Kinetics and Thermodynamics of Fast Square-planar–Octahedral Interconversion. Part 3.[1] The Reaction of [Biacetyl bis-α-hydroxybenzylidenehydrazone(2−)-$N^1N^{1'}OO'$]nickel(II) † with Bidentate Heterocyclic Amines in Chlorobenzene

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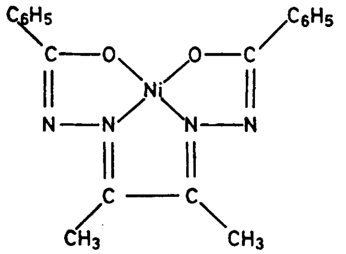
The square-planar complex [Ni(bbh)] [bbh = biacetyl bis-α-hydroxybenzylidenehydrazone(2−)-$N^1N^{1'}OO'$] reacts with 2,2'-bipyridine and substituted 1,10-phenanthrolines to give octahedral adducts in which, presumably, the ligand bbh behaves as a tridentate ligand and a hydroxy-group of the water present in the solvent occupies one of the positions around the nickel atom. A comparative thermodynamic and kinetic study of these reactions has been made. The mechanism proposed implies a nickel-to-oxygen bond breaking as the rate-determining step. Thermodynamic and activation parameters associated with the reactions are discussed.

We have previously [1] carried out a comparative thermodynamic and kinetic study of the reaction between the square-planar complex [Ni(bbh)] [bbh = biacetyl bis-α-hydroxybenzylidenehydrazone(2—)-N^1N^1OO'] and various heterocyclic amines in chlorobenzene. It turned out that the lability of the amines, co-ordinated in a mutually *trans* position to nickel, in the addition products [Ni(bbh)(amine)$_2$], can be correlated to the pK_a of the amines themselves and to the formation constants of the adducts.



[Ni(bbh)]

The Lewis-acid character of [Ni(bbh)] is also exerted on bidentate nitrogen bases. Recently a 1 : 1 adduct between the complex and 1,10-phenanthroline has been isolated [2] from ethanol. The configuration of this compound, as shown by *X*-ray diffractometry, is octahedral. The two nitrogen atoms of phenanthroline are both co-ordinated in relative *cis* positions and the hydrazone bbh behaves as a tridentate ligand, the oxygen of one of the benzoyl groups being non-co-ordinated and in enolic form. The sixth co-ordination site of the complex is occupied by an ethoxy-group of the solvent. Surprisingly we found that the reaction between [Ni(bbh)] and 1,10-phenanthroline also takes place in aprotic and poorly co-ordinating solvents like benzene, toluene, chloroform, and chlorobenzene. In particular, we verified that in the latter solvent the complex interacts with several heterocyclic bidentate amines. The singularity of this finding has prompted us to investigate the nature of these reactions. In this paper we report the results of a thermodynamic and kinetic study of the interaction between [Ni(bbh)] and the nitrogen bidentate bases 1,10-phenanthroline (phen), 5-nitro-1,10-phenanthroline (nphen), 5-chloro-1,10-phenanthroline (cphen), 5-methyl-1,10-phenanthroline (mphen), 2,9-dimethyl-1,10-phenanthroline (dmphen), and 2,2'-bipyridine (bipy) in chlorobenzene. Thermodynamic parameters associated with the reactions are discussed.

EXPERIMENTAL

Materials.—The complex [Ni(bbh)] was prepared according to the method reported in the literature.[3] The adducts between [Ni(bbh)] and L–L (L–L = 1,10-phenanthroline, 5-methyl-1,10-phenanthroline, or 2,9-dimethyl-1,10-phenanthroline) were prepared by mixing equimolar amounts of the complex and the ligand in chlorobenzene. The brown solids which crystallized slowly on cooling at −30 °C were washed with cold chlorobenzene and then dried *in vacuo* over P_4O_{10}. The same procedure was followed to prepare the adduct between [Ni(bbh)] and 1,10-phenanthroline in ethanol. All the adducts were characterized by elemental analysis. 2,2'-Bipyridine and the phenanthrolines (K. and K.) were used without further purification. Chlorobenzene was used either as a commercial product (spectroscopic grade) or after progressive treatment with 4 Å molecular sieves to make it anhydrous. Absolute ethanol was of spectroscopic grade.

