in the presence of excess pyridine and all attempts to isolate it were unsuccessful.

(*d*) Brown xanthic acid nickel immediately formed a green paramagnetic (μ = 3.32 B.M.) complex with pyridine. On evaporation the solution deposited green crystals that rapidly returned to the original brown compound. Here again it was not found possible to isolate any pyridine addition compound.

(*e*) Klemm and Raddatz[11] claim to have isolated two forms of bis-N-methylsalicylaldimine nickel, both green in color, one of which is diamagnetic (*trans*-form) and the other paramagnetic, with a moment of 3.18 B.M. (*cis*-form). The latter form, though it gave the same analysis as the former, was obtained only by accident, and reverted to the diamagnetic form on standing for several weeks. It seemed important in connection with the present investigation to repeat the work of these authors.

The diamagnetic form (I) was easily obtained, as described by Klemm and Raddatz, by warming together the calculated quantities of nickel acetate solution, salicylaldehyde and ethylenediamine, and recrystallizing the precipitate from chloroform-petroleum ether.

Anal. of (I). Found: N, 8.53. Calcd. for $C_{16}H_{16}O_2N_2Ni$: N, 8.56.

Difficulty however was experienced in preparing the paramagnetic form. The above reaction was carried out at 0° and the product repeatedly recrystallized from pyridine. After drying between porous plates the substance smelt strongly of pyridine; in this condition it was paramagnetic (II).

Removal of the residual pyridine from (II), either by repeated recrystallization from chloroform or by maintaining the specimen under a pressure of about 0.005 mm. for eighteen hours and condensing the pyridine vapor in a liquid-air trap resulted in the production of the diamagnetic form (I).

This work shows that, in the solid state, bis-N-methylsalicylaldimine nickel is only paramagnetic when it contains pyridine, and that when this pyridine is removed, the compound becomes diamagnetic. Whether the pyridine is coördinated to the nickel atom or present as pyridine of crystallization it is difficult to say.

Discussion

A wide range in values for the magnetic moment of nickel in different complexes in various solvents was observed. The values at the extremes of the range (μ = 0 and μ = 3.2 B.M.) are perhaps the most easily accounted for.

Those diamagnetic complexes which enter solution without any change of moment require no comment. The moments of μ = 3.0–3.2 B.M. were only found in pyridine solutions, and it is significant that in each case distinct evidence of change on entering solution was observed, and that the observed values of μ correspond to those found for solid paramagnetic complexes containing either tetrahedrally[5] (ionic) or octahedrally[12] bound nickel. Since pyridine molecules readily coördinate with transition-metal ions, it is reasonable to suppose that the change in moment of, say, bis-salicylaldoxime nickel when dissolved in pyridine, arises from the formation of an octahedral complex:

$$[Ni(C_7H_6O_2N)_2] + 2py \rightleftharpoons [Ni\,py_2(C_7H_6O_2N)_2]$$

with the equilibrium predominantly in favor of the octahedral complex. As pointed out above, although the compounds formed are stable in the presence of excess pyridine, all attempts to isolate them have shown them to be very unstable in the solid state. This instability has been noted by Morgan and Smith[13] for the case of diammino-bis-acetylacetone nickel, and the fact that square nickel complexes add on pyridine less readily than tetrahedral ones has been noted by Dwyer and Mellor[12] and also by Pfeiffer.[14]

The most difficult cases to explain are those

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[9] Eigenberger, *J. prakt. Chem.*, **130**, 75 (1931).

[10] Stoner, "Magnetism and Matter," Methuen, London, 1936, p. 38.

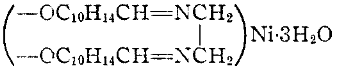
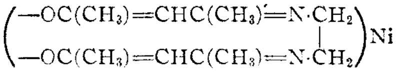
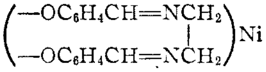
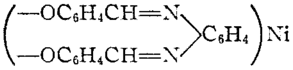
[11] Klemm and Raddatz, *Z. anorg. allgem. Chem.*, **250**, 207 (1942).

[12] Dwyer and Mellor, THIS JOURNAL, **63**, 81 (1941).

