Spectrophotometric and Calorimetric Studies on the Formation of Binary (2,2'-Bipyridine)nickel(II) and Ternary (2,2'-Bipyridine)chloronickel(II) Complexes in *N,N*-Dimethylformamide

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Formation of binary (2,2'-bipyridine)nickel(II) and ternary (2,2'-bipyridine)chloronickel(II) complexes has been studied by spectrophotometry and calorimetry in *N,N*-dimethylformamide (dmf) at 25 °C. Both spectrophotometric and calorimetric data obtained are well explained in terms of the formation of binary $[Ni(bipy)]^{2+}$ (bipy = 2,2'-bipyridine), $[Ni(bipy)_2]^{2+}$, and $[Ni(bipy)_3]^{2+}$ and ternary $[NiCl(bipy)]^+$, $[NiCl(bipy)_2]^+$, $[NiCl_2(bipy)]$, and $[NiCl_2(bipy)_2]$ complexes, and their formation constants, enthalpies, and entropies were determined. Electronic spectra of the individual complexes suggest that all the ternary complexes have an octahedral six-co-ordinate structure, as have the binary complexes in solution.

We have studied spectrophotometrically and calorimetrically the formation of ternary (2,2'-bipyridine)bromocopper(II)[1] and (2,2'-bipyridine)chlorozinc(II)[2] complexes in *N,N*-dimethylformamide (dmf). In the copper(II) system are formed $[CuBr(bipy)]^+$ (bipy = 2,2'-bipyridine), $[CuBr(bipy)_2]^+$, and $[CuBr_2(bipy)]$ complexes. It is suggested that $[CuBr(bipy)]^+$ has a five-co-ordinate structure in solution, *i.e.* two solvent molecules bind to the copper(II) ion. Copper(II) is also five-co-ordinated within $[CuBr(bipy)_2]^+$ in solution as well as in $[CuX(bipy)_2]^+$ (X = Cl, Br, or I) in the crystal.[3-7] In the zinc(II) system are formed only the $[ZnCl(bipy)]^+$ and $[ZnCl_2(bipy)]$ complexes. It is suggested that zinc(II) ion within $[ZnCl_2(bipy)]$ is four-co-ordinated in solution[2] as well as in the crystal,[8] and that within $[ZnCl(bipy)]^+$ it is four-co-ordinated with a solvent molecule in the primary solvation sphere.[2]

Ternary nickel(II) complexes with halide ions and 2,2'-bipyridine such as $[NiCl_2(bipy)_2]$ and $[NiCl_2(bipy)]$ have been obtained by thermal decomposition of $[Ni(bipy)_3]Cl_2{\cdot}7H_2O$.[9] No thermodynamic investigation has so far been carried out on the formation of the ternary (2,2'-bipyridine)chloronickel(II) complexes in any solution. In this work, therefore, we aimed to investigate the formation of such complexes in dmf in comparison with that of the ternary copper(II) and zinc(II) complexes. It is known that, in dmf, nickel(II) forms a series of $[NiCl]^+$, $[NiCl_2]^0$, $[NiCl_3]^-$, and $[NiCl_4]^{2-}$ complexes with chloride ions. Calorimetric and spectrophotometric data obtained for the ternary system were analysed on the basis of the thermodynamic quantities and electronic spectra of the individual nickel(II) chloro complexes determined in previous work.[10]

Experimental

Reagents.—All chemicals used were of reagent grade. 2,2'-Bipyridine was used without further purification and dried in vacuum over P_2O_5 in a desiccator. Other chemicals were prepared or purified as described elsewhere.[9] *N,N*-Dimethylformamide was dried for several weeks over molecular sieve 4A 1/16, then distilled under reduced pressure, and stored over molecular sieve in a dark bottle with a P_2O_5 drying-tube.

Measurements.—All calorimetric and spectrophotometric titrations were carried out by using fully automatic on-line systems in a room thermostatted at 25 ± 0.2 °C. All dmf solutions prepared contained NEt_4ClO_4 as an ionic medium to keep the ionic strength at 0.4 mol dm^{-3}.

Spectrophotometry. An aliquot of a nickel(II) perchlorate solution (25 cm^3) was placed in a vessel under a dry nitrogen atmosphere and then titrated with either 0.25 mol dm^{-3} 2,2'-bipyridine or 0.4 mol dm^{-3} NEt_4Cl solution. Electronic spectra were measured with a flow cell (pathlength 0.5 cm) connected to a titration vessel. Absorbances thus measured at each titration point were recorded every 1 nm over the range 450—850 nm. Absorbance data at 50 selected wavelengths over this range were used for the least-squares calculation of formation constants.

