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Studies in Coördination Chemistry. VII. Recent Investigations on the Magnetically Anomalous Nickel(II) Complexes of N-Alkylsalicylaldimines

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The magnetic susceptibility of a series of bis-(N-alkylsalicylaldimine)-nickel(II) complexes has been measured over a wide range of temperature, both in solution and in the molten state. The experimental data are discussed in the light of the recent ligand field treatments for the anomalous nickel complexes, implying an equilibrium between planar molecules in triplet and singlet states. The equation proposed for the variation of the magnetic susceptibility with temperature has been verified and the values of the energy separation $h\nu_1$ between the lowest singlet and triplet states have been calculated. The results are consistent with such a theoretical treatment. The temperature dependence of μ and $h\nu_1$ for solutions and melts confirms that the mechanism of the transition from diamagnetism to paramagnetism is substantially the same in both cases. The results of viscosity measurements of the complexes in the molten state appear to indicate that in the melts there is no temperature dependent association implying a planar-octahedral equilibrium.

Introduction

The paramagnetism shown by some diamagnetic four-coördinated nickel(II) complexes, such as, for example, bis-(N-methylsalicylaldimine)-nickel (II) when dissolved in organic solvents was attributed, (a) to the formation of six-coördinate adducts with two molecules of strongly polar solvents such as pyridine and (b) to a planar-tetrahedral equilibrium in the case of "inert" solvents.[1–4]

On the other hand, the dielectric polarization data of solutions of nickel complexes of N-alkylsalicylaldimines were taken to indicate that both the diamagnetic and the paramagnetic species of the complexes, dissolved in "non-coördinating" solvents, have a planar structure.[5,6] Later it was shown that the paramagnetism occurs even when the complexes are in the molten state[7] and that the complex bis-(N-methylsalicylaldimine)-nickel(II) is transformed on heating into a paramagnetic isomer, probably of octahedral polymeric structure.[8] An X-ray diffraction investigation has ruled out the existence of Ni–Ni bonds with spin pairing in the diamagnetic solid form.[9]

Recently Ballhausen and Liehr[10] and independently Gilda Maki[11] have treated this problem in terms of modern ligand theory. Both treatments lead to the conclusion that a planar complex of Ni(II) has a number of singlet and triplet states lying within a narrow range of energy. The relative energies of the electronic states depend upon the intensity and symmetry (*cis*, *trans*, etc.) of the electrostatic field of the ligands. The ground state of a planar nickel(II) complex will therefore be a singlet (diamagnetic complex) or a triplet (paramagnetic complex), depending on the ligand field.

On melting or dissolving a four-coördinated nickel complex, the effective ligand field acting on the nickel(II) will change. According to Ballhausen and Liehr this is due to changes in the bond lengths and bond angles, as well as to solvation effects, while according to Maki the change is mainly due to the axial electrostatic perturbation

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(1) T. B. Willis and D. P. Mellor, THIS JOURNAL, **69**, 1237 (1947).

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

(3) F. Basolo and W. R. Matoush, THIS JOURNAL, **75**, 5663 (1953).

(4) S. Fujii and M. Sumitani, *Sci. Repts. Tôhoku Imp. Univ., First Series*, **37**, 49 (1953).

(5) L. Sacconi, P. Paoletti and G. Del Re, THIS JOURNAL, **79**, 4062 (1957).

(6) L. Sacconi, M. Ciampolini, F. Maggio and G. Del Re, *ibid.*, **82**, 815 (1960).

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

(8) L. Sacconi, P. Paoletti and R. Cini, International Symposium on the Chemistry of the Coördination Compounds, Rome, September 1957; *J. Inorg. & Nuclear Chem.*, **8**, 492 (1958); THIS JOURNAL, **80** 3583 (1958); C. M. Harris, S. L. Lenzer and R. L. Martin, *Aust. J. Chem.*, **11**, 331 (1958).

(9) E. Frasson, C. Panattoni and L. Sacconi, *J. Phys. Chem.*, **63**, 1908 (1959).

(10) C. J. Ballhausen and A. D. Liehr, THIS JOURNAL, **81**, 538 (1959).

(11) Gilda Maki, *J. Chem. Phys.*, **28**, 651 (1958); **29**, 162 (1958); **29**, 1129 (1958).