Thermodynamics.—The equilibrium constants for the reactions were determined spectrophotometrically using an Optica CF 4R recording spectrophotometer equipped with a thermostatted cell holder. Mixtures of the complex and the ligand, both of known concentrations, were left to equilibrate thermally at the desired temperature and their absorbances were recorded in the region 380—580 nm. The temperature of the solution was controlled to ±0.1 °C by means of a thermocouple immersed in the spectrophotometric cell.

Kinetics.—The rates of reaction were followed spectrophotometrically by measuring the changes in optical density (absorbance) (at a suitable wavelength in the visible region) of the reaction mixture as a function of time. A stopped-flow Durrum D-110 provided with a Kel-F flow system was used to monitor the course of the reaction. The exponential traces were photographed and the values of $k_{obs.}$ were

† [4,5-dimethyl-1,8-diphenyl-2,3,6,7-tetra-azaocta-1,3,5,7-tetraene-1,8-diolato(2−)-N^3,N^6,O,O']nickel(II).

evaluated by matching the experimental traces with similar ones produced by an exponential generator [4] on the same oscilloscope. For a full list of $k_{\mathrm{obs.}}$ values see Supplementary Publication No. SUP 22832 (6 pp.).*

RESULTS

When increasing amounts of ligand L–L are added to a chlorobenzene solution of [Ni(bbh)], a gradual, but immediate, spectral change characterized by two sharp isosbestic points (Figure 1) is observed. Spectrophotometric titrations of the complex with the base L–L show that the stoicheiometric ratio of the two substances in the reaction product is in each case unity. Nevertheless, the formation of a 1 : 1 adduct between the complex and the ligand cannot be conceived [2] on the basis of the relative structures of the two compounds. Accordingly, the elemental analysis of the products does not conform to its simple formulation as [Ni(bbh)(L–L)]. In addition, the absorbance of [Ni(bbh)]–L–L depends on the amount of water present as impurity in the solvent. In particular, the regression of the reaction equilibrium as the chlorobenzene becomes increasingly anhydrous indicates that water must be involved in the reaction stoicheiometry and may be present in the reaction products. The formulation of these as [Ni(bbh)(L–L)(OH_2)] agrees well with the elemental analysis (Table 1).

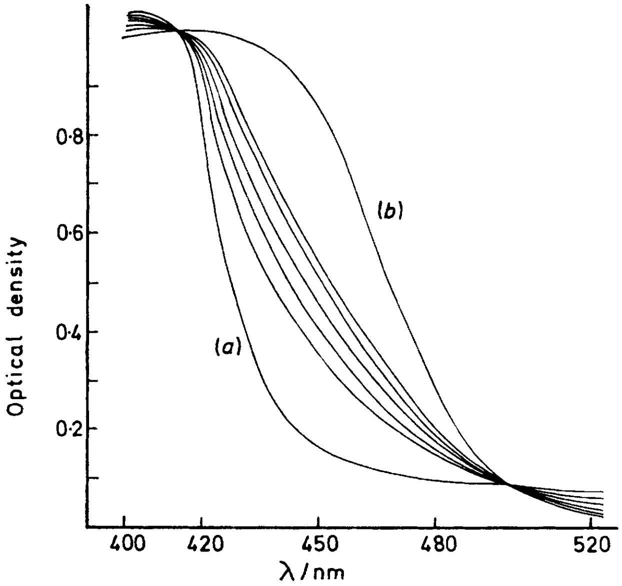


FIGURE 1 Spectral variations for reaction of [Ni(bbh)] with 2,2′-bipyridine in chlorobenzene, [Ni(bbh)] = 1 × 10^{-4} mol dm^{-3}. (*a*) [Ni(bbh)], (*b*) [Ni(bbh)] + excess of bipy

