Metal Complexes of Sulphur–Nitrogen Chelating Agents. Part 11.† Synthesis, Characterisation, and Thermodynamics of Nucleophilic Substitution Reactions of Monohalogeno Nickel(II) Complexes of Tridentate ligands of the Type SNN in Solution and the Solid State

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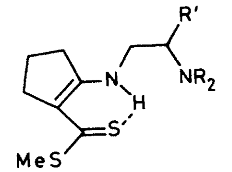
Square-planar nickel(II) complexes [NiLX] (X = Cl, Br, I, or SCN) have been obtained through deprotonation of the ligands methyl 2-(β-aminoethylamino)cyclopent-1-enedithiocarboxylate (HL^1), methyl 2-(β-aminoisopropylamino)cyclopent-1-enedithiocarboxylate (HL^2), and methyl 2-(β-diethylaminoethylamino)cyclopent-1-enedithiocarboxylate (HL^3). Diamagnetic complexes of composition $[NiL(MeCN)][ClO_4]$ ($L = L^1$—L^3) and $[Ni_2L_2(HL)][ClO_4]_2$ ($L = L^1$ or L^2) have also been synthesised. The equilibrium constants for the nucleophilic substitution reaction $[NiL^2X] + B \rightleftharpoons [NiL^2(B)]^+ + X^-$ (X = Cl, Br, or I; B = pyridine and its methyl-substituted derivatives) have been determined spectrophotometrically in the temperature range 25—50 °C. A linear correlation has been obtained between the $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ values. The enthalpy changes (ΔH_2) and activation energies (E_a^*) for the thermal dissociation $[NiL^2(B)]X(s) \longrightarrow [NiL^2X](s) + B(g)$ have been determined. A linear correlation has been found between the (ΔS_2) and E_a^* values.

Introducing 2-aminocyclopent-1-enedithiocarboxylic acid and its derivatives as the building blocks for metal complexes, we [1-7] as well as others [8-12] have investigated bonding, stereochemistry, and structural aspects of various metal complexes. In a recent publication [6] we have reported some reactivities of the palladium(II) complexes of the ligands methyl 2-(β-aminoalkylamino)cyclopent-1-enedithiocarboxylate (HL^1—HL^3). As part of our current interest in polar cycloaddition and homogeneous catalytic reactions we have been interested to generate square-planar nickel(II) complexes from mono-anionic tridentate ligands so that the fourth co-ordination site could be occupied by an easily replaceable unidentate ligand. The known co-ordination chemistry of nickel(II) with SNN donors is practically confined to those obtained with neutral ligands, which owing to their weaker ligand-field strengths form either octahedral bis-complexes or in combination with donor anions, high-spin five-co-ordinate species.[13-15] We report here the formation of square-planar nickel(II) complexes [NiLX] ($L = L^1$—L^3; X = Cl, Br, I, or SCN). Substitutional lability of the halide ions has been demonstrated by investigating thermodynamics of the reaction equilibrium $[NiL^2X] + B \rightleftharpoons [NiL^2(B)]^+ + X^-$ (B = pyridine and its methyl-substituted derivatives) in solution. We have also determined the activation energies and enthalpy changes involved in the thermal dissociation $[NiL^2(B)]X \longrightarrow [NiL^2X] + B$, in the solid state. Some useful conclusions have been drawn from these thermodynamic parameters.

Experimental

Materials and Methods.—All chemicals were reagent grade and used as received. Pyridine and monomethylpyridines were purified by refluxing over anhydrous K_2CO_3 followed by distillation using an efficient fractionating column. 2,6-Dimethylpyridine and 2,4,6-trimethylpyridine were treated with *ca.* 20 mol% BF_3 which selectively combines with sterically non-hindered isomers; the hindered isomers were then separated by fractionation. Nickel(II) iodide and thiocyanate were prepared according to a previously described method.[16] The ligands HL^1—HL^3 were obtained as reported earlier.[6]



HL

R = R′ = H (HL^1)
R = H, R′ = Me (HL^2)
R = Et, R′ = H (HL^3)

Preparation of the Complexes.—[NiLX] ($L = L^1$—L^3; X = Cl, Br, I, *or* SCN). To a methanol solution (40 cm³) containing the ligand and triethylamine (4 mmol each) the nickel salt (4 mmol) dissolved in methanol (15 cm³) was added in small portions with stirring. The compound formed on mixing was stirred additionally for 1 h. The product was collected by filtration, washed first with benzene (in which the ligand is highly soluble) and then with methanol. All but the compounds of L^1 and L^2 with X = I or SCN were recrystallised from chloroform.

