164. *Studies in Co-ordination Chemistry. Part III.* The Thermodynamics of Interaction between Heterocyclic Bases and (Diacetyl Bisbenzoylhydrazone)nickel(II) in Benzene.*

By L. Sacconi, G. Lombardo, and P. Paoletti.

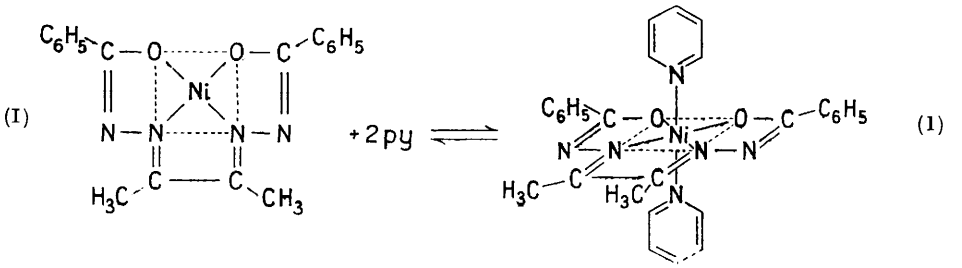
The planar complex (diacetyl bisbenzoylhydrazone)nickel(II) is diamagnetic, with dsp^2 hybridisation, and forms addition compounds with various nitrogen bases containing two molecules of base. The different absorption characteristics of the two co-ordination compounds allow the formation constants of the complexes in non-polar solvents to be determined by spectrophotometry. The main factors controlling the stability of the complexes have been investigated and the relationship between the base strength and co-ordinating tendency toward (diacetyl bisbenzoylhydrazone)nickel(II) is discussed in terms of electronic and steric factors. From the measurements of the temperature dependence of the formation constants we calculated the heats of reaction and free-energy and entropy changes; these are discussed. The different orders of entropy change observed can be explained as a particular type of "*ortho*-effect" and by the π-bond character ascribed to the co-ordinate links between nickel and the nitrogen atom of the heterocyclic amines.

The number of thermodynamic data, *e.g.*, heats and entropies of reaction, for complex equilibria is very small.[1] Most investigations have been carried out in aqueous solution and so refer to displacement reactions, *i.e.*, water for another ligand. Since the thermodynamic data relative to such hydration processes cannot be determined unequivocally, the results are generally uncertain.

* Part II, Sacconi, Paoletti, and Maggio, *J. Amer. Chem. Soc.*, 1957, **79**, 4067.

[1] Rasmussen, *Acta Chem. Scand.*, 1956, **10**, 1279.

The study of the equilibria between (diacetyl bisbenzoylhydrazone)nickel(II) (I) and a series of bases, in a " non-co-ordinating " solvent, is free from these limitations: the reactants are uncharged and anhydrous, and no displacement of ligands occurs during the



reaction, which consists solely in the addition of two molecules of base to the square planar nickel complex. Owing to the nature of the metal atom and the peculiar steric requirements of the reference complex molecule, these equilibria are valuable for study of the structure of the bases and the bond types involved.

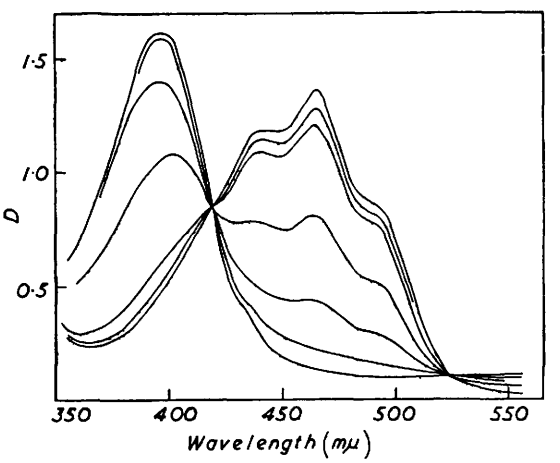


FIG. 1. *Absorption curves of (diacetyl bisbenzoylhydrazone)nickel(II) in benzene and benzene–pyridine solutions.*

(Diacetyl bisbenzoylhydrazone)nickel(II), [Ni(DBH)], (I), described previously,[2] is diamagnetic and a square planar structure with dsp^2 hybridation has been suggested. It gives green diamagnetic solutions in " non-co-ordinating " solvents, *e.g.*, chloroform and benzene, and the solutions in donor solvents are yellow-brown and paramagnetic (*e.g.*, in pyridine $\mu_{eff.} = 3{\cdot}2$ B.M.). This can be attributed to the formation of an octahedral complex (II) according to (I).

