$$\mathrm{Pt(NH_3)_2Y(H_2O)^{++} + Y \xrightarrow{k_6} Pt(NH_3)_2Y_2^{++} + H_2O} \quad (14)$$

By using the steady-state assumption for the concentration of the intermediates $Pt(NH_3)_2(H_2O)Cl^-$, $Pt(NH_3)_2YCl^+$ and $Pt(NH_3)_2Y(H_2O)^{++}$, the rate equation reduces to

$$\frac{d[\mathrm{Cl^-}]}{dt} = 2k_1\left(1 - \frac{k_2[\mathrm{Cl^-}]}{k_2[\mathrm{Cl^-}] + k_3[\mathrm{Y}]}\right)[\mathrm{Pt(NH_3)_2Cl_2}] \quad (15)$$

It actually has been observed that the initial, rather rapid, rate of liberation of Cl^- drops to a much lower value even before half of the total chlorine has been liberated, and that the smaller the concentration of the incoming group, Y, in the solution, the earlier this drop off occurs. Furthermore, if chloride ion is added to the solution to begin with, then for the same concentration of Y, the slowing down takes place earlier. Addition of more Y at this stage again speeds up the reaction. These are all expected on the basis of eq. 15. Eventually all of the chloride ion is replaced by pyridine or aniline (see Experimental). Hence, the rate constant for the initial rate has been divided by two for the data given in Table I for these two reagents, namely, aniline and pyridine in their reaction with *trans*-$Pt(NH_3)_2Cl_2$.

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

Studies in Coördination Chemistry. I. The Effect of Solvents on Some Bis-(N-alkylsalicylaldimine)-nickel(II) Complexes

BY LUIGI SACCONI, PIERO PAOLETTI AND GIUSEPPE DEL RE

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A series of bis-(N-alkylsalicylaldimine)-nickel(II) complexes in the solid state and in solution of organic solvents was submitted to magnetic, spectrophotometric and electric moment measurements. The results of dipole moment determination afford evidence against the hypothesis of a tetrahedral structure of such complexes when dissolved in "non-coördinating" solvents. The paramagnetism developed in such solutions and some characteristic features of the absorption spectra can be understood with the hypothesis of an equilibrium involving an "outer orbital" $4s4p^24d$ planar configuration. The magnetic behavior and the absorption spectral data of these complexes in the solid state are discussed in terms of this concept. Observations on the influence of the length of the *n*-alkyl chains attached to the nitrogen atoms on these properties are reported. The zigzag shape of the curves of magnetic moments, atomic polarizations and melting points for this series of complexes are correlated with changes of base strength and coördination power of the parent amines. The smaller the coördination power of the amine, the greater the polarity and thus the "outer orbital" character of the coördinate bonds of the complex. This is also accompanied by a greater ease of bending vibrations of the chelate rings and a greater tendency for interactions between the polarizable molecules in the crystals.

The magnetic behavior of nickel complexes has proved of considerable value in obtaining useful information concerning the bond type and the stereochemistry of such compounds.

Generally magnetic measurements have been carried out on metal complexes in the solid state. However, some measurements also have been made on complexes dissolved in organic solvents. French, Magee and Sheffield,[1] postulate that the weak paramagnetism (1.9 B.M.) exhibited by a methanol solution of diamagnetic bis-(formylcamphor)-ethylenediaminenickel(II) is caused by a partial conversion of the planar complex to a tetrahedral form. Subsequently Willis and Mellor[2] found that a number of tetracovalent nickel(II) complexes, diamagnetic in the solid state, exhibit paramagnetism in various solvents such as pyridine, alcohols, dioxane, chloroform and benzene. The paramagnetism observed in pyridine solutions, corresponding to two unpaired electrons, was attributed to an expansion of the coördination number to six. This solvation reaction was confirmed by Basolo and Matoush[3] through the isolation of the corresponding paramagnetic complexes containing two molecules of pyridine.

Some complexes such as bis-(formylcamphor)-ethylenediaminenickel(II), bis-(salicylaldoxime)-nickel(II) and bis-(N-methylsalicylaldimine)-nickel(II), diamagnetic in the solid state, exhibit paramagnetism even in "non-coördinating" solvents such as benzene and chloroform.[2] In such cases, where the magnetic moment is intermediate between 0 and 3.2 B.M., it was suggested that a proportion of the molecules of the complex is converted from a planar to a tetrahedral configuration.[2]

In this connection Basolo and Matoush[3] found that no direct correlation exists between the magnetic moment of bis-(formylcamphor)-ethylenediaminenickel(II) in methylbenzenes and the base strength of these solvents. They concluded that the paramagnetism must therefore not be due to solvation but rather to formation of tetrahedral nickel(II) compounds.