Calorimetry. A nickel(II) perchlorate solution (50 cm^3) was placed in a stainless-steel vessel, the inside wall of which was coated with Teflon. The vessel was inserted in an aluminium block thermostatted at 25.0 ± 0.0001 °C in an air-bath. The solution under a dry nitrogen atmosphere in the vessel was then titrated with either 0.05 or 0.1 mol dm^{-3} 2,2'-bipyridine solution by using an autoburette (ABP-118, Kyoto Electronics). Heats of complexation at each titration point were measured in the range 0.1—2.5 J with a certainty ±0.02 J. They were corrected for the heat of dilution of the titrant which had been determined by separate experiments by titrating a 0.4 mol dm^{-3} NEt_4ClO_4 solution with a solution containing 2,2'-bipyridine (0.05 or 0.1 mol dm^{-3}) and 0.4 mol dm^{-3} NEt_4ClO_4. The heat of dilution observed in this measurement was very small.

Analysis of Data.—If the formation of only mononuclear complexes is assumed, the overall formation of the $[NiCl_n(bipy)_m]^{(2-n)+}$ complex can be defined as in equations (1) and (2). The absorbance A_{ij} in the solution i at a given wavelength λ_j

$$Ni^{2+} + nCl^- + m\text{bipy} \longrightarrow [NiCl_n(bipy)_m]^{(2-n)+} \quad (1)$$

$$\beta_{1nm} = [NiCl_n(bipy)_m{}^{(2-n)+}]/[Ni^{2+}][Cl^-]^n[bipy]^m \quad (2)$$

is thus expressed by using the formation constant β_{1nm} and the molar absorption coefficient $\varepsilon_{1nm}(\lambda_j)$ of $[NiCl_n(bipy)_m]^{(2-n)+}$ with various combinations of n and m as in equation (3).

$$A_{ij} = \Sigma\Sigma\varepsilon_{1nm}(\lambda_j)\beta_{1nm}[Ni^{2+}]_i[Cl^-]_i^n[bipy]_i^m + \varepsilon_{Ni}(\lambda_j)[Ni^{2+}]_i + \varepsilon_{Cl}(\lambda_j)[Cl^-]_i \quad (3)$$

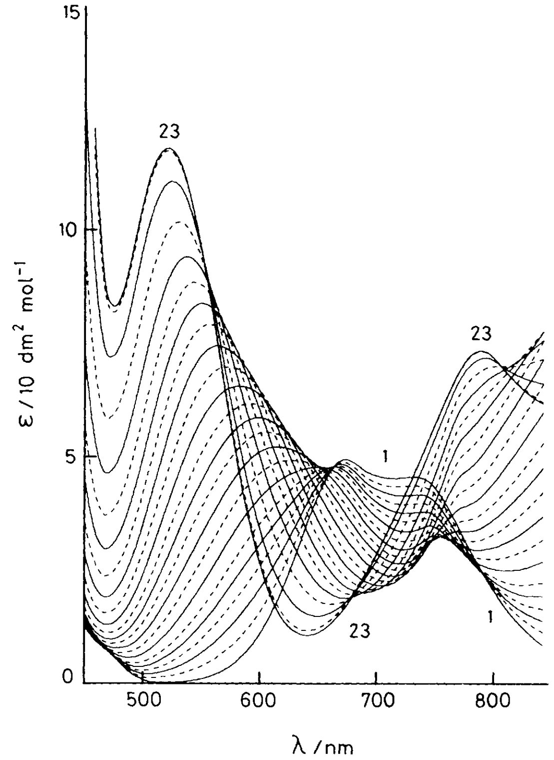

Figure 1. Measured electronic spectra of (2,2′-bipyridine)nickel(II) complexes in dmf. Intensities are normalized for the concentration of nickel(II) ion. The initial concentration of nickel(II) perchlorate was 0.075 38 mol dm^{-3} and the solution (25.0 cm^3) was titrated with 0.256 mol dm^{-3} 2,2′-bipyridine. Volumes of the titrant added are 0.0 (spectrum 1), 0.7 (2), 1.4 (3), 2.1 (4), 2.8 (5), 3.5 (6), 4.5 (7), 5.5 (8), 6.5 (9), 7.5 (10), 8.5 (11), 9.5 (12), 10.7 (13), 11.9 (14), 13.1 (15), 14.3 (16), 15.5 (17), 16.7 (18), 18.0 (19), 19.5 (20), 21.0 (21), 22.5 (22), and 24.0 (23) cm^3