[13] Morgan and Smith, *J. Chem. Soc.*, 912 (1926).

[14] Pfeiffer, Bucholtz and Bauer, *J. prakt. Chem.*, **129**, 163 (1931).

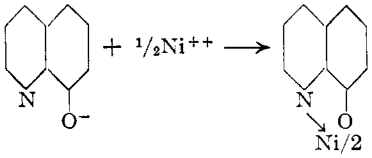
TABLE I

Substance	μ(solid), B.M.	Solvent	Concn., g./g.	Temp., °C.	$\chi_A \times 10^6$	μ, B.M.
Class I						
bis-Salicylaldehyde nickel $(-OC_6H_4CHO)_2Ni$	3.2	Py	0.0215	20	4520	3.26[a]
Class II						
bis-8-Hydroxyquinoline nickel $(-OC_9H_6N)_2Ni$	3.3	Py	.0237	21	4400	3.24[a]
bis-Formylcamphor-ethylenediamine nickel	0.0	Chloro	.0531	19	Diamag	0.0
 $\left(\begin{array}{l}-OC_{10}H_{14}CH=NCH_2\\ \qquad\qquad\quad \vert\\ -OC_{10}H_{14}CH=NCH_2\end{array}\right)Ni\cdot 3H_2O$			.0571			
		Bz	.0308	19	260	0.8
		MeOH	.0195	19	850	1.4
		Py	.0946	21	Diamag	0.0[b]
bis-Acetylacetone-ethylene Diamine nickel	.0	Chloro	.0144	22	Diamag	.0
 $\left(\begin{array}{l}-OC(CH_3)=CHC(CH_3)=N\cdot CH_2\\ \qquad\qquad\qquad\qquad\qquad\quad \vert\\ -OC(CH_3)=CHC(CH_3)=N\cdot CH_2\end{array}\right)Ni$		EtOH	.0105	23	Diamag	.0
bis-Salicylaldoxime nickel $(-OC_6H_4CH=NOH)_2Ni$	.0	Chloro	.0035	20	510	1.1
		Bz	.0045	20	Diamag	0.0
		Py	.0236	20	4030	3.10[c]
bis-Salicylaldehyde-ethylene Diamine nickel  $\left(\begin{array}{l}-OC_6H_4CH=NCH_2\\ \qquad\qquad\quad \vert\\ -OC_6H_4CH=NCH_2\end{array}\right)Ni$	.0	Py	.0095	21	Diamag	0.0
bis-Salicylaldehyde-*o*-phenylene Diamine nickel	.0	Py	.0108	21	2700	2.54
 $\left(\begin{array}{l}-OC_6H_4CH=N\\ \qquad\qquad\qquad >C_6H_4\\ -OC_6H_4CH=N\end{array}\right)Ni$			.0136		2720	2.55
bis-N-Methylsalicylaldimine nickel	.0	Chloro	.0317	20	2260	2.30
			.0161		2010	2.19
			.0064		2030	2.20
$(-OC_6H_4CH=NCH_3)_2Ni$		Bz	.0297	21	2450	2.4
		EtOH	.0023	21	2470	2.4
		Diox	.0219	22	1990	2.2
			.0106		2320	2.3
		Py	.0750		4070	3.10
			.0383	21	3840	3.04
			.0156		4040	3.09
			.0099		4070	3.10
bis-Salicylaldimine nickel $(OC_6H_4CH=NH)_2Ni$	.0	Py	.0075	21	2250	2.3
Class III						
bis-4,4′-Dimethyldiazoaminobenzene Nickel[a]	.0	Chloro	.0156	19	Diamag	0.0
		Py	.0127	22	Diamag	.0
bis-Methylglyoxime nickel $(CH_3C(=NOH)CH=NO)_2Ni$	.0	Py	.0151	22	990	1.5
Classes IV and V						
(No compounds examined)						
Class VI						
bis-Xanthic acid nickel $(-SC(OC_2H_5)=S)_2Ni$	.0	Chloro	.0258	22	Diamag	0.0
		Diox	.0126	21	Diamag	.0
		Py	.0235	22	4640	3.32[d]

[a] bis-4,4′-Dimethyldiazoaminobenzene nickel is probably a binuclear compound.[12]

where the moment is between 0 and 3.2 B.M. Such intermediate values are found in some of the pyridine solutions, and in all the non-pyridine solutions in which nickel has a paramagnetic moment. In these latter solutions there appears to be little likelihood of the solvent forming octahedral complexes with the metal atom, so that equilibrium of the type postulated above is out of the question.

