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Reactivity of Metal Chelates of Sulphur Containing Ligands towards Lewis Bases. Part IV. Reaction of Bis[2(1-methyl-2-oxo-propylidenehydrazine-*S*-methylcarbodithioato)NSO(−1)] nickel(II) with Amines

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Abstract

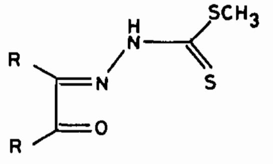
The reactions of octahedral bis[2(1-methyl-2-oxo-propylidenehydrazine-*S*-methylcarbodithioato)NSO-(−1)]nickel(II) (**3**, R = CH_3) with aromatic heterocyclicamines (pyridine, 3- and 4-methylpyridine), secondary aliphatic amines (diethyl, di-n-propyl and di-n-butylamine) and alicyclic amines (piperidine and morpholine) have been studied in benzene.

Spectrophotometric studies revealed that these reactions proceed by nucleophilic displacement of the two coordinated carbonyl oxygens to give the corresponding bis(amine) adducts.

The kinetic measurements of these reactions indicate first-order dependence on the substrate and second-order dependence on the amine concentration. A comparison of the activation parameters suggests the formation of a π adduct in the transition state in the case of the pyridines. In the case of the secondary aliphatic amines, hydrophobic interactions between the alkyl chains and the in-plane ligand is proposed.

Introduction

The ligand of the type **1** (R = CH_3 or C_6H_5) shows different coordination abilities towards nickel(II) depending on the nature of R [1]. The bisligand nickel(II) complex with **1** (R = C_6H_5) is square planar (**2**), in which the hydrazone molecule acts as mononegative bidentate ligand, and where the carbonyl oxygen remains uncoordinated. With **1** (R = CH_3), however, the isolated bisligand complex is octahedral (**3**), implying the tridentate nature of this ligand [1]. The octahedral arrangement of the two tridentate ligands around the central nickel(II) was confirmed by X-ray structural analysis [2]. Each of the tridentate ligands is coordinated to nickel(II) by carbonyl oxygen, azomethine nitrogen and the thiol sulphur. The donor atoms of each ligand are arranged approximately coplanar and the two planes are perpendicular to each other.



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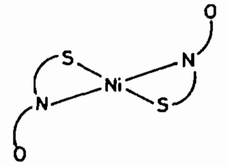

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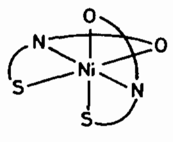

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A careful study of the previously reported electronic spectral data [1] suggests that both square planar **2** and octahedral **3** complexes can react with coordinating solvents such as pyridine to give pyridine adducts. Similar to other square planar nickel(II) complexes with NS bidentate ligands [3, 4], the reaction of **2** with pyridine may proceed by direct coordination of one or two pyridine molecules giving either mono- or bispyridine adducts. However, in the case of **3**, the formation of the analogous adducts must involve nucleophilic displacement of one or two coordinated carbonyl oxygens.

The present work is devoted to studying the kinetics and mechanism of the reaction of **3** with aliphatic and alicyclic secondary amines, as well as pyridines in benzene.

Results and Discussion

The reaction of **3** with N-heterocyclic aromatic amines (pyridine, 3-methylpyridine and 4-methylpyridine), alicyclic secondary amines (piperidine and morpholine) and aliphatic secondary amines (diethyl-, di-n-propyl- and di-n-butyl-amine) have been studied spectrophotometrically in benzene solution. The