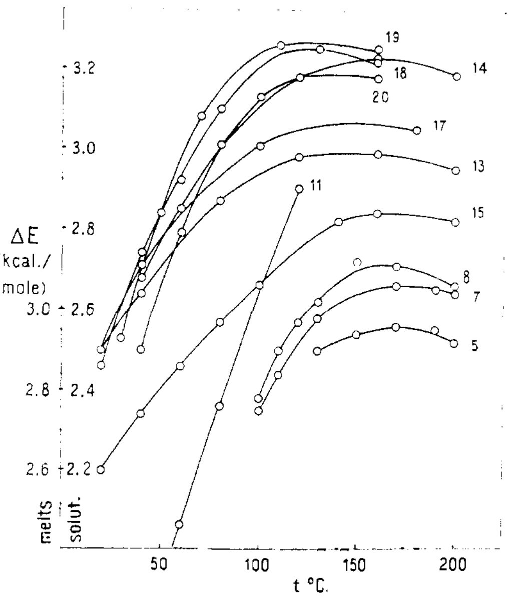

Fig. 1.—Plot of energy separation ΔE *vs.* temperature. The numbers are from Tables I and II.

caused by solvent molecules acting as dipoles (along the z-axis). In all cases the consequence is a decrease of the energy of the lowest triplet state relative to the energy of the lowest singlet state.

If the energy separation between the low-lying energy levels becomes comparable with the thermal energy, the molecules will distribute between these states according to the Maxwell–Boltzmann law, and the complex will be paramagnetic with a magnetic moment intermediate between 0 and 3.2 B.M. The paramagnetism exhibited in solution and in the molten state by the "magnetically anomalous" nickel chelates cannot, therefore, according to the above mentioned treatments, be attributed to conformational equilibria. The structure of the complexes will remain planar, as already inferred from the dielectric polarization data obtained for bis-(N-alkylsalicylaldimine)-nickel(II) complexes.[5]

From the above considerations, Ballhausen and Liehr proposed the following general expression, correlating χ and T and valid for any electronic system having both a low-lying singlet and a low-lying triplet

$$\chi_{\mathrm{A}} = \frac{2g^2\beta^2N}{3kT}(1 + {}^1/_3 \exp h\nu_1/kT)^{-1} + N\alpha \quad (1)$$

where g is the Landé factor for the triplet, N Avogadro's number, k the Boltzmann constant, β the Bohr magneton, $N\alpha$ the temperature independent part of the susceptibility and $h\nu_1$ the energy separation between the lowest singlet and triplet state. It had not, however, been possible until now to verify this expression, because of the lack of detailed susceptibility *vs.* temperature studies. For this reason we think it worth while to publish the results of magnetic suceptibility of bis-(N-alkylsalicylaldimine)-nickel(II) complexes, in solution and in the molten state, over a range of temperature. A preliminary communication on this subject appeared two years ago.[7]

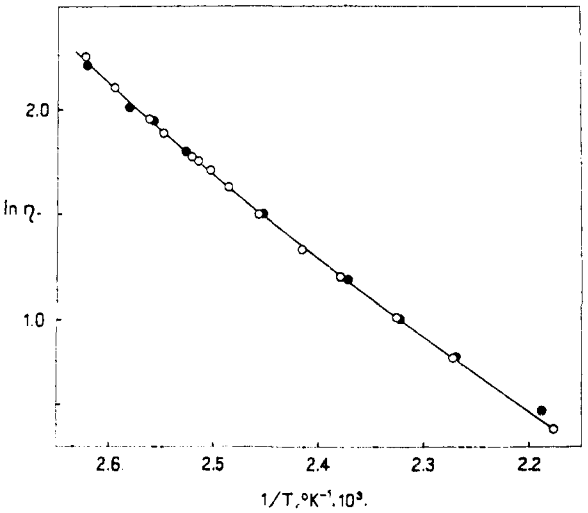

Fig. 2.—Plot of ln η *vs.* $1/T$: ●, bis-N-nonyl-salic.-Ni; ○, bis-N-decyl-salic.-Ni.