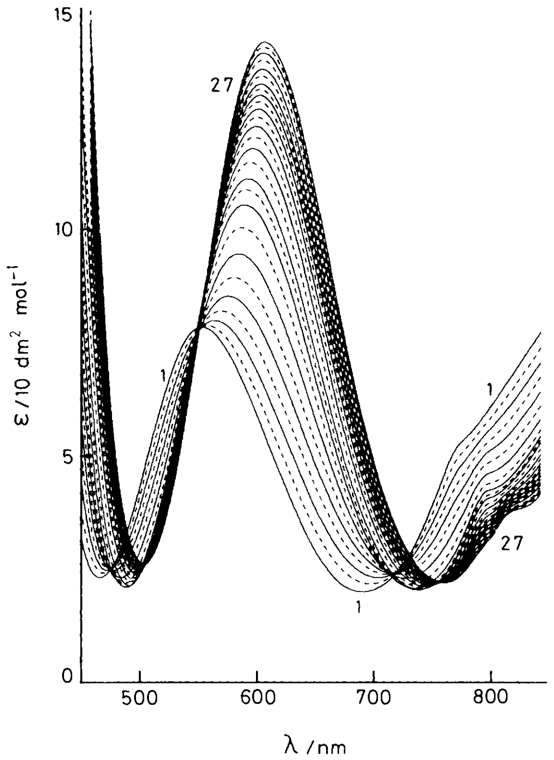

Figure 2. Typical measured electronic spectra of (2,2′-bipyridine)-chloronickel(II) complexes at a given concentration ratio of 2,2′-bipyridine to $Ni(ClO_4)_2$ (2.02) with varying concentrations of NEt_4Cl in dmf. Intensities are normalized for the concentration of nickel(II) ion. The initial total concentration of nickel(II) ions was 0.062 68 mol dm^{-3} and the nickel(II) 2,2′-bipyridine solution was titrated with a 0.4014 mol dm^{-3} NEt_4Cl solution. Volumes of the titrant solution are 0.0 (spectrum 1), 0.8 (2), 1.6 (3), 2.4 (4), 3.2 (5), 4.0 (6), 4.8 (7), 5.6 (8), 6.4 (9), 7.2 (10), 8.0 (11), 9.5 (12), 11.0 (13), 12.5 (14), 14.0 (15), 15.5 (16), 17.0 (17), 18.5 (18), 20.0 (19), 21.5 (20), 23.0 (21), 25.5 (22), 28.0 (23), 32.0 (24), 36.0 (25), 40.0 (26), and 44.0 (27) cm^3

Similarly, a heat q_i measured at the ith titration point is expressed by using both formation constants β_{1nm} and overall enthalpies $\Delta H^{\circ}_{\beta 1nm}$ as in equation (4) where V denotes the volume of the test solution. In equations (3) and (4) the

$$q_i = -(V_i\Sigma\Sigma\beta_{1nm}\Delta H^{\circ}_{\beta 1nm}[\mathrm{Ni}^{2+}]_i[\mathrm{Cl}^-]_i^n[\mathrm{bipy}]_i^m - V_{i-1}\Sigma\Sigma\beta_{1nm}\Delta H^{\circ}_{\beta 1nm}[\mathrm{Ni}^{2+}]_{i-1}[\mathrm{Cl}^-]_{i-1}^n[\mathrm{bipy}]_{i-1}^m) \quad (4)$$

concentrations of free Ni^{2+} and Cl^- ions and 2,2′-bipyridine are related to their total concentrations, $c_{M,i}$, $c_{X,i}$, and $c_{L,i}$, respectively, in the solution i by the mass-balance equations (5)—(7).

$$c_{M,i} = [\mathrm{Ni}^{2+}]_i + \Sigma\Sigma\beta_{1nm}[\mathrm{Ni}^{2+}]_i[\mathrm{Cl}^-]_i^n[\mathrm{bipy}]_i^m \quad (5)$$

$$c_{X,i} = [\mathrm{Cl}^-]_i + \Sigma\Sigma n\beta_{1nm}[\mathrm{Ni}^{2+}]_i[\mathrm{Cl}^-]_i^n[\mathrm{bipy}]_i^m \quad (6)$$

$$c_{L,i} = [\mathrm{bipy}]_i + \Sigma\Sigma m\beta_{1nm}[\mathrm{Ni}^{2+}]_i[\mathrm{Cl}^-]_i^n[\mathrm{bipy}]_i^m \quad (7)$$

Formation constants and molar absorption coefficients of (2,2′-bipyridine)chloronickel(II) complexes were simultaneously determined by minimizing $\Sigma\Sigma(A_{ij,\mathrm{obs.}} - A_{ij,\mathrm{calc.}})^2$ by using a non-linear least-squares program according to an algorithm proposed by Marquardt.[11] Enthalpies of formation of the complexes were then determined by minimizing $\Sigma(q_{i,\mathrm{obs.}} - q_{i,\mathrm{calc.}})^2$ on the basis of the formation constants obtained by spectrophotometry.

