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Reactivity of Metal Chelates of Sulphur Containing Ligands towards Lewis Bases. Part II. Reaction of Bis(S-methyl-N-arylidenehydrazinecarbodithioate)nickel(II) Chelates with Pyridines and 2,2′-Bipyridyl

M. F. ISKANDER*, L. EL-SAYED, L. LABIB and A. EL-TOUKHY

University of Alexandria Research Centre (UNARC) and Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt

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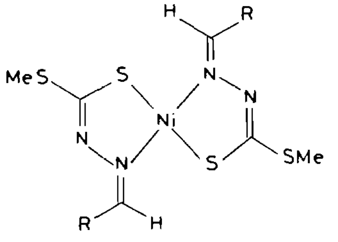
The reaction of bis(S-methyl-N-arylidenehydrazinecarbodithioate)nickel(II) chelates with pyridine, 3-methylpyridine, 4-methylpyridine and 2,2′-bipyridyl has been studied in benzene solution. The stability constants as well as the thermodynamic parameters for adduct formation were measured spectrophotometrically. The obtained results suggest the formation of octahedral bis-adducts with unidentate pyridines, while cis-octahedral monoadducts are formed from the reaction of 2,2′-bipyridyl with p-methoxy, p-methyl and unsubstituted chelates. The p-chloro derivative, however, forms a five-coordinate monoadduct where one of the hydrazone molecules behaves as unidentate ligand. The kinetics of bipyridyl adduct formation were followed by means of stopped flow techniques. The kinetic data suggest the rapid formation of five-coordinate intermediate, in which the bipyridyl molecule reacts as a unidentate ligand, followed by slow rate determining bipyridyl ring closure.

Introduction

Due to their carcinostatic activity, there has been much recent interest in the transition metal chelates of Schiff bases derived from S-methylhydrazinecarbodithioate [1, 2]. A detailed study of the interaction of these chelates with different types of nitrogenous Lewis bases may increase the understanding of the mode of action within the biological systems [3].



(I)

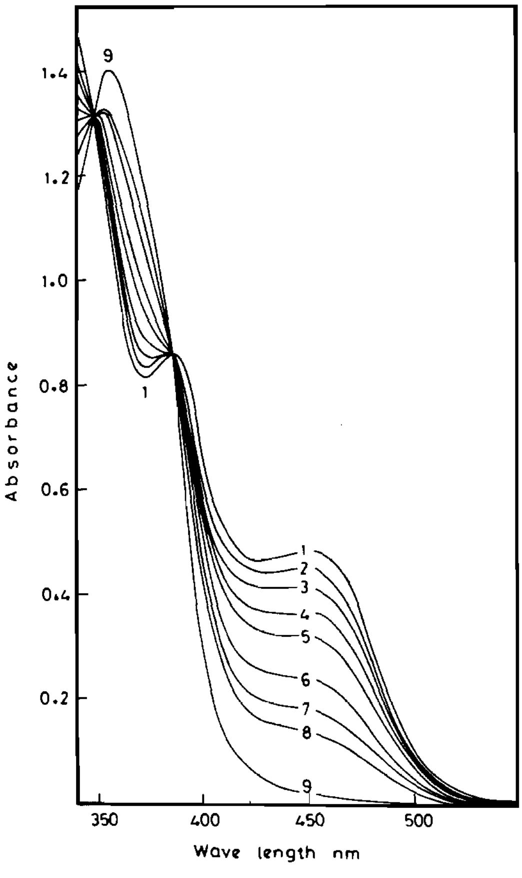


Fig. 1. Spectrophotometric titration of $Ni(p\text{-}MeC_6H_4CH{=}N{-}N{=}CSSMe)_2$ (8.86×10^{-5} mol dm^{-3}) with pyridine in benzene-solution at 25 °C; C_{Py} mol dm^{-3}: 1) 0.000, 2) 0.1235, 3) 0.2470, 4) 0.3705, 5) 0.4940, 6) 0.7410, 7) 0.9880, 8) 1.2350 and 9) 6.1735.

In the present report, the thermodynamics and kinetics of the reaction between square planar bis(S-methyl-N-arylidenehydrazinecarbodithioate)nickel(II) chelates (I) [4, 5] with pyridine type bases, as

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*Author to whom correspondence should be addressed.

