Thermodynamics of Formation of Binary and Ternary Complexes of Zinc(II) with Halide and Thiocyanate Ions and 2,2′-Bipyridine in Dimethylformamide

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The formation of binary and ternary complexes of zinc(II) with bromide, iodide, and thiocyanate ions and 2,2′-bipyridine (bipy) has been studied by calorimetry in dimethylformamide (dmf) at 25 °C. The formation of the ternary complexes $[ZnX_m(bipy)_n]^{(2-m)+}$ (denoted as [1*mn*]), such as [111], [112], and [121] for X = Br and I and [111], [112], [121], and [122] for X = SCN is revealed, along with the binary complexes $[ZnX_n]^{(2-n)+}$ (*n* = 1—3 for X = Br, *n* = 2 or 3 for X = I, and *n* = 1, 3, or 4 for X = SCN) and $[Zn(bipy)_n]^{2+}$ (*n* = 1—3), and their formation constants, reaction enthalpies, and entropies were obtained. The thermodynamic parameters are discussed together with those for the (2,2′-bipyridine)chlorozinc(II) complexes previously determined. A four-co-ordinate structure is suggested for $[ZnX_2(dmf)_2]$ (X = Br or I), $[ZnX_3(dmf)]^-$ (X = Br, I, or SCN), and $[Zn(NCS)_4]^{2-}$, and thus the six-co-ordinate, octahedral structure of $[Zn(dmf)_6]^{2+}$ changes upon complexation. The complexes $[Zn(NCS)(dmf)_5]^+$ and $[Zn(bipy)_n]^{2+}$ (*n* = 1—3) remain octahedral. The extent of formation of the [111] complex is weak in all halide systems. The [121] complex is dominant in the chloride system, significant in the bromide, but very weak in the iodide system, and the reaction enthalpies and entropies suggest that an octahedral–tetrahedral equilibrium, $[ZnX_2(bipy)(dmf)_2]$ $(O_h) \rightleftharpoons [ZnX_2(bipy)]$ (T_d) + 2dmf (X = Cl or Br), is established in solution. On the other hand, the [112] complex, which is not found in the chloride system, becomes dominant in the bromide and especially so in the iodide system. The formation of the $[ZnI(bipy)_2]^+$ complex, $[Zn(bipy)_2]^{2+} + I^- \longrightarrow [ZnI(bipy)_2]^+$, is accompanied by unusual ΔH° and ΔS° values, implying that a specific interaction operates between iodide ion and 2,2′-bipyridine molecules in the vicinity of the zinc(II) ion.

Various $[ZnL_2X_2]$ complexes [L = pyridine (py) or its derivatives; X = Cl, Br, or I] were prepared and characterized,[1] and the tetrahedral structure of $[ZnX_2(py)_2]$ (X = Cl or I) has been established.[2,3] Pyridine is known to be a good π acceptor of metal π donors, while d^{10} Zn^{II} is a rather poor donor,[4] *i.e.* σ bonding is stronger than π bonding in zinc(II) complexes.[5,6] Indeed, the Zn^{II}–Cl distance changes little among $[ZnCl_2(4R\text{-}py)_2]$ complexes of various pyridine derivatives,[5] suggesting that no pyridine–chloride ion interaction occurs through the central zinc(II) ion. This is supported by free energies of transfer of $ZnCl_2$ from pyridine to other solvents.[7] With regard to ternary zinc(II) systems involving 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen), such complexes as $[ZnX_2L]$ (X = Cl, Br, I, or SCN; L = bipy or phen), $[Zn(O_2CMe)_2(bipy)]$, $[Zn(O_2CMe)_2(bipy)_2]$, and $[ZnA(bipy)]^+$, $[ZnA_2(bipy)]$, and $[ZnA(bipy)_2]^+$ (HA = an amino acid) have been characterized.[8,9] For the $[ZnCl_2L]$ (L = bipy or phen) complex, tetrahedral geometry has been established.[10,11] On the other hand, $[Zn(bipy)_2(NO_2)]^+$ and $[Zn(phen)_2(NCS)_2]$ possess six-co-ordinate, *cis*-octahedral geometry.[12,13] However, investigations of the ternary complexation of zinc(II) ions in solution have been limited, and thermodynamic data, such as reaction enthalpies and entropies, are especially scarce.[14] To elucidate interactions in the ternary zinc(II) system in more detail, precise thermodynamic data are indispensable. In our previous work on the ternary Zn^{II}–Cl^-–bipy system in dimethylformamide (dmf)[15] the formation of the ternary complexes $[ZnCl(bipy)]^+$ and $[ZnCl_2(bipy)]$ was established, and their reaction enthalpies and entropies determined. Here, we extend these studies to the ternary systems Zn^{II}–X^-–bipy (X = Br, I, or SCN) in dmf.