Nyholm[4] recently suggested that the intermolecular crystalline forces in solids may sometimes favor the square configuration, whereas in solution, the tetrahedral arrangement of lowest potential energy may be adopted by the isolated molecule.

The magnetic measurements by Fujii and Sumitani[5] and by Clark and Odell[6] on solutions of such complexes in non-coördinating solvents over a

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(1) H. S. French, M. Z. Magee and E. Sheffield, THIS JOURNAL, **64**, 1924 (1942).

(2) J. B. Willis and D. P. Mellor, *ibid.*, **69**, 1237 (1947).

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

(4) R. S. Nyholm, *Chem. Revs.*, **53**, 263 (1953).

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

(6) H. C. Clark and A. L. Odell, *J. Chem. Soc.*, 3131 (1955).

temperature range of 100°, confirmed the occurrence of temperature-dependent equilibria between dia- and paramagnetic forms. Calculation of the thermodynamic quantities associated with the equilibria were retained as supporting Nyholm's suggestion that for certain complexes in solution the paramagnetic, probably tetrahedral, form is the state of lowest energy. However no direct experimental evidence has as yet been reported in support of the hypothesis that the tetrahedral form is responsible for the paramagnetism in benzene and in chloroform solutions.

Clark and Odell[7] correlated their magnetic data with the absorption spectra in various solvents at different temperatures. While the spectral data for solutions in coördinating solvents are consistent with the results of the magnetic measurements, absorption spectra of bis-(formylcamphorethylenediamine)-nickel(II), bis-(salicylaldoxime)-nickel(II) and bis-(N-methylsalicylaldimine)-nickel(II) complexes in non-polar solvents do not correlate the results of magnetic measurements.

In order to obtain more definitive information on the effect of solvents on these nickel complexes, we have investigated the series of nickel(II) complexes of N-alkylsalicylaldimines, where the alkyl group increase from methyl through *n*-amyl. Chloroform, benzene and dioxane solutions of these complexes were submitted to dipole moment, magnetic and spectrophotometric measurements. Magnetic and spectrophotometric measurements also were made on the solid compounds. Relatively few spectral investigations of complexes in the crystalline state are reported in the literature.[8]

Experimental

Preparation of Compounds.—The following general method was used: bis-salicylaldehydenickel(II) dihydrate was suspended in excess of an aqueous alcoholic solution of *n*-alkylamine and heated on the water-bath under reflux for several minutes. The crystalline products obtained were then recrystallized from alcohol or from chloroform and petroleum ether. The olive-green complexes are soluble in alcohol, ether, benzene and chloroform. The solubility in non-polar solvents increases with increasing *n*-alkyl chain length.

Bis-(N-methylsalicylaldimine)-nickel(II) was prepared according to Klemm and Raddatz.[9] This compound melts between 192 and 202°.

Bis-(N-ethylsalicylaldimine)-nickel(II): m.p. 173–174°. *Anal.* Calcd. for $C_{18}H_{20}O_2N_2Ni$: N, 7.89; Ni, 16.53. Found: N, 8.05; Ni, 16.31.

Bis-(N-propylsalicylaldimine)-nickel(II): m.p. 160–161°. *Anal.* Calcd. for $C_{20}H_{24}O_2N_2Ni$: N, 7.32; Ni, 15.33. Found: N, 7.55; Ni, 15.22.

Bis-(N-butylsalicylaldimine)-nickel(II): m.p. 140–141°. *Anal.* Calcd. for $C_{22}H_{28}O_2N_2Ni$: N, 6.82; Ni, 14.27. Found: N, 6.97; Ni, 14.05.

Bis-(N-amylsalicylaldimine)-nickel(II): m.p. 142–143°. *Anal.* Calcd. for $C_{24}H_{32}O_2N_2Ni$: N, 6.38; Ni, 13.36. Found: N, 6.37; Ni, 13.24.

Magnetic Susceptibility Measurements.—Susceptibility measurements on the solids were made with the modified Bhatnagar balance described previously.[10] Magnetic measurements on the complexes dissolved in the different solvents were executed using a Gouy-type magnetic balance. The susceptibilities of the complexes were determined according to the formula

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

where x = fraction by weight of complex in solution. After calculation of the molar susceptibilities, diamagnetic corrections for the organic ligands were computed from Pascal's constants.[11] The solutions employed were of equivalent concentration. The only exception to this was the chloroform solution of the first complex, which is very sparingly soluble in this solvent.