$[Ni_2L_2(HL)][ClO_4]_2$ ($L = L^1$ *or* L^2). $Ni(ClO_4)_2\cdot 6H_2O$ (1.1 g, 3 mmol) dissolved in methanol (5 cm³) was added to a stirred solution of the ligand (6 mmol) in chloroform (15 cm³). After 5 min a yellowish brown compound began to separate. Stirring was continued for 0.5 h, after which the product was filtered and washed several times with methanol and chloroform. Attempted recrystallisation of the compound from boiling methanol or acetone caused appreciable decomposition.

$[NiL(MeCN)][ClO_4]$ ($L = L^1$—L^3). [NiLCl] (6 mmol) was dissolved in acetonitrile (50 cm³) and dry $Ag(ClO_4)$ (1.25 g, 6 mmol) was added to it. AgCl precipitated and the solution turned deep green. The mixture was stirred for 0.5 h and then filtered. The filtrate was concentrated to *ca.* 5 cm³ in a rotary evaporator, filtered, and the filtrate was kept in a refrigerator overnight. The green crystals deposited were collected by filtration, and recrystallised by dissolving in a minimum volume of acetonitrile followed by cooling at −5 °C for 12 h.

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† Part 10 is ref. 6.

Table 1. Analytical data for selected compounds

	Analysis * (%)			
Complex	C	H	N	Ni
$[NiL^1Cl]$	35.15 (34.9)	4.7 (4.85)	8.9 (9.05)	18.85 (19.0)
$[NiL^2Br]$	32.45 (32.65)	4.7 (4.6)	7.45 (7.65)	16.15 (15.95)
$[NiL^3I]$	34.4 (34.15)	4.9 (5.05)	5.95 (6.15)	12.7 (12.85)
$[NiL^3(SCN)]$	43.05 (43.35)	5.8 (5.93)	10.65 (10.85)	15.05 (15.15)
$[NiL^1(4Me\text{-}py)]Cl$	44.45 (44.75)	5.35 (5.45)	10.25 (10.45)	14.8 (14.6)
$[NiL^2(2,4,6Me_3\text{-}py)]I$	40.05 (40.35)	5.1 (5.25)	7.6 (7.85)	11.15 (10.95)
$[NiL^1(py)]ClO_4$	37.55 (37.15)	4.25 (4.4)	8.95 (9.3)	13.15 (13.0)
$[NiL^1(MeCN)][ClO_4]$	32.1 (31.8)	4.55 (4.35)	9.95 (10.15)	14.25 (14.15)
$[Ni_2L^1_2(HL^1)][ClO_4]_2$	33.9 (33.65)	5.0 (4.8)	8.55 (8.75)	12.35 (12.2)

* Calculated values are given in parentheses.

Table 2. Selected i.r. data (cm^{-1}) for the complexes

Complex	$\nu_{asym}(N-H)$	$\nu_{sym}(N-H)$	$\delta(NH_2)$	$\nu(C{\cdots}C)$	$\nu(C{\cdots}C + C{\cdots}N)$
$[NiL^1Cl]$	3 270m	3 200w 3 130w	1 585w	1 560s	1 470s
$[NiL^2Br]$	3 270m	3 220m 3 140m	1 590m	1 565m	1 470s
$[NiL^1(SCN)]$	3 280m	3 200m 3 130w	1 580 (sh)	1 565s	1 470s
$[NiL^2(MeCN)][ClO_4]$	3 240m	3 200m 3 120w	1 570m	1 550m	1 455m
$[NiL^1(py)][ClO_4]$	3 290m	3 240m 3 160w	1 595m	1 555m	1 460s
$[Ni_2L^1_2(HL^1)][ClO_4]_2$	3 280w	3 230w 3 160w 3 100w	1 600s		1 495s 1 475s

$[NiL(B)]X$ [$L = L^1$ *or* L^2; B = *pyridine* (py), *2-methyl-*(2Me-py), *3-methyl-*(3Me-py), *4-methyl-*(4Me-py), *2,6-dimethyl-*($2,6Me_2$-py), *or 2,4,6-trimethyl-pyridine* ($2,4,6Me_3$-py); X = Cl, Br, *or* I]. About 0.5 g of [NiLX] was stirred with the pyridine derivative (15 cm^3) for 5 h when most of the material went into solution and a deep red colour developed. This was filtered and the filtrate was then flooded with a large volume of dry diethyl ether. The precipitated red compound was collected by filtration, washed with n-heptane and dry diethyl ether, and finally dried in air.

$[NiL(py)][ClO_4]$ ($L = L^1$ *or* L^2). These compounds were prepared from $[NiL(MeCN)][ClO_4]$ in the same way as described above.

Analytical data for selected compounds are given inTable 1.

