TABLE VI

	ΔH^0_f, kcal./mole	ΔF^0_f, kcal./mole	ΔS^0, cal./mole/deg.
$CdCl^+$	−56.72	−52.67	9.8
$CdCl_2$	−96.3	−84.96	27.6
$CdCl_3^-$	−132.8	−115.5	47.4

The decrease of ΔH with increasing ionic strength is most pronounced in the ionic strength range 0 to 0.5; as the ionic strength increases to the higher range the rate of decrease becomes much less. The values of ΔS likewise decrease rapidly in the low range, but exhibit a minimum and then increase with ionic strength at higher concentrations. Consequently in the low range ΔF will decrease rapidly due to the combined variations in ΔH and ΔS being in the same sense. This is in accord with the observations of Newton and Arcand,[12] who found a small variation of ΔH and larger variations of ΔF and ΔS in the region of lower ionic strengths. In the region where ΔS increases while ΔH decreases, the variation in ΔF will be lessened; whether ΔF eventually passes through a maximum and falls off again will depend on the relative rates of variation of ΔH and $T\Delta S$; in this system a maximum in ΔF is found, followed by a gradual decrease with ionic strength.

The relatively large variation of ΔS in the range 0 to 0.5 emphasizes that intercomparisons for complexes of different metals and ligands should be limited to comparable ionic strengths. On the other hand, the relatively small variation of ΔH suggests that this quantity is probably fairly characteristic of the complex itself, and that intercomparisons for ΔH values are considerably less limited with respect to ionic strengths.

LINCOLN, NEBRASKA

[12] T. W. Newton and G. M. Arcand, THIS JOURNAL, **75**, 2449 (1953).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

Changes in Configuration of Some Nickel(II) Complexes[1]

BY FRED BASOLO AND WILLIAM R. MATOUSH[2]

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Diamagnetic nickel(II) complexes were allowed to react with anhydrous pyridine. In several instances it was possible to isolate well-defined crystalline compounds of hexacoördinated nickel(II) containing two molecules of pyridine. These solid compounds were paramagnetic and removal of pyridine at reduced pressures yielded the original diamagnetic materials. It is therefore concluded that the paramagnetism of certain pyridine solutions of diamagnetic nickel(II) complexes results from an expansion of coördination to yield hexa-coördinated nickel(II) compounds. It was also observed that no direct correlation exists between the magnetic susceptibility of solutions of bis-(formylcamphor)-ethylenediiminenickel(II) in methyl benzenes and the base strength of these solvents. This would indicate that the paramagnetism of these solutions is due not to solvation but rather to formation of tetrahedral nickel(II) compounds.

The complex compounds of nickel(II) are of particular interest because of the variety of spatial configurations which are encountered. Nickel(II) may have a coördination number of either four or six. If the coördination number is four and the bonds are essentially covalent then the complex has a planar configuration and is diamagnetic (dsp^2) whereas if the bonds are ionic the complex has a tetrahedral configuration and is paramagnetic (sp^3) (Table III). With a coördination number of six the structure of the compound is that of an octahedron. However, if the bonds are primarily covalent the compound is diamagnetic (d^2sp^3)[3] and if ionic it is paramagnetic (sp^3d^2) (Table III).

Lifschitz, Bos and Dijkema[4] have shown that changes in the configuration of some nickel(II) complexes occur with considerable ease. The observation that diamagnetic bis-(formylcamphor)-ethylenediiminenickel(II) was weakly paramagnetic (1.9 B.M.) in methanol solution led French, Magee and Sheffield[5] to postulate a partial conversion of the planar complex to a tetrahedral form. A more extensive investigation of this phenomenon by Willis and Mellor[6] has revealed that a number of diamagnetic nickel(II) complexes exhibit paramagnetic behavior in various organic solvents. The paramagnetism was observed to be especially high in pyridine solutions. They suggested that this may result from the reaction of the diamagnetic complex with two molecules of pyridine to form an octahedral complex but attempts to isolate such compounds were not successful. However, Willis and Mellor[6] postulated that in solvents such as alcohol, benzene and chloroform, any paramagnetism observed must be caused by the formation of some tetrahedral complex. It should perhaps be noted that there is no direct experimental evidence in support of either of these postulates. Hall and Willeford[7] found that in general the nickel(II) complexes which form paramagnetic solutions undergo exchange with radionickel.