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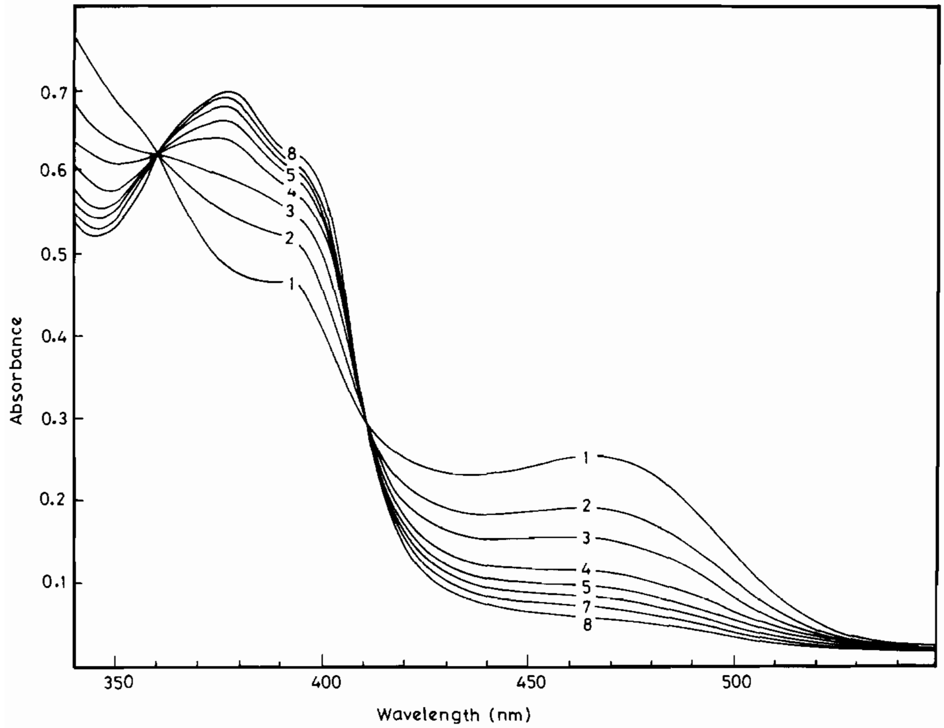


Fig. 2. Spectrophotometric titration of Ni(p-ClC$_6$H$_4$CH=N–N=CSSMe)$_2$ (2.50×10^{-5} mol dm^{-3}) with 2,2'-bipyridyl in benzene solution at 25 °C. $C_{bipy} \times 10^4$ mol dm^{-3}: 1) 0.00, 2) 0.500, 3) 1.000, 4) 2.000, 5) 3.000, 6) 4.000, 7) 6.000, 8) 7.000.

well as 2,2'-bipyridyl in benzene, have been studied. In spite of the limited number of substituents (I, R = p-MeOC$_6$H$_4$, p-MeC$_6$H$_4$, Ph and p-ClC$_6$H$_4$) studied, due to insolubility factors, attention has been directed towards determining how substituents on the in-plane ligands can modify the thermodynamics and kinetics of Lewis acid–base interaction.

Results and Discussion

Formation Constants and Thermodynamic Parameters

Addition of pyridine type base, B (pyridine, 3-methylpyridine or 4-methylpyridine) to a benzene solution of bis(S-methyl-N-arylidenehydrazinecarbodithioate)nickel(II) chelate, NiL$_2$ (I, R = Ph, p-MeOC$_6$H$_4$, p-MeC$_6$H$_4$ or p-ClC$_6$H$_4$) results in pronounced spectral changes. Typical spectral variations as the Lewis base B concentration increases are shown in Fig. 1. Within the base concentration range (0.00–6.175 mol dm^{-3}), the successive absorption curves pass through sharp isosbestic points at 350 and 380 nm. Analysis of the previous spectrophotometric titrations by means of the graphical method of Coleman *et al.* [6] reveals the presence of only two absorbing species, namely the square planar Ni(II) chelate (NiL$_2$) and the base adduct NiL$_2$B$_n$. Such equilibria can be represented by the stoichiometric equation

$$NiL_2 + nB \rightleftharpoons NiL_2B_n$$

In these systems, a large excess of the Lewis base was used to achieve complete adduct formation and it is assumed that $C_B = [B]$. The adduct formation constant K can be calculated using the logarithmic eqn. 1:

$$K = [NiL_2B_n]/[NiL_2]\,[B]_n$$

$$\log (A_o - A)/(A - A_\infty) = \log K + n \log C_B \qquad (1)$$

where A_o, A, A_∞ and n have their usual significance [7].

For all systems studied, plots of log $(A_o - A)/(A - A_\infty)$ against log C_B gave straight lines and from the gradient and intercept of these lines both n and log K can be evaluated.

The spectral variations of I (R = Ph, p-MeOC$_6$H$_4$, p-MeC$_6$H$_4$ and p-ClC$_6$H$_4$) as the concentration of 2,2'-bipyridyl increases were also recorded and typical series of spectra are shown in Fig. 2. Here again sharp isosbestic points at 360 and 412 nm are observed.

Due to the stability of the bipyridyl adducts, the logarithmic eqn. 1 used for the determination of adduct formation constants with unidentate Lewis bases cannot be applied for bipyridyl adducts. Instead, however, eqn. 2 [8] was adequately used for computing bipyridyl adduct formation constants:

TABLE I. Stability Constants and Thermodynamic Parameters of Bis- and Monoadducts in Benzene at 25 °C.