Physical Measurements.—The equipment used for physical measurements was as reported earlier.[6,17]

Thermal Analyses.—Thermal analyses (t.g.a. and d.t.a.) were carried out on a Shimadzu DT-30 thermal analysis system under a nitrogen atmosphere with a heating rate of 5 °C min^{-1}. For measuring heats of dissociation a Perkin-Elmer DSC-2 differential scanning calorimeter (d.s.c.) was used. The change in heat content of a sample was obtained by comparing the area of its thermogram with the one obtained for the fusion of indium (3.27 kJ mol^{-1}).[18]

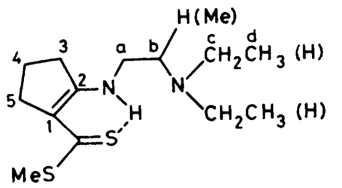
Equilibrium Constants.—The equilibrium constants for the reaction $[NiL^2X] + B \rightleftharpoons [NiL^2(B)]^+ + X^-$ (X = Cl, Br, or I; B = py, 2Me-py, 3Me-py, 4Me-py, $2,6Me_2$-py, or 2,4,6-Me_3-py) were determined spectrophotometrically at several temperatures (25—50 °C) by recording a series of spectra of $[NiL^2X]$ in dimethyl sulphoxide (dmso) mixed with varying quantities of the Lewis base (B). The concentration of $[NiL^2X]$ was *ca.* 2×10^{-3} mol dm^{-3} and that of the base varied in the range 2×10^{-2} to 1.5×10^{-1} mol dm^{-3}.

Results and Discussion

All of the [NiLX] complexes are diamagnetic and non-electrolytes. Molecular weight determination of $[NiL^3Cl]$ (found, 350; calc. 365) in chloroform confirmed the monomeric composition of the complexes. The compounds $[NiL(B)]X$ ($L = L^1$ or L^2), $[NiL(MeCN)][ClO_4]$ ($L = L^1$—L^3), and $[Ni_2L_2(HL)][ClO_4]_2$ ($L = L^1$ or L^2) are also diamagnetic. In methanol or dmso the compounds $[NiL(B)]X$ behave as non-electrolytes, but their conductivity values approach that of an 1 : 1 electrolyte in the presence of excess of base (B). The conductivity data of $[NiL(MeCN)][ClO_4]$ and $[Ni_2L_2(HL)][ClO_4]_2$ are consistent with 1 : 1 and 1 : 2 electrolytes, respectively.

Some i.r. frequencies that are diagnostic of metal–ligand bonding are set out in Table 2 for representative compounds. The band assignments have been made in accordance with our previous studies.[1-6] For the compounds [NiL(SCN)] a strong band due to the thiocyanate is observed at 2 100 cm^{-1} which implies that the bonding with the metal ion is through the sulphur and not through the nitrogen (which is observed near and below 2 050 cm^{-1}) or SCN bridge (usually observed well above 2 100 cm^{-1}).[19] In the complexes $[NiL(MeCN)][ClO_4]$, the $\nu(C{\equiv}N)$ vibration of the metal bound acetonitrile appears at *ca.* 2 220 cm^{-1} (free MeCN vibration occurs at 2 250 cm^{-1}).[20] The perchlorate ion in these compounds seems to be co-ordinated [21-24] to the metal ion in the solid state, as a sharp band at 1 150 cm^{-1} and a strong doublet at 1 105 and 1 065 cm^{-1} are observed compared with a broad band centred at 1 100 cm^{-1} observed due to the ionic perchlorates in the compounds $[NiL(B)][ClO_4]$ and $[Ni_2L_2(HL)][ClO_4]_2$. Several new bands have been observed for all of the complexes in the

Table 3. Hydrogen-1 n.m.r. spectral data for the ligands and [NiLX] complexes



Compound [a]	Chemical shifts (δ/p.p.m.) [b]
HL^1 [c]	1.13br (NH_2), 1.92m (4-CH_2), 2.52s (SCH_3), 2.83m (b-CH_2 + 3,5-CH_2) [d], 3.33q (a-CH_2), 12.7br (N–H ··· S)
$[NiL^1Cl]$ [e]	3.80t (NH_2), 1.77m (4-CH_2), 2.27t (a-CH_2), 2.50s (SCH_3), 2.60m (3,5-CH_2), 3.20m (b-CH_2)
$[NiL^1Br]$ [e]	3.55t (NH_2), 1.80m (4-CH_2), 2.48s (SCH_3), 2.3—3.1 [f]
HL^2 [c]	1.07br (NH_2), 1.20m (b-CH_3), 1.88m (4-CH_2), 2.52s (SCH_3), 2.75 (b-CH + 3,5-CH_2) [d], 3.19q (a-CH_2), 11.0br (N–H ··· S)
$[NiL^2Cl]$ [e]	3.80br (NH_2), 1.17d (b-CH_3), 1.77m (4-CH_2), 2.48s (SCH_3), 2.7—3.3 [f]
$[NiL^2Br]$ [e]	3.52br (NH_2), 1.17d (b-CH_3), 1.80m (4-CH_2), 2.47s (SCH_3), 2.2—3.0 [f]
HL^3 [c]	1.06t (d-CH_3), 1.83m (4-CH_2 + b-CH_2) [d], 2.52s (SCH_3), 2.70m (c-CH_2 + 3,5-CH_2) [d], 3.33q (a-CH_2), 9.7br (N–H ··· S)
$[NiL^3Cl]$ [c]	1.71 (d-CH_3) [g], 1.80m (4-CH_2) [g], 2.61s (SCH_3), 2.3—2.8 [f], 3.30q (c-CH_2)
$[NiL^3Br]$ [c]	1.73 (d-CH_3), 1.80m (4-CH_2) [g], 2.58s (SCH_3), 2.2—3.0 [f], 3.30q (c-CH_2)

