[CONTRIBUTION FROM THE INSTITUTE OF GENERAL CHEMISTRY, THE UNIVERSITY OF PALERMO]

Studies in Coördination Chemistry. IV. A Paramagnetic Form of Bis-(N-methylsalicylaldimine)-nickel(II) Complex[1]

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The diamagnetic complex bis-(N-methylsalicylaldimine)-nickel(II) turns into a paramagnetic complex of the same composition when heated above 180°, which is insoluble in non-coördinating solvents. The μ_{eff} value was found to be 3.4 B.M. The process was followed by means of magnetic balance measurements. The value of the heat of transition from the diamagnetic into the paramagnetic form was found to be -806 cal. A polymeric structure is proposed for the paramagnetic complex implying octahedral configuration and $4s4p^34d^2$ hybridation.

The complexes of nickel (II) with N-alkylsalicylaldimines exhibit an unusual behavior. They are diamagnetic in the solid state but become paramagnetic when dissolved in organic solvents[2] and when in the molten state.[3]

The first member of the series, bis-(N-methylsalicylaldimine)-nickel(II) differs somewhat from the other members of the series. Its paramagnetism, both in solution and in the molten state, is appreciably higher than that of the other complexes of the homologous series. The electric dipole moment of the methyl derivative is also higher than that of the others, and its ultraviolet spectrum, done in KBr discs, is anomalous.[2d]

Klemm and Raddatz[4] reported the isolation, together with a diamagnetic form of an unstable green paramagnetic form of bis-(N-methylsalicylaldimine)-nickel(II). The latter turned into the diamagnetic form within a few weeks. Other workers[2a] maintain that the paramagnetic compound exists only if contaminated with pyridine of crystallization.

A special behavior of the methyl member of this series is also displayed when heated. This can be observed under a microscope. On gradual heating, the green crystals begin to turn to a crystalline white powder above 160°. Between 190–202° the mixture of green and white crystals melts. Above the last temperature the liquid mixture solidifies again and at 280° is still solid. On rapid heating, *e.g.*, placing it in a muffle which is at 205–210°, the polymorphic change occurs rapidly without melting. Evidently the transition point lies below the melting point of the green complex compound. The analytical data of the product, whether the heating was carried out in a sealed tube or in an open vessel, were found to be identical to those of the starting material. The product thus obtained was, in the bulk, light green with pink reflections. Unlike the starting material, it is insoluble in all non-polar solvents, such as benzene, chloroform, etc. It dissolves slowly on prolonged boiling in pyridine to give a solution with the same absorption spectrum as that of a corresponding solution of the original green complex. On removal of the solvents the green diamagnetic compound is recovered.

The product of the thermal reaction is paramagnetic with μ_{eff} equal to 3.4 B.M. The conversion of the diamagnetic form into the paramagnetic form has been followed at 180° by measuring the magnetic susceptibility change from time to time. A plot of the atomic susceptibility *vs.* time is shown in Fig. 1. The conversion is virtually complete within two hours to yield a corresponding final χ_A value of 3236×10^{-6} u.c.g.s. Per cent. of reaction thus can be made to correspond to any intermediate susceptibility value while the conversion is in progress.

The temperature dependence of the atomic susceptibility of this paramagnetic complex from 20 to 200° fits fairly well into Curie's law This is shown by these magnetic susceptibility data

T, °K.	$\chi_A \times 10^6$	μ_{eff}
293	5028	3.45
343	4278	3.44
403	4658	3.45
453	3236	3.44
473	3116	3.45

The powder diagrams of the diamagnetic and paramagnetic forms, as obtained by use of the Cu Kα radiation, are completely different from each other. Since the paramagnetic form is insoluble in organic solvents, the ultraviolet spectrum has been measured in the solid state by use of the potassium bromide technique. The spectrum is identical to that of the diamagnetic form.[2d] On varying the charge of the sample and the pressure used for the preparation of the potassium bromide disc, no appreciable change in the spectrum is noted. This makes it improbable that the identity in the two spectra is caused by reaction of the two compounds with potassium bromide. On the other hand, prolonged grinding by mechanical vibrator was found to render the paramagnetic form soluble in those solvents, such as benzene and chloroform, in which it was not soluble prior to the treatment. The spectra of the solutions thus obtained are identical to those of the diamagnetic form. The finely ground material is some 20% less strongly paramagnetic than the non-ground compound. The above observations can be taken as evidence that grinding initiates a conversion process of the paramagnetic into the diamagnetic form. This is further enhanced by the high compression used for the preparation of the pellet.

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(1) Presented in part to the Symposium on the Chemistry of Coordination Compounds, Rome, September, 1957.

(2) (a) J. B. Willis and D. P. Mellor, THIS JOURNAL, **69**, 1237 (1947); (b) F. Basolo and W. Matoush, *ibid.*, **75**, 5663 (1952); (c) H. C. Clark and A. L. Odell, *J. Chem. Soc.*, 3431 (1955); 520 (1956); (d) L. Sacconi, P. Paoletti and G. Del Re, THIS JOURNAL, **79**, 4062 (1957).