In order to clarify the nature of the reaction products, we have compared by u.v. and i.r. spectroscopy the adducts between [Ni(bbh)] and 1,10-phenanthroline in chlorobenzene and ethanol. The structure of the compound formed in the latter solvent is known.[2] The electronic spectra of the two compounds in the visible and u.v. region are almost identical in a variety of solvents. Furthermore, the i.r. spectra (Nujol mull) of the compounds are very similar and both exhibit the characteristic stretching frequency of OH attributable to the enolic form of the unco-ordinated benzoyl group of the ligand hbbh⁻ (hbbh = the monoenolic form of bbh). These findings strongly suggest that the two compounds have similar configurations. We assume, therefore, that the structure of the reaction products between [Ni(bbh)] and the ligands L–L in chlorobenzene is that shown below. Accordingly the stoicheiometry of the reactions is given by (1).

$$\underset{\text{square planar}}{[\mathrm{Ni(bbh)}]} + \mathrm{L{-}L} + \mathrm{H_2O} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \underset{\text{octahedral}}{[\mathrm{Ni(hbbh)(L{-}L)(OH)}]} \quad (1)$$

Because of the dependence of the equilibrium position, and, in some cases, of the rate constants on the water content of chlorobenzene, the whole set of experiments was performed using the same stock of solvent. The amount of water in the solvent and its uniformity with time were determined by Karl–Fisher titration.

TABLE 1

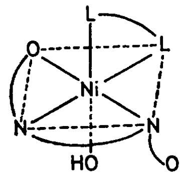
Elemental analysis for the product of the reaction between [Ni(bbh)] and 1,10-phenanthroline in chlorobenzene

Analysis (%) *					
C	H	N	O	Ni	Total
62.3	4.5	14.5	8.4	10.1	99.8
(64.4)	(4.3)	(15.1)	(5.7)	(10.5)	(100)
[62.4]	[4.5]	[14.6]	[8.3]	[10.2]	[100]

* Calculated values are given in parentheses: round brackets for [Ni(bbh)(phen)] and square brackets for [Ni(bbh)(phen)(OH_2)].

The equilibrium constants for the reaction of [Ni(bbh)] with the bases L–L were determined spectrophotometrically (see Experimental section) from the slopes of the plots of $(1 - \alpha)/\alpha$ against [L–L], where α is the ratio of the difference in absorbance between the octahedral and the square-planar forms of the complex and [L–L] is the concentration of the free ligand, *i.e.* $C_L - (1 - \alpha)C_C$ where C_L and C_C are the concentrations of ligand and complex respectively. These values are reported in Table 2. Actually, the values obtained in such a way do not represent the equilibrium constants, K, for reaction (1) but rather the product $K[H_2O] = K'$. Nevertheless, owing to the uniformity of the term $[H_2O]$ these values are homogeneous and, therefore, comparable.

For most of the processes, the equilibrium at room temperature lies far to the right. For this reason the experimental determinations of equilibrium constants were carried out at higher temperatures (35—65 °C), taking advantage of the largely negative reaction enthalpies. The equilibrium constants at 25 °C were obtained by extrapolation from the Van t'Hoff plots by supposing $\Delta H^\ominus$ constant throughout the temperature range. These values are reported in Table 3 along with those of the thermodynamic parameters $\Delta H^\ominus$, $\Delta S^\ominus$, and $\Delta G^\ominus$ obtained through the usual relation (2).