Results and Discussion

Spectrophotometric Results.—Measured electronic spectra of (2,2′-bipyridine)nickel(II) complexes are depicted in Figure 1. In the binary system the absorbance data were well explained terms of the formation of $[Ni(bipy)]^{2+}$, $[Ni(bipy)_2]^{2+}$, and $[Ni(bipy)_3]^{2+}$, and their formation constants were determined. The $\log(\beta_{10m}/dm^{3m}\ mol^{-m})$ values of the $[Ni(bipy)_m]^{2+}$ complex thus obtained are 6.04 (3σ = 0.17), 11.29 (0.34), and 15.52 (0.49) for m = 1, 2, and 3, respectively, which involve rather large uncertainties, however. Typical electronic spectra of the ternary (2,2′-bipyridine)chloronickel(II) complexes measured are depicted in Figure 2. In the ternary system we assumed the formation of various types of mono- and poly-nuclear complexes in solution. Under the experimental conditions examined the absorbance data are well explained in terms of the formation of $[NiCl(bipy)]^+$, $[NiCl_2(bipy)]$, $[NiCl(bipy)_2]^+$, and $[NiCl_2(bipy)_2]$. The formation of $[NiCl_3(bipy)]^-$, $[NiCl_3(bipy)_2]^-$ and polynuclear complexes is practically negligible. Finally the formation constants of all the binary $[Ni(bipy)]^{2+}$, $[Ni(bipy)_2]^{2+}$, and $[Ni(bipy)_3]^{2+}$ and ternary $[NiCl(bipy)]^+$, $[NiCl_2(bipy)]$, $[NiCl(bipy)_2]^+$, and $[NiCl_2(bipy)_2]$ complexes were simultaneously optimized by using the whole absorbance data obtained in both binary and ternary systems. The results are listed in Table 1. The certainties for the binary (2,2′-bipyridine)nickel(II) complexes are sufficiently improved in this calculation. Figures 3 and 4 show distribution curves of both binary and ternary complexes calculated as

Table 1. Least-squares refinement of the formation constants, log (β_{1nm}/dm$^{3(n+m)}$ mol$^{-(n+m)}$), and enthalpies, $\Delta H^\circ_{\beta 1nm}$/kJ mol^{-1}, of [NiCl$_n$(bipy)$_m$]$^{(2-n)+}$ in *N*,*N*-dimethylformamide at 25 °C

Complex	Symbol	log β_{1nm}	$\Delta H^\circ_{\beta 10m}$	$\Delta H^\circ_{\beta 1nm}$
[Ni(bipy)]$^{2+}$	[101]	5.90 (0.08)	−31.1 (0.7)	−31.1[a]
[Ni(bipy)$_2$]$^{2+}$	[102]	11.18 (0.14)	−63.8 (0.7)	−63.8[a]
[Ni(bipy)$_3$]$^{2+}$	[103]	15.43 (0.19)	−92.2 (0.8)	−92.2[a]
[NiCl(bipy)]$^+$	[111]	9.58 (0.10)		−22.7 (0.8)
[NiCl$_2$(bipy)]	[121]	10.69 (0.10)		−7.4 (2.0)
[NiCl(bipy)$_2$]$^+$	[112]	14.95 (0.19)		−55.9 (1.0)
[NiCl$_2$(bipy)$_2$]	[122]	15.84 (0.19)		−45.4 (2.4)
U[b]		0.026 67	0.0258	0.219
R[c]		0.006 58	0.0263	0.0205
N[d]		7 068	84	130

Values in parentheses refer to three standard deviations (3σ). The formation constants and enthalpies of the nickel(II) chloro complexes used in the analysis are given in ref. 10. [a] Determined in the binary system, and kept constant in the course of the calculation. [b] Error-square sum. [c] The Hamilton R factor. [d] The number of data points.