Alternatively the magnetic moment could be caused by partial dissociation of the complex into free Ni^{++} ion and chelate molecules, but this possibility is ruled out by measurements made in this laboratory on the stability constants of some internal nickel complexes by the method of Calvin and Wilson.[15] For the reaction



the constant $K = 10^{8.5}$ was found, while for the corresponding reaction, using salicylaldehyde and Ni^{++}, K was $10^{4.2}$. Electrical conductivity measurements on pyridine, chloroform and ethanol solutions of bis-8-thiolquinoline nickel, bis-N-methylsalicylaldimine nickel and bis-4,4′-dimethyl-diazoaminobenzene nickel indicated stability constants of at least the above order: the conductivity of these solutions is so small that it may well be largely due to impurities. It is clear, then, that the dissociation of internal nickel complexes is very small, and entirely inadequate to account for the magnetic moments observed in the present work.

It is conceivable that the difference of stability of square and tetrahedral nickel complexes is in some instances so small that, under the influence of the solvent molecules, as suggested by French, Magee and Sheffield,[4] some of the square-coordinated molecules are converted to a tetrahedral configuration, for which $\mu = 3.2$ B.M., so that the complex shows a paramagnetic moment whose magnitude depends on the proportion of molecules thus converted. Lifschitz, Bos and Dijkema[16] have prepared isomeric, easily interconvertible, cationic nickel complexes, in which one form is bluish-green and paramagnetic and the other form yellow and diamagnetic. It would appear that, under some circumstances, transition from a diamagnetic to a paramagnetic form does not require very much energy. Steric deformation has been proposed[5,17] to account for the paramagnetism, even in the solid state, of certain nickel complexes which, from the nature of the nickel–chelate bonds, would be expected to be diamagnetic.

With one exception already referred to (see note (*b*) following the Table), in every case the magnetic moment reported is shown immediately the compound goes into solution, and the substance when crystallized from solution becomes diamagnetic once more. In the few cases where measurements were possible at more than one concentration, there was no significant variation of moment with concentration, within the limits of experimental accuracy. It is not possible to determine how the moment in various solvents varies with the class of compound studied, since not enough compounds of Classes IV, V and VI were available for study.

Acknowledgments.—The authors wish to thank the Commonwealth Research Committee of the University of Sydney for a grant to purchase the Curie–Chéneveau balance and for the award of a Scholarship to one of them (J. B. W.) Mr. W. A. Rawlinson kindly carried out some preliminary magnetic measurements on one of the compounds, and Mr. L. Maley determined the stability constants for two compounds. The micro-analyses were carried out by Miss J. Fildes.

Summary

1. A number of nickel complexes which are diamagnetic in the solid state show magnetic moments of up to 3.2 Bohr magnetons when dissolved in various solvents.

2. Where pyridine is used as a solvent, interaction between solvent and solute sometimes occurs, presumably with the formation of octahedral complexes containing two molecules of pyridine; the magnetic moment in such cases is that expected for d^2sp^3 bonds, *viz.*, 3.0–3.2 B.M.

3. In other cases, where the moment is less than that corresponding to two unpaired spins, it is suggested that under the influence of the solvent molecules a proportion of the molecules of the complex is converted from a planar (diamagnetic) to a tetrahedral (paramagnetic) formation, thus giving the complex as a whole a paramagnetic moment of less than 3.2 B.M.

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[15] Calvin and Wilson, THIS JOURNAL, **67**, 2003 (1945).

[16] Lifschitz, Bos and Dijkema, *Z. anorg. allgem. Chem.*, **242**, 97 (1939).

[17] Mellor and Lockwood, *J. Proc. Roy. Soc. N. S. Wales*, **74**, 141 (1940).