Spectrophotometric Measurements.—Absorption spectra were obtained with a Beckman DU spectrophotometer. The silica absorption cells had a 1-cm. light path. The concentrations of the complexes in solutions were between 1.7×10^{-4} and 2.07×10^{-2} mole per liter depending upon the degree of absorption. Measurements in the solid state were made by the potassium bromide method.[12] Extinction coefficients for the ultraviolet spectra by the disk method were calculated from the familiar equation $E = 1/cd \log_{10}(I_0/I)$ in which c is reported in moles per liter of potassium bromide, and d is the length of the light path (0.080–0.085 cm.).

Dipole Moment Measurements.[13]—The dielectric constants of the solutions relative to those of the solvents were determined with a heterodyne oscillator and a cell as previously described.[14] The solvents (benzene and dioxane) were purified by the standard procedures. In each case 4 or 5 solutions were measured. The refractive indices were determined with a Pulfrich refractometer. Densities were measured with a pycnometer. The main source of error in the determinations was the low solubility of the compounds investigated, especially for the benzene solution of the first member of the series.

The molar polarizations of the solutes at infinite dilution ($P_{2\infty}$) were determined by the method of Halverstadt and Kumler.[15] The plots of dielectric constants ϵ_{12} and densities d_{12} *vs.* molar fractions were found to be straight lines with slopes α and β, respectively. The extrapolated values (ϵ_1 and d_1) for $f_2 = 0$ were always close to the experimental values for the pure solvents. The P_E values were determined experimentally, and varied according to the additivity rule of molar refractions.

Results and Discussion

The diamagnetism exhibited by these complexes in the solid state (*cf.* Table I) is indicative of a covalent dsp^2 planar configuration. Table I and Fig. 1 report the values of magnetic moments of the complexes dissolved in dioxane, benzene and chloroform.

The values of the magnetic moments found for bis-(N-methylsalicylaldimine)-nickel, ranging from 1.9 to 2.3 B.M. depending on the solvent used, are in good agreement with the results of Willis and Mellor[2] and with those of Clark and Odell.[6,7] The susceptibilities of the successive members of the series are much lower. In benzene and dioxane solutions they vary between 0.3 and 0.8 B.M. In chloroform the values are higher, ranging from 0.9 to 1.2 B.M. It may be remarked that the plot of $\mu_{\text{eff.}}$ *vs.* the number of carbon atoms in the *n*-alkyl chain has the shape of a zigzag. In this plot the lower points correspond to alkyl chains with an even number, the upper points to alkyl chains with an odd number of carbon atoms.

The values of magnetic moments, which vary between zero and that required for two unpaired

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[7] H. C. Clark and A. L. Odell, *J. Chem. Soc.*, 520 (1956).

[8] *Cf.* J. P. Faust and J. V. Quagliano, THIS JOURNAL, **76**, 5346 (1954).

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

[10] L. Sacconi, THIS JOURNAL, **76**, 3402 (1954).

[11] P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, pp. 51–55.

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

[13] These measurements were made at the Istituto di Chimica Organica dell'Università, Napoli.

[14] G. Speroni, G. Del Re and C. Caselli, *Ricerca Sci.*, **26**, 3115 (1956).

[15] I. Halverstadt and W. Kumler, THIS JOURNAL, **64**, 2988 (1942).

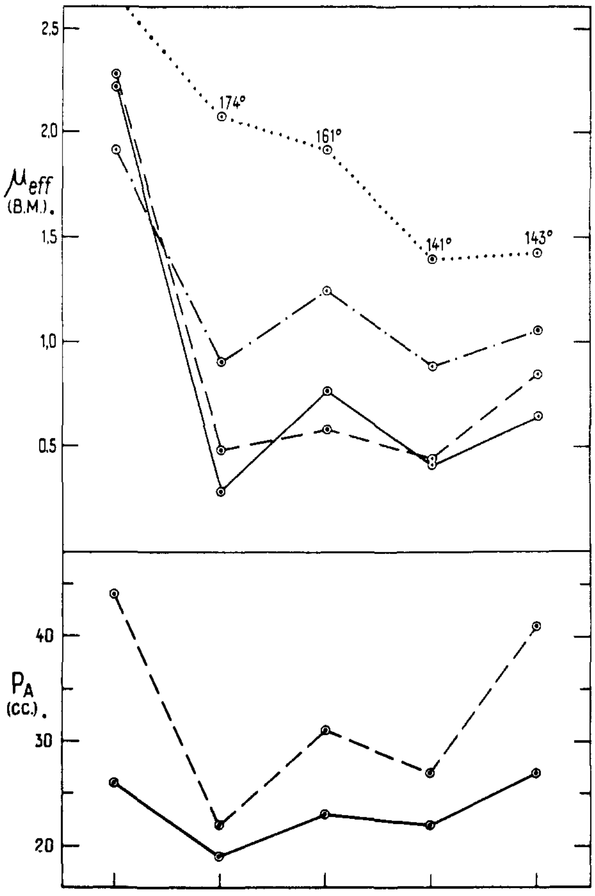

Fig. 1.—Plot of magnetic moments, atom polarizations and melting points of the bis-N-alkylsalic.-Ni complexes *vs.* R = *n*-alkyl chain. Solvents: benzene (———); dioxane (- - - -); chloroform (-·-·-·). In the curve (......) only the upper values of melting points are reported.