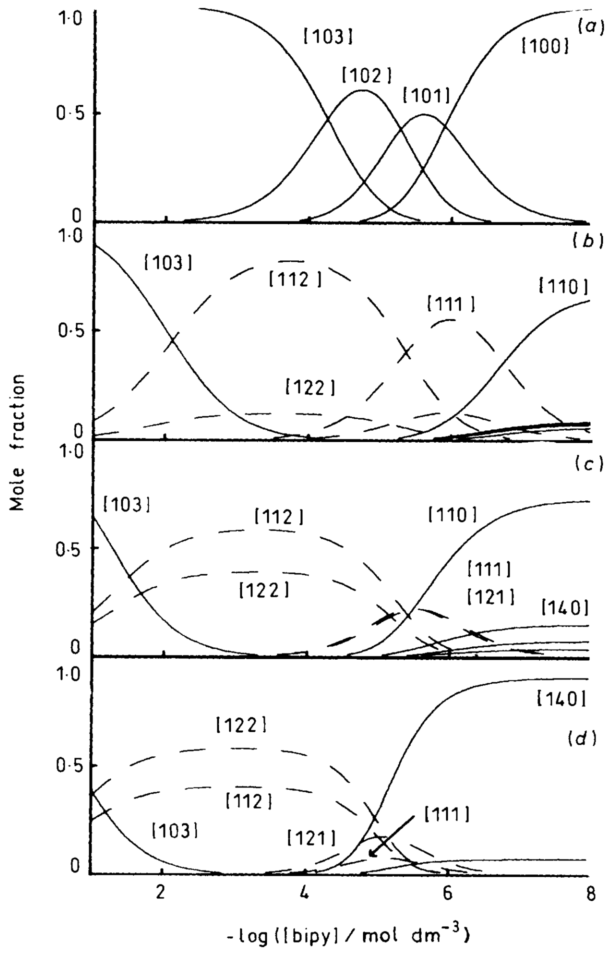

Figure 3. Distribution of (2,2′-bipyridine)chloronickel(II) complexes in dmf as a function of −log([bipy]/mol dm^{-3}). The [NiCl$_n$(bipy)$_m$]$^{(2-n)+}$ complex is represented as [1*nm*]. c_M = 0.01 mol dm^{-3}; c_X = 0 (*a*), 0.03 (*b*), 0.1 (*c*), and 0.2 mol dm^{-3} (*d*)

−log([bipy]/mol dm^{-3}) and −log([Cl$^-$]/mol dm^{-3}), respectively, at a given total concentration of nickel(II) (0.01 mol dm^{-3}).

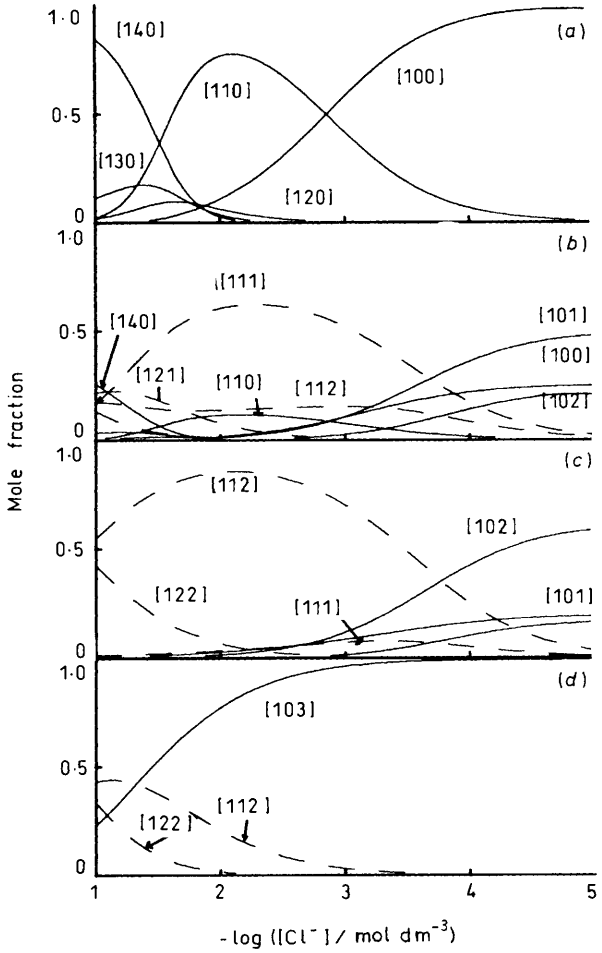

Figure 4. Distribution of (2,2′-bipyridine)chloronickel(II) complexes in dmf as a function of −log([Cl$^-$]/mol dm^{-3}). The [NiCl$_n$(bipy)$_m$]$^{(2-n)+}$ complex is represented as [1*nm*]. c_M = 0.01 mol dm^{-3}; c_L = 0 (*a*), 0.01 (*b*), 0.02 (*c*), and 0.04 mol dm^{-3} (*d*)

Electronic Spectra of Individual (2,2′-Bipyridine)chloronickel(II) *Complexes*.—In Figure 5 are shown electronic spectra of individual binary [Ni(bipy)]$^{2+}$, [Ni(bipy)$_2$]$^{2+}$, [Ni(bipy)$_3$]$^{2+}$ (solid lines), and ternary [NiCl(bipy)]$^+$, [NiCl$_2$(bipy)], [NiCl(bipy)$_2$]$^+$, and [NiCl$_2$(bipy)$_2$] complexes (broken lines). The (2,2′-bipyridine)nickel(II) complexes that may have octahedral structures in solution show an absorption peak in the range 500—700 nm which shifts to shorter wavelengths (blue shift) with the number of 2,2′-bipyridine molecules within the complexes. On the other hand, the peak position of the ternary complexes shifts to longer wavelengths (red shift) and its intensity increases upon addition of Cl$^-$ to the [Ni(bipy)$_m$]$^{2+}$ complex. Molar absorption coefficients of the ternary (2,2′-bipyridine)chloronickel(II) complexes are similar to those of the binary (2,2′-bipyridine)nickel(II) ones, and it is thus suggested that nickel(II) is six-co-ordinated within the ternary complexes in solution, *i.e.* the [NiCl(bipy)]$^+$, [NiCl$_2$(bipy)], and [NiCl(bipy)$_2$]$^+$ complexes respectively involve three, two, and one dmf molecules bound to the central nickel(II), while [NiCl$_2$(bipy)$_2$] contains no dmf molecule in the co-ordination shell.