(3) L. Sacconi, R. Cini and F. Maggio, *ibid.*, **79**, 3933 (1957).

(4) W. Klemm and K. H. Raddatz, *Z. anorg. allgem. Chem.*, **250**, 207 (1942).

On the other hand, the occurrence of polymorphic transitions in crystalline products caused by vigorous pelleting procedures recently has been reported.[5]

The value of the heat of transition from the diamagnetic into the paramagnetic form was found to be −806 cal. at 298°K. This value can be compared with the heats of transformation of the diamagnetic form into the soluble paramagnetic form of this complex found by Clark and Odell[2c]: −7210 cal. in chloroform, −9990 cal. in benzene; −10,700 cal. in toluene.

Because of the difficulties experienced in the preparation of crystals of the paramagnetic form suitable for a detailed structural analysis, we can only speculate as to its structure.

It is well known that the paramagnetism of nickel(II) complexes resulting from two unpaired electrons can be alternatively accounted for in terms of the following configurations: (a) tetrahedral, with $4s4p^3$ hybridation; (b) square planar with $4s4p^24d$ outer orbital hybridation; (c) octahedral with $4s4p^34d^2$ hybridation. Sutton[6] suggests in terms of ligand field theory that the splitting and therefore the stabilization is much less for the tetrahedral arrangement than for a regular octahedral one. In this case the coördination number will increase to six through polymerization. Nyholm[7] pointed out that this occurs for most of the compounds in which the nickel(II) atom is supposed to be four-covalent.

This seems applicable to the case described here. The non-solubility of the paramagnetic bis-N-methyl complex in inert solvents is in agreement with the hypothesis of a polymeric octahedral structure.

Experimental

Paramagnetic bis-(N-methylsalicylaldimine)-nickel(II) was prepared by heating the diamagnetic bis-(N-methylsalicylaldimine)-nickel(II) complex at 210° for two hours.

Anal. Calcd. for $C_{16}H_{18}O_2N_2Ni$: N, 8.56; Ni, 17.95. Found: N, 8.67; Ni, 17.87.

Magnetic Measurements.—Magnetic susceptibilities were determined with the use of a Gouy-type magnetic balance which will be described elsewhere. A finely ground sample of the substance was heated quickly to the desired temperature by means of a circulating paraffin bath regulated to within 0.4°.

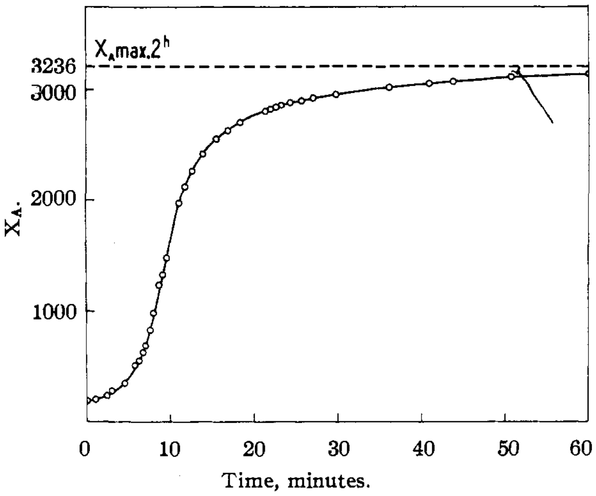

Fig. 1.—Magnetic data on the transformation of bis-(N-methylsalicylaldimine)-nickel(II) at 180°.

Absorption Spectra.—Spectrophotometric measurements in the solid state were made with a Beckman DU spectrophotometer by the potassium bromide technique.[8] The applied pressure was 12 ton cm.$^{-2}$. Grinding was accomplished with a Hilger type ball vibrator.

Calorimetric Measurements.—Measurements of the heat of transition from the diamagnetic to the paramagnetic form were made in a calorimeter of the type described by Davies, Singer and Staveley.[9] From the heats of reaction of the complexes with 6 *N* hydrochloric acid the heat of transition was calculated according to the formula: $\Delta H = L_{\text{diam}} - L_{\text{param}}$. The calorimetric data are the following: $L_{\text{diam}} = -27{,}471 \pm 6$ cal.; $L_{\text{param}} = -26{,}665 \pm 60$ cal.; $\Delta H = -806 \pm 70$ cal.

The spectra of the hydrochloric acid solutions of the two forms were found to be identical. This indicates that in each case the reaction with hydrochloric acid causes the formation of the same final products.

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(5) A. W. Baker, *J. Phys. Chem.*, **61**, 450 (1957).

(6) L. E. Sutton, "Theory of Bonding in Metal Complexes," Proceedings of the Symposium on the Chemistry of Coördination Compounds, Rome, September, 1957.

(7) R. S. Nyholm, "Complex Compounds of Transition Metals," Proceedings of Tenth Solvay Conference, Brussels, May, 1956.

(8) M. M. Stimson and M. J. O'Donnell, THIS JOURNAL, **74**, 1805 (1952).

(9) T. Davies, S. S. Singer and L. A. K. Staveley, *J. Chem. Soc.*, 2304 (1954).