Experimental

Reagents.—All chemicals used were of reagent grade. The dmf solvates of zinc(II) perchlorate were prepared as described elsewhere.[16] Tetraethylammonium perchlorate, thiocyanate, bromide, and iodide were recrystallized once from water and dried in a vacuum oven at 100 °C. 2,2′-Bipyridine was used without further purification and dried *in vacuo* in a desiccator over P_2O_5. Dimethylformamide was dried for several weeks over molecular sieve 4A 1/16, then distilled under reduced pressure and stored with molecular sieves in a dark bottle with a P_2O_5 drying tube.

Measurements.—Calorimetric measurements were carried out using a fully automatic on-line calorimetry system,[17] in a room thermostatted at 25 ± 0.2 °C. All zinc(II) perchlorate and 2,2′-bipyridine solutions contained NEt_4ClO_4 as an inert ionic medium (0.16, 0.10, and 0.40 mol dm^{-3} for Br, I, and SCN systems, respectively). A solution (40 cm^3) containing zinc(II) perchlorate and 2,2′-bipyridine was placed in a stainless-steel vessel, the inside wall of which was coated with Teflon. The vessel, filled with dry nitrogen gas and isolated from moisture with a P_2O_5 drying tube, was inserted into an aluminium block thermostatted at 25.0 ± 0.0001 °C in an air-bath. The titrant was a 0.16 mol dm^{-3} NEt_4Br, 0.1 mol dm^{-3} NEt_4I, or 0.40 mol dm^{-3} NEt_4SCN solution. Similarly, a solution containing zinc(II) perchlorate and NEt_4X (X = Br, I, or SCN) was titrated with a 0.1 mol dm^{-3}, 2,2′-bipyridine solution. Portions of the titrant solution were added to the test solution by using an autoburette (APB-118, Kyoto Electronics), and heats of complexation at each titration point were measured with a certainty of ±0.02 J, and corrected for the heat of dilution of