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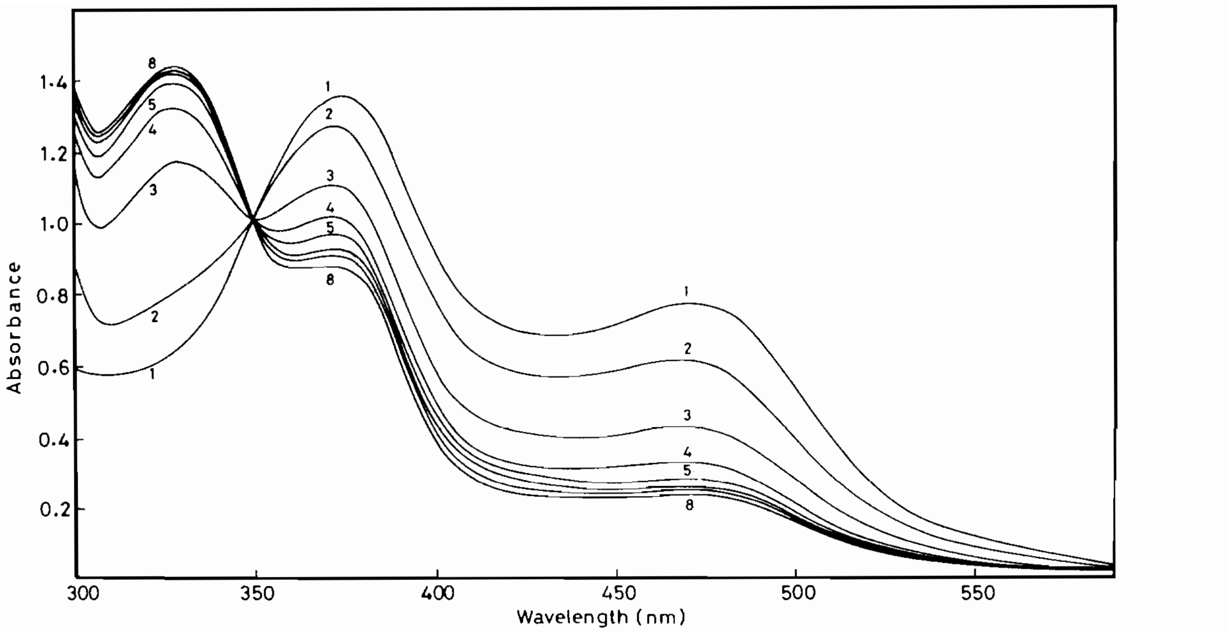


Fig. 1. Variation of the absorption spectra of 3 (5.90×10^{-6} mol dm^{-3}) in the presence of pyridine (1.33 mol dm^{-3}) as a function of time (min) in benzene at 25.0 °C: 1, 00.0; 2, 12.0; 3, 24.0; 4, 34.0; 5, 44.0; 6, 62.0; 7, 87.0; 8, 132.0.

spectra of **3** in the presence of any of these amines were found to be time dependent and similar spectral changes with a fixed isosbestic point at 350 nm were observed for all systems studied. A typical spectral variation as a function of time is shown in Fig. 1. Analysis of these spectrophotometric data using the graphical method of Coleman *et al.* [5], revealed the presence of two light absorbing species namely the parent NiL_2 (3, $R = CH_3$) and the formed amine adduct, (NiL_2B_n) as given by eqn. (1).

In the case of alicyclic and aliphatic secondary amines, the change of absorbance measured at 470 nm, after equilibration, as a function of C_B/C_{NiL_2} shows an inflection at a 2:1 molar ratio implying the formation of a highly stable bisamine adduct. However, in the case of pyridines, a very large excess of amine concentration was required to achieve complete reaction. The stoichiometry of these reactions was established by using eqn. (2).

$$NiL_2 + nB \rightleftharpoons NL_2Bn \qquad (1)$$

$$\log (A_0 - A)/(A - A_\infty) = \log K + n \log C_B \qquad (2)$$

where

$K = [NiL_2B_n]/[NiL_2][B]^n$

and A_0, A and A_∞ have their usual significance [6]. Plots of log $(A_0 - A)/(A - A_\infty)$ versus log C_B give straight lines with slopes (n) equal to (2.0 ± 0.2). The uncertainty in the values of A measured after equilibration, especially at low amine concentration makes accurate determination of the equilibrium constant K rather difficult. The values of log K (at 25.0 °C) estimated from the slopes of these lines for pyridine, 3-methylpyridine and 4-methylpyridine bisadducts are 0.26, 0.85 and 1.10 mol^{-1} dm^6, respectively.

