The Interaction of Aliphatic Amines with Transition-metal Complexes of Aromatic Di-imines. Part 1. Kinetics and Thermodynamics of Reaction of the Tris(5-nitro-1,10-phenanthroline)nickel(II) Cation with Aliphatic Amines in Dimethylformamide †

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Addition of aliphatic amines to the complex $[Ni(nphen)_3][ClO_4]_2$ (nphen = 5-nitro-1,10-phenanthroline) in dipolar aprotic solvents gives deep red solutions. A spectrophotometric investigation of these processes leading to the formation of 1 : 2 adducts of complex : amine, most likely ' Meisenheimer ' complexes, has been carried out in dimethylformamide. Both equilibrium and rate constants for adduct formation between $[Ni(nphen)_3][ClO_4]_2$ and piperidine, n-propylamine, or benzylamine have been calculated by low-temperature stopped-flow techniques. The reactions are exothermic; the equilibrium data at −50 °C show that co-ordination of the ligand to nickel(II) largely increases the stability of the adduct between nphen and piperidine. Kinetic data are in agreement with a stepwise mechanism in which nucleophilic attack of the amine at the ligand is followed by proton transfer from the species formed to a second amine molecule. Proton transfer is either fast or rate determining depending on the nature of the amine.

Transition metal complexes of aromatic di-imines frequently undergo nucleophilic attack at the co-ordinated ligand by a variety of bases.[1-3] The investigations on this subject have dealt mainly with the reaction of oxygen bases such as hydroxide or alkyloxides with platinum(II),[4] iron(II),[5] and ruthenium(II)[6] complexes of substituted 2,2′-bipyridine and 1,10-phenanthroline.

Very little is known, therefore, on the reactivity of nitrogen bases with this type of substrate. During the course of our studies on substitution reactions at transition metal complexes we have noticed that several alpihatic amines interact with the nickel(II) complex $[Ni(nphen)_3][ClO_4]_2$ (nphen = 5-nitro-1,10-phenanthroline) to give deeply coloured adducts. This reaction can be observed also with nphen complexes of other transition metals such as platinum(II), palladium(II), and iron(II); no interaction occurs, however, when the co-ordinated 1,10-phenanthroline in these complexes bears a substituent other than a nitro- or sulphonato-group. This behaviour is in line with the possibility of nucleophilic attack of the amine at one of the carbon atoms of nphen to give a σ-adduct. The reaction between nitroaromatics and aliphatic amines, which leads to the formation of Meisenheimer complexes, is well known to organic chemists.[7,8] In this paper we report the results of spectrophotometric investigations on the stability and the rate of formation of the adducts between $[Ni(nphen)_3][ClO_4]_2$ and n-propylamine, benzylamine, or piperidine (pip) in dimethylformamide (dmf) at various temperatures.

Experimental

Materials.—The complex $[Ni(nphen)_3][ClO_4]_2$ was prepared following essentially the procedure[9] used to obtain the analogous complex with 1,10-phenanthroline. No attempt was made to separate the possible geometric isomers of this compound. Piperidine, n-propylamine, and benzylamine were distilled over potassium hydroxide pellets. Piperidinium perchlorate, n-propylammonium perchlorate, and benzylammonium perchlorate were obtained on mixing equimolar amounts of the appropriate amine and perchloric acid in ethanol. The resulting solutions were evaporated under reduced pressure and the oily substances obtained were crystallised twice from absolute ethanol. Dimethylformamide was distilled under reduced pressure and then stored over molecular sieves. The other products were of reagent grade.

Kinetics.—The kinetics were performed under pseudo-first-order conditions with respect to the complex, in the temperature range −50 to −10 °C. The reaction course was followed spectrophotometrically by using a HI-TECH SF-3 stopped-flow spectrophotometer. The oscilloscopic traces, stored on a Gould Advance 054100 oscilloscope and then recorded on a Radiometer REC 61 potentiometric recorder, were analysed on plotting the values of $\ln(A_\infty - A_t)$ against time; A_t is the mixture absorbance at time t and A_∞ the mixture absorbance after six to seven half-lives. The observed rate constants (see SUP 23870) were determined at seven or more different amine concentrations, the complex concentration being usually in the range 5×10^{-5} to $2 \cdot 10^{-4}$ mol dm^{-3}. The concentrations were corrected for density change with the temperature. The $k_{obs.}$ values, reproducible to better than ±5%, were independent of the wavelength. Under the experimental conditions used the effect of ionic strength proved to be negligible.