Calorimetric Results.—In the binary nickel(II)–2,2′-bipyridine system, observed enthalpy values remain practically unchanged over the range c_L/c_M = 0—2, which implies that the formation constants of [Ni(bipy)]$^{2+}$ and [Ni(bipy)$_2$]$^{2+}$ are not determin-

Table 2. Thermodynamic quantities, $\log(K/\mathrm{dm^3\ mol^{-1}})$, ΔG°/kJ mol^{-1}, ΔH°/kJ mol^{-1}, and ΔS°/J K^{-1} mol^{-1}, for the reaction $[\mathrm{NiCl}_n(\mathrm{bipy})_{m-1}]^{(2-n)+}$ + bipy $\longrightarrow [\mathrm{NiCl}_n(\mathrm{bipy})_m]^{(2-n)+}$ in *N,N*-dimethylformamide at 25 °C

Reaction	log *K*	ΔG°	ΔH°	ΔS°
$\mathrm{Ni^{2+}} + \mathrm{bipy} \longrightarrow [\mathrm{Ni(bipy)}]^{2+}$	5.90	−33.7	−31.1	9
$[\mathrm{Ni(bipy)}]^{2+} + \mathrm{bipy} \longrightarrow [\mathrm{Ni(bipy)_2}]^{2+}$	5.28	−30.1	−32.7	−9
$[\mathrm{Ni(bipy)_2}]^{2+} + \mathrm{bipy} \longrightarrow [\mathrm{Ni(bipy)_3}]^{2+}$	4.25	−24.3	−28.4	−14
$[\mathrm{NiCl}]^{+} + \mathrm{bipy} \longrightarrow [\mathrm{NiCl(bipy)}]^{+}$	6.73	−38.4	−31.3	23
$[\mathrm{NiCl(bipy)}]^{+} + \mathrm{bipy} \longrightarrow [\mathrm{NiCl(bipy)_2}]^{+}$	5.37	−30.6	−33.2	−9
$[\mathrm{NiCl_2(bipy)}] + \mathrm{bipy} \longrightarrow [\mathrm{NiCl_2(bipy)_2}]$	5.15	−29.4	−38	−29

Table 3. Thermodynamic quantities, $\log(K/\mathrm{dm^3\ mol^{-1}})$, ΔG°/kJ mol^{-1}, ΔH°/kJ mol^{-1}, and ΔS°/J K^{-1} mol^{-1}, for the reaction $[\mathrm{NiCl}_{n-1}(\mathrm{bipy})_m]^{(3-n)+} + \mathrm{Cl^-} \longrightarrow [\mathrm{NiCl}_n(\mathrm{bipy})_m]^{(2-n)+}$, in *N,N*-dimethylformamide at 25 °C

Reaction	log *K*	ΔG°	ΔH°	ΔS°
$\mathrm{Ni^{2+}} + \mathrm{Cl^-} \longrightarrow [\mathrm{NiCl}]^{+}$	2.85	−16.3	8.6	83
$[\mathrm{Ni(bipy)}]^{2+} + \mathrm{Cl^-} \longrightarrow [\mathrm{NiCl(bipy)}]^{+}$	3.68	−21.0	8.4	98
$[\mathrm{Ni(bipy)_2}]^{2+} + \mathrm{Cl^-} \longrightarrow [\mathrm{NiCl(bipy)_2}]^{+}$	3.77	−21.5	7.9	99
$[\mathrm{NiCl(bipy)}]^{+} + \mathrm{Cl^-} \longrightarrow [\mathrm{NiCl_2(bipy)}]$	1.11	−6.3	15.3	73
$[\mathrm{NiCl(bipy)_2}]^{+} + \mathrm{Cl^-} \longrightarrow [\mathrm{NiCl_2(bipy)_2}]$	0.89	−5.1	10.5	52