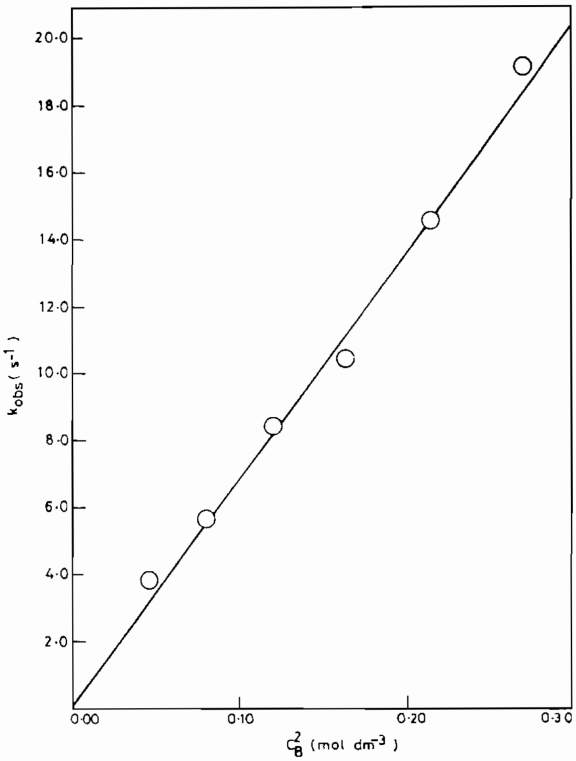


Fig. 2. Variation of k_{obs} (s^{-1}) as a function of C_B^2 for the reaction of **3** with 4-methylpyridine in benzene at 25.0 °C.

These spectrophotometric studies indicate that the reaction of **3** with different amines proceeds via a nucleophilic displacement of the two carbonyl oxygens by two amine molecules giving the bisamine adduct 7 or 8. Similar nucleophilic displacements were reported for the reaction of the green octahedral bis(*N*-*o*-methoxybenzaldehyde-*p*-methoxybenzoylhydrazinato)nickel(II) with pyridine, where the two coordinated methoxyl oxygens have been displaced by two pyridine molecules [7].

The observed first-order rate constants k_{obs} (s^{-1}) were measured under pseudo first-order conditions at different large excesses of amine concentrations. In all cases, plots of k_{obs} versus C_B^2 gave straight lines passing through the origin, (Fig. 2) and accordingly the rate law can be expressed by

$$k_{obs} = k_f C_B^2 \qquad (3)$$

where k_f ($mol^2\ dm^{-6}\ s^{-1}$) is the third-order rate constant and C_B is the analytical concentration of the amine used. The values of k_f calculated from the slopes of best fitting linear least-square lines at different temperatures are listed in Table 1. These data reveal the dependence of k_f on the nature of the amines used, where the reactivity increases in the order pyridine < 3-methylpyridine < 4-methylpyridine < di-n-propylamine < di-n-butylamine < diethylamine < morpholine < piperidine.

Correlation of the values of log k_f with nucleophile basicities as measured either by the acidity constants (pK_a) of the amines in water, or the equilibrium constants (log K_{eq}) of bisamine adduct formation

TABLE 1. Third-order rate constants (k_f) for the reaction of 3 with different amines at different temperature in benzene