$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus \quad (2)$$

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

TABLE 2

Rate and equilibrium constants for reaction of [Ni(bbh)] with heterocyclic bidentate amines L–L in chlorobenzene at various temperatures [a]

Amine L–L	θ_c/°C	10^3[L–L]/ mol dm^{-3}	No. of experiments	$k_{obs.}$/s^{-1}	10^{-3} k_b/ dm^3 mol^{-1} s^{-1}	k_a/s^{-1}	10^2 (gradient/intercept dm^3 mol^{-1}	10^{-2} K'[b] dm^3 mol^{-1}
nphen	5.8	0.1—0.5	8	20—98	196 ± 4			2 890 ± 52
	10.5	0.1—0.5	9	24—114	229 ± 3			1 570 ± 28
	15	0.15—0.4	6	40—108	267 ± 8			888 ± 16
	20	0.125—0.5	9	41—154	309 ± 6			482 ± 8
	25	0.125—0.45	7	45—164	363 ± 3			267 ± 7
cphen	5.5	0.35—2	5	12—71	350 ± 3			14 800 ± 280
	10	0.35—2	7	13—79	401 ± 9			7 300 ± 140
	15	0.35—1.75	6	15—76	435 ± 9			4 040 ± 70
	20	0.35—2	7	18—101	531 ± 26			2 110 ± 40
	25	0.35—2	7	22—120	598 ± 7			1 130 ± 20
bipy	6.6	0.8—8	9	18—123	14.4 ± 0.7	4.15 ± 0.52	34.8	37.5 ± 4.1
	10.6	0.8—6	8	21—107	16.4 ± 0.3	7.67 ± 1.0	21.4	21.0 ± 2.3
	15	0.8—8	7	26—152	17.5 ± 0.4	14.5 ± 1.6	12	11.8 ± 1.2
	20	0.8—5	7	43—125	19.8 ± 0.4	26.5 ± 1.1	7.5	6.0 ± 0.6
	20 [c]	0.75—4.5	6	66—140	19.9 ± 0.5	50.0 ± 1.3		
	25	1—6	7	80—186	21.9 ± 0.5	56.6 + 1.9	3.9	3.2 ± 0.3
phen	6	0.2—0.5	7	112—283	567 ± 3			41 600 ± 2 130
	10	0.2—0.45	6	140—300	653 ± 17			22 000 ± 1 170
	15	0.1—0.4	7	75—287	725 ± 24			10 900 ± 570
	20	0.1—0.35	6	86—293	846 ± 17			5 530 ± 280
	25	0.1—0.35	6	95—340	982 ± 7			2 870 ± 150
mphen	5.5	0.035—0.2	7	23—127	613 ± 49			57 800 ± 3 130
	10	0.035—0.2	7	28—151	739 ± 34			30 000 ± 1 590
	15	0.035—0.2	7	33—182	883 ± 28			14 700 ± 760
	20	0.035—0.2	7	37—220	1 100 ± 24			7 400 ± 380
	25	0.035—0.175	6	47—218	1 240 ± 25			3 820 ± 200
dmphen	5	5—20	5	26—58	2.16 ± 0.12	13.9 ± 1.5	1.5	1.5 ± 0.2
	10	5—20	5	35—72	2.61 ± 0.14	20.8 ± 1.7	1.2	1.1 ± 0.1
	15	5—20	5	51—103	3.38 ± 0.14	34.3 ± 1.7	0.9	0.8 ± 0.0
	20	5—20	5	83—144	4.13 ± 0.13	62.1 ± 1.6	0.6	0.6 ± 0.0
	25	5—20	5	117—197	5.31 ± 0.16	89.5 ± 2.0	0.5	0.4 ± 0.0

[a] Concentration of [Ni(bbh)] $\leqslant 1 \times 10^{-4}$ mol dm^{-3}; $[H_2O] = 5.5 \times 10^{-2}$ mol dm^{-3} unless otherwise stated; the gradient and inter cept refer to the plot of $k_{obs.}$ against [L–L]. [b] Determined spectrophotometrically. [c] $[H_2O] = 2.7 \times 10^{-2}$ mol dm^{-3}.