This paper reports the isolation of paramagnetic hexacoördinated nickel(II) complexes containing two molecules of pyridine. The suggestion of Willis and Mellor[6] that a solvation reaction takes place in pyridine solutions has therefore been confirmed. Some attempt has also been made to determine what occurs in methylbenzene solutions.

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[1] Presented at the Chicago Meeting of the American Chemical Society, September, 1953.

[2] Taken in part from a thesis submitted by William R. Matoush in partial fulfillment of the requirements for the M.S. degree, 1952.

[3] F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

[4] I. Lifschitz, J. G. Bos and K. M. Dijkema, *Z. anorg. Chem.*, **242**, 97 (1939); *Rec. trav. chim.*, **59**, 407 (1940); *ibid.*, **60**, 581 (1941).

[5] H. S. French, M. F. Magee and E. Sheffield, THIS JOURNAL, **64**, 1924 (1942).

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

[7] N. F. Hall and B. R. Willeford, *ibid.*, **73**, 5419 (1951).

TABLE I

ANALYTICAL AND MAGNETIC SUSCEPTIBILITY DATA FOR NICKEL(II) COMPLEXES

		Parent complex				Addition complex						Residue			
		Nickel			$\mu_{eff.}$[6] (in py)[j]	Nickel		Pyridine		χ_m		Nickel		χ_m	
	-nickel	Calcd.	Found	$\mu_{eff.}$		Calcd.	Found	Calcd.	Found	$\times 10^{-6}$	$\mu_{eff.}$	Calcd.	Found	$\times 10^{-6}$	μ_{eff}
Class I															
1	Bis-(salicylaldehyde)[a]	17.42 (2H_2O)	17.5	3.1[a]	3.26	12.76 (2py)	12.8	34.47 (2py)	34.3	3350	2.8	19.47	19.5	3790	3.0
Class II															
2	Bis-(8-hydroxyquinoline)[b]	16.91	17.4	3.3[6]	3.24	10.05 (3py)	9.93	40.62 (3py)	41.1	3230	2.8	16.91	16.8	4150	3.2
3	Bis-(salicylaldoxime)[c]	17.73	17.7	0.0[6]	3.10	12.00 (2py)	11.6	32.35 (2py)	34.5	2990	2.7	17.73	17.7	Diamagnetic	
		Microanal. Calcd.: C, 50.81; H, 3.66; N, 8.47. Found: C, 51.07; H, 3.63; N, 8.62.				*Microanal.* Calcd.: C, 58.90; H, 4.53; N, 11.45. Found: C, 58.47; H, 4.39; N, 11.37						*Microanal.* Calcd.: C, 50.81; H, 3.66; N, 8.47. Found: C, 51.00; H, 3.62; N, 9.01.			
4	Bis-(N-methylsalicylaldimine)[d]	17.95	17.9	0.0[6]	3.10	12.10 (2py)	12.1	32.62 (2py)	32.6	3950	3.1	17.95	18.2	Diamagnetic	
5	Bis-(N-phenylsalicylaldimine)	13.01	13.0	0.0		8.53 (3py)	8.54	34.47 (3py)	34.4	3490	2.9	13.01	13.0	Diamagnetic	
6	Bis-(formylcamphor)-ethylenediimine[e]	13.31	13.3	0.0[6]	3.15					2110	2.3				
		Microanal. Calcd.: C, 65.33; H, 7.78; N, 6.35. Found: C, 65.78; H, 8.18; N, 63.37				*Microanal.* Calcd.: C, 68.12; H, 7.39; N, 9.33. Found: C, 67.00; H, 6.16; N, 9.42.									
7	Bis-(salicylaldehyde)-*o*-phenylenediimine[f]	15.74	15.7	0.0[6]	2.54 2.55	12.98 (1py)	12.9	17.50 (1py)	18.6	Diamagnetic		15.74	15.8		
8	Bis-(salicylaldehyde) ethylenediimine[g,f]	18.06	18.1	0.0[6]	0.0	14.52 (1py) 16.7 (0.372py)	16.6	19.57 (1py) 8.28 (0.372py)	8.28	Diamagnetic		18.06	18.1		
9	Bis-(salicylaldimine)[h]	19.65	19.7	0.0[6]	2.3	19.65 (0py)	19.7		0.0						
Class III															
10	Bis-(dimethylglyoxime)	20.32	20.3	0.0[6]	1.5	20.32 (0py)	20.3		0.0						
Class VI															
11	Bis-(xanthic acid)[i]	19.45	19.5	0.0[6]	3.32	12.76 (2py)	12.2	34.45 (2py)	35.8	2990	2.7	19.45	19.1	Diamagnetic	