Amine	Temperature (°C)	[Base] (mol dm^{-3})	No. of runs	k_f (mol^{-2} dm^6 s^{-1})
Pyridine	30.3	0.679–1.359	8	$(7.62 \pm 0.38)10^{-4}$
	33.2		7	$(8.14 \pm 0.55)10^{-4}$
	35.1		7	$(8.60 \pm 0.48)10^{-4}$
	37.8		7	$(8.94 \pm 0.51)10^{-4}$
	41.2		7	$(9.49 \pm 0.51)10^{-4}$
3-Methylpyridine	25.0	0.332–0.797	8	$(13.18 \pm 0.70)10^{-4}$
	30.2		8	$(14.25 \pm 1.21)10^{-4}$
	33.5		8	$(15.23 \pm 1.23)10^{-4}$
	41.5		8	$(17.10 \pm 0.25)10^{-4}$
4-Methylpyridine	30.1	0.215–0.603	6	$(64.14 \pm 2.09)10^{-4}$
	33.6		6	$(68.09 \pm 2.74)10^{-4}$
	37.7		6	$(72.91 \pm 1.78)10^{-4}$
	41.2		5	$(78.28 \pm 2.20)10^{-4}$
Morpholine	25.0	0.200–0.500	8	$(17.58 \pm 0.82)10^{-2}$
	30.0		6	$(19.97 \pm 1.13)10^{-2}$
	35.0		6	$(22.58 \pm 1.97)10^{-2}$
	40.0		6	$(26.83 \pm 1.10)10^{-2}$
Piperidine	24.9	0.020–0.080	8	12.48 ± 1.24
	30.0		8	14.69 ± 0.71
	35.0		6	16.69 ± 0.60
	40.0		6	19.09 ± 0.99
Diethylamine	25.0	0.341–0.886	8	$(5.83 \pm 0.10)10^{-2}$
	30.0		8	$(6.74 \pm 0.22)10^{-2}$
	35.0		8	$(7.68 \pm 0.20)10^{-2}$
	40.0		8	$(8.62 \pm 0.28)10^{-2}$
Dipropylamine	25.0	0.491–0.910	8	$(1.84 \pm 0.08)10^{-2}$
	30.0		8	$(2.10 \pm 0.09)10^{-2}$
	35.0		6	$(2.38 \pm 0.10)10^{-2}$
	40.0		6	$(2.78 \pm 0.07)10^{-2}$
Dibutylamine	25.0	0.576–1.080	6	$(2.25 \pm 0.12)10^{-2}$
	30.0		6	$(2.63 \pm 0.11)10^{-2}$
	35.0		6	$(3.05 \pm 0.12)10^{-2}$
	40.0		6	$(3.54 \pm 0.10)10^{-2}$

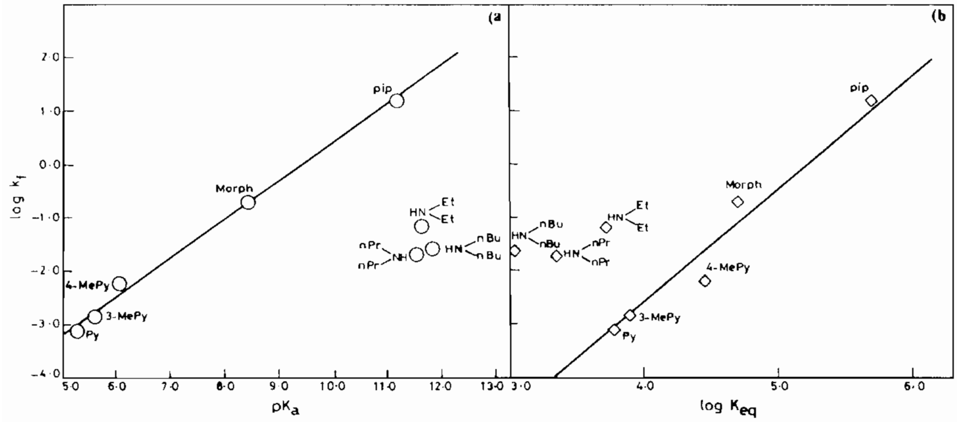
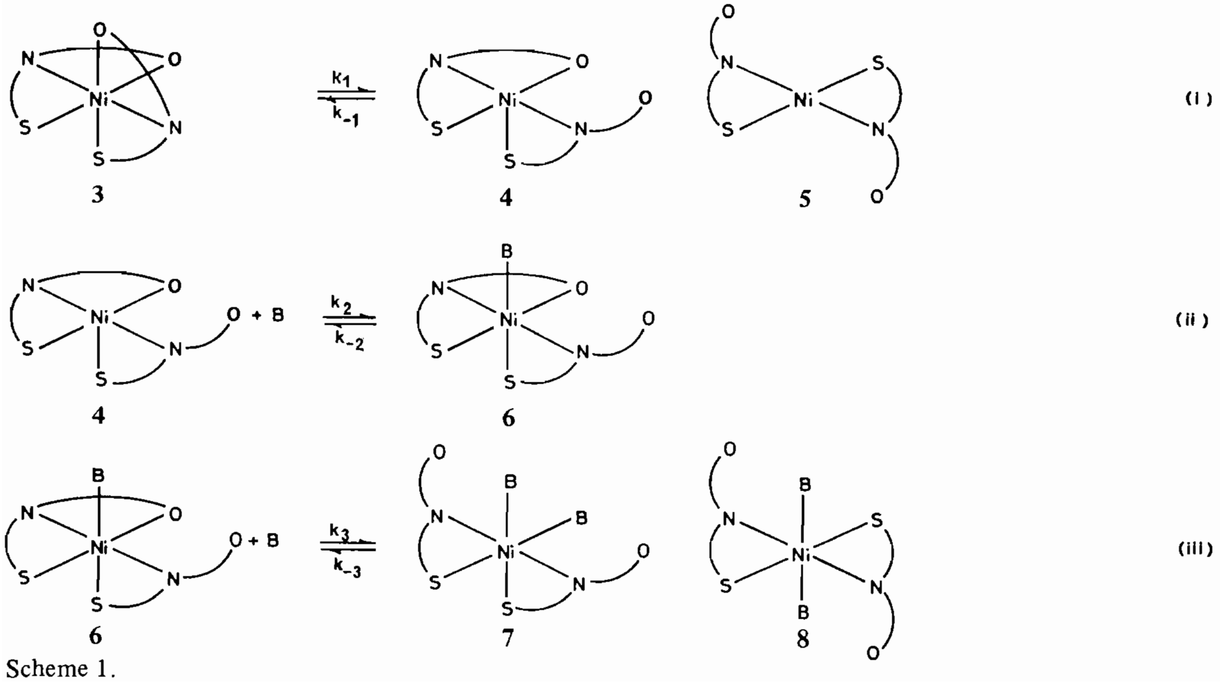