[a] See above for labelling of carbon atoms. [b] Chemical shifts were measured relative to $SiMe_4$; d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. [c] In $CDCl_3$. [d] Overlapping multiplets with the indicated centre of gravity. [e] In $[^2H_6]$dmso. [f] Unresolvable multiplets. [g] Apparent multiplet.

Table 4. Electronic spectral data for selected compounds

Complex	$\tilde{\nu}$/cm^{-1}(ε/dm^3 mol^{-1} cm^{-1})	Δ_1/cm^{-1} [a]
$[NiL^1Cl]$ [b]	15 750 (52); 23 530 (5 100); 28 170 (3 390); 31 050 (10 200); 35 100 (20 500)	18 500
$[NiL^1Br]$ [b]	15 630 (50); 23 300 (5 000) [c]	18 430
$[NiL^1I]$ [b]	14 930 (68); 23 000 (4 480) [c]	17 730
$[NiL^1(SCN)]$ [d]	17 240 (100); 23 250 (3 000) [c]	20 040
$[NiL^1(py)]Cl$ [e]	18 500 [c]	
$[NiL^1(py)]Cl$ [f]	18 200 (92) [c]	21 000
$[NiL^1(MeCN)][ClO_4]$ [g]	16 640 (70); 23 300 (4 850) [c]	19 440
$[NiL^1_2(HL^1)][ClO_4]_2$ [d]	17 550 (145) [c]	
$[NiL^2I]$ [d]	16 450 (78); 24 270 (3 900); 28 740 (3 700)	19 250
$[NiL^2(py)]Cl$ [h]	18 700 (105) [c]	21 500
$[NiL^2(py)]I$ [h]	18 500 (110) [c]	21 300
$[NiL^2(py)][ClO_4]$ [g]	18 300 (96) [c]	21 100
$[NiL^2(MeCN)][ClO_4]$ [g]	17 120 (80); 25 250 (7 800); 30 860 (4 420); 35 460 (26 950)	20 000
$[NiL^3Cl]$ [b]	15 240 (110); 22 830 (5 600); 27 470 (4 400); 31 250 (12 900); 33 560 (26 900)	18 040
$[NiL^3Br]$ [b]	14 700 (100); 22 730 (4 200) [c]	17 500
$[NiL^3I]$ [b]	14 290 (105); 22 730 (4 800) [c]	17 080
$[NiL^3(SCN)]$ [b]	16 500 (215); 23 800 (5 300) [c]	19 300

[a] Obtained from the relation proposed by B. G. Werden, E. Billig, and H. B. Gray, *Inorg. Chem.*, 1966, **5**, 78. [b] In chloroform. [c] Higher energy bands were not recorded. [d] In dmso. [e] In Nujol mull. [f] In chloroform–pyridine. [g] In acetonitrile. [h] In dmso–pyridine.

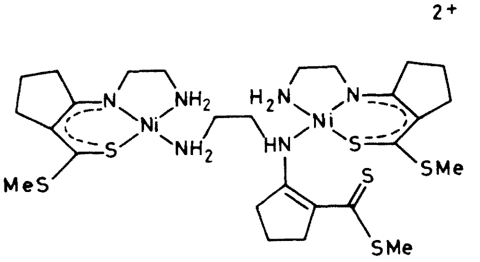
range 600—300 cm^{-1}, of which a medium intensity band around 550 cm^{-1} and a sharp band at *ca.* 375 cm^{-1} are most likely to be due to Ni–N [6,25,26] and Ni–S [6,27–29] stretchings respectively.