In fact a pyridine adduct can easily be prepared by carrying out reaction (1) in chloroform. It is paramagnetic ($\mu_{eff.} = 2{\cdot}5$ B.M.) and presumably octahedral with d^2sp^3 hybridisation, with the pyridine molecules in the *trans*-position. Low magnetic susceptibilities have frequently been observed in similar adducts.[3]

Equilibrium (1) can be studied spectrophotometrically because the complex (I) and its pyridine adduct absorb at different wavelengths with absorption maxima at 392 mμ (in benzene) and 466 mμ (in 0·15M-pyridine solution in benzene) respectively. These absorption curves, and those of intermediate composition, form a family with an isosbestic point at their intersection, 421 mμ (Fig. 1), indicating the presence of only two

[2] Sacconi, *Z. anorg. Chem.*, 1954, **275**, 249.

[3] Cf. Basolo and Matoush, *J. Amer. Chem. Soc.*, 1953, **75**, 5663; Draney and Cefola, *ibid.*, 1954, **76**, 1975.

complex species in solution. Similar graphs with sharp isosbestic points are obtained for all the bases employed.

Experimental

Preparation of (Diacetyl Bisbenzoylhydrazone)nickel(II),2Pyridine.—Pyridine (2 g.) was added to the complex (I) (1 g.) in chloroform, and the solution evaporated to a few c.c., and diluted with light petroleum. The brown precipitate was filtered off and washed with light petroleum, and, dried between filter paper at room temperature, gave brilliant brown *leaflets* (Found: N, 16·6; Ni, 17·4. $C_{18}H_{16}O_2N_4Ni,2C_5H_5N$ requires N, 16·6; Ni, 17·4%). On storage in an evacuated desiccator (H_2SO_4) it lost pyridine and reverted to the black starting material.

Calculation of Formation Constants.—The total formation constants for equilibria of type (1) are given by

$$K = [\text{Ni(DBH),2Base}]/[\text{Ni(DBH)}][\text{Base}]^2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Solutions of the nickel complex (I) in benzene and pyridine–benzene obey Beer's law and its concentration and that of its adduct with two molecules of base can be obtained directly by spectrophotometry. If α is the fraction of " free " complex and D the observed optical density at a given wavelength, then, as c and l are kept constant ($c = 1 \times 10^{-4}$),

$$D = D_1\alpha + D_2(1 - \alpha); \quad \alpha = (D - D_2)/(D_1 - D_2)$$

where D_1 and D_2 are the observed optical densities of Ni(DBH) and Ni(DBH),2Base at $1{\cdot}0 \times 10^{-4}$M.

Then eqn. (2) becomes $K = (1 - \alpha)/(\alpha[\text{Base}]^2)$. The concentration of the " free " base, [Base], is the difference between the concentration of base added and twice the concentration of the adduct, the latter being $(1 - \alpha) \times 10^{-4}$.

Spectrophotometry.—Visible and ultraviolet absorption spectra were measured with a Beckman DU quartz spectrophotometer fitted with a thermostated cell compartment.[4] Measurements were made at 10°, 25°, and 45° in 1·00 cm. stoppered silica cells. During measurements at 10° care was taken to prevent the formation of a film of moisture on the cells by circulation of dried air in the cell compartment. The solutions used contained 10^{-4} mole per litre of the complex and known and varying amounts of each base. The solution used as a blank contained the same concentration of base as the sample.

Calculation of Thermodynamic Properties.—The standard molar thermodynamic quantities ΔG, ΔH, and ΔS associated with the formation of the complexes were calculated by means of the usual relationships $-2{\cdot}303\boldsymbol{R}T \log K = \Delta G = \Delta H - T\Delta S$ and $\Delta H = 2{\cdot}303\boldsymbol{R}T_1T_2 \times (\log K_2 - \log K_1)/(T_2 - T_1)$.

ΔH is constant within the experimental error over the range of temperatures investigated as shown by the linear plot of $\log K$ against $1/T$ in Fig. 2.

Magnetic Measurements.—The magnetic susceptibility of (diacetyl bisbenzoylhydrazone)-nickel(II) in pyridine was determined by the Gouy method.[5] The susceptibilities of the solid and the solid pyridine adduct were measured by means of the interferometric Bhatnagar balance [6] with the Faraday method. The molar susceptibility of the addition compound was calculated by using an effective molecular weight derived from the actual concentration of pyridine present in the compound. Diamagnetic corrections were calculated from Pascal's constants.