Ni(II) chelate R	Log K	$-\Delta G°$ kJ mol^{-1}	$-\Delta H°$ kJ mol^{-1}	$-\Delta S°$ J mol^{-1} K^{-1}
i) *Bispyridine adducts*				
$p-MeOC_6H_4$	0.037 ± 0.018	−0.21	50.5 ± 3.2	170 ± 11
$p-MeC_6H_4$	0.287 ± 0.010	1.64	51.0 ± 4.0	166 ± 12
Ph	0.580 ± 0.012	3.32	51.5 ± 2.8	162 ± 10
$p-ClC_6H_4$	1.120 ± 0.025	6.38	67.0 ± 3.4	203 ± 10
ii) *Bis-3-methylpyridine adducts*				
$p-MeOC_6H_4$	0.127 ± 0.009	0.73	52.0 ± 2.9	172 ± 10
$p-MeC_6H_4$	0.510 ± 0.014	2.91	53.0 ± 3.3	168 ± 12
Ph	0.905 ± 0.017	5.17	60.0 ± 2.8	184 ± 10
$p-ClC_6H_4$	1.510 ± 0.020	8.62	66.0 ± 2.5	193 ± 10
iii) *Bis-4-methylpyridine adducts*				
$p-MeOC_6H_4$	0.529 ± 0.020	3.02	54.0 ± 3.0	171 ± 10
$p-MeC_6H_4$	0.819 ± 0.027	4.68	55.0 ± 2.8	169 ± 10
Ph	1.160 ± 0.018	6.63	70.2 ± 2.5	213 ± 8
$p-ClC_6H_4$	1.850 ± 0.020	10.57	79.0 ± 2.8	230 ± 11
iv) *Mono-bipyridyl adducts*				
$p-MeOC_6H_4$	3.06 ± 0.030	17.47	47.0 ± 3.1	99 ± 10
$p-MeC_6H_4$	3.32 ± 0.028	18.96	51.2 ± 2.6	108 ± 8
Ph	3.65 ± 0.025	20.84	58.4 ± 2.7	126 ± 10
$p-ClC_6H_4$	3.92 ± 0.020	22.37	47.0 ± 2.0	83 ± 7

$$(A_o - A)/(A - A_\infty) =$$

$$= K[C_{bipy} - n(A_o - A)/(A_o - A_\infty)C_{NiL_2}]^n \qquad (2)$$

Plots of $(A_o - A)/(A - A_\infty)$ against $[C_{bipy} - n(A_o - A)/(A_o - A)C_{NiL_2}]^n$ gave straight lines passing through the origin only when n = 1. The values of K were obtained from the gradients of these plots. The enthalpy ($-\Delta H°$) and entropy ($-\Delta S°$) changes for both pyridines and bipyridyl adduct formation reactions can be calculated from the variation of log K with temperature (20–40 °C). The formation constants and the thermodynamic parameters are listed in Table I.

The present spectrophotometric data suggest that the reaction of I (R = Ph, $p-MeOC_6H_4$, $p-MeC_6H_4$ and $p-ClC_6H_4$) with pyridine, 3-methylpyridine and 4-methylpyridine in benzene affords hexacoordinate bis-base adducts NiL_2B_2 (n = 2) [9], while bipyridyl affords the corresponding monoadduct. With different axial unidentate Lewis bases, the measured values of log K and therefore of $-\Delta G°$ show the expected increase with the donor power of heterocyclic nitrogen atoms, as measured by the acidity constant pK_a of the base. It is also apparent from the data given in Table I that the substituents on the in-plane ligands influence greatly the Lewis acidity of the square planar nickel(II) chelates. This is evident from the linear correlation between log K and the Hammett substituent constant (σ), Fig. 3. The presence of an electron-withdrawing substituent results in an increase of the formal positive charge on the Ni(II) and thereby increases the acidity of the square planar nickel(II) chelate. The reverse situation is observed with electron-releasing groups.

The adduct formation reactions of these unidentate pyridine type bases with (I) form an isoequilibrium series with temperature β = 422 K [10]. Since the experimental temperature range (298–312 K) is far enough away from the determined isoequilibrium temperature, the observed trend in log K values is a sensitive measure of acidity of the parent square planar nickel(II) chelates.

The observed extra stability of bipyridyl adducts as indicated by the high $-\Delta G°$ values relative to the corresponding bispyridine adducts suggests the expected bidentate nature of the bipyridyl molecule in these adducts. A correlation of log K for bipyridyl adduct formation reaction with Hammett substituent constant (σ), Fig. 4, shows that the