The chemical shifts observed in the ^1H n.m.r. spectra of the ligands HL^1—HL^3 undergo considerable modification in the compounds [NiLX] (X = Cl or Br) (Table 3). An interesting feature is the lower field shift of the NH_2 resonance of the chloro-complexes compared to the bromo-analogue in [NiLX] (L = L^1 or L^2). This is due to the fact that the more electronegative chloride ion induces greater withdrawal of electron density from the NH_2 group in these compounds, *via* the metal ion. In contrast, no significant variation in the chemical shifts of the c-CH_2 and d-CH_3 resonances (see Table 3 for the labelling of the carbon atoms) is observable when the chlorine atom is replaced by bromine in $[NiL^3X]$. This observation can be rationalised by taking into consideration the electron-releasing capacity of the alkyl substituents which allow the NEt_2 group to act as a strong donor for the meta ion.

Table 4 summarises the electronic spectral features of the complexes. The high-intensity bands observed above 27 000 cm^{-1} are due to internal ligand transitions. All of the compounds are characterised by a single *d–d* ($^1A_{1g}\rightarrow{}^1A_{2g}$) transition in the range 19 000—14 000 cm^{-1}. The position and intensity of this band with a particular ligand is dependent on the co-ordinated anion (X). Apparently other *d–d* transitions that could have been observed are masked by the intense charge-transfer band (L→M) appearing at *ca.* 24 000 cm^{-1}. The crystal-field separation energies, Δ_1 ($d_{xy}\rightarrow d_{x^2-y^2}$), for the compounds shown in Table 4 reveal that the decreasing order of the ligand-field splitting in terms of the fourth donor site is: py > SCN > MeCN > Cl > Br > I, which incidentally is the normal spectrochemical series.

From preliminary spectral and conductivity measurements it turned out that the complexes [NiL(B)]X undergo extensive dissociation in solution. The labile nature of a NiL(B)X compound does not give any information as to whether it has a square-planar configuration {*i.e.* [NiL(B)]X} or a low-spin five-co-ordinate environment {*i.e.* [NiL(B)X]}. Normally a core like NiN_3SX that contains four hard donors should be high-spin type. However, it is known that apical elongation in square-pyramidal complexes favours the low-spin state.[15] In apically elongated square-pyramidal complexes the energy for a $d_{xy} \longrightarrow d_{x^2-y^2}$ transition will be somewhat less than that observed in square-planar complexes.[30] Inspection of Table 4 reveals that the compounds NiL(B)X exhibit a band whose energy is greater than any of the corresponding [NiLX] species. Moreover, the absorption energy and intensity of all NiL(py)X type of complexes (X = Cl, Br, I, or ClO_4) are almost identical (Table 4). This clearly shows that the compounds [NiL(B)]X have square-planar geometry. The lack of formation of $[NiL^3(B)]X$ due to steric reasons is also consistent with the above explanation.

The complexes of composition $[Ni_2L_2(HL)][ClO_4]_2$ deserve some comments. They are diamagnetic, 1 : 2 electrolytes, and their electronic spectra are consistent with square-planar geometry. I.r. spectra have features similar to the [NiLX] type of compounds. On the basis of this information the metal–ligand binding as shown below seems quite plausible.



The lack of formation of a similar compound with HL^3 on steric ground appears to be consistent with the above proposal.

Thermodynamics of Substitution Reactions.—The equilibrium constants for the nucleophilic substitution reaction (1)

$$[NiL^2X] + B \rightleftharpoons [NiL^2(B)]^+ + X^- \qquad (1)$$

(X = Cl, Br, or I) have been determined for a number of Lewis bases (B = py, 2Me-py, 3Me-py, 4Me-py, $2,6Me_2$-py, and $2,4,6Me_3$-py). The reaction equilibrium (1) exemplified by Figure 1 shows the spectral changes occurring upon addition of pyridine to a solution of $[NiL^2Cl]$ in dmso at 30 °C. The limiting spectrum is indistinguishable from that observed for $[NiL^2(py)]Cl$ in the solid state. The spectrum of $[NiL^2(py)]Cl$ dissolved in neat pyridine remains unchanged indicating that a higher association product, *viz.* $[NiL^2(py)_2]Cl$, does not form. The successive absorption curves shown in Figure 1 pass through two isosbestic points at 530 and 585 nm. Similar spectral behaviour has been observed for the other systems. The presence of only two light-absorbing species in solution was further verified by a standard graphical treatment[31] of the absorption curves. The equilibrium constants were computed by linear regression analysis of the data obtained from spectrophotometric titrations using a modified version[32] of the relation due to Benesi and Hildebrand.[33]