Materials.—Benzene was carefully purified by standard methods.[7] The amines, which were good-quality commercial products (Fluka), were purified until their physical constants agreed closely with the values in the literature. Usually they were refluxed for several hours over potassium hydroxide or barium oxide, fractionated through a column of 40 theoretical plates packed with Fenske glass helices, and the constant-boiling middle fractions collected.

Results.—The equilibrium constants for reactions of type (1) at 10°, 25°, and 45° are in Table 1. K_H is the value of the acid dissociation constants of the amines and K_{Ag} some of the

[4] Bell and Stryker, *Science*, 1947, **105**, 415.
[5] Sacconi, Paoletti, and Del Re, *J. Amer. Chem. Soc.*, 1957, **79**, 4062.
[6] Sacconi, *ibid.*, 1954, **76**, 3400.
[7] Weissberger, " Organic Solvents," Interscience Publishers, Inc., New York, 1955.

corresponding formation constants with silver(I) from the literature. $R = \log K/pK_H$ and $R' = \log K_{Ag}/pK_H$. Q_N is the calculated charge density on the nitrogen atom.

In Fig. 3 log K is plotted against pK_H for the bases. The precision of the values was ± 0.02 for log K, ± 0.02 kcal. mole^{-1} for ΔG and ΔH (± 0.3 kcal. mole^{-1} for quinoline and *iso*quinoline), and ± 0.1 e.u. for ΔS (± 1 for quinoline and *iso*quinoline).

FIG. 2. *Plot of* log K *against* $1/T$ (*for numerals, see Tables*).

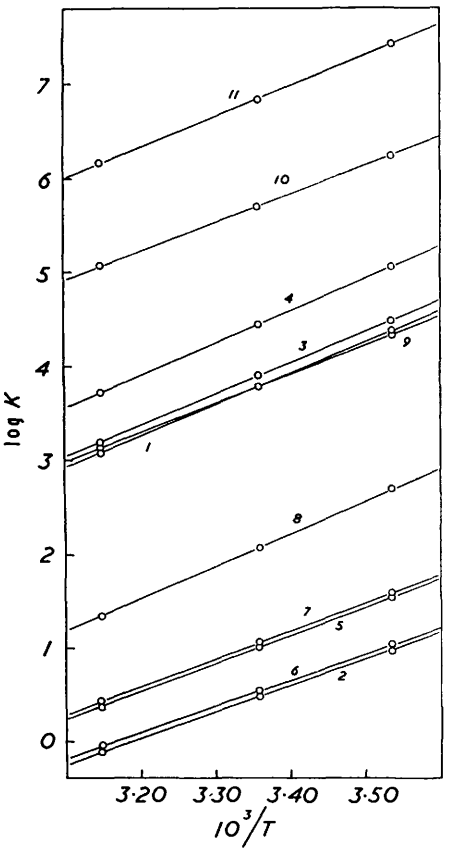
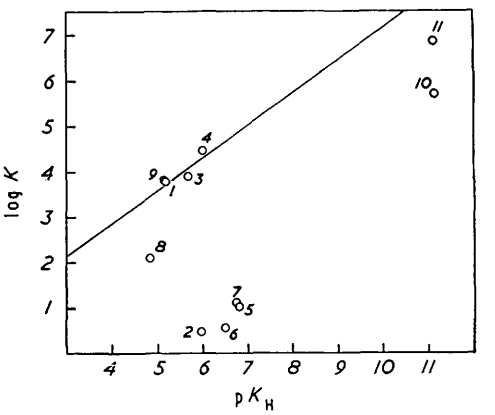


FIG. 3. *Plot of* log K *against* pK_H (*for numerals, see Tables*).



DISCUSSION

The values of log K for pyridine and substituted pyridines fall into two main groups: the first includes pyridine and 3-, 4-, and 3 : 4-substituted pyridines with values of R ranging from 0·69 to 0·74. The values of log K for such bases on the plot in Fig. 3 lie roughly on one straight line of slope equal to the mean values of R. The second group includes the 2-methylpyridines, *i.e.*, 2-methyl- and 2 : 4-, 2 : 5-, 2 : 6-dimethyl-pyridine. Their values of log K are more than 3·5 logarithmic units lower than those of the first group and the values of R range from 0·08 to 0·15. The values of log K for the quinoline and for the secondary amines piperidine and pyrrolidine lie apart from these two groups.