TABLE I

MAGNETIC SUSCEPTIBILITY DATA FOR BIS-(N-ALKYLSALICYLALDIMINE)-NICKEL(II) COMPLEXES AT 20°

Bis-N-alkyl-Ni-complex	$-\chi \times 10^6$ (solid)	Solvent	Concn. g./g.	Concn. mM/g.	$\chi_A \times 10^6$	$\mu_{eff.}$ (B.M.)
N-Methyl-	0.329	Chl	2.12	6.5	1586	1.92
		Bz	1.70	5.2	2106	2.22
		Diox	1.50	4.6	2246	2.28
		Pyr	2.10	6.42	4296	3.16
N-Ethyl-	.435	Chl	2.86	8.06	357	0.91
		Bz	1.85	5.2	36	.29
		Diox	1.63	4.6	103	.49
		Pyr	2.28	6.42	4174	3.12
N-Propyl-	.519	Chl	3.09	8.06	665	1.25
		Bz	1.99	5.2	271	0.78
		Diox	1.76	4.6	148	.59
		Pyr	2.46	6.42	4294	3.16
N-Butyl-	.437	Chl	3.32	8.06	337	0.89
		Bz	2.14	5.2	78	.42
		Diox	1.89	4.6	85	.45
		Pyr	2.64	6.42	4247	3.14
N-Amyl-	.521	Chl	3.54	8.06	478	1.06
		Bz	2.28	5.2	184	0.65
		Diox	2.02	4.6	304	.84
		Pyr	2.82	6.42	4121	3.11

TABLE II

DIELECTRIC POLARIZATION DATA FOR BIS-(N-ALKYLSALICYLALDIMINE)-NICKEL(II) AND COPPER(II) COMPLEXES AT 25°

Bis-N-alkylsalic. complex	Solvent	ϵ_1	α	d_1	β	R_D (cc.)	$P_{2\infty}$ (cc.)	$P_{2\infty} - R_D$ (cc).	$\mu_{app.}$ (D) 10%	$\mu_{app.}$ (D) 20%
N-Methyl-Ni	Bzn	2.2714	3.52	0.8724	1.43	99	125	26	0.88	0.54
	Diox	2.2077	5.30	1.0280	1.02	99	143	44	1.29	1.08
N-Ethyl-Ni	Bzn	2.2787	3.13	0.8726	1.46	109	128	19	0.63	..
	Diox	2.2189	3.74	1.0277	0.82	108	130	22	.73	..
N-Propyl-Ni	Bzn	2.2739	2.89	0.8736	1.24	117	140	23	.73	..
	Diox	2.2251	4.25	1.0265	0.88	117	148	31	.96	0.63
N-Butyl-Ni	Bzn	2.2758	2.92	0.8732	1.29	127	149	22	.66	..
	Diox	2.2221	4.06	1.0258	0.82	127	154	27	.83	0.31
N-Amyl-Ni	Bzn	2.2714	3.18	0.8726	1.18	138	165	27	.79	..
	Diox	2.2189	3.70	1.0268	0.66	138	179	41	1.17	0.80
N-Methyl-Cu	Diox	2.2194	5.40	1.0276	1.01	94	146	52	1.45	1.21
N-Ethyl-Cu	Diox	2.2222	6.66	1.0272	0.95	107	174	67	1.66	1.50

electrons, suggest the occurrence of an equilibrium between diamagnetic and paramagnetic forms of such complexes. This is more evident for the odd members of the series.