Fig. 3. Correlation between log k_f with (a) the acidity constants (pK_a) for aqueous solution of different bases at 25.0 °C and (b) the equilibrium constants (log K_{eq}) of the reaction of diacetyl(bisbenzoylhydrazonato)nickel(II) with different bases in benzene at 25.0 °C.

reactions between these amines and a standard Lewis acid, diacetyl(bisbenzoylhydrazonato)nickel(II) in benzene [8–10] are shown in Fig. 3a and b. With the exception of the aliphatic secondary amines, a reasonable linear correlation is observed. The deviation from linearity of the data for the aliphatic secondary amines is mainly attributed to the steric requirements imposed by the alkyl groups. The similarity of the pK_a values measured in water may also contribute to the observed deviation.

To account for the results of the presented kinetic measurements a multistep mechanism has to be proposed. In this mechanism the two carbonyl oxygens are displaced in two successive steps by two amine molecules as shown in Scheme 1. The first amine molecule may either react directly with the octahedral (**3**) or with the five coordinate (**4**) and/or the square planar (**5**) form which may be present in equilibrium with the six coordinate species. The electronic spectra of **3** in benzene solution over the temperature range 5.0–45.0 °C, (Fig 4) confirm the presence of reversible equilibria, most probably between **3** and **4** or **5**. Similar equilibria, in aprotic solvents, have been previously reported for many octahedral nickel(II) complexes with tridentate ligands, where one or more coordination sites are displaced [11].

The reactions of these amines with the four coordinate species **5** to give the bisamine adducts are expected to proceed very fast and cannot account for



Scheme 1.

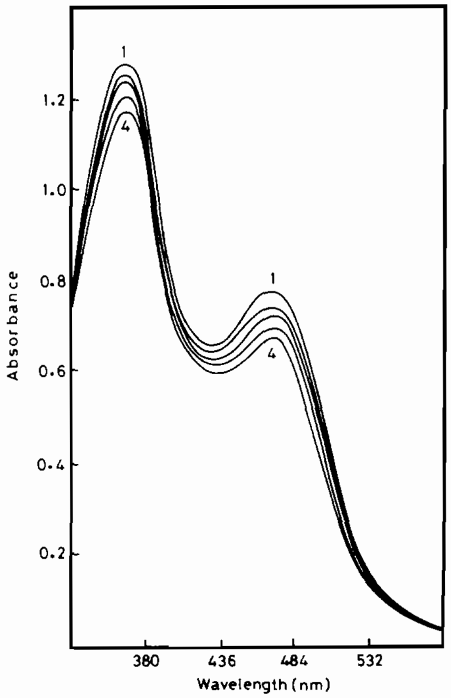


Fig. 4. Spectral changes of **3**, in benzene, with temperature (°C): 1, 6.0; 2, 25.0; 3, 38.0; 4, 45.0.