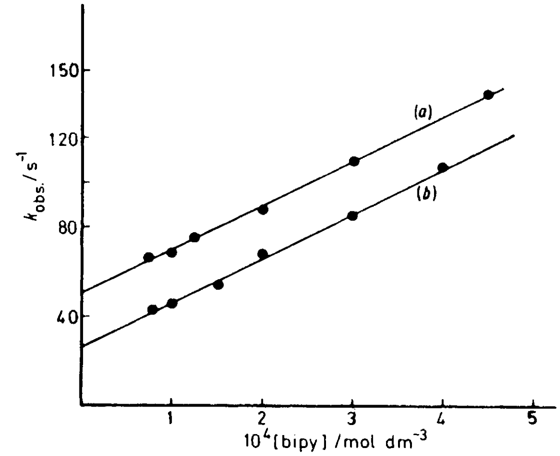


FIGURE 2 Plot of $k_{obs.}$ against [bipy] at various water concentrations: (a) $[H_2O] = 2.7 \times 10^{-2}$; (b) $[H_2O] = 5.5 \times 10^{-2}$ mol dm^{-3}; [Ni(bbh)] $\leqslant 1 \times 10^{-4}$ mol dm^{-3}; temperature = 20 °C

The kinetics were performed under pseudo-first-order conditions with respect to the complex by using at least a ten-fold excess of L–L. The water concentration (5.5 mol dm^{-3}) was in each case much larger than that of the complex. The rate constants, $k_{obs.}$, conform to the rate

$$k_{obs.} = k_a + k_b[L\text{–}L] \qquad (3)$$

law (3). The term k_a is appreciable only in those cases in which the reaction does not proceed to completion, *i.e.* when L–L is 2,2′-bipyridine or 2,9-dimethyl-1,10-phenanthroline. For this reason we assume that k_a refers to the reverse reaction. The ratio gradient : intercept (*i.e.* k_b/k_a) of the plots $k_{obs.}$ against [L–L] is in any case equal to (4).

$$k_b/k_a = [Ni(hbbh)(L\text{–}L)(OH)]/[Ni(bbh)][L\text{–}L] = K[H_2O] = K' \qquad (4)$$

The effect of water on the rate constants $k_{obs.}$ was determined by studying the reaction between [Ni(bbh)] and 2,2′-bipyridine at two different known water concentrations. Two parallel straight lines (Figure 2) were obtained from the plot of the two sets of $k_{obs.}$ values against [bipy], the lower referring to the higher water concentration. The term k_b was practically unaffected by the presence of H_2O, while the term k_a nearly doubled on halving $[H_2O]$. Therefore, the overall rate law is expressed by (5). The values of k_a

$$k_{obs.} = k_a'/[H_2O] + k_b[L\text{–}L] \qquad (5)$$

and k_b at various temperatures are reported in Table 2. The activation parameters $\Delta H^‡$ and $\Delta S^‡$, obtained from the Arrhenius plots, are listed in Table 4.

DISCUSSION

Inspection of Table 3 shows that both rate constants, k_b, and equilibrium constants, K', for the reactions studied are dependent on the nature of the ligand L–L. More specifically, if we consider only the substituted 1,10-phenanthrolines, the values of equilibrium constants and those of rate constants increase linearly as the pK_a in water of the phenanthrolines increases. Plots of log K' and log k_b for the reaction of a given phenanthroline against the pK_a of the phenanthroline itself are shown in Figure 3. The slopes of these plots, 0.70 ± 0.02 and 0.33 ± 0.02 respectively, indicate that the equilibrium constants, K', are more sensitive to the change in the basicity of the phenanthroline than the corresponding rate constants, k_b, for the same reactions. This is an obvious indication that the reverse rate constants, k_a, for reaction (1) are also dependent on the basicity of the group L–L. The large deviation from linearity for 2,9-dimethyl-1,10-phenanthroline in both plots reflects the effects of steric hindrance of this ligand to co-ordination. When the complex itself, rather than the proton, is used as a reference, all the kinetic values can be correlated. Thus, if the values of rate constants, k_b, are compared with those of equilibrium constants, K', the linear free-energy relationship (6) holds for all the reactions studied (Figure 4: $a = 2.82 \pm 0.28$; $b =$

$$\log k_b = a + b \log K' \qquad (6)$$

0.59 ± 0.02). In this case the lack of deviation for 2,9-dimethyl-1,10-phenanthroline shows that the steric hindrance of this ligand is exerted both on the forward and the reverse reaction. It is interesting to note that the values of k_b are of the same order of magnitude as those calculated for the addition of bidentate ligands to square-planar complexes of the type $[Ni(L-L)_2]$ (L–L = OO'-disubstituted phosphorodithioate[6] and OO'-disubstituted xanthate[7]).