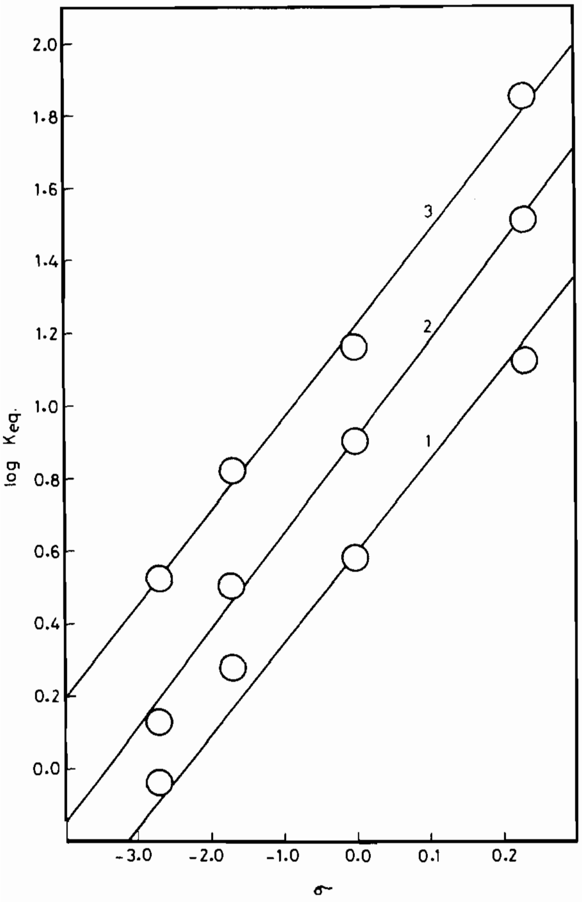


Fig. 3. Plots of log K_{eq} for 1) pyridine, 2) 3-Methylpyridine and 3) 4-Methylpyridine adduct formation with I (R = p-$MeOC_6H_4$, p-MeC_6H_4, Ph and p-ClC_6H_4) chelates against Hammett substituent constants (σ).

p-chloro derivative (I, R = p-ClC_6H_4) deviates from linearity as compared with other substituents (I, R = p-$MeOC_6H_4$, p-MeC_6H_4 and Ph). Also a plot of $-\Delta H^\circ$ against $-\Delta S^\circ$ (Fig. 5) shows that the p-$MeOC_6H_4$ and p-MeC_6H_4 derivatives, as well as the unsubstituted member, form an isoequilibrium series while the corresponding p-chloro derivative does not belong to any such series. Furthermore, the data cited in Table I reveal that the values of $-\Delta H^\circ$ for the monobipyridyl adduct formation of I (R = p-$MeOC_6H_4$, p-MeC_6H_4 and Ph) are more or less similar and equal to those measured for the corresponding bispyridine adducts. This is expected, since $-\Delta H^\circ$ is a measure of the bond energy and two Ni–N bonds are formed in both bispyridine and monobipyridyl adducts. Consequently the extra stability of bipyridyl systems can be attributed to entropy effects. In the case of (I, R = p-ClC_6H_4) however, the measured $-\Delta H^\circ$ of monobipyridyl adduct is much smaller than that measured for the corresponding bispyridine adduct.

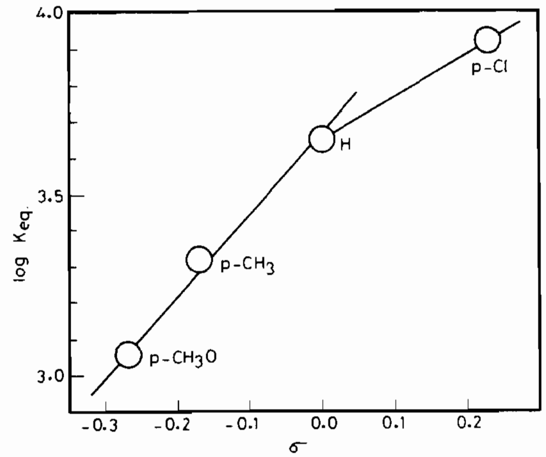


Fig. 4. Plots of log K_{eq} for 2,2'-bipyridyl addition to I (R = p-$MeOC_6H_4$, p-MeC_6H_4, Ph and p-ClC_6H_4) against Hammett substituent constants (σ).

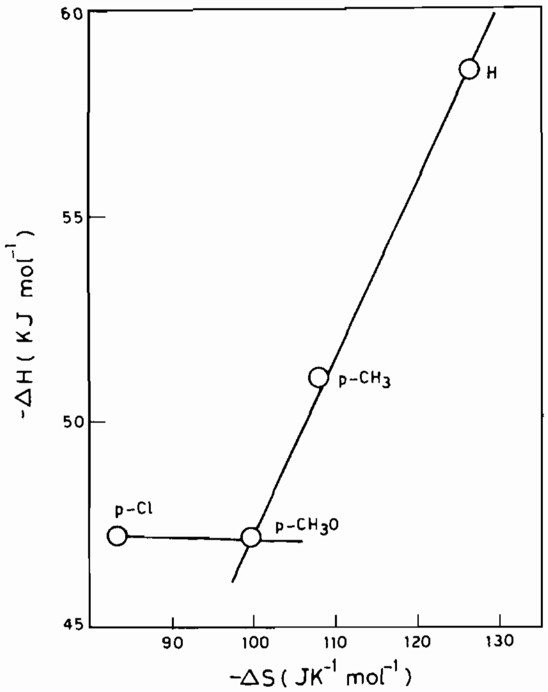


Fig. 5. Isoequilibrium relationship for 2,2'-bipyridyl addition to I (R = p-$MeOC_6H_4$, p-MeC_6H_4, Ph and P-ClC_6H_4).