The electron density Q_N at the nitrogen atoms of the heterocyclic bases depends on the environment of the nitrogen atom through operation of the inductive and mesomeric effect of the substituent. In the picolines and lutidines the inductive ($+I$) and the hyperconjugative effect of the methyl group increase the charge density on the nitrogen atom.[8] Values of Q_N and pK_H (Table 1) show that the base strengths of pyridine, the picolines,

[8] Cf. H. C Brown and Barbaras, *J. Amer. Chem. Soc.*, 1947, **69**, 1137.

and *iso*quinoline run parallel to the charge densities on nitrogen atoms. The values of log K now observed for all these bases except 2-picoline also run parallel to the charge densities on the nitrogen atom. This suggests that the availability of electrons on the

TABLE 1. *Formation constants of (diacetyl bisbenzoylhydrazone)nickel(II) with heterocyclic bases, and related data.*

No.		t (°C)	log K	pK_H	log K_{Ag}	R	R'	Q_N	Refs.
1	Pyridine	10	4·36						
		25	3·78	5·23	4·22	0·72	0·81	1·274	*a, b, c, d*
		45	3·09						
2	2-Methylpyridine	10	0·98						
		25	0·48	5·97	4·68	0·08	0·78	1·494	*a, b, c, d*
		45	−0·11						
3	3-Methylpyridine	10	4·49						
		25	3·90	5·68	—	0·69	—	1·368	*a, d*
		45	3·20						
4	4-Methylpyridine	10	5·06						
		25	4·45	6·02	4·70	0·74	0·78	1·521	*a, c, d*
		45	3·73						
5	2 : 4-Dimethylpyridine	10	1·55						
		25	1·02	6·79	5·18	0·15	0·76	—	*a, c*
		45	0·39						
6	2 : 5-Dimethylpyridine	10	1·03						
		25	0·54	6·51	—	0·08	—	—	*a*
		45	−0·04						
7	2 : 6-Dimethylpyridine	10	1·58						
		25	1·05	6·75	—	0·15	—	—	*a*
		45	0·42						
8	Quinoline	10	2·68						
		25	2·08	4·85	—	0·43 *	—	1·326	*a, d*
		45	1·34						
9	*iso*Quinoline	10	4·34						
		25	3·78	5·14	—	0·73 *	—	1·278	*a, d*
		45	3·14						
10	Piperidine	10	6·24						
		25	5·70	11·13	6·48	0·51	0·58	—	*a, c*
		45	5·06						
11	Pyrrolidine	10	7·42						
		25	6·84	11·11	—	0·61	—	—	*e*
		45	6·16						

[a] H. C. Brown, McDaniel, and Hatliger, "Dissociation Constants" in Braude and Nachod, "Determination of Organic Structures by Physical Methods," Academic Press Inc., New York, 1955. [b] Gero and Markham, *J. Org. Chem.*, 1951, **16**, 1835. [c] Bruehlman and Verhoek. *J. Amer. Chem. Soc.*, 1948, **70**, 1401. [d] D. A. Brown and M. J. S. Dewar, *J.*, 1953, 2406. Briegleb, *Z. Elektrochem.*, 1949, **53**, 355.

* At 20°.

TABLE 2. *Thermodynamic functions for equilibrium reactions of type* (1) *at* 25°.

No.		ΔG (kcal. mole^{-1})	ΔH (kcal. mole^{-1})	ΔS (cal. deg.$^{-1}$ mole^{-1})
1	Pyridine	−5·15	−14·95	−32·9
2	2-Methylpyridine	−0·65	−12·83	−40·9
3	3-Methylpyridine	−5·32	−15·17	−33·1
4	4-Methylpyridine	−6·03	−15·65	−32·3
5	2 : 4-Dimethylpyridine	−1·39	−13·64	−41·2
6	2 : 5-Dimethylpyridine	−0·74	−12·58	−39·7
7	2 : 6-Dimethylpyridine	−1·43	−13·64	−41·0
8	Quinoline	−2·84	−15·80	−43·5
9	*iso*Quinoline	−5·15	−14·13	−30·1
10	Piperidine	−7·76	−13·88	−20·5
11	Pyrrolidine	−9·33	−14·94	−18·8

nitrogen atom is the main factor determining the co-ordinating ability of the pyridine bases toward the (diacetyl bisbenzoylhydrazone)nickel(II) as well as the proton. That log K for 2-picoline is much smaller than that expected on the basis of its proton affinity can be ascribed to an F-strain between its methyl group and the plane of the Ni(DBH).

This hindrance, of course, is absent when the reference acceptor is the proton. The same *F*-strain would account for the lower values of log *K* for all the 2-substituted pyridines of the second group.