TABLE 3

Rate and equilibrium constants for reaction of [Ni(bbh)] with heterocyclic bidentate amines in chlorobenzene at 25 °C

Amine	pK_a[a]	log k_b	log k_a	log K'
nphen	3.6	5.56	1.13	4.43
cphen	4.3	5.77	0.72	5.05
bipy	4.3	4.34	1.74[b]	2.53
phen	5.0	5.98	0.52	5.46
mphen	5.2	6.10	0.52	5.58
dmphen	5.9	3.72	1.95[b]	1.60

[a] pK_a of the conjugate acid in water. Values of pK_a from ref. 5. [b] Evaluated directly.

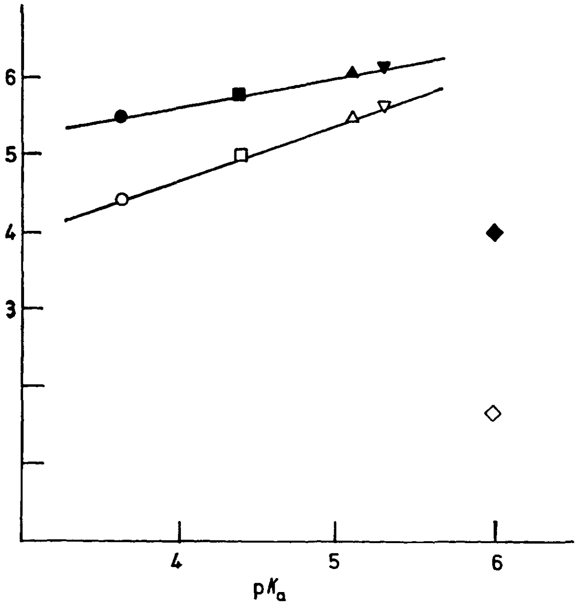


FIGURE 3 Plot of log K' (open symbols) and log k_b (filled symbols) for the reaction of [Ni(bbh)] with various bidentate amines L–L at 25 °C against pK_a for L–L: nphen (○,●); cphen (□,■); phen (△,▲); mphen (▽,▼); and dmphen (◇,♦)

The mechanism compatible with the kinetic data is drawn in the Scheme (charges are omitted for simplicity). The complex and the ligand rapidly react to form a five-co-ordinate intermediate.* This is followed by a slow rate-determining step in which the second nitrogen atom of L–L binds to nickel while one of the nickel-to-oxygen bonds breaks. The fast co-ordination of a water molecule to the complex, and the proton transfer from the oxygen of the co-ordinated water to the oxygen of the free arm of the ligand, lead to the product. The rate law derived for the mechanism in the Scheme, under pseudo-first-order conditions, applying the stationary state to the intermediates and assuming that $k_3 \gg k_{-2}$, is given by (7).

$$k_{\text{obs.}} = K_0 k_2[L-L] + k_{-2}/K_3[H_2O] \qquad (7)$$

The mechanistic nature of the rate-determining step of the reactions is difficult to establish. Both I_d or I_a mechanisms are conceivable. Nevertheless, the existence of a Brönsted relation with a slope less than one would suggest an I_a mechanism. It is assumed, in fact, that in octahedral substitutions for a series of related reactions a mechanism of type I_d usually implies a linear correlation with a slope of unity between kinetic and thermodynamic parameters of the reactions, whereas for an I_d mechanism the slope is less than one.[9-11]