An inspection of the previous results reveals that the nature of the monobipyridyl adduct formed with the p-chloro chelate (I, R = p-ClC_6H_4) differs from that of the other members of this series. It seems reasonable to assume that the reaction of bipyridyl with I (R = p-$MeOC_6H_4$, p-MeC_6H_4 and Ph) chelates, in benzene, proceeds with the formation of bis-octahedral monoadducts (III-a). However, the presence of electron-attracting p-chloro substituent on the in-plane ligands undoubtedly will increase the Lewis acidity of (I) as evident from the higher $-\Delta G^\circ$ rela-

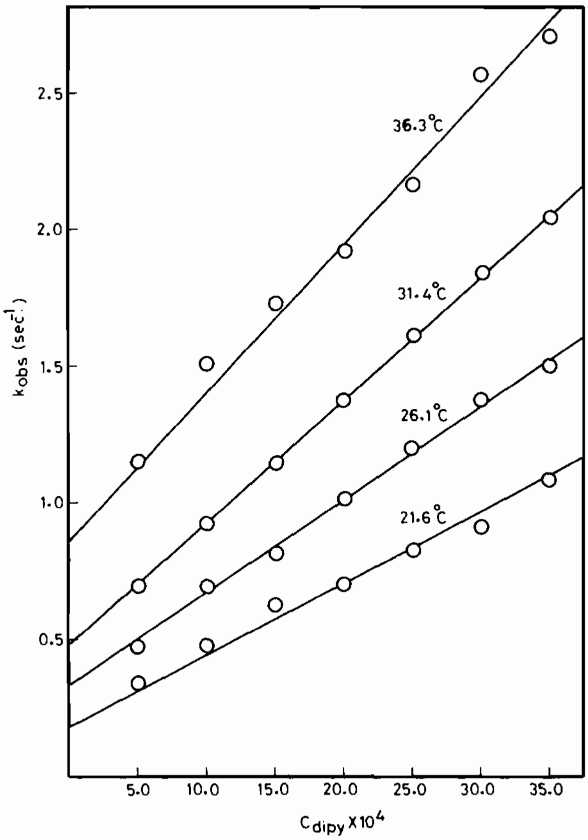
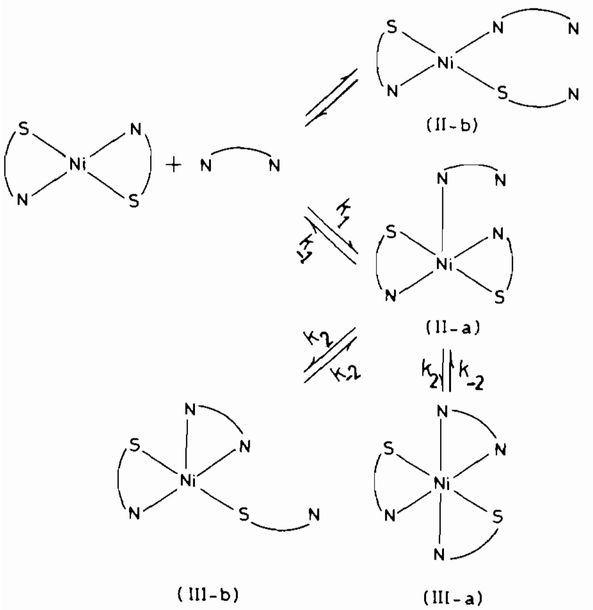


Fig. 6. Pseudo first order rate constants, k_{obs}, as a function of 2,2′-bipyridyl concentration for Ni(p-MeC$_6$H$_4$CH=NN=CSSMe)$_2$ at different temperatures.



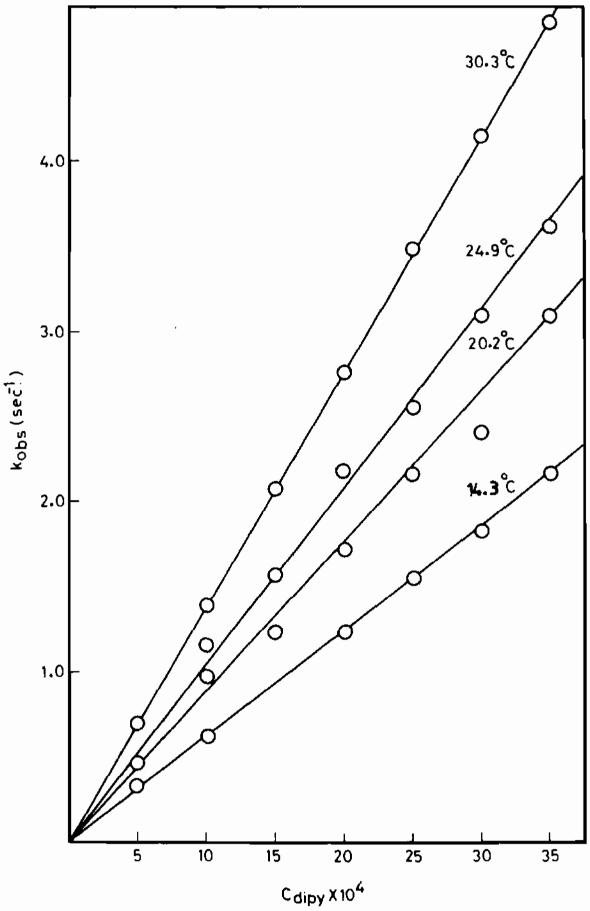


Fig. 7. Pseudo first order rate constants, k_{obs}, as a function of 2,2′-bipyridyl concentration for Ni(p-ClC$_6$H$_4$CH=N–N=CSSMe)$_2$ at different temperatures.