Thermodynamics.—The equilibrium constants were determined spectrophotometrically. The equilibrium concentration of the red adduct was evaluated on the basis of the absorbance of the reaction mixture read directly, at one wavelength in the range 400—500 nm, on the stopped-flow oscilloscope immediately after the colour-forming reaction was complete. The absorption coefficients of the adducts between $[Ni(nphen)_3][ClO_4]_2$ and the three amines were evaluated from the absorbance of mixtures of the complex at a known concentration and a large excess of amine. In the spectral range used, species other than the red adducts have negligible absorption. Amine (NR^1R^2H) and $NR^1R^2H_2^+$ concentrations were in all cases much larger than that of the complex; consequently their equilibrium concentrations could be considered equal to the analytical ones. The ionic strength of the solutions was kept constant at 0.005 mol dm^{-3} by means of $NaClO_4$. The values of

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† *Non-S.I. unit employed:* 1 cal = 4.184 J.

Supplementary data available (No. SUP 23870, 5 pp.): observed rate constants and equilibrium constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

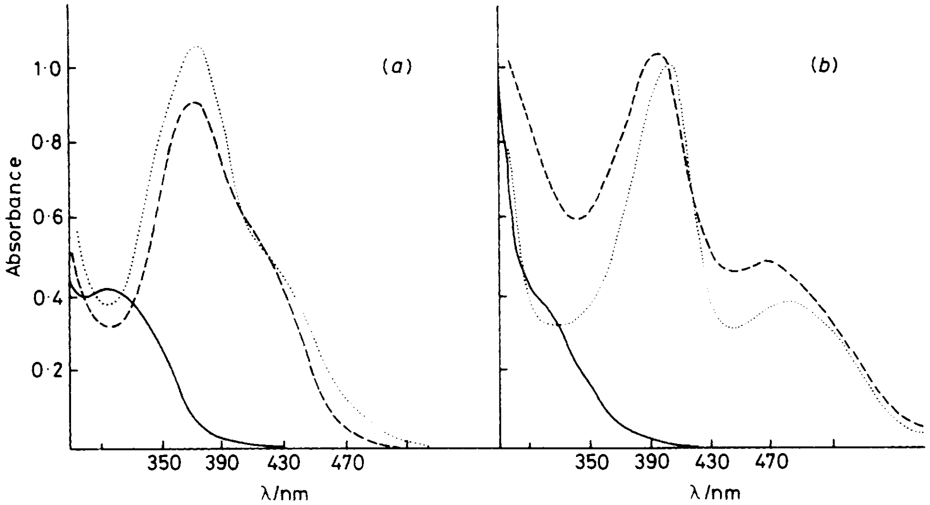

Figure 1. Spectra of nphen and $[Ni(nphen)_3][ClO_4]_2$ in the presence of bases: (*a*) [nphen] = 1×10^{-4} mol dm^{-3} (——), + OMe^- (3×10^{-2} mol dm^{-3}) (— — —), + pip (3 mol dm^{-3}) (· · · · ·); (*b*) $[Ni(nphen)_3][ClO_4]_2$ = 7.5×10^{-5} mol dm^{-3} (——), + OMe^- (3×10^{-2} mol dm^{-3}) (— — —), + pip (3×10^{-2} mol dm^{-3}) (· · · ·)

the equilibrium constants, which are averages of at least three determinations, were reproducible to better than ±10%.

Results and Discussion

On addition of aliphatic amines to a dmf solution of $[Ni(nphen)_3][ClO_4]_2$ a deep red colour develops instantly. The visible and u.v. spectrum of the reaction mixture is characterised by the two maxima at 470—500 and 390—410 nm, typical of σ-Meisenheimer complexes.[7,8] These spectral variations (Figure 1) compare well with those relative to the analogous reaction of the unco-ordinated ligand nphen either with amines or sodium methoxide. The last process, in the solvent dimethyl sulphoxide (dmso), has been shown[10] by ^1H n.m.r. to lead to the formation of a σ-adduct by attack of OMe^- at carbon C-6 of nphen. In the present case, unfortunately, as often observed for transition metal complexes of aromatic di-imines, ^1H n.m.r. measurements are prevented by spectral broadening in dmf or dmso solutions of $[Ni(nphen)_3][ClO_4]_2$.

As expected for nucleophilic addition at nitroaromatics,[7,8] neither tertiary aliphatic amines * nor aromatic amines interact with nphen either in its free form or co-ordinated to nickel(II) in the complex here studied. In the reaction between $[Ni(nphen)_3][ClO_4]_2$ and aliphatic amines, the initial formation of a red adduct is followed by several slow processes leading to unidentified products. This behaviour is observed in many dipolar aprotic solvents such as dmf, dmso, MeCN, *etc.*; however, when the reaction is performed in hydroxylic solvents both the colour intensity and the fading time of the red adduct are strongly reduced so that the process can hardly be observed.