[a] G. N. Tyson and S. C. Adams, THIS JOURNAL, **62**, 1228 (1940). [b] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1946, pp. 78–81. [c] E. G. Cox, F. W. Pinkard, W. Wardlow and K. C. Webster, *J. Chem. Soc.*, 459 (1935). [d] W. Klemm and K. H. Raddatz, *Z. anorg. Chem.*, **250**, 207 (1942). [e] P. Pfeiffer, W. Christelheit, T. Hesse, H. Pfitzer and H. Thielert, *J. prakt. Chem.*, **150**, 261 (1938). [f] P. Pfeiffer, E. Breith, E. Lubbe and T. Tsumaki, *Ann.*, **503**, 84 (1933). [g] J. V. Dubsky and A. Sokol, *Coll. Czech. Chem. Comm.*, **3**, 548 (1931). [h] P. Pfeiffer, H. Buchholz and O. Bauer, *J. prakt. Chem.*, 129, 170 (1931). [i] M. Delépine and L. Compin, *Bull. soc. chim.*, **27**, 469 (1920).

Experimental

Preparation of Compounds.—Nickel complexes used in the preparation of pyridine addition compounds were obtained by well-known procedures appearing in the literature and references for these are listed at the bottom of Table I. Only compound 5 (Table I) merits individual mention, having been prepared by a method that Pfeiffer and Krebs[8] used to obtain the analogous copper compound. Preparation of the nickel complex was accomplished by heating a suspension of bis-salicylaldehyde nickel dihydrate in excess aniline for 4 hr. at 115°. The crude product obtained on cooling the reaction mixture was extracted with small portions of ether and then recrystallized from chloroform to yield blackish-green crystals of the phenyl substituted complex.

Nickel analyses for starting compounds, performed either by precipitation with dimethylglyoxine or by electrodeposition, are listed in Table I. Microanalyses were performed only on compounds 3 and 6.

Reaction of Complexes with Pyridine.—The pyridine used in preparing addition compounds was a C.P. grade, dried over KOH and then distilled. The addition compounds were obtained by dissolving the appropriate parent complex in pyridine warmed to steam-bath temperature and then allowing slow crystallization. Large crystal formation was desirable to the extent that the adherent solvent was then more easily removed. The crystals were collected on a filter, washed several times with ligroin and then carefully dried of this solvent by light suction with an aspirator. Analyses and magnetic susceptibility measurements were then performed without delay, since many of the addition compounds lost pyridine quite rapidly. The weight which was lost *in vacuo* over concentrated sulfuric acid, assumed to be entirely due to loss of pyridine, was then determined. In the case of addition compounds of diamagnetic complexes complete removal of pyridine was accomplished within a few days at room temperature, or within a few hours when heated to 100° in an Abderhalden pistol. On the other hand, pyridine adducts of the paramagnetic complexes, 1 and 2, required heating at 100° for five to six weeks time in order to expel the pyridine completely. The residues left after removal of pyridine were again analyzed and the magnetic susceptibilities determined.