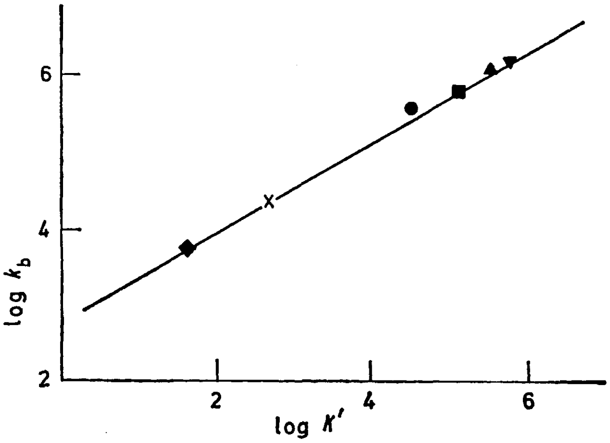


FIGURE 4 Linear free-energy relationship between log k_b and log K' for the reaction of [Ni(bbh)] with bidentate amines nphen (●); cphen (■); phen (▲); mphen (▼); dmphen (♦); and bipy (×)

* When L–L is one of the phenanthrolines, the intermediate can be better described as having a structure in which the ligand is unidentate but rapidly exchanges[8] its point of attachment to the central atom.

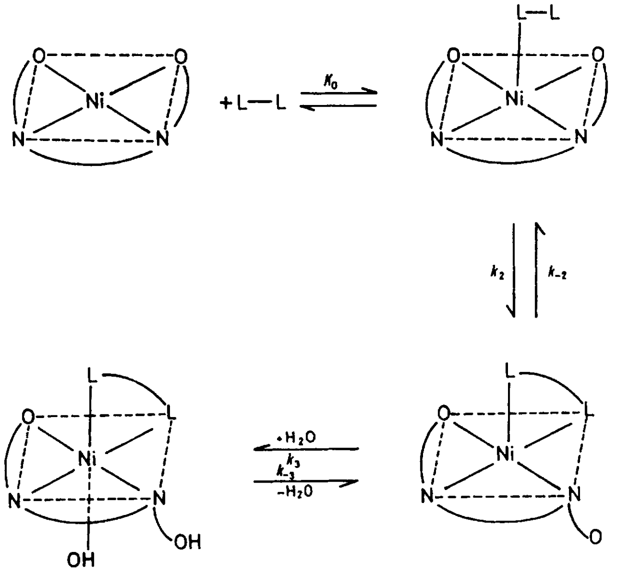
TABLE 4

Activation and thermodynamic parameters associated with the reaction of [Ni(bbh)] with heterocyclic bidentate amines in chlorobenzene *

Amine	$\Delta H^{\ddagger}$ / kcal mol^{-1}	$\Delta S^{\ddagger}$ / cal K^{-1} mol^{-1}	$\Delta H^{\ominus}$ / kcal mol^{-1}	$\Delta S^{\ominus}$ / cal K^{-1} mol^{-1}	$\Delta G^{\ominus}$ / kcal mol^{-1}
nphen	4.6 ± 0.1	−18 ± 0.2	−20.5 ± 0.0	−48.5 ± 1.1	−6.04 ± 0.01
cphen	4.0 ± 0.4	−19 ± 1.4	−21.8 ± 0.3	−50.0 ± 0.8	−6.89 ± 0.01
bipy	3.1 ± 0.2	−28 ± 1.0	−22.2 ± 0.8	−63.0 ± 2.0	−3.45 ± 0.06
phen	4.2 ± 0.2	−17 ± 1.0	−22.8 ± 0.8	−51.5 ± 2.5	−7.44 ± 0.03
mphen	5.5 ± 0.3	−12 ± 1.0	−23.0 ± 0.8	−51.6 ± 1.4	−7.61 ± 0.03
dmphen	6.8 ± 0.3	−19 ± 1.0	−10.9 ± 0.4	−29.2 ± 1.5	−2.20 ± 0.06

* 1 cal = 4.184 J.