The isolation of a stable solid paramagnetic isomer of bis-(N-methylsalicylaldimine)-nickel(II) for which an octahedral polymeric structure has been postulated,[8] might suggest that the paramagnetism of the molten chelates is due to a similar type of polymerization. If so, the change of the magnetic susceptibility of the melts with temperature should be accompanied by a variation of the degree of association. In order to verify this hypothesis we measured the viscosity of the melts over a wide range of temperature.

Experimental

Preparation of the Metal Complexes.—The nickel complexes from hexyl- to decyl-, which already have been described by Charles,[12] were prepared according to the method used for the corresponding ethyl-amyl complexes.[5]

Bis-(N-hexylsalicylaldimine)-nickel(II).—M.p. 121°.

Anal. Calcd. for $C_{26}H_{36}O_2N_2Ni$: Ni, 12.56; N, 5.99. Found: Ni, 12.52; N, 5.96.

Bis-(N-heptylsalicylaldimine)-nickel(II).—M.p. 119–120°

Anal. Calcd. for $C_{28}H_{40}O_2N_2Ni$: Ni, 11.85; N, 5.65. Found: Ni, 11.68; N, 5.69.

Bis-(N-octylsalicylaldimine)-nickel(II).—M.p. 99–100°.

Anal. Calcd. for $C_{30}H_{44}O_2N_2Ni$: Ni, 11.21; N, 5.35. Found: Ni, 11.13; N, 5.50.

Bis-(N-nonylsalicylaldimine)-nickel(II).—M.p. 102–103°.

Anal. Calcd. for $C_{32}H_{48}O_2N_2Ni$: Ni, 10.64; N, 5.08. Found: Ni, 10.63; N, 5.16.

Bis-(N-decylsalicylaldimine)-nickel(II).—M.p. 91–92°.

Anal. Calcd. for $C_{34}H_{52}O_2N_2Ni$: Ni, 10.13; N, 4.83. Found: Ni, 9.75; N, 4.98.

Magnetic Susceptibility Measurements.—Susceptibility measurements were made with the Gouy method using an iron clad coils electromagnet working with 2 kw. of power, 20,000 oersteds of field strength.[13] The samples were placed in a double ended glass tube surrounded by a glass jacket. Temperatures from 20 to 200° were obtained by circulating paraffin oil from a thermostat regulating to ± 0.2°. All measurements were referred to freshly boiled distilled water, the specific susceptibility of which was assumed to be $-0.720 \cdot 10^{-6}$ at 20°. The mixtures of two complexes in the molten state contained the components in the molecular ratio 1:1. The mean molecular weight of the two complexes was taken as the effective molecular weight of the mixture. The susceptibilities of the complexes dissolved in dibutyl phthalate were calculated as described for analogous solutions[5] in the first paper of this series.

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(12) R. G. Charles, *J. Org. Chem.*, **22**, 677 (1957).

(13) F. Bitter and F. Everett Reed, *Rev. Sci. Instr.*, **22**, 171 (1951); R. Cini, *Ricerca Sci.*, **29**, 172 (1959).