Table II contains the dielectric polarization data obtained for the five nickel(II) complexes and for two analogous copper(II) chelates. The values of the "apparent" moment for the nickel complexes range from 0.63 to 0.88 *D* for the benzene solutions and from 0.83 to 1.29 *D* for the dioxane solutions. These data were obtained by assuming P_A = 10% P_E, *i.e.*, by using P_A values ranging from 10 to 14 cc., both for benzene and dioxane solutions. In this connection it may be remembered that Sutton and co-workers[16] showed that the P_A values for several metal acetylacetonates greatly exceed the 10% P_E, being *ca.* 30 cc. For a series of copper(II) and nickel(II) chelates of analogs of bis-(acetylacetone)-ethylenediimine, where the metal is joined to two oxygen and two nitrogen atoms at the center of three ortho condensed chelate rings, McCarty and Martell[17] made the allowance for P_A of 36–41 cc. = 35–50% P_E. Besides MacQueen and J. W. Smith[18] computed P_A values ranging from 21 to 31 cc. for a number of *trans*-planar complexes of copper(II) and nickel(II) in benzene and

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[16] A. Finn, G. Hamps and L. Sutton, *J. Chem. Soc.*, 1254 (1938); I. Coop and L. Sutton, *ibid.*, 1269 (1938).

[17] J. McCarty and A. E. Martell, THIS JOURNAL, **78**, 2106 (1956).

[18] J. MacQueen and J. W. Smith, *J. Chem. Soc.*, 1821 (1956); J. W. Smith, "Electric Dipole Moments," Butterworths Scientific Publications, London, 1955, pp. 276–279.

dioxane solutions. In our measurements if allowance is made for P_A = 17–26% P_E in benzene and 21–44% P_E in dioxane, the values of μ (D) become equal to zero. If, according to the treatment of MacQueen and Smith,[18] we interpret the difference between P_2 and R_D as atom polarizations, values of P_A ranging from 19 to 27 cc. for benzene solutions are found. This fact leads to the conclusion that the dipole moments are practically zero when correct allowance for the atom polarization is made. On the basis of these data both the *cis*-planar and the tetrahedral structure are to be rejected and therefore a *trans*-planar configuration can be ascribed to all the nickel chelates in Table II. This conclusion is corroborated by the results of dipole moment measurements on some analogous copper(II) chelates. For bis-(N-methylsalicylaldimine)-copper(II), where a *trans*-planar configuration is generally accepted, if allowance is made[19] for P_A = 20% P_E, then the same value of $\mu_{app.}$ = 1.21 D (solvent dioxane) is found. Besides the value of P_A of *ca.* 50 cc., computed from the difference between $P_{2\infty}$ and R_D agrees with the value of 54 cc. calculated by MacQueen and Smith from the data of Charles and Freiser[19] for this copper chelate. The complex bis-(N-ethylsalicylaldimine)-copper(II) in dioxane exhibits a still higher moment of 1.50 D (P_A = 20% P_E)(*cf.* Table II).

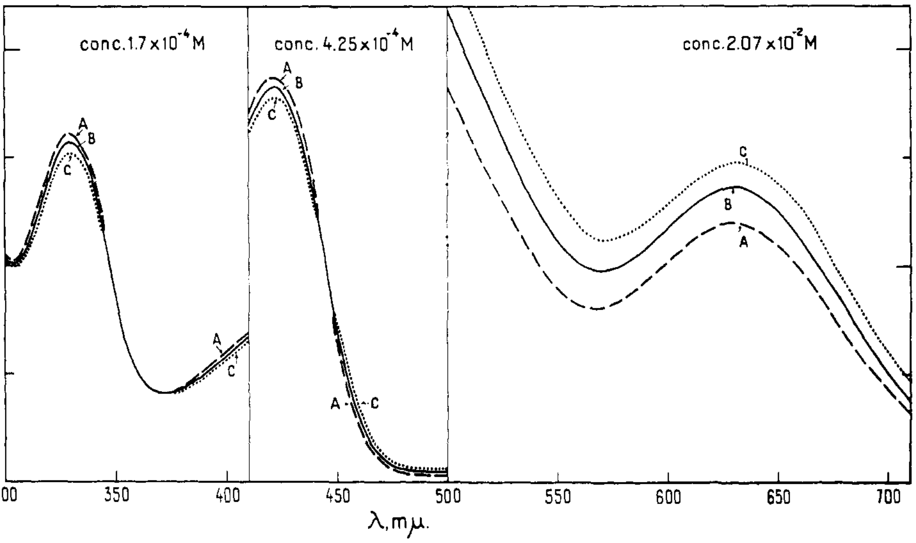

Fig. 3.—Absorption curves of bis-N-methylsalic.-Ni(II) complex in benzene at different temperatures: A (- - - - -), 10°; B (———), 25°; C (......), 45°. At *ca.* 445 mμ the isosbestic point.

Furthermore it is remarkable that the values of $P_{2\infty}$ and $P_{2\infty} - R_D$ found for all the complexes investigated in solution of dioxane are slightly higher than those in benzene, in accordance with the results of both Sutton and MacQueen and Smith. In accordance with the conclusions of these authors, the high P_A values found for the square complexes of the series of N-alkyl-salicylaldimine can be explained as principally due to bending vibrations of the rings as units relative to the remainder of the molecule. These vibrations of the six-membered rings would involve a folding or twisting of the molecule as a whole.