tive to other substituents, but at the same time will decrease the Ni–N bond strength in the parent square planar chelate making it more susceptible to bond rupture on adduct formation. The resulting adduct may attain the five-coordinate structure (III-b) in which one of the hydrazone molecules behaves as a unidentate ligand and coordinates to the Ni(II) ion *via* the thiol sulphur, while the other hydrazone ligand retains its bidentate nature. The observed lower enthalpy of the monobipyridyl adduct of the p-chloro derivative ($-\Delta H^{\circ}_{bipy}$) as compared to that of the corresponding bispyridine adduct ($-\Delta H^{\circ}_{py}$) is in agreement with this assumption. The difference $\Delta H^{\circ}_{bipy} - \Delta H^{\circ}_{py}$ can be related to the energy required for the in-plane Ni–N bond breaking on adduct formation. A similar explanation was proposed by Dakternieks and Graddon [11] to account for the low value of $-\Delta H^{\circ}$ for the addition of 2,9-dimethyl-1,10-phenanthroline to the bis(dialkylphosphorodithioate)nickel(II) chelate in which Ni–S bond rupture is confirmed [12].

Kinetic Measurements and Reaction Mechanism

It was possible to follow the kinetics of bipyridyl addition to I (R = p-MeOC$_6$H$_4$, p-MeC$_6$H$_4$, Ph and

TABLE II. Rate and Equilibrium Constants for the Reaction of 2,2'-Bipyridyl with (I) Chelates in Benzene at Different Temperatures.*

Ni(II) Chelate R	Temp. °C	No. of solns	k_f ($dm^3\ mol^{-1}\ sec^{-1}$)	k_b (sec^{-1})	$10^{-2}\ k_f/k_b$ ($dm^3\ mol^{-1}$)
p-$MeOC_6H_4$	21.2	12	266 ± 2	0.179 ± 0.02	14.63 ± 1.93
	26.4	10	342 ± 8	0.328 ± 0.02	10.45 ± 0.62
	30.4	10	451 ± 3	0.478 ± 0.07	9.44 ± 0.15
	35.3	8	545 ± 33	0.857 ± 0.07	6.35 ± 0.67
p-MeC_6H_4	21.6	10	371 ± 12	0.143 ± 0.02	26.04 ± 3.24
	26.1	8	430 ± 12	0.238 ± 0.02	18.09 ± 1.66
	31.4	10	594 ± 36	0.406 ± 0.06	14.63 ± 2.37
	36.3	8	729 ± 37	0.687 ± 0.01	10.62 ± 1.09
Ph	25.0	10	554 ± 4	0.132 ± 0.01	41.87 ± 4.03
	30.0	6	609 ± 4	0.195 ± 0.01	31.87 ± 2.02
	35.0	6	753 ± 3	0.347 ± 0.01	21.73 ± 0.52
	40.0	8	949 ± 10	0.598 ± 0.03	15.88 ± 0.86
p-ClC_6H_4	14.3	12	632 ± 5		
	20.2	10	874 ± 8		
	24.9	10	1062 ± 8		
	30.3	10	1382 ± 22		

*C_{bipy} varies from 5.00 to 200.0 × 10^{-4} mol dm^{-3}.

p-ClC_6H_4) by means of stopped flow techniques. However, the formation of the corresponding pyridine and substituted pyridine adducts was too fast to be measured. All kinetic runs were conducted at constant concentration of the square planar nickel(II) chelates (5 × 10^{-5} mol dm^{-3}) and in the presence of a large excess of bipyridyl (5–200 × 10^{-4} mol dm^{-3}). Under these conditions all runs follow pseudo first-order kinetics up to four to six half-lives. The reaction was monitored at 450 nm and only one relaxation was observed. Measurements at wavelengths below and above the isosbestic points also gave one relaxation with the same k_{obs} value.

For the reaction of I (R = p-$MeOC_6H_4$, p-MeC_6H_4 and Ph) with bipyridyl, plots of k_{obs} against C_{bipy}, Fig. 6, give straight lines with positive intercepts and k_{obs} can be adequately represented by

$$k_{obs} = k_f C_{bipy} + k_d \tag{3}$$

where k_f/k_d = K. In the case of p-chloro derivative (I, R = p-ClC_6H_4) the k_{obs} – C_{bipy} plots, Fig. 7, are also linear but with a zero intercept (*i.e.* k_d = 0.0) and k_{obs} can be expressed by

$$k_{obs} = k_f C_{bipy} \tag{4}$$

The second order rate constants k_f calculated from the gradients of these plots are listed in Table II.