TABLE I

MAGNETIC SUSCEPTIBILITY DATA FOR BIS-(N-ALKYLSALICYLALDIMINE)-NICKEL(II) IN THE MOLTEN STATE

Bis-N-alkyl-Ni-complex	Temp., °C.	d	X_g ($\times 10^6$)	X_A ($\times 10^6$)	μ_{eff} (B.M.)	ΔE (kcal./mole)
N-ethyl-	180	1.191	+0.333	+308	1.06	3.09
	190	1.183	+ .378	+324	1.10	3.09
	200	1.175	+ .441	+347	1.15	3.07
N-propyl-	168	1.147	+0.052	+233	0.91	3.25
	180	1.138	+ .100	+251	0.96	3.27
	190	1.130	+ .139	+266	1.00	3.27
	200	1.121	+ .191	+286	1.04	3.27
N-butyl-	148	1.130	+0.012	+242	0.91	2.96
	155	1.125	+ .027	+248	.92	2.96
	170	1.113	+ .071	+266	.97	2.98
	190	1.097	+ .153	+300	1.06	2.98
	200	1.089	+ .202	+320	1.10	2.92
N-amyl-	150	1.092	−0.041	+243	0.91	2.96
	160	1.085	− .019	+253	.94	2.97
	170	1.078	+ .010	+265	.97	2.98
	179	1.072	+ .042	+279	1.01	2.98
	200	1.057	+ .126	+317	1.10	2.92
N-hexyl-	130	1.080	−0.106	+236	0.87	2.90
	150	1.065	− .081	+247	.92	2.94
	170	1.050	− .033	+270	.98	2.96
	190	1.035	+ .038	+303	1.06	2.95
	200	1.027	+ .075	+320	1.10	2.92
N-heptyl-	130	1.057	−0.219	+200	0.81	3.02
	150	1.042	− .197	+211	.85	3.10
	170	1.027	− .148	+236	.92	3.06
	190	1.012	− .080	+269	1.00	3.05
	200	1.004	− .039	+290	1.05	3.04
N-octyl-	101	1.074	−0.187	+235	0.84	2.75
	111	1.067	− .214	+221	.83	2.84
	131	1.051	− .227	+214	.84	2.98
	170	1.021	− .172	+243	.93	3.06
	199	0.999	− .084	+289	1.05	3.04
N-decyl-	100	1.025	−0.273	+223	0.82	2.78
	110	1.019	− .300	+207	.80	2.90
	120	1.012	− .309	+202	.80	2.97
	130	1.005	− .313	+200	.81	3.02
	150	0.991	− .298	+208	.84	3.12
	170	.977	− .262	+229	.91	3.11
	200	.957	− .179	+277	1.03	3.06
Ethyl + octyl- 1:1	130	1.161	−0.061	+234	0.87	
	151	1.146	− .027	+249	.92	
	169	1.133	+ .024	+271	.98	
	190	1.117	+ .091	+301	1.06	
	200	1.110	+ .129	+318	1.10	
Hexyl + heptyl- 1:1	100	1.091	−0.134	+233	0.84	
	110	1.083	− .158	+221	.83	
	125	1.072	− .172	+214	.83	
	131	1.067	− .175	+213	.83	
	170	1.037	− .108	+245	.93	
	199	1.015	− .006	+294	1.06	

Spectrophotometric Measurements.—The absorption spectra of the bis-(N-nonylsalicylaldimine)-nickel(II) complex in benzene solution (at 20°) and in the molten state (at 100°) were measured with a Beckmann DU spectrophotometer fitted with a thermostated cell compartment. The silica absorption cell had a 1.00 cm. light path for the solution and 0.01 cm. for the molten sample.

Viscosity Measurements.—The viscosity measurements were carried out in an Ostwald type viscosimeter using *ca.* 2 ml. volumes of the molten complexes. Temperatures were held constant to ±0.1° by means of an oil filled thermostated bath. Flow times for the molten complexes were of about 150 and 40 sec. at room temperature and at 180°, respectively. The viscosimeter was calibrated carefully with water at 98°, 1,2-dibromoethylene at 105°, toluene at 107° and paraffin oil at 120 and 150°. The viscosity of this substance at these temperatures was determined previously with a Höppler viscosimeter. Literature values[14] for the density of water, 1,2 dibromoethylene and toluene were used. The density of paraffin oil and molten complexes were determined in the standard manner using a pycnometer.

The accuracy of the viscosity measurements was ± 2%.

Results and Discussion

The results are reported in Tables I and II and in Figs. 1 and 2.

All complexes are diamagnetic in the solid state. When melted they attain a partial paramagnetism with μ from 0.8 to 1.15 B.M. The plots of μ *vs.* T have similar shapes for all complexes, μ increasing steadily from 120 up to 200°; when the complexes or mixtures of complexes have melting points lower than 120°, a minimum corresponding to this temperature appears in the curves.

If dibutyl phthalate (b.p. 340°) is used as a solvent, the magnetic susceptibility of the solutions can be measured over a wider range of temperature (20–200°). The μ values so found range from 0.5 to 1.6 B.M. The curves of μ *vs.* T for dilute solutions have a positive slope, which increases with temperature. The solutions of bis-(N-octylsalicylaldimine)-nickel(II), which is highly soluble in dibutyl phthalate, show a minimum which is shifted toward higher temperatures for higher concentrations. For concentrations corresponding to 10.3, 19.9, 34.4 and 45.9%, the minima of the curves lie at about 40, 60, 70 and 80°, respectively. From these values it appears that on increasing the concentration the temperature corresponding to the minimum of the curve approaches the value 120° found for the complex in the molten state, that is, under the conditions of highest concentration.