R for quinoline, 0·43, is much higher than those of the other 2-substituted bases (0·08—0·15), and reflects a significant structural difference between quinoline and the 2-substituted pyridines. In fact the planar molecules of the aromatic bases which co-ordinate to the nickel atom will tend to arrange themselves in one of the two planes perpendicular to the co-ordination plane of the nickel(II) atom so as to bisect one of the N–Ni–O and N–Ni–N bond angles. Thus the hydrogen atom of the *ortho* C–H group of the quinoline can come between two adjacent ligand atoms. In the case of 2-picoline, on the other hand, the free rotation of the 2-methyl group prevents any hydrogen atom of the methyl group from penetrating easily between two adjacent co-ordinated atoms. As a consequence the approach of the base to the central nickel atom will be hindered.

Acridine does not produce a change in colour of the benzene solution of (diacetyl bisbenzoylhydrazone)nickel(II). This is rather surprising because the nitrogen atom has a fairly high electron density ($Q_N = 1{\cdot}431$) and it is a good base ($pK_H = 5{\cdot}60$ at 20°). It is even more remarkable in view of the fact that 2 : 6-lutidine does actually form an adduct.

The value of *R* for the piperidine complex is smaller than that for the pyridine complex (0·512 and 0·732 respectively), probably owing, at least in part, to the smaller size of the pyridine molecule. However, the piperidine and pyridine complexes of silver(I) have ratios, *R'*, which are related to the corresponding ones in the Ni(DBH) system, *R*, by a factor which is very close to 1·4 in each case. There is evidence that π-bonds are formed between silver and heterocyclic bases [9] and in view of the striking similarity in the ratio of *R* to *R'*, and despite the two systems' being so different, π-bonds are probably operative also in the case of Ni(DBH),2Base. This could contribute to a value of *R* which is larger in the case of the pyridine complex than in that of the piperidine complex.

Heat of Reaction.—A negative value of ΔG is essential to form a stable complex so it is of great assistance if ΔH is negative; our values range from −12·58 to −15·81 kcal. mole^{-1}. This small change in ΔH shows that the largest part in the change in ΔG is in ΔS of the reactions.

The values of ΔH for the 2-substituted pyridines (−12·58 to −13·64 kcal. mole^{-1}) are lower than those for the other substituted pyridines (−14·13 to −15·80 kcal. mole^{-1}). If ΔH is considered to measure bond strength this difference confirms the presence of steric hindrance in the formation of adducts of 2-substituted pyridines.

Entropy Changes.—Table 2 shows that the entropy changes for the formation of the hexaco-ordinate complexes are always negative, the values of ΔS ranging from −18·8 to −43·5 e.u. A negative entropy is expected for a system such as this where (i) the number of free particles decreases and (ii) the nickel complex and the aromatic base lose independent motion upon combination. The values of ΔS can be collected in two groups: one group of the secondary amines with ΔS −18·8 and −20·5, and another group of the pyridine bases with ΔS −30·1 to −43·5 e.u. This large difference between the two sets of values can be accounted for in terms of a reduction in the freedom of rotation of the pyridine bases around the Ni–N bond with respect to that of piperidine and pyrrolidine. Indeed, if double-bonding is involved in the bonds between nickel and the nitrogen of the pyridine bases, it should result in a hindrance of rotation of the amine. This loss in entropy therefore corroborates the hypothesis of π-bond character of such co-ordinate links.

The values of ΔS for the pyridine bases can be further subdivided into two groups. The former, from −39·7 to −43·5, correspond to all the *ortho*-substituted pyridines; the second, from −30·1 to −33·1, refers to the non-*ortho*-substituted pyridine bases. The large negative entropy changes for the *ortho*-substituted pyridines can be attributed to a

[9] Chatt and Williams, *J.*, 1951, 3061; 1954, 4403; Chatt, Duncanson, and Venanzi, *J.*, 1955, 4456; Murman and Basolo, *J. Amer. Chem. Soc.*, 1955, **74**, 3484.

restriction of free rotation of the *ortho*-methyl group about the C–C bond due to the penetration of a hydrogen atom of the methyl group between two adjacent ligand atoms of the plane of the nickel central atom. This "*ortho*-effect," already verified also for the entropies of hydration of the same substituted pyridines,[10] appears probably as an important factor in determining the rigidity of the octahedral complex molecules.

We are indebted to the Italian "Consiglio Nazionale delle Ricerche" for financial support.

ISTITUTO DI CHIMICA GENERALE DELL'UNIVERSITÀ,
PALERMO, ITALY.

[*Received, August 22nd,* 1957.]

[10] Andon, Cox, and Herington, *J.*, 1954, 3188.