the present kinetic data [10]. Accordingly the preexistence of the square planar species in benzene solution can be ruled out. Hence, it seems fair to assume that the first amine molecule can preferentially react with **4** rather than **5** giving the octahedral monoamine intermediate **6**. The nucleophilic displacement of the second carbonyl oxygen of **6** by a second amine molecule gives the *cis* bisadduct **7**. Further rearrangement to the *trans* isomer **8** is also possible.

Applying the steady state treatment of **6** and neglecting the reverse reaction (k_{-3}) gives

$$k_{\text{obs}} = \frac{K_1 k_2 k_3 [\text{B}]^2}{k_{-2} + k_3 [\text{B}]} \tag{4}$$

The observed second-order dependence on amine concentration, eqn. (3), suggests that k_3 [B] $< k_{-2}$ and accordingly eqn. (4) is reduced to

$$k_{\text{obs}} = K_1 K_2 k_3 [\text{B}]^2 \tag{5}$$

This kinetic behaviour indicates that the formation of **7** from **6** is the rate determining step while steps (i) and (ii) in Scheme 1 are fast preequilibria. The measured third-order rate constant k_f is equal to $K_1 K_2 k_3$.

Further insight into the mechanism of these nucleophilic substitution reactions is provided from the measured activation parameters ($\Delta H^{\neq}{}_f$ and $\Delta S^{\neq}{}_f$). Table 2 shows that the values of $\Delta H^{\neq}{}_f$ measured for pyridines are more or less similar while higher values are observed for alicyclic and aliphatic secondary amines. Furthermore, the reaction of the pyridines are characterized by more negative $\Delta S^{\neq}{}_f$ values relative to the alicyclic and aliphatic secondary amines.

The rate expression (eqn. (5)) suggests that both $\Delta H^{\neq}{}_f$ and $\Delta S^{\neq}{}_f$ respectively, can be related to the appropriate enthalpy and entropy terms for the individual steps given in Scheme 1 by

$$\Delta H^{\neq}{}_f = \Delta H^{\circ}{}_1 + \Delta H^{\circ}{}_2 + \Delta H^{\neq}{}_3 \tag{6}$$

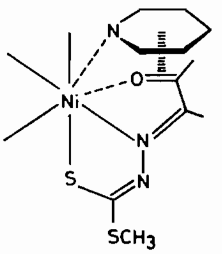
$$\Delta S^{\neq}{}_f = \Delta S^{\circ}{}_1 + \Delta S^{\circ}{}_2 + \Delta S^{\neq}{}_3 \tag{7}$$

The value of $\Delta H^{\circ}{}_1$ is positive as a result of Ni–O bond rupture and is independent on the kind of base. The term $\Delta H^{\circ}{}_2$ which is a measure of the Ni–N bond strength formed in **6** is always negative and is within the range 25.0–37.0 kJ mol^{-1} [12]. More negative or at least comparable $\Delta H^{\circ}{}_2$ values should be expected for the reactions of the more basic alicyclic and aliphatic secondary amines as compared to the less basic pyridines. Hence, the observed low $\Delta H^{\neq}{}_f$ values for pyridines are mainly due to low $\Delta H^{\neq}{}_3$ values rather than the negative contribution of the $\Delta H^{\circ}{}_2$ term. Accordingly, the low values of the third-order rate constants (k_f) measured for the pyridines are due to the more negative entropy terms.