From the variable-temperature equilibrium constant measurements the thermodynamic parameters have been obtained from the plots of ln *K* *vs.* T^{-1}. These are listed in Table 5 along with log *K* at 298 K and pK_H of the bases. The substitution of chloride by pyridine and its derivatives is neither an isoenthalpic nor an isoentropic process. The plot of $\Delta H^{\ominus}$ against $\Delta S^{\ominus}$ gives a good linear fit (Figure 2) with a slope of 0.34 which implies an 'isothermodynamic temperature' of 67 °C. A further implication of the linear relation is that all of the heterocyclic bases share a common interaction mechanism. A comparison of the equilibrium constants involving $[NiL^2X]$ (X = Cl, Br, or I) and pyridine (Table 5) reveals that the ease with which the halogen atoms are replaced is I > Br > Cl, showing again that the Ni–X bond is predominantly ionic in character. It may be noted that when the heterocyclic bases offer no steric hindrance, the equilibrium constants exhibit the expected trend with the basicity of the donors. For example, in the cases of py, 3Me-py, and 4Me-py a linear variation of log *K* with pK_H is obtained. Even with the bases 2Me-py, $2,6Me_2$-py, and $2,4,6Me_3$-py that offer varying degree of steric hindrances, the equilibrium constants are qualitatively related to the basicity of the donors.

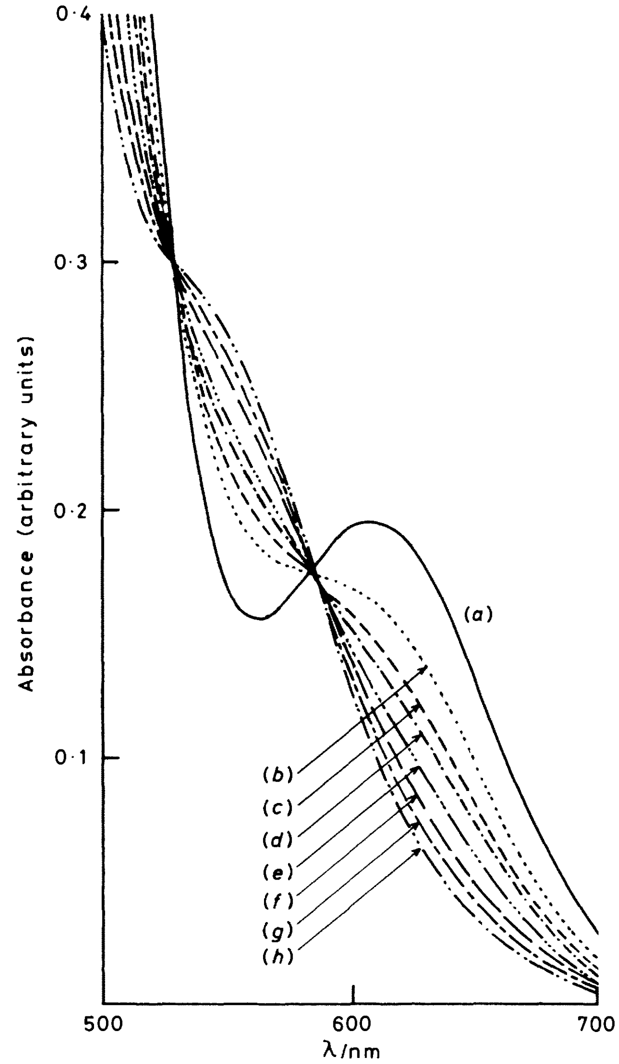


Figure 1. Spectral changes of (*a*) $[NiL^2Cl]$ (2.99×10^{-2} mol dm^{-3}) in dmso at 30 °C and with the addition of varying amounts of pyridine: (*b*) 1.486×10^{-2}; (*c*) 2.97×10^{-2}; (*d*) 4.46×10^{-2}; (*e*) 7.43×10^{-2}; (*f*) 14.86×10^{-2}; (*g*) 22.29×10^{-2}; (*h*) 37.15×10^{-2} mol dm^{-3}

Thermal Studies.—Preliminary thermal analysis of the compounds $[NiL^2X]$ showed that they do not decompose

Table 5. Equilibrium constants and thermodynamic parameters for the reaction $[NiL^2X] + B \rightleftharpoons [NiL^2(B)]^+ + X^-$ in dmso solutions

$[NiL^2X]$	B	log K/dm^3 mol^{-1} [a]	$-\Delta H^\ominus_1$/kJ mol^{-1}	$-\Delta S^\ominus_1$/J K^{-1} mol^{-1}	pK_H
$[NiL^2Cl]$	py	1.62 ± 0.02	17 ± 2	25 ± 5	5.22 [b]
$[NiL^2Cl]$	2Me-py	1.67 ± 0.03	12 ± 2	10 ± 4	5.96 [b]
$[NiL^2Cl]$	3Me-py	1.76 ± 0.03	19 ± 3	30 ± 5	5.63 [b]
$[NiL^2Cl]$	4Me-py	1.91 ± 0.04	25 ± 4	48 ± 6	5.98 [b]
$[NiL^2Cl]$	2,6Me$_2$-py	1.56 ± 0.02	11 ± 1	7 ± 2	6.75 [c]
$[NiL^2Cl]$	2,4,6Me$_3$-py	1.83 ± 0.04	18 ± 3	25 ± 5	
$[NiL^2Br]$	py	2.50 ± 0.05			
$[NiL^2Br]$	3Me-py	2.73 ± 0.06			
$[NiL^2Br]$	4Me-py	2.90 ± 0.04			
$[NiL^2Br]$	2,4,6Me$_3$-py	2.88 ± 0.06			
$[NiL^2I]$	py	2.78 ± 0.05			