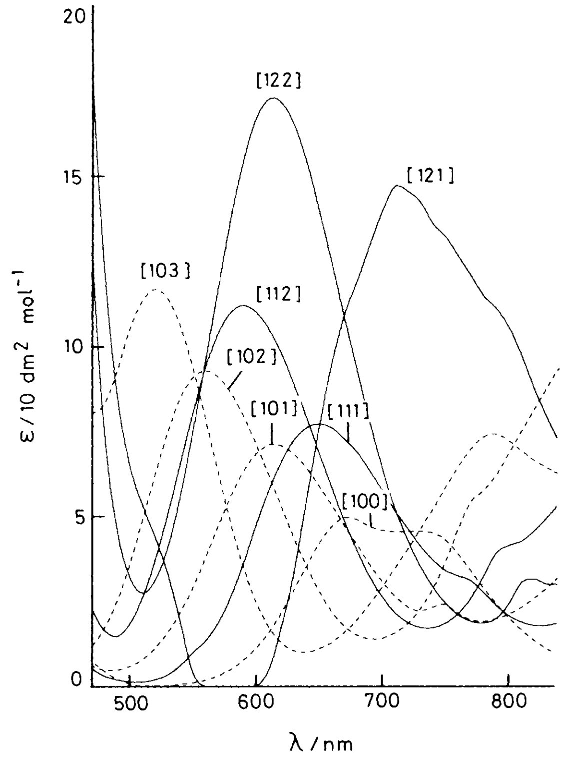

Figure 5. Electronic spectra of individual (2,2′-bipyridine)nickel(II) and (2,2′-bipyridine)chloronickel(II) complexes in dmf at 25 °C. The $[\mathrm{NiCl}_n(\mathrm{bipy})_m]^{(2-n)+}$ complex is represented as [1*nm*]

able from the analysis of the calorimetric data. Therefore, in the present work calorimetric data obtained in both binary and ternary systems were analysed on the basis of the formation constants of the complexes determined by spectrophotometry. The enthalpies thus obtained are also listed in Table 1. In Figure 6 are shown calorimetric titration curves obtained in the ternary nickel(II) systems in dmf. The term $-q/(\delta v c_{\mathrm{L,tit}})$ is plotted against $c_\mathrm{L}/c_\mathrm{M}$, where q and δv are the heat evolved and the volume of an aliquot of the titrant added, respectively, at each titration point, and $c_{\mathrm{L,tit}}$ denotes the concentration of 2,2′-bipyridine in the titrant solution. The solid curves calculated by using the constants of relevant complexes in Table 1 well reproduce the experimental points.

Stepwise Thermodynamic Quantities.—The stepwise thermodynamic quantities are summarized in Tables 2 and 3. As discussed in a previous section, nickel(II) within the (2,2′-bipyridine)nickel(II) and (2,2′-bipyridine)chloronickel(II) complexes may be six-co-ordinated in dmf and they are thus represented as $[\mathrm{Ni(bipy)(dmf)_4}]^{2+}$, $[\mathrm{Ni(bipy)_2(dmf)_2}]^{2+}$, $[\mathrm{Ni(bipy)_3}]^{2+}$, $[\mathrm{NiCl(bipy)(dmf)_3}]^{+}$, $[\mathrm{NiCl(bipy)_2(dmf)}]^{+}$, $[\mathrm{NiCl_2(bipy)(dmf)_2}]$, and $[\mathrm{NiCl_2(bipy)_2}]$. It is noted that the solvated nickel(II) ion and monochloronickel(II) complex are also six-co-ordinated in dmf and described as $[\mathrm{Ni(dmf)_6}]^{2+}$ and $[\mathrm{NiCl(dmf)_5}]^{+}$, respectively.[10]

As seen in Table 2 the ΔH° values for reactions (8) and (9) are

$$\mathrm{Ni^{2}} + \mathrm{bipy} \longrightarrow [\mathrm{Ni(bipy)}]^{2+} \qquad (8)$$

$$[\mathrm{NiCl}]^{+} + \mathrm{bipy} \longrightarrow [\mathrm{NiCl(bipy)}]^{+} \qquad (9)$$

negative and practically the same, and the corresponding ΔS° values are positive and not largely different. Similar ΔH° values to those for reactions (8) and (9) are also observed for reactions (10) and (11). The ΔS° values for reactions (10) and (11) are the

$$[\mathrm{Ni(bipy)}]^{2+} + \mathrm{bipy} \longrightarrow [\mathrm{Ni(bipy)_2}]^{2+} \qquad (10)$$

$$[\mathrm{NiCl(bipy)}]^{+} + \mathrm{bipy} \longrightarrow [\mathrm{NiCl(bipy)_2}]^{+} \qquad (11)$$

same. Considering the six-co-ordinate structure for all the complexes involved in these reactions (8)—(11), we expect that two dmf molecules bound to nickel(II) are replaced by a bidentate 2,2′-bipyridine in the course of the reactions. It is thus suggested that the energy for the replacement of two dmf molecules bound to nickel(II) with 2,2′-bipyridine does not significantly change in the presence and in the absence of a ligating Cl$^-$ ion. It may be expected that Cl$^-$ bound to nickel(II) weakens both metal–dmf and metal–bipy bonds. However, this influence may not be significant and the weakening of the bonds may occur to the same extent. On the other hand, the ΔH° and ΔS° values for reaction (12) are appreciably more negative than

$$[\mathrm{NiCl_2(bipy)}] + \mathrm{bipy} \longrightarrow [\mathrm{NiCl_2(bipy)_2}] \qquad (12)$$