The k_f values are sensitive to substituents on the in-plane ligands and are found to increase as the electron-withdrawing character of R in (I) increases. The data shown in Table II indicate a linear relationship, Fig. 8, between log k_f and the Hammett substituent constant (σ). A linear correlation between log K and the intrinsic acidity of nickel(II) chelates, as measured by log K for pyridine bis-adducts, Fig. 8b, is also observed. Furthermore, the ratios k_f/k_d calculated for I (R = p-$MeOC_6H_4$, p-MeC_6H_4 and Ph) are in good agreement with the formation constants (see Table I) determined spectrophotometrically.

The formation of either cis-octahedral (III-a) or five-coordinate (III-b) bipyridyl adducts from the reaction of square planar nickel(II) chelates (I) with bipyridyl most probably proceeds *via* a stepwise mechanism. The first step is the formation of five-coordinate intermediate (II-a) where the bipyridyl molecule reacts as a unidentate ligand. The second step involves ring closure of the bidentate Lewis base with a simultaneous re-arrangement of the in-plane ligands to give (III-a) (R = p-$MeOC_6H_4$, p-MeC_6H_4 and Ph), or Ni–N bond rupture as in the case of p-chloro derivative to give (III-b).

The present spectrophotometric titrations as well as stopped flow experiments do not provide evidence for the existence of the five-coordinate intermediate (II-a). Accordingly the formation of (II-a) from (I) may be considered either as the slow rate-determining step, followed by relatively fast ring closure, then k_{obs} can be expressed by eqn. 5 [13],

TABLE III. Thermodynamic and Activation Parameters for the Reaction of 2,2′-Bipyridyl with (I) Chelates in Benzene at 25 °C.

R	p-MeOC$_6$H$_4$	p-MeC$_6$H$_4$	Ph	p-ClC$_6$H$_4$
k_f (dm^3 mol sec^{-1})	332	421	532	1083
k_b (sec^{-1})	0.277	0.277	0.208	
K_{kin} (dm^3 mol^{-1})	1199	2024	4156	
K_{spec} (dm^3 mol^{-1})	1211	2089	4467	
$\Delta H_f^{\ddagger}$ (kJ mol^{-1})	39.8 ± 1.8	34.5 ± 3.2	24.4 ± 3.9	32.8 ± 1.2
$\Delta S_f^{\ddagger}$ (J mol^{-1} K^{-1})	−63.2 ± 6.1	−78.9 ± 10.8	−110.9 ± 12.7	−76.7 ± 4.1
$\Delta H_b^{\ddagger}$ (kJ mol^{-1})	81.4 ± 2.2	78.3 ± 4.7	72.0 ± 6.3	
ΔH^{o}_{kin} (kJ mol^{-1})	−41.6	−43.8	−47.6	

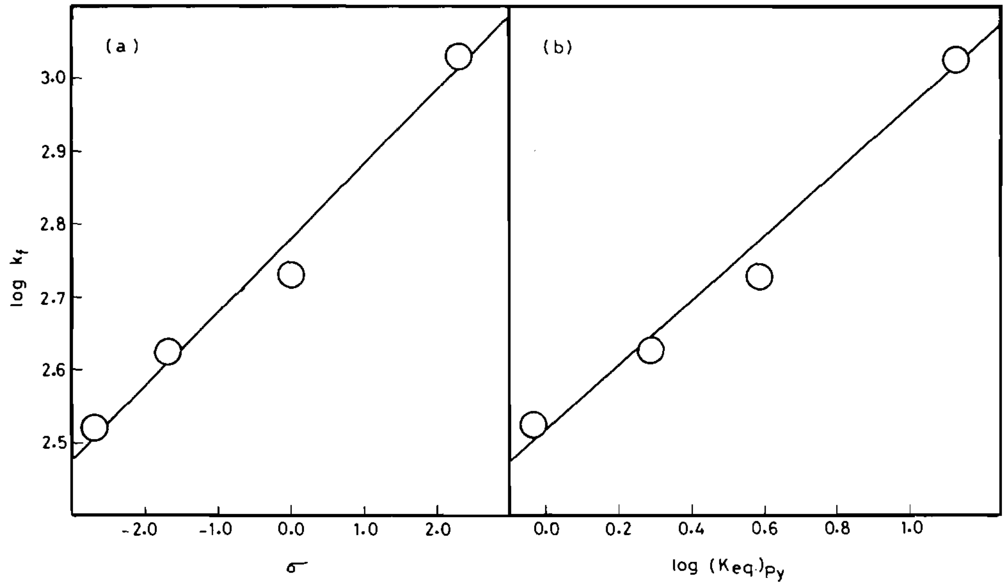


Fig. 8. Plots of log k_f (at 25 °C) against a) Hammett substituent constants (σ) and b) log K_{eq} for the corresponding pyridine adducts at 25 °C.

$$k_{obs} = k_1 C_{bipy} + k_{-1} \qquad (5)$$

or as a fast pre-equilibrium step followed by the rate controlling ring closure step and in this case

$$k_{obs} = k_2 K C_{bipy} (1 + K C_{bipy}) + k_{-2} \qquad (6)$$

where $K = k_1/k_{-1}$ [13]. However, the steric requirement of the bipyridyl molecule will reduce the stability of the formed five-coordinate intermediate (II-a) and $K \cdot C_{bipy}$ may be very much less than unity so that eqn. 6 reduces to

$$k_{obs} = k_2 K C_{bipy} + k_{-2} \qquad (7)$$

Thus the observed dependence of k_{obs} on C_{bipy}, Figs. 6 and 7, as well as the effect of substituents on k_f, cannot provide any kinetic evidence to distinguish the rate-determining step in Scheme I.