TABLE 2. Rate constants and activation parameters for the reaction of **3** with different amines at 25 °C in benzene

Amine	k_f (mol^{-2} dm^{-6} s^{-1})	$\Delta H^{\neq}{}_f$ (kJ mol^{-1})	$-\Delta S^{\neq}{}_f$ (J mol^{-1} K^{-1})
Pyridine	6.77×10^{-4}	13.61 ± 0.98	260.0 ± 3.2
3-Methylpyridine	1.32×10^{-3}	9.79 ± 0.19	267.3 ± 0.6
4-Methylpyridine	5.08×10^{-3}	11.71 ± 0.51	248.5 ± 1.6
Morpholine	1.76×10^{-1}	19.10 ± 0.99	195.5 ± 3.2
Piperidine	1.25×10	18.84 ± 0.74	160.7 ± 2.4
Diethylamine	5.83×10^{-2}	18.14 ± 0.44	207.8 ± 1.5
Dipropylamine	1.84×10^{-2}	18.40 ± 0.58	216.5 ± 1.9
Dibutylamine	2.25×10^{-2}	20.89 ± 0.10	206.7 ± 0.3

It is apparent from the preceding discussion that in case of the pyridines, the transition state resulting from the addition of a second amine molecule to **6** is more stabilized relative to the other amines. Also, in aprotic solvents such as benzene, no appreciable change in solvation between the ground states and the corresponding transition states is expected. Thus, the more negative entropy assigned for pyridines can be related to a more rigid transition state in the rate controlling step. The pecularity of the reactions of pyridines can be rationalized, on the basis of a possible π interaction in the transition state, between the incoming aromatic pyridines and the leaving carbonyl oxygen or the carbonyl π electrons as shown by **9**. Such a π interaction between the incoming aromatic pyridine ring and the delocalized π system of the in-plane ONS ligand **10** appears also possible. This indicated transition state could account for the low $\Delta H^{\neq}_f$, the more negative $\Delta S^{\neq}_f$, as well as the low k_f values observed for aromatic pyridines relative to other aliphatic amines, where such interactions are not possible. A π interaction in the ground state between the carbonyl π electrons and the aromatic pyridines (**11**) in the monopyridine adduct (**6**) seems also possible, and would give rise to more negative ΔH°_2 and ΔS°_2, values, which in turn lower the corresponding measured $\Delta H^{\neq}_f$ and $\Delta S^{\neq}_f$ values. Indeed, it has previously been indicated that stacking interactions between aromatic ring systems of ligands may influence the rate of complex formation in aqueous solution [13].



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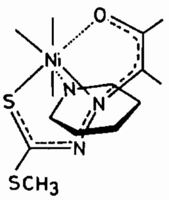

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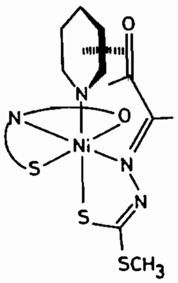

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Furthermore, the more negative entropies of activations associated with reactions of secondary aliphatic amines relative to alicyclic amines might possibly be related to an intramolecular hydrophobic interaction between the aliphatic alkyl side chain of the amine molecule and the delocalized pseudo aromatic in-plane ligand either in the five coordinate intermediate **4** or in the transition state leading to the octahedral bisadduct 7. Such type of interactions would result in more negative ΔS°_2 or $\Delta S^{\neq}_3$ terms relative to alicyclic secondary amines. Hydrophobic interactions between aromatic moieties and aliphatic side chains have been reported for many ternary complexes [14, 15].

Experimental

Materials

Bis[2(1-methyl-2-oxo-propylidenehydrazine-*S*-methylcarbodithioato)NSO(−1)]nickel(II) (3, R = CH_3) was prepared and crystallized as previously described [1]. Analar benzene (Merck) was dried and distilled over sodium before use. Pyridine, 3-methylpyridine and 4-methylpyridine were kept over KOH for two weeks and distilled before use. Piperidine was refluxed for two hours over sodium and distilled. Morpholine was purified by the method described by Perrin *et al.* [16]. Analar diethyl-, di-n-propyl- and di-n-butylamines (Aldrich Chem. Co) were used without further purification.

Kinetic Measurements

The kinetics of these reactions were measured spectrophotometrically using a Pye-Unicam SP-1800 or a Durrum D-101 stopped flow spectrophotometer as described previously [4, 17]. The observed first-order (k_{obs}) and third-order (k_f) rate constants, as well as the activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) were calculated using the previously described procedures [17].

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