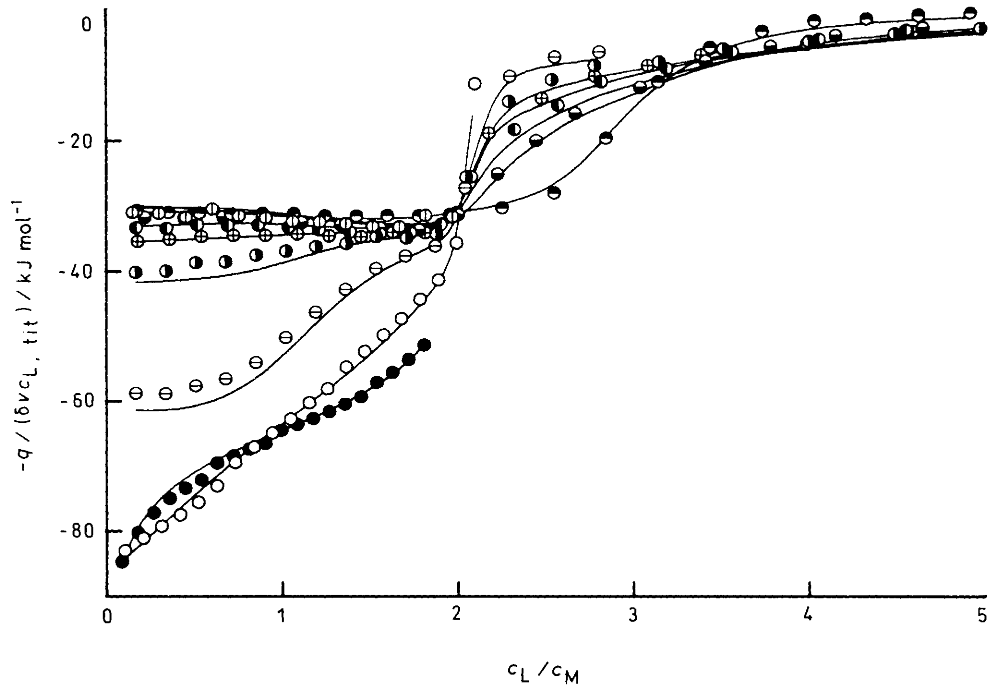

Figure 6. Calorimetric curves obtained by titrating various nickel(II) chloride solutions with 2,2′-bipyridine in dmf. Concentrations of nickel(II) and chloride ions, $c_{\text{M,init}}$ and $c_{\text{X,init}}$/mmol dm^{-3}, in the initial test solutions: (◓) 5.17, 2.59; (⦶) 4.04, 6.48; (◒) 4.13, 8.11; (◐) 4.13, 11.60; (⊕) 3.38, 13.80; (◑) 4.19, 20.80; (⊖) 4.80, 40.10; (○) 10.94, 106.30; (●) 12.66, 190.70 mmol dm^{-3}. The solid lines were calculated by using the constants in Table 1

the respective values for (8)—(11). In this reaction also two dmf molecules may be replaced by a 2,2′-bipyridine molecule. The more negative ΔH° and ΔS° values suggest that the ligating Cl^- ions influence largely the Ni–dmf and Ni–bipy bonds within $[NiCl_2(bipy)(dmf)_2]$ and $[NiCl_2(bipy)_2]$.

As seen in Table 3, positive ΔH° values are observed for reactions (13)—(15) implying that a dmf molecule bound to

$$Ni^{2+} + Cl^- \longrightarrow [NiCl]^+ \qquad (13)$$

$$[Ni(bipy)]^{2+} + Cl^- \longrightarrow [NiCl(bipy)]^+ \qquad (14)$$

$$[Ni(bipy)_2]^{2+} + Cl^- \longrightarrow [NiCl(bipy)_2]^+ \qquad (15)$$

nickel(II) is liberated in each reaction. It should be noted that the ΔH° values for these reactions are close to each other, which indicates that the energy needed to break the Ni–dmf bond to form the Ni–Cl bond is not largely influenced by binding of 2,2′-bipyridine molecules. Also the corresponding ΔS° values are slightly larger for reactions (14) and (15) than for (13), the favourable formation of the ternary nickel(II) complexes compared with the binary ones is consequently dominated by the entropies.

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