Magnetic Susceptibility Measurements.—The magnetic susceptibilities of solid pyridine addition compounds were measured at room temperature (approx. 27°), using a Faraday apparatus. The force on a sample suspended in an inhomogeneous magnetic field was measured by means of the vertical distortion of a supporting quartz fiber coil. The apparatus was standardized with a sample of dry sugar. During the determination, samples were surrounded by an atmosphere of nitrogen gas.

The values for the molar susceptibilities of the addition compounds were calculated using an effective molecular weight derived from the actual per cent. of pyridine found by weight loss. A diamagnetic correction calculated from Pascal's constants[9] was applied for all organic ligands except

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(8) P. Pfeiffer and H. Krebs, *J. prakt. Chem.*, **155**, 77 (1940).

(9) P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, pp. 51–55.

pyridine. The correction for the latter was based on a separate determination of its susceptibility using a Gouy balance. The effective moment in Bohr magnetons was calculated from the expression

$$\mu_{\text{eff}} = 2.84\sqrt{x_{\text{m}}T}$$

for $T = 300$°K.

The principal advantage of the Faraday method for purposes of this investigation was in the small sample of nickel complex required in the determination. The apparatus was, however, not well adapted to samples having a large paramagnetism. In such cases, the size of the samples was of necessity quite small, with consequent introduction of sizable weighing errors. In the several instances where the susceptibilities were also measured with a Gouy apparatus, agreement was shown to be within 10%.

The magnetic susceptibilities of bis-(formylcamphor)-ethylenediiminenickel(II) in benzene, toluene, *o*-, *m*- and *p*-xylene and mesitylene solutions were determined at 25°. The solutions were prepared on a weight basis using doubly distilled solvents. Densities required for calculation of the magnetic susceptibilities were determined by use of a Westphal balance, while the magnetic measurements were made by the Gouy method. The solutions were maintained at 25° (±0.1°) in a constant temperature bath, except for the brief intervals when the susceptibilities were being measured. The solutions attained the full value of their paramagnetism only after standing approximately two weeks at 25°, which behavior was observed by Willis and Mellor[6] with pyridine solutions of this same nickel(II) complex. The precision of these results is somewhat limited because of the small apparent weight change of the sample in the Gouy apparatus; however, the error in the magnetic moment does not exceed 0.2 B.M.

Results

The compounds studied are arranged in four groups in Table I according to the method of classification used by Mellor and Craig.[10] In each case analyses are given for the original complex, its pyridine reaction product and the residue after removal of pyridine. The magnetic susceptibilities listed for the parent complexes and their pyridine solutions were taken from values given in the literature. The values reported for the pyridine addition compounds and the final residues were determined by the Faraday method.

The magnetic susceptibilities for methylbenzene solutions of bis-(formylcamphor)-ethylenediaminenickel(II) are shown in Table II. These measurements were made by the Gouy method.

TABLE II

MAGNETIC SUSCEPTIBILITIES FOR METHYLBENZENE SOLUTIONS OF BIS-(FORMYLCAMPHOR)-ETHYLENEDIIMINENICKEL

Solvent	Concn., % Ni	$x_{\text{m}} \times 10^6$	$\mu_{\text{eff.}}$ (25°)	Relative base strength[a]	No. of positions available[b]	Dielectric const.[c]
Benzene	0.612	490	1.1	.....	6	2.28(20°)
Toluene	.615	440	1.0	0.01	4	2.38(20°)
o-Xylene	.561	550	1.1	3	3	2.58(17°)
p-Xylene	.577	250	0.8	1	2	2.25(17°)
m-Xylene	.625	70	0.4	9	2	2.37(20°)
Mesitylene	.595	60	0.4	1400	0	2.35(20°)

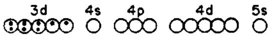
[a] D. A. McCaulay and A. P. Lien, THIS JOURNAL, 73, 2013 (1951). [b] R. S. Mulliken, *ibid.*, 74, 811 (1952). [c] "International Critical Tables," Vol. VI, pp. 83, 88, 90–94.