Addition of increasing amounts of amine to a dmf solution of the complex, at fixed concentration, leads to increased absorbance. By contrast, addition of acid or protonated amine ($NR^1R^2H_2^+$) causes fading or disappearance of the colour, which can, however, be restored by further addition of amine. The quantitative effect of amine and $NR^1R^2H_2^+$ on the process has been examined by the analysis of the spectral variations observed on treating fixed amounts of amine and/or $NR^1R^2H_2^+$. Although the colour-forming reaction and that of subsequent fading are under most experimental conditions well separated in time-scale, it was found convenient to evaluate the absorbance of the reaction mixture from the infinity value of the exponential curves obtained, by the stopped-flow technique, on mixing the complex with the amine and/or $NR^1R^2H_2^+$. In this way it could also be established that the colour-forming reaction occurs only in one step at all the wavelengths used. Due to the fact that at room temperature the reactions lie well over to the left, most of the experiments were performed at low temperature, taking advantage of the exothermicity of the process.

The experimental results (Table 1), obtained at a fixed ionic strength of 0.005 mol dm^{-3}, show that the equilibrium for the red adduct formation obeys equation (1). Accordingly the process conforms to the stoicheiometry of equation (2).

$$K = \frac{[(\text{red adduct})^+][NR^1R^2H_2^+]}{[Ni(nphen)_3{}^{2+}][NR^1R^2H]^2} \qquad (1)$$

$$[Ni(nphen)_3]^{2+} + 2\,NR^1R^2H \rightleftharpoons (\text{red adduct})^+ + NR^1R^2H_2^+ \qquad (2)$$

The $\Delta H^\ominus$ values for the reactions studied have been obtained from the dependence of the equilibrium constants K on temperature; the entropy changes have been evaluated by the relation (3). These thermodynamic parameters together with the

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus \qquad (3)$$

equilibrium constants at 25 °C are listed in Table 1. Inspection of this Table shows that the equilibrium constants vary with the nature of the amine; in fact the order of increasing stability parallels that of increasing basicity of the amines, as expressed by their pK_a values in water. The adducts between aliphatic amines and uncomplexed nphen are far less stable. Complexation of nphen with nickel(II) enhances by *ca.* 1 000 fold the stability of the adduct with piperidine, the values of K at −50 °C in dmf being 0.03 dm^3 mol^{-1} for nphen and 20.63 dm^3 mol^{-1} for $[Ni(nphen)_3][ClO_4]_2$. The equilibrium

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* Actually, solutions of triethylamine and $[Ni(nphen)_3][ClO_4]_2$ in dmf slowly turn red. However, after careful purification of the amine the colour intensity is dramatically reduced; so it seems that impurities present in the triethylamine, possibly primary or secondary amines, rather than the triethylamine itself are responsible for the colour formation.

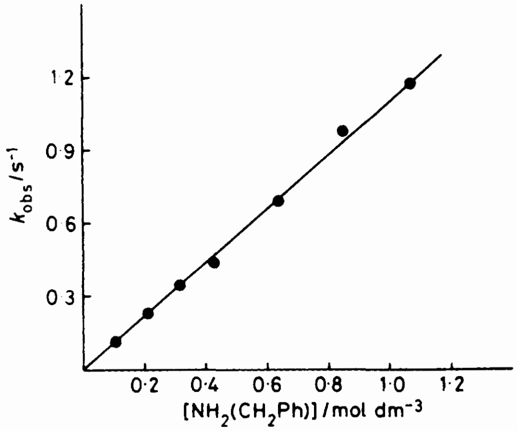


Figure 2. Dependence on amine concentration of the observed rate constant, $k_{obs.}$, of the colour-forming reaction between $[Ni(nphen)_3][ClO_4]_2$ and benzylamine in dmf at −50 °C