[a] At 298 K. [b] A. Fischer, W. J. Galloway, and J. Vaughan, *J. Chem. Soc.*, 1964, 3591. [c] L. Sacconi, G. Lombardo, and P. Paoletti, *J. Inorg. Nucl. Chem.*, 1958, **8**, 217.

Table 6. Enthalpy change and activation energy for the thermal dissociation $[NiL^2(B)]X(s) \longrightarrow [NiL^2X](s) + B(g)$

Compound	T_m/K	ΔH_2 [a]/kJ mol^{-1}	ΔS_2/J K^{-1} mol^{-1}	E_a* [b]/kJ mol^{-1}
$[NiL^2(py)]Cl$	394	55	140	151
$[NiL^2(py)]Br$	423	58	137	167
$[NiL^2(py)]I$	434	59	136	176
$[NiL^2(2Me\text{-}py)]Cl$	405	57	141	142
$[NiL^2(3Me\text{-}py)]Cl$	427	59	138	159
$[NiL^2(4Me\text{-}py)]Cl$	438	60	137	163
$[NiL^2(2,6Me_2\text{-}py)]Cl$	418	56	134	180

Error limit ±2 kJ mol^{-1}. [b] Error limit ±4 kJ mol^{-1}.

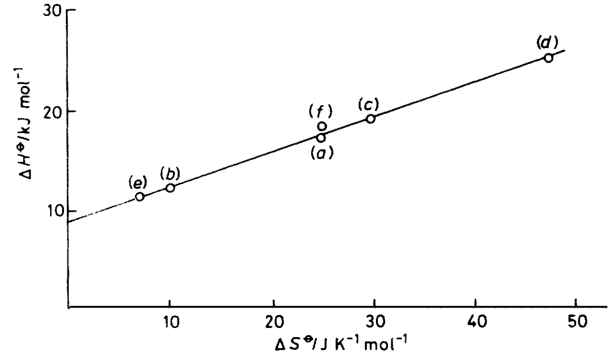


Figure 2. Relationship between $\Delta H^\ominus$ and $\Delta S^\ominus$ in the reaction equilibrium $[NiL^2Cl] + B \rightleftharpoons [NiL^2(B)]^+ + Cl^-$, where B = py (*a*); 2Me-py (*b*); 3Me-py (*c*); 4Me-py (*d*); 2,6Me$_2$py (*e*); 2,4,6Me$_3$-py (*f*)

below 230 °C, above which the decomposition mechanism is complicated. All of the $[NiL^2(B)]X$ compounds undergo thermal dissociation between 100 and 220 °C [equation (2)].

$$[NiL^2(B)]X(s) \longrightarrow [NiL^2X](s) + B(g) \qquad (2)$$

The temperature of decomposition depends upon the base and halogen atom associated. Thermogravimetric analysis shows that liberation of the heterocyclic bases takes place quantitatively (within ±0.5% of the calculated weight loss). The changes in heat content (ΔH_2) for the reaction (2) as determined by d.s.c. measurements are set out in Table 6. These values are, however, not directly comparable with the heats of formation (ΔH_1) measured in solution. They are related by the following thermochemical cycle and by Hess's law (below). In this relation ΔH_4 refers to the heat of vaporisation of a heterocyclic base at 25 °C and values reported in the literature[34] for ΔH_4 of the bases under consideration are as follows: py, 40.4; 2Me-py, 42.92; 3Me-py, 45.23; 4Me-py, 45.33; 2,6Me$_2$-py, 46.06 kJ mol^{-1}. Taking these and the values of ΔH_1 and ΔH_2 into consideration, the combined enthalpy changes due to other processes ($\Delta H_3 + \Delta H_5 - \Delta H_6$) are found to vary among the compounds investigated in the range 2—10 kJ mol^{-1}. This seems quite reasonable because ΔH_3 and ΔH_6, which oppose in sign, are of comparable magnitudes as the gross stereochemistry of $[NiL^2X]$ and $[NiL^2(B)]X$ remains unchanged. Thus the major contribution arises due to solvation of the heterocyclic bases in dmso.