The curve for N-methyl derivative in dibutyl phthalate is different from those of the analogous complexes containing longer alkyl chains. The values of μ decrease from 1.6 to 0.9 B.M. as the temperature rises from 20 to 120°. Above this temperature, μ increases again, but the results obtained at high temperatures are unreliable, since the compound transforms slowly into the insoluble stable paramagnetic form, which can be separated from the solution by centrifugation.

The values so obtained can be interpreted with the aid of a modified form of the expression 1. Since $\mu_{eff}^2 = (3kT/N)X_A$ and the term $N\alpha$ can be neglected, the equation becomes

$$\mu_{eff} = (2g^2\beta^2)^{1/2}\,(1 + {}^1/_3 \exp \Delta E/RT)^{-1/2} \qquad (2)$$

where $\Delta E = Nh\nu_1$ is the energy separation per mole between the lowest singlet and triplet state. ΔE is therefore positive or negative according to whether the ground state is dia- or paramagnetic. Since for a paramagnetic complex of nickel(II) the actual value of the expression $(2g^2\beta^2)^{1/2}$ is generally equal to 3.2 B.M.

$$\mu_{eff} = 3.2\,(1 + {}^1/_3 \exp \Delta E/RT)^{-1/2} \qquad (3)$$

If the lowest energy state is a singlet, ΔE will vary from 0 to $+\infty$, and the corresponding values

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(14) "International Critical Tables," Vol. II. J. Timmermans, Physico-chemical Constants of Pure Organic Compounds, Elsevier Publishing Co., Inc., New York, N. Y., 1950.

TABLE II

MAGNETIC SUSCEPTIBILITY DATA FOR BIS-(N-ALKYLSALICYLALDIMINE)-NICKEL(II) COMPLEXES IN DIBUTYL PHTHALATE

Bis-N-alkyl-Ni-complex	Temp., °C.	Concn., g., %	X_g ($\times 10^6$)	X_A ($\times 10^6$)	μ_{eff} (B.M.)	ΔE (kcal./mole)
N-methyl-	32	2.36	+2.44	+964	1.54	1.39
	40		+1.86	+774	1.40	1.58
	60		+0.81	+430	1.07	2.10
	80		+ .45	+312	0.95	2.41
	100		+ .24	+245	.86	2.71
	120		+ .17	+222	.84	2.90
	160		+ .35	+280	.99	2.88
	200		+ .28	+256	.99	3.14
N-ethyl-	23	2.56	+0.16	+248	0.77	2.28
	60		+ .20	+261	.84	2.45
	100		+ .19	+258	.88	2.67
	160		+ .37	+320	1.06	2.75
	200		+ .51	+372	1.19	2.75
N-ethyl-	20	6.97	−0.045	+174	0.64	2.50
	32		− .052	+172	.65	2.58
	40		− .062	+169	.65	2.64
	60		− .052	+172	.68	2.75
	80		− .057	+170	.69	2.89
	121		− .030	+201	.80	2.98
	160		+ .15	+244	.92	2.99
	200		+ .33	+308	1.08	2.96
N-propyl-	40	7.54	−0.15	+157	0.63	2.68
	60		− .17	+149	.63	2.85
	80		− .18	+144	.64	3.01
	101		− .15	+155	.68	3.09
	120		− .15	+155	.70	3.18
	160		− .050	+194	.82	3.23
	199		+ .082	+244	.97	3.19
N-butyl-	20	8.12	+0.086	+272	0.80	2.22
	40		+ .082	+271	.83	2.32
	100		+ .046	+256	.88	2.66
	140		+ .11	+280	.97	2.86
	160		+ .11	+282	.99	2.88
	200		+ .27	+349	1.15	2.83
N-hexyl-	20	9.14	−0.41	+ 94	0.47	2.86
	38		− .41	+ 92	.48	3.02
	100		− .35	+122	.67	3.10
	180		− .056	+259	.97	3.05
N-octyl-	20	10.34	−0.29	+179	0.65	2.47
	40		− .34	+154	.62	2.71
	100		− .32	+165	.70	3.03
	180		− .15	+254	.96	3.07
N-octyl-	22	19.93	−0.29	+179	0.65	2.49
	26		− .31	+169	.64	2.54
	36		− .34	+154	.62	2.66
	42		− .36	+142	.60	2.76
	56		− .39	+131	.59	2.91
	70		− .39	+128	.59	3.03
	110		− .38	+134	.64	3.26
	130		− .34	+156	.71	3.25
	160		− .26	+196	.83	3.22
N-octyl-	30	34.40	−0.27	+191	0.68	2.50
	34		− .30	+178	.66	2.57
	39		− .31	+169	.65	2.63
	41		− .35	+148	.61	2.73
	60		− .39	+128	.59	2.94
	80		− .41	+119	.58	3.14
	98		− .40	+122	.60	3.25
	160		− .27	+192	.82	3.25
N-octyl-	41	45.90	−0.24	+206	0.72	2.51
	45		− .27	+194	.70	2.58
	50		− .29	+181	.69	2.64
	60		− .32	+165	.66	2.79
	80		− .35	+147	.65	2.98
	100		− .35	+148	.67	3.13
	120		− .34	+157	.71	3.18
	160		− .24	+209	.85	3.18