Discussion

The spatial configurations, orbital hybridizations and expected magnetic moments for nickel(II) complexes are summarized in Table III. It is apparent from these values that the paramagnetism of nickel(II) compounds is a good indication that the bonds are primarily ionic but does not allow for any distinction between specific types 1, 2 and 4 shown in Table III. Willis and Mellor[6] have suggested that the paramagnetic behavior of certain solutions of some diamagnetic nickel(II) compounds may result from: (1) dissociation of the complex—No. 1; (2) formation of an octahedral complex—No. 4; (3) rearrangement to a tetrahedral configuration—No. 2. They rule out the dissociation process on the basis of the large stability constants of these complexes and the extremely small conductivity of their solutions. Since pyridine is known to coördinate readily with transition metal ions, it was suggested that the change in magnetic moment in pyridine solutions was caused by the formation of an octahedral complex (No. 4). In the "non-coördinating" solvents such as alcohol, benzene and chloroform Willis and Mellor[6] regard the change in moment as resulting from a rearrangement of the square complex to a tetrahedral configuration (No. 2). No direct experimental evidence was cited in support of either of these postulates.

TABLE III

ORBITAL HYBRIDIZATIONS, MAGNETIC SUSCEPTIBILITIES AND CONFIGURATIONS ASSIGNED NICKEL(II) COMPLEXES

Coördination no.	Orbital hybridization	μ_{eff}	Configuration
Ni^{+2}		2.83	——
4		2.83	Tetrahedral
4		0.0	Square
6		2.83	Octahedral
6		0.0	Octahedral

The isolation of paramagnetic complex containing two molecules of pyridine from pyridine solutions of some diamagnetic nickel(II) complexes affords a direct confirmation of the formation of an octahedral complex in this solvent. It is also of interest that the removal of pyridine from these compounds results in the regeneration of the original diamagnetic nickel(II) complex. These results are in accord with some of the unpublished work of Calvin and his students.[11]

Pfeiffer, Bucholtz and Bauer[12] and Dwyer and Mellor[13] have observed that square nickel(II) complexes add pyridine less readily than do analogous tetrahedral compounds. Essentially the same observation was made during our experiments but in the reverse direction. For example, by heating *in vacuo* at 100° pyridine was completely removed within several hours from complexes that were originally diamagnetic. However, removal of pyridine from the paramagnetic complexes (compounds 1 and 2) at these same conditions required six weeks. It also was observed that although it was possible to isolate pyridine compounds of some diamagnetic nickel(II) complexes, other quite analogous dia-

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

[11] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, pp. 216–217.

[12] P. Pfeiffer, E. Bucholtz and O. Bauer, *J. prakt. Chem.*, **129**, 63 (1931).

[13] F. P. Dwyer and D. P. Mellor, THIS JOURNAL, 63, 81 (1941

magnetic compounds did not appear to coördinate with pyridine. This is clearly illustrated by the fact that compounds 4 and 5 coördinate with pyridine whereas the similar compounds 8 and 7, respectively, do not appear to react under these same conditions. Since the inductive effects of the groups attached to nickel(II) must be approximately the same, one is then inclined to search for an explanation of this difference in behavior on the basis of steric factors. Compounds 7 and 8 contain a tetradentate molecule so that the complex has three chelate rings as compared to only two for compounds 4 and 5. The fact that compounds 9 and 10 do not yield pyridine addition complexes may also be attributed to increased chelation resulting from hydrogen bonding.[14] On the basis of the observation that the amount of chelation appears to play an important role with regard to the addition of pyridine, it is noted that compounds 3 and 6 do not show the expected behavior. It is not apparent from a consideration of molecular models why the more highly chelated complexes should in general show a smaller tendency to coördinate with pyridine.