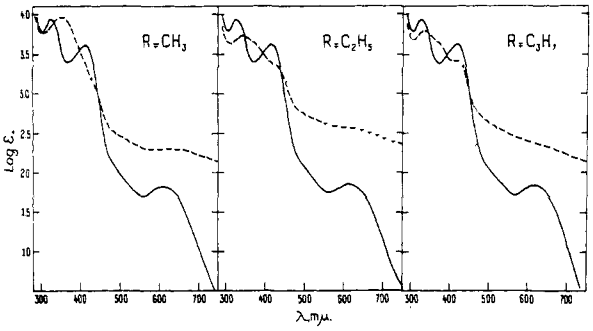

Fig. 2.—Absorption curves of bis-N-alkylsalic.-Ni complexes in chloroform (———) and in the solid state (- - - -). The spectra of bis-N-butyl and bis-N-amyl complexes are very similar to that of the bis-N-propyl complex and therefore are not shown.

The spectra of the complexes in chloroform solutions (see Table III and Figs. 2 and 3) show three bands in the 326, 414–418 and 610–620 mμ regions. The absorption curves of the chelate groups in dioxane and benzene solutions are quite similar, excepting a shift of 2–20 and 3–25 mμ toward the red in dioxane and benzene solutions, respectively. This shift increases gradually with increasing λ_{max} of the bands. The very strong absorption band at *ca.* 420 mμ (log $\epsilon > 3.5$) may be identified as the band characteristic of covalent nickel chelates.[20] The weak band at 610–640 mμ can be considered as due to the central metallic cation.[21] The intensity of this band (log $\epsilon < 2$) is that typical of a forbidden transition, probably 3d-3d.[22] This fact leads to the assumption of the existence of unoccupied 3d levels in these complexes when dis-

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[19] R. G. Charles and H. Freiser, THIS JOURNAL, **73**, 5223 (1951).

[20] J. E. Mills and D. P. Mellor, *ibid.*, **64**, 181 (1942); **69**, 1237 (1947); H. A. McKenzie, D. P. Mellor, J. E. Mills and L. N. Short, *J. Proc. Soc., N. S. Wales*, **78**, 70 (1944).

[21] *Cf.* K. Sone, THIS JOURNAL, **75**, 5204 (1953).

[22] R. J. P. Williams, *J. Chem. Soc.*, 137 (1955).

TABLE III

SPECTROPHOTOMETRIC ABSORPTION DATA FOR BIS-(N-ALKYLSALICYLALDIMINE)-NICKEL(II) COMPLEXES[a]

Bis-N-alkylsalic. Ni-complexes	Solvent	λ_1	$\log \epsilon_1$	λ_2	$\log \epsilon_2$	λ_3	$\log \epsilon_3$	λ_4	$\log \epsilon_4$
N-Methyl-	Chl	326	3.94			414	3.61	610	1.82
	Diox	328	3.94			418	3.62	625	1.75
	Bz	330	3.96			422	3.64	628	1.82
	Solid			354	3.95				
N-Ethyl-	Chl	327	3.93			416	3.62	615	1.85
	Diox	328	3.91			420	3.62	625	1.85
	Bz	330	3.96			426	3.64	640	1.85
	Solid	343	3.73	(~360)	3.68	(~430)	3.35		
N-Propyl-	Chl	327	3.93			418	3.63	620	1.84
	Diox	328	3.90			422	3.58	630	1.84
	Bz	330	3.95			424	3.64	640	1.86
	Solid	338	3.79	(~360)	3.70	(~420)	3.4		
N-Butyl-	Chl	327	3.93			417	3.64	615	1.84
	Diox	328	3.90			422	3.61	635	1.83
	Bz	330	3.96			426	3.66	640	1.86
	Solid	338	3.67	(~360)	3.59	(~420)	3.3		
N-Amyl-	Chl	327	3.93			418	3.63	615	1.85
	Diox	328	3.86			422	3.59	630	1.80
	Bz	330	3.95			424	3.67	635	1.86
	Solid	345	3.61	(~360)	3.55	(~420)	3.20		

[a] The values of the wave lengths of the inflections are enclosed in parentheses.

solved in the above solvents, in accordance with the results of magnetic measurements.