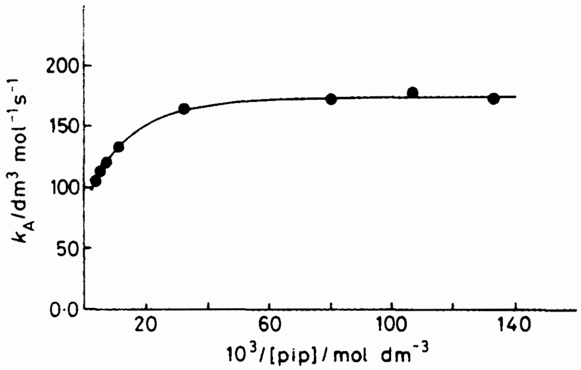
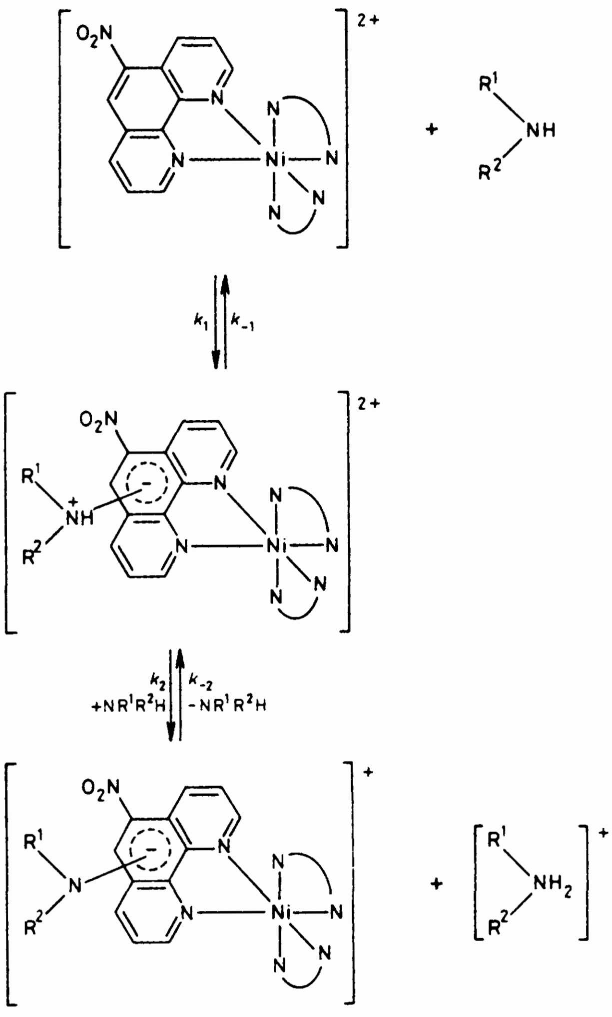


Figure 3. Dependence on amine concentration of the second-order rate constant, k_A ($k_{obs.}/[NR^1R^2H]$), for colour formation between $[Ni(nphen)_3][ClO_4]_2$ and piperidine in dmf at −50 °C

constants between nphen and n-propylamine or benzylamine were too low to be evaluated even at −50 °C. As expected for processes largely shifted to the left, the $\Delta G^\ominus$ values at 25 °C are all positive. The instability of the adducts produced, at room temperature, is due to entropic factors; in fact, although the reactions are exothermic, the entropy values are so largely negative as to lead to positive values of free energy. Negative values of $\Delta S^\ominus$ are in agreement with the nature of the reactions in which the number of free particles decreases; the change of solvation from reactants to products probably leads also to a decrease in entropy.

The values of observed rate constants, $k_{obs.}$, were obtained at low temperature, by using a large excess of amine with respect to the complex. This was necessary, both to assure pseudo-first-order conditions and to force the reactions to completion. The $k_{obs.}$ values thus obtained are independent of the ionic strength of the solutions but increase in all cases on increasing amine concentration. However, the dependence of the rate coefficients on the amine concentration changes according to the type of amine. Thus, while in the case of n-benzylamine and n-propylamine the observed rate constants increase linearly on increasing amine concentration (Figure 2), when piperidine is considered plots of $k_A = k_{obs.}/[pip]$ *versus* [pip] are curved and level off at high base concentration (Figure 3).

The kinetic behaviour of the complex $[Ni(nphen)_3][ClO_4]_2$ can be interpreted in terms of the stepwise mechanism (4), in



(4)

which the nucleophilic attack of the amine at one of the carbon atoms of the aromatic ring is followed by proton transfer from the species formed to a second amine molecule (under the high amine concentrations used proton transfer to dmf is a possible but negligible route). For such a mechanism, if we apply the steady-state hypothesis to the transient species $[Ni(nphen)_2(nphen{\cdot}NR^1R^2)]^{2+}$, rate law (5) is obtained. When NR^1R^2H is sufficiently high so that $k_2[NR^1R^2H] \gg k_{-1}$, k_A is equal to k_1. Equation (5) can be rearranged to give equation (6). This last

$$k_A = \frac{k_{obs.}}{[NR^1R^2H]} = \frac{k_1k_2[NR^1R^2H]}{k_{-1} + k_2[NR^1R^2H]} \qquad (5)$$

$$\frac{1}{k_A} = \frac{1}{k_1} + \frac{k_{-1}}{k_1k_2[NR^1R^2H]} \qquad (6)$$

relation was used to evaluate the k_1 values for reaction of piperidine, from the intercept of the straight lines obtained on plotting $[pip]/k_{obs.}$ *versus* [pip]. These values are reported in Table 2. In the case of n-propylamine and benzylamine, for which $k_A = k_1$ over the entire range of amine concentrations used, the k_1 values could be obtained directly from the slopes of the linear plots of $k_{obs.}$ *versus* $[NR^1R^2H]$. These values, together with those of the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are also reported in Table 2.