Further information concerning the mechanism of the bipyridyl addition to (I) can be obtained from the effect of R on the activation parameters ($\Delta H_f^{\ddagger}$) and ($\Delta S_f^{\ddagger}$). The observed variation of both $\Delta H_f^{\ddagger}$ and $\Delta S_f^{\ddagger}$ (see Table III) with substituents on the in-plane ligands is mainly due to electronic effects as the para substituents do not impose any steric effects on adduct formation. Accordingly it would be expected that the increase in electrophilicity of Ni(II) will stabilize the transition state(s) by incipient Ni–N bond formation and both ($\Delta H_f^{\ddagger}$) and ($\Delta S_f^{\ddagger}$) will consequently decrease in the order p-MeOC$_6$H$_4$ > p-MeC$_6$H$_4$ > Ph > p-ClC$_6$H$_4$. However, the higher $\Delta H_f^{\ddagger}$ and $-\Delta S_f^{\ddagger}$ measured for the p-chloro derivative as compared with those of the unsubstituted member are in agreement with the assumed in-plane Ni–N bond rupture. This also suggests that in case of the p-chloro derivative the rate controlling step must involve the dissociation of this in-plane Ni–N bond.

Thus the labilization of Ni–N bond may occur simultaneously either on the approach of the first bipyridyl nitrogen, giving a four-coordinate intermediate (II-b) *via* a highly distorted transition state, or on bipyridyl ring closure of the five-coordinate intermediate. The formation of (II-b) as the rate controlling step is rather unlikely since the formation of five-coordinate intermediate (II-a) is well established for both substitution reactions where in-plane bond rupture is required [14, 15] and adduct formation reactions [8, 16–18]. Consequently bipyridyl ring closure to give (III-a) can be assumed to be the rate controlling step, and from eqn. 7 it is apparent that $k_f = k_2K$ and $\Delta H_f^{\ddagger} = \Delta H_f^{\circ} + \Delta H_2^{\ddagger}$. A similar situation can be ascribed for other substituents since severe re-arrangement of the in-plane ligands is required to form the cis-octahedral adducts (III-a).

Gray *et al.* [16–18] however suggest that the rate determining process for the addition of bidentate ligands to bis(dithiophosphato)nickel(II) is the coordination change from four to five, the rate being determined primarily by steric requirements of the bidentate ligands. This assumption may be valid for the bipyridyl addition to (I) (R = p-$MeOC_6H_4$, p-MeC_6H_4 and Ph), and if this is the case, then we are actually dealing with two different rate determining steps, namely, the bipyridyl ring closure (IIa) $\rightleftharpoons$ (III-b) in case of p-chloro derivative and the formation of five-coordinate intermediate (I) $\rightleftharpoons$ (II-a) for other substituents (R = p-$MeOC_6H_4$, p-MeC_6H_4 and Ph). The linear relationship between log k_f and σ, Fig. 8, however, indicates that the addition of bipyridyl to (I) chelates most likely proceeds *via* the same rate determining step. The rate of these addition reactions is controlled mainly by the bipyridyl ring closure rather than by the formation of five-coordinate intermediate. The agreement between the values of K obtained spectrophotometrically and those calculated from the kinetic data ($k_2 K_1/k_{-2}$), Table III, confirms this assignment.

Experimental

Materials

Bis(S-methyl-N-arylidenehydrazinecarbodithioate)-nickel(II) chelates were prepared as previously described [4] and crystallized from benzene–petroleum (60–80 °C). Pyridine and substituted pyridines were of AR grade and were distilled over KOH before use. 2,2′-bipyridyl (Merck) was used without further purification. The solvent was analytical grade benzene which was dried and distilled over sodium before use.

Physical Measurements

The electronic spectra were recorded on a Pye Unicam SP 1801 spectrophotometer equipped with a thermostatted cell holder. The actual temperature of the solution was measured by a calibrated thermocouple. Kinetic measurements were made by using a Durrum D-101 stopped flow spectrophotometer. Traces were recorded on a Tektronix storage oscilloscope and were transferred directly from the screen onto graph paper. Pseudo first-order rate constants (k_{obs}) were calculated from the gradients of ln ($A_t - A_\infty$) *versus* time (t, seconds) plots. Enthalpies and entropies of activation were estimated from plots of ln (k_f/T) *versus* 1/T. The gradients and intercepts, as well as their estimated standard deviations of the best fitting straight lines, were computed using a weighted least-squares program.

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