of μ from 2.8 to 0. If the ground state is a triplet, ΔE will vary from 0 to $-\infty$ and μ from 2.8 to 3.2 B.M. As the experimental values of μ range from 0.5 to 1.6 for dibutyl phthalate solutions and from 0.8 to 1.15 for the melts, the ground state for all bis-(N-alkylsalicylaldimine)-nickel(II) complexes, both in solution and in the melts, in the range of temperature we investigated is diamagnetic as in the solid state.

Equation 3 shows that μ is a decreasing function of the ratio $\Delta E/RT$. As the curve of μ *vs.* T has a minimum, the ratio $\Delta E/RT$ must show a maximum. It is therefore to be expected that, on increasing the temperature, ΔE first increases more rapidly and then less rapidly then RT. On introducing in equation 3 the values of μ measured at various temperatures, the corresponding values of the molar energy separation ΔE are obtained. They are listed in the last column in Tables I and II and shown graphically in Fig. 1.

In the melts and in the solutions, ΔE increases up to a temperature of about 120° and in most cases shows a decrease in the proximity of 200°. Since for all complexes, the N-methyl derivative excepted, ΔE ranges between 2.2 and 3.2 kcal./mole, the values of the energy separation $h\nu_1$ lie between 770 and 1100 cm.$^{-1}$, so that a transition between the lowest singlet and triplet states should result in a feeble spin forbidden band in this region of the spectrum.

The variation of μ with T can be explained by assuming that ΔE depends on such temperature-dependent quantities as the geometrical dimensions, average axial electrostatic perturbations by neighbors, etc. On varying the temperature, these factors may influence ΔE in different ways. For instance, an increase in temperature should be accompanied by an increase in the average intermolecular distances, as well as by a decrease in the orientation of the solvent molecules.[15] The axial perturbation will then become smaller and the tetragonal distortion stronger, thus causing ΔE to increase. On the other hand, since the bond lengths between the nickel ion and the ligand atoms in the plane of the molecule increase with the temperature, a decrease of the effective electrostatic field acting on the central ion is to be expected, and the low-lying triplet state should therefore be stabilized with respect to the singlet ground state. Consequently the energy separation should be expected to decrease. The curves of ΔE *vs.* T show that up to 120° at least the first effect prevails and results in a further separation of the energies of the two lowest states. The dependence of μ values on T is satisfactorily interpreted from the above considerations. At low temperature the energy sepa-

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(15) C. J. Ballhausen and C. K. Jörgensen, *Acta Chem. Scand.*, **9**, 397 (1955).

ration is relatively small, so that an appreciable proportion of molecules will populate the lowest triplet state; but on increasing the temperature since the energy separation increases more rapidly than RT, the number of molecules in the triplet state will become smaller. Above a certain temperature ΔE remains practically constant, so that the increase of thermal energy causes an increase of the population of the lowest triplet state.

As shown in Tables I and II, the values of ΔE at a given temperature are nearly identical for the solutions and the melts. Also the spectra of the melt and of benzene solution, although measured at different temperatures, are found to be very similar. This confirms that fusion, *i.e.*, self-solution, alters the effective ligand field around the nickel ion, in a way very similar to that of dissolution in a solvent.