The spectrum of bis-(N-methylsalicylaldimine)-nickel(II) in the solid state presents a maximum at *ca.* 354 mμ. This band in the spectra of the other complexes is gradually shifted and split toward the positions of the two bands of the solutions at *ca.* 326 and 416 mμ as the number of *n*-alkyl carbon atoms increases. As a result a band envelope in the 320–430 mμ region appears in the spectra. In this envelope three components at *ca.* 340, 360 and 430 mμ are detectable, the intermediate maximum being only slightly apparent. The longer the *n*-alkyl chain which hinders the close packing of the molecules of the complexes the greater is the similarity between the spectra of the solid and those of the solutions in the 320–430 mμ region.

The absorption curves of bis-(N-methylsalicylaldimine)-nickel(II) in benzene at 10, 25 and 45° have a isosbestic point at *ca.* 445 mμ. This indicates an equilibrium between two differently absorbing species. The $\epsilon_{\max}$ of the band at 610 mμ increases with increasing temperature, an increase which takes place also by dilution at constant temperature. The two forms in equilibrium correspond, evidently, to the diamagnetic and the paramagnetic one revealed by the magnetic measurements of Clark and Odell.[6]

Our observation that the paramagnetic form possesses a non-polar, planar structure can be explained by assuming that the four bonds from the nickel atom in this form are of the "outer orbital" $4s4p^24d$ type. This signifies that the equilibrium existing in such solutions is not between a planar and a tetrahedral form but probably between an "inner" and an "outer orbital" one. In the solid, only the "inner orbital" $3d4s4p^2$ form probably exists, owing to the influence of the crystalline field which forces a complete spin coupling.

In this connection it should be remembered that the existence of tetrahedral Ni(II) complexes has not been proven and at present it is being more and more regarded as doubtful.[4,23]

The zigzag shape of the curves of P_A and $\mu_{eff.}$ of the complexes can be accounted for by correlating such quantities with the basic strength of the parent amines, as measured by their pK_a values. The pK_a values of the *n*-alkylamines from methyl- to *n*-butylamine, vary as follows: methyl-, 10.64; ethyl-, 10.67; *n*-propyl-, 10.58; *n*-butylamine, 10.61.[24] The complexes derived from the more basic amines (those with an even-numbered carbon chain) exhibit lower values of both P_A and $\mu_{eff.}$. This can be understood, keeping in mind that the nitrogen atoms of the more basic amines have a stronger donor property, thus favoring the formation of bonds with lower polarity and more "inner orbital" character. The rings containing such bonds will possess a smaller capacity of bending vibrations.[18]

An analogous zigzag decrease is shown by the plot of the melting points. Odd-numbered complexes which have more polar bonds, exhibit relatively higher melting points, presumably as a consequence of a stronger interaction between the molecules. It is probable, however, that steric factors of the type which are operative in melting of normal alkanes,[25] expressed in terms of different orientation of the carbon chain within the unit

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(23) J. Bjerrum and C. K. Joergensen, *Rec. trav. chim.*, **75**, 661 (1956); C. J. Ballhausen, *ibid.*, 665, 669; R. S. Nyholm, "Complex Compounds of Transition Metals," Proceedings of Tenth Solvay Conference, Brussels, May, 1956.

(24) *Cf.* E. A. Braude and F. C. Nachod, "Determination of Organic Structure by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 573. See also J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

(25) *Cf.* E. A. Braude and F. C. Nachod, ref. 24, pp. 3–12; J. A. A. Ketelaar, "Chemical Constitution," Elsevier Publishing Co., Amsterdam, 1953, pp. 350, 368.

cell, may play some role also in the phenomenon considered here.

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Studies in Coördination Chemistry. II. Spectrophotometric Investigation of Some Hydrazidic Tetracovalent Nickel(II) Complexes

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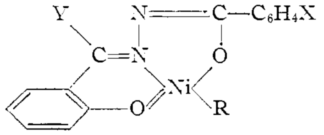
The ultraviolet absorption spectra of a number of hydrazidic tetracovalent nickel(II) complexes have been measured. The effect of certain atomic grouping adjacent to the chelate ring has been studied and discussed in terms of the hypothesis of dative π-bond in metal complexes.

The concept of double bond formation between metals and donor atoms is now regarded as of great importance in many complexes.[1]

Pauling was the first to explain the unusual strength and shortening of some metal–ligand bonds in certain coördination compounds by the hypothesis of double bonding.[2] In the case of nickel complexes it was suggested that the formation of double bond using d_π electron pairs of the metal and a vacant p or d orbital of the donor atom is an important factor influencing the formation of the square arrangement.[3]

With the aim to collect new experimental observations on the problem of dative π-bonding in metal complexes,[4] spectrophotometric measurements have been carried out on two groups of hydrazidic nickel(II) complexes in which two six-membered rings, the chelate and the aromatic one, are present. In compounds of the type I, namely, nickel complexes with acylhydrazones of *o*-oxyaldehydes and ketones, the rings are condensed; in those of the type II, namely, nickel complexes with acylhydrazones of benzoylacetone, the rings are joined by a C–C bond.