It can be seen that the k_1 value is much larger for piperidine than it is for benzylamine and n-propylamine; this is in line with the higher basicity of the secondary amines with respect

Table 1. Equilibrium and thermodynamic data for reaction of $[Ni(nphen)_3][ClO_4]_2$ (1×10^{-4} mol dm^{-3}) with amines in dmf; $I = 5 \times 10^{-3}$ mol dm^{-3}

Amine (NR^1R^2H)	T/°C	10^2[pip]/ mol dm^{-3}	10^3[Hpip·ClO_4]/ mol dm^{-3}	K/ dm^3 mol^{-1}	ln K [a]	$\Delta H^{\ominus}$/ kcal mol^{-1}	$\Delta S^{\ominus}$/ cal K^{-1} mol^{-1}	$\Delta G^{\ominus}$/ kcal mol^{-1}
Piperidine	−50			20.6 (0.03) [b]	0.185	−9.0 ± 0.2	−33 ± 1	1.0 ± 0.1
	−30	1.5	1.5	5.69				
		5.0	1.0	5.35				
		5.0	5.0	5.64				
		5.0	10.0	5.75				
		7.5	1.5	5.39				
		15.0	1.5	5.42				
	−20			2.76				
	−10			1.33				
	0			0.72				
n-Propylamine	−30			1.85	0.123	−7.2 ± 0.1	−28 ± 1	1.3 ± 0.0
	−20			1.05				
	−10			0.59				
	0			0.36				
Benzylamine	−30			0.16	0.0075	−7.9 ± 0.5	−36 ± 1	2.9 ± 0.1
	−20			0.08				
	−10			0.04				
	0			0.03				

[a] Values extrapolated at 25 °C. [b] Value refers to un-co-ordinated nphen.

Table 2. Kinetic and activation parameters for reaction of $[Ni(nphen)_3][ClO_4]_2$ with amines in dmf

Amine (NR^1R^2H)	k_1/dm^3 mol^{-1} s^{-1}	T/°C	k_{25} */ dm^3 mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
Piperidine	135 ± 3	−50	4.275×10^3	5.6 ± 0.3	−19 ± 1
	219 ± 5	−40			
	420 ± 12	−30			
	675 ± 32	−20			
n-Propylamine	4.57 ± 0.11	−50	205.25	6.0 ± 0.2	−24 ± 1
	8.99 ± 0.26	−40			
	15.16 ± 0.12	−30			
	26.24 ± 0.62	−20			
Benzylamine	1.13 ± 0.03	−50	49.38	6.1 ± 0.2	−26 ± 1
	2.09 ± 0.06	−40			
	3.80 ± 0.03	−30			
	6.70 ± 0.17	−20			

* Extrapolated values.

to the primary ones. While the activation entropy values, in agreement with the associative character of the reaction, are largely negative, the activation enthalpies are all very small. This seems to be a feature of this type of process; similar activation parameters have been reported by Orvik and Bunnett [11] for the analogous reaction between 2,4-dinitro-1-naphthyl ethyl ether and n-butylamine in dmso.

The experimental data show that, while in the case of n-propylamine and benzylamine proton transfer from $[Ni(nphen)_2(nphen{\cdot}NR^1R^2)]^{2+}$ is fast under all experimental conditions used, when piperidine is considered proton transfer is fast only at high amine concentration. The plot of Figure 3 clearly implies, in fact, that there is a change in the rate-determining step with concentration; at low amine concentration, when $k_{-1} \leqslant k_2$[pip], proton transfer is rate determining. Proton transfer from NH-acids to N-bases is usually assumed to be diffusion controlled. Nevertheless, recent investigations [12,13] have shown that steric effects can reduce the rate of proton transfer below that expected for diffusion-controlled processes; it has been stated that deprotonation of Meisenheimer-like complexes by amines is usually lowered by a factor of over 100 due to steric factors. Our reactions seem to be in line with such a statement in that proton transfer is rate determining for the system involving the secondary amine piperidine, for which steric effects are likely to be larger than for the primary amines.

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