$$\begin{tikzcd}
{[NiL^2X](s) +} \arrow[dd, "\Delta H_3"] & B(g) \arrow[d, "\Delta H_4"] & {[NiL^2(B)]X(s)} \arrow[l, "\Delta H_2"'] \arrow[dd, "\Delta H_6"] \\
 & B(l) \arrow[d, "\Delta H_5"] & \\
{[NiL^2X](sol) +} & B(sol) \arrow[r, "\Delta H_1"] & {[NiL^2(B)]X(sol)}
\end{tikzcd}$$

$$\Delta H_2 = \Delta H_1 + \Delta H_3 + \Delta H_4 + \Delta H_5 - \Delta H_6$$

The activation energies (E_a*) for the thermal dissociation (2) of the compounds have been determined from the t.g.a. curves by the method of Horowitz and Metzger[35] and are listed in Table 6. It may be noted that the E_a* values lie in the range 140—180 kJ mol^{-1}. A comparison of the data pertaining to the triad $[NiL^2(py)]X$ shows that the decreasing order of the activation energies is $[NiL^2(py)]I > [NiL^2(py)]Br > [NiL^2(py)]Cl$, which is also the trend observed for the decomposition temperatures of these compounds. In the series $[NiL^2(B)]Cl$ where the halogen atom is fixed (Cl), the trend in E_a* with respect to the heterocyclic base is: 2,6Me$_2$-py > 4Me-py > 3Me-py > py > 2Me-py.

An attempt can be made to correlate the thermal stabilities with the bond energies *vis-a-vis* equilibrium constants of the complexes. On this basis the compounds $[NiL^2(py)]X$ (X = Cl, Br, or I) show the expected trend. However, the situation

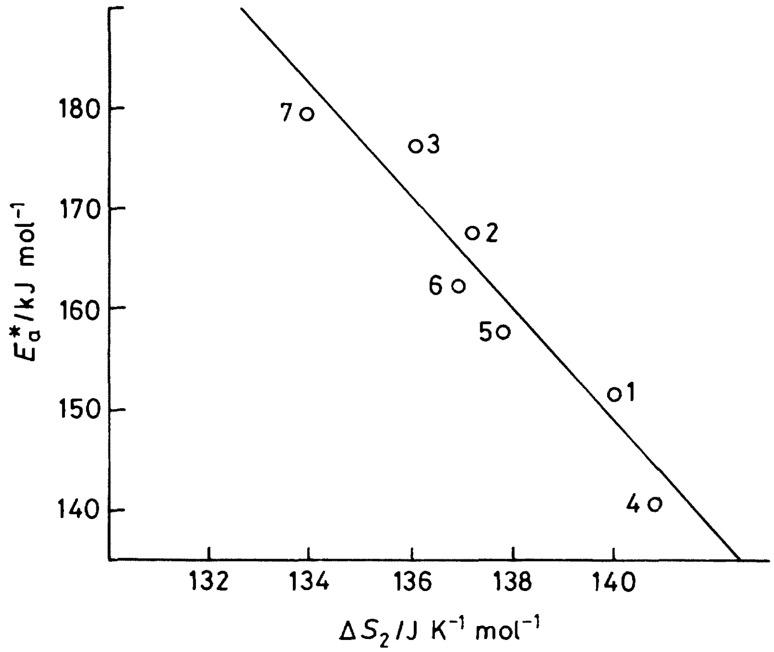


Figure 3. Plot of ΔS_2 *vs.* E_a^* for the thermal dissociation [NiL^2(B)]X(s) → [NiL^{2}X](s) + B(g). (1) [NiL^2(py)]Cl; (2) [NiL^2(py)]Br; (3) [NiL^2(py)]I; (4) [NiL^2(2Me-py)]Cl; (5) [NiL^2(3Me-py)]Cl; (6) [NiL^2(4Me-py)]Cl; (7) [NiL^2(2,6Me$_2$-py)]Cl

is not that simple in the compounds where the heterocyclic bases are varied with a fixed halogen (*i.e.* X = Cl). A reasonable premise for finding a correlation among the observed parameters, namely ΔH, T_m, and E_a^*, would be to compare the entropies of thermal dissociation (ΔS_2) with the activation energies. The entropy values may be obtained as $\Delta S_2 = \Delta H_2/T_m$ where T_m is the peak temperature of the d.s.c. thermogram. It is easy to see that a system having higher entropy will require less energy (E_a^*) for its thermal dissociation. In other words, for closely related systems, one can expect to find a linear correlation between ΔS and E_a^* values. The E_a^* *vs.* ΔS_2 plot shown in Figure 3 gives a reasonably good straight line. Considering the uncertainties involved in measuring both E_a^* and ΔH_2, the observed linear correlation is quite satisfying.

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