The assumption of a bond breaking in the reaction sequence accounts for the relatively low values of observed rate constants relative to the square-planar–octahedral interconversion. The addition reactions of unidentate ligands to the complex [Ni(bbh)], which lead to the formation of *trans*-octahedral complexes without requiring bond breakings or bond rearrangements, are extremely fast and cannot be followed by stopped-flow techniques.



SCHEME

According to the proposed mechanism, the variations in the values of k_f through the series of reactions examined reflect the influence of the nature of L–L both on the values of K_0 and k_2. The formation constant for a five-co-ordinate complex usually increases on increasing basicity of the adding ligand.[12-14] On the other hand, in the subsequent step, the nickel-to-oxygen bond breaking and the co-ordination of the second nitrogen atom of the ligand L–L are favoured by the decrease in electrophilicity of the nickel in the five-co-ordinate species. This is consistent with the observed trend of the k_b values for phenanthrolines. The structure of the ligand should also be of importance in determining the value of the forward rate constant k_b. Thus, the greater tendency of 5-chloro-1,10-phenanthroline, with respect to the more flexible 2,2′-bipyridine, to chelate with the nickel atom should be reflected in a higher rate constant k_2. As a matter of fact, the calculated value of k_b for the former ligand is larger, although the equilibrium constants, K_0, for 5-chloro-1,10-phenanthroline and 2,2′-bipyridine should be very similar as expected on the basis of their pK_a's (4.26 and 4.30 respectively). The rate constant k_b for 2,9-dimethyl-1,10-phenanthroline reflects the influence of steric hindrance to co-ordination in the two steps of the reaction.

The values of reverse rate constants, k_a, which have been evaluated directly for 2,9-dimethyl-1,10-phenanthroline and 2,2′-bipyridine and derived from the values of k_b/K' for the other amines (see Table 3), show a gradual decrease with increasing pK_a of phenanthrolines, as well as a strong dependence on the structure of the ligand. In this case an analysis of the trend of the reverse rate constants, k_a, in terms of relative variations of k_{-2} and K_3 ($k_a = k_{-2}/K_3$) is difficult in that both these constants are affected in the same way, but certainly to a different extent, by the nature of the ligand L–L.

The activation parameters of the reactions (Table 4) are consistent with the proposed mechanism. The very low values of activation enthalpy derivable from the rate constants k_b can be directly related to the composite nature of the forward rate constant k_f. In fact, k_f is the product of the rate constant k_2, which increases on increasing temperature, and the equilibrium constant K_0, which decreases [12-14] on increasing temperature. Therefore, the experimentally determined values of activation enthalpy $\Delta H_f^{\ddagger}$, are the balance of a positive term, $\Delta H_2^{\ddagger}$, and a negative one, $\Delta H_0^{\ominus}$, equation (8).

$$\Delta H_f^{\ddagger} = \Delta H_2^{\ddagger} + \Delta H_0^{\ominus} \qquad (8)$$

As expected for processes in which there is a loss of freedom of the free particles due to association, thermodynamic parameters associated with the reactions studied here are characterized by largely negative values of entropy. In contrast with the uniformity of the entropy values in the series of 5-substituted 1,10-phenanthrolines, enthalpy values, which are also negative, show gradual slight variations. Therefore, the increase in stability of the adducts, on increasing basicity of phenanthrolines, as shown by the values of $\Delta G^{\ominus}$, is mainly due to enthalpic factors. The value of the enthalpy change for the formation of [Ni(bbh)-

(bipy)] is similar to that of [Ni(bbh)(phen)]. The lower stability of the former adduct is attributable to the larger negative entropy change due to the greater loss of freedom of 2,2′-bipyridine with respect to the rigid phenanthrolines on bonding with [Ni(bbh)]. The peculiarity of the reaction with 2,9-dimethyl-1,10-phenanthroline is also reflected in its activation parameters. The lower values of $\Delta H^\ominus$ and $\Delta S^\ominus$, with respect to those for the other reactions, are probably attributable to the steric hindrance of the ligand to co-ordination.

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