All of these complexes, from orange to red in color are diamagnetic, therefore planar with respect to the four dsp^2 covalent bonds. One of the coördinative valences of the nickel central atom is saturated by ammonia, ethylamine or triethylphosphine.



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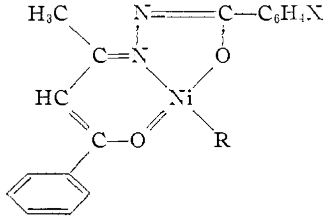

II

Y = H, CH_3; X = H, Cl; R = NH_3, $NH_2C_2H_5$, $P(C_2H_5)_3$

Experimental

Preparation of Compounds.—Salicylidenebenzoylhydrazonenickel(II)-ammine, salicylidene-*p*-chlorobenzoylhydrazonenickel(II)-ammine, *o*-oxyacetophenonebenzoylhydrazonenickel(II)-ammine, benzoylacetonebenzoylhydrazonenickel (II)-ammine and benzoylacetone-*p*-chlorobenzoylhydrazonenickel(II)-ammine complexes were prepared as previously described.[5]

***o*-Oxyacetophenone-*p*-chlorobenzoylhydrazone.**—*p*-Chlorobenzoylhydrazide (1.3 g.) in 8 ml. of alcohol and *o*-oxyacetophenone (1.1 g.) in 3 ml. of alcohol were refluxed over a water-bath for few minutes; water was then added in order to obtain a crystalline precipitate melting at 223–225°.

Anal. Calcd. for $C_{15}H_{13}O_2N_2Cl$: N, 9.70. Found: N, 9.68.

***o*-Oxyacetophenone-*p*-chlorobenzoylhydrazonenickel(II)-ammine.**—A mixture of 0.9 g. of nickel(II) acetate in 10 ml. of concd. ammonia and 1 g. of *o*-oxyacetophenone-*p*-chlorobenzoylhydrazone suspended in 15 ml. of alcohol was heated on a water-bath. Orange needles which do not melt at 270° were obtained.

Anal. Calcd. for $C_{15}H_{14}O_2N_3ClNi$: N, 11.59; Ni, 16.19. Found: N, 11.63; Ni, 16.10.

Salicylidenebenzoylhydrazonenickel(II)-ethylamine.—A mixture of 1 g. of nickel(II) acetate in 16 ml. of 50% alcohol and 8 ml. of 33% ethylamine and 0.66 g. of salicylidenebenzoylhydrazone in 30 ml. of alcohol was warmed on a water-bath to obtain red needles of m.p. 132° dec.

Anal. Calcd. for $C_{16}H_{17}O_2N_3Ni$: N, 12.28; Ni, 17.16. Found: N, 12.19; Ni, 17.17.

Salicylidenebenzoylhydrazonenickel(II)-triethylphosphine.—Nickel(II) acetate (1 g.) in 16 ml. of 50% alcohol and 1 g. of triethylphosphine was mixed with 0.66 g. of salicylidenebenzoylhydrazone in 30 ml. of alcohol. The mixture was warmed on a water-bath under reflux. Orange tablets of m.p. 105–106° dec. were obtained.

Anal. Calcd. for $C_{20}H_{25}O_2N_2PNi$: N, 6.75; P, 7.47; Ni, 14.14. Found: N, 6.97; P, 8.05; Ni, 14.40.

***o*-Oxyacetophenonebenzoylhydrazonenickel(II)-ethyl-**

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[1] R. S. Nyholm, *Rev. Pure Appl. Chem. (Australia)*, **4**, 15 (1954); A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 160; Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules," Butterworths Sci. Publ., London, 1950, p. 361.

[2] L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1948, p. 250.

[3] R. S. Nyholm, *Chem. Revs.*, **53**, 276 (1953).

[4] *Cf.* G. E. Coates, *J. Chem. Soc.*, 2003 (1951); J. Chatt and A. A. Williams, *ibid.*, 3061 (1951); J. Chatt and R. G. Wilkins, *ibid.*, 273, 4300 (1952); R. S. Nyholm and F. H. Burstall, *ibid.*, 3570, 3579 (1952); J. Chatt, L. A. Duncanson and L. M. Venanzi, *ibid.*, 4461 (1955); R. K. Murmann and F. Basolo, THIS JOURNAL, **77**, 3484 (1955).

[5] L. Sacconi, *Gazz. chim. ital.*, **83**, 884 (1953); *Z. anorg. allgem. Chem.*, **275**, 249 (1954); THIS JOURNAL, **75**, 5434 (1953).