That hexacoördinated nickel(II) complexes are more readily formed from tetracoördinated complexes of a tetrahedral configuration than from those of a square structure is not compatible with the stereochemical changes that must accompany these reactions. However, the formation of a paramagnetic hexacoördinated nickel(II) complex from a square diamagnetic compound requires unpairing of two electrons since dsp^2 yields an sp^3d^2 orbital hybridization. The energy required to effect this transformation is expected to be larger than that which requires no unpairing of electrons as is true of the tetrahedral paramagnetic complex where sp^3 yields sp^3d^2 type hybridization.

It is also of interest that the residues of compounds 1 and 2 after removal of coördinated pyridine have essentially the same magnetic moment as that of the starting material. If it is assumed that the two pyridine molecules occupy *trans* positions in order to keep the steric strain at a minimum then the two chelate rings are forced into a planar configuration. Removal of the pyridine molecules from the solids does not visually appear to disturb the crystal structure. In such a case the coplanar structure may not be distorted and the sample might be expected to have a somewhat lower magnetic moment. Since no decrease in paramagnetism was observed, it must be concluded that either the pyridine complex is the *cis*-isomer or what appears more likely is that the prolonged heating required to remove the pyridine has allowed for regeneration of the tetrahedral complex.

Analysis of the pyridine addition product of compound 2 (Table I) shows that it contains three molecules of pyridine. It is not believed that the coördination number of nickel(II) has increased to seven but instead that the additional molecule of pyridine is held as solvent of crystallization. Likewise compounds 7 and 8 yield products which contain a small amount of pyridine. However, since these materials are diamagnetic it would appear that the pyridine is not directly coördinated to the central metal atom.

An attempt was made to determine what changes occur in "non-coördinating" solvent by measuring the magnetic moments in a series of solvents exhibiting a regular variation of properties. The solvents employed by Willis and Mellor[6] differed in type, structure and dielectric constant. Choice of methylbenzene solvents was made because these substances are of similar structure, have approximately the same dielectric constant, but differ greatly in base strength. One may expect that if the amount of paramagnetism of these solutions is a direct consequence of solvation then there should be a good correlation between the magnetic moment observed and the base-strength of the solvent. The results obtained and shown in Table II indicate the non-existence of such a correlation. There is however one added complication in the interpretation of these data, which arises from the possible effect of steric hindrance due to the methyl groups. Mulliken[15] has called attention to the fact that the stability of the methylbenzene complexes of silver(I)[16] are not in direct accord with their base strengths toward a protonic acid. He suggests that this is caused by the presence of methyl groups which make unavailable for coördination the adjacent positions. It is therefore plausible to assume that similar steric hindrance must be involved in any coördination of the substituted benzenes, *e.g.*, with bis-(formylcamphor)-ethylenediiminenickel-(II). However, if one considers merely the solvents *p*-xylene and *m*-xylene, both having the same number of positions available for coördination but the latter being a stronger base, it is again apparent that the amount of paramagnetism is not related to the base strength. Although these results give no conclusive proof as to what occurs in these solvents, it is believed that, unlike the case with the solvent pyridine, the evidence is more nearly consistent with a rearrangement of the planar complex to a tetrahedral configuration than with formation of hexacoördinated nickel(II).

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EVANSTON, ILLINOIS

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[14] R. E. Rundle and M. Parasol, *J. Chem. Phys.*, **20**, 1487 (1952).

[15] R. S. Mulliken, THIS JOURNAL, **74**, 821 (1952).

[16] L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949); **72**, 3113, 5034 (1950).