In the case of the bis-(N-methylsalicylaldimine)-nickel(II) complex the values of the energy separation are lower than in the other complexes, ranging from 1.3 at 20° to 2.9 at 120°. The values of ΔE for the same complex, calculated using Clark's data for magnetic measurements in $CHCl_3$ and toluene,[2] are even lower, becoming negative at temperature below $-10°$. Under these conditions, therefore, the triplet state is the most stable.

Another peculiar feature of the methyl complex is the fact that, on heating above 150°, it transforms into a paramagnetic solid isomer with $\mu_{\text{eff}} = 3.4$ B.M.[8] This has been attributed to the attainment of a six-coördinated structure, through the formation of intermolecular bonds along the z-axis, between nickel and donor atoms of two adjacent molecules of the complex. The crystal field acting on the nickel atom would in this case approach a distorted octahedron, and the ground state would be paramagnetic.

A similar explanation implying an equilibrium between diamagnetic planar monomers and octahedral paramagnetic polymers could also be postulated for the temperature dependent paramagnetism in the melts. Such a suggestion, however, does not agree with the results of the viscosity measurements. In fact in our measurements of the viscosity of the octyl- and nonyl-complexes we found a practically linear relationship between ln η and $1/T$ over a wide range of temperature(Fig. 2). As is well known this behavior is peculiar to unassociated liquids.

This conclusion does not contradict the above assumption that the molecular interactions decrease as the temperature increases. In fact, a comparison of the values of μ and ΔE, for the melts and for the corresponding solutions in solvents such as benzene and dibutyl phthalate, shows that they are almost equal and quite different from those of the solutions in pyridine. The molecular interactions responsible for the axial perturbation of the field acting on the nickel ion in the melts must therefore be weak and almost equal to those established between the molecules of the complex and of the inert solvents. Thus it is not surprising that the variation of viscosity with the temperature is "normal."

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[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO]

The Infrared Spectra of the Complexes of Iron(II), Cobalt(II) and Nickel(II) with Biacetyldihydrazone

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The infrared spectra of the complexes of iron(II), cobalt(II) and nickel(II) with biacetyldihydrazone (BdH) have been determined. Assignments have been made in the case of twelve different absorptions. The position of the C=N stretching frequency of BdH is sensitive to the type of complex which is formed. The data, which are presented herein, are consistent with the formation of multiple bonds (both sigma- and pi-bonds) in the diamagnetic complex, tris-(biacetyldihydrazone)-iron(II) iodide. The spectra of the paramagnetic cobalt(II) and nickel(II) complexes indicate that the interaction between the metal atom and the imine nitrogen atom of the ligand molecule is not as great as that which exists in the diamagnetic iron(II) complex. The conformation of biacetyldihydrazone is discussed.

Introduction

It has been demonstrated that the complexes which biacetyldihydrazone forms with iron(II), cobalt(II) and nickel(II) are very similar to the complexes which these dipositive metal ions form with ligand molecules of the dipyridyl type, *e.g.*, 2,2'-bipyridine and *o*-phenanthroline.[1b] Tris-(biacetyldihydrazone)-iron(II) iodide is diamagnetic whereas the corresponding three-to-one cobalt(II) and nickel(II) complexes are paramagnetic. The two-to-one complexes of cobalt(II) and nickel(II), *viz.*, $[Co(BdH)_2Cl_2]$ and $[Ni(BdH)_2Cl_2]$, are also highly paramagnetic, indicating three and two unpaired electrons, respectively.

Of the complexes formed by these metal ions with aromatic heterocyclic diamines, acyclic diimines and dihydrazones, only the iron(II) complexes are consistently highly colored. It has been suggested by other investigators that the properties of these iron(II) complexes which distinguish them from those of cobalt and nickel are a consequence of pi-bonding between the conjugated ligand molecules (all of which contain the conjugated dimethine group) and the t_{2g} (non-bonding) electrons of the iron atom.[2,3]

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[1] (a) University of Florida, Gainesville. (b) R. C. Stoufer and D. H. Busch, THIS JOURNAL, **78**, 6016 (1956).

[2] P. Krumholz, *ibid.*, **75**, 2163 (1953).

[3] D. H. Busch and J. C. Bailar, Jr., *ibid.*, **78**, 1137 (1956).