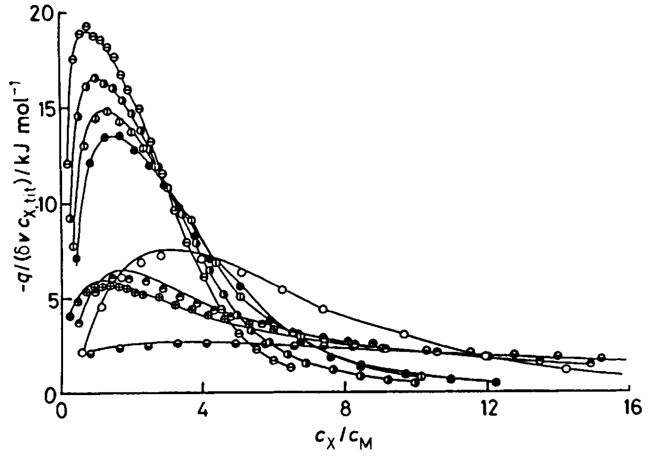

Figure 1. Calorimetric titration curves for the Zn^{II}–I^-–bipy system obtained in dimethylformamide containing 0.10 mol dm^{-3} NEt_4ClO_4 at 25 °C. Concentrations of Zn^{II} and 2,2′-bipyridine in the initial solutions, c_M,c_L/mmol dm^{-3}: 2.143, 0 (○); 5.773, 0 (●), 7.206, 0 (⌽); 9.529, 0 (◑); 15.03, 0 (⊖); 5.056, 5.711 (◓); 10.55, 18.75 (⊕); and 5.924, 15.84 (◒). The titrant is a 0.10 mol dm^{-3} NEt_4I solution. The solid lines are calculated by using the constants in Table 4

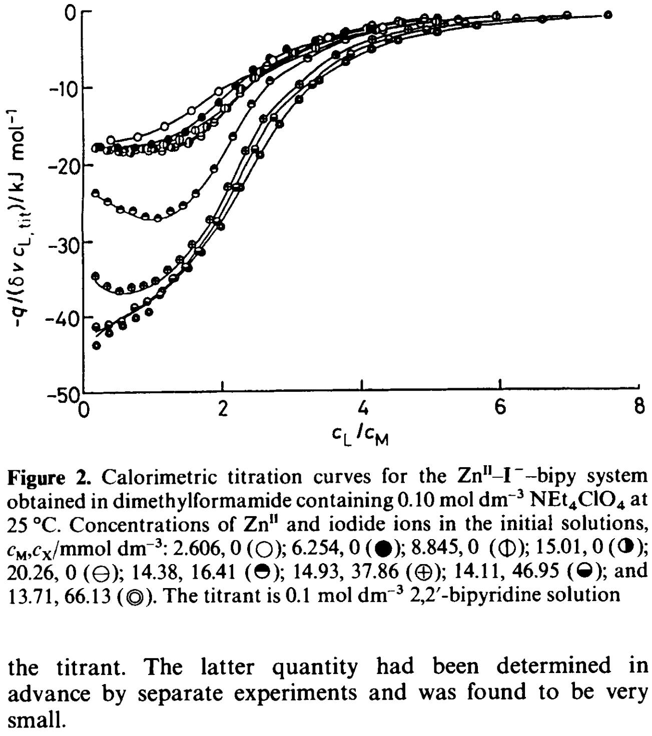

Figure 2. Calorimetric titration curves for the Zn^{II}–I^-–bipy system obtained in dimethylformamide containing 0.10 mol dm^{-3} NEt_4ClO_4 at 25 °C. Concentrations of Zn^{II} and iodide ions in the initial solutions, c_M,c_X/mmol dm^{-3}: 2.606, 0 (○); 6.254, 0 (●); 8.845, 0 (⌽); 15.01, 0 (◑); 20.26, 0 (⊖); 14.38, 16.41 (◓); 14.93, 37.86 (⊕); 14.11, 46.95 (◒); and 13.71, 66.13 (◎). The titrant is 0.1 mol dm^{-3} 2,2′-bipyridine solution

the titrant. The latter quantity had been determined in advance by separate experiments and was found to be very small.

Data Analysis.—If the formation of only mononuclear complexes is assumed, the system can be defined as in equations (1) and (2). A heat q_i measure at the ith titration point is

$$Zn^{2+} + mX^- + n\text{bipy} \rightleftharpoons [ZnX_m(\text{bipy})_n]^{(2-m)+} \quad (1)$$

$$\beta_{1mn} = [ZnX_m(\text{bipy})_n{}^{(2-m)+}]/[Zn^{2+}][X^-]^m[\text{bipy}]^n \quad (2)$$

expressed by using both formation constants β_{1mn} and overall enthalpies $\Delta H^\circ_{\beta 1mn}$, equation (3), where V denotes the volume of the test solution. The concentrations of free Zn^{2+} and X^- 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 according to the mass-balance equations (4)—(6).

$$q_i = -(V_i\Sigma\Sigma\beta_{1mn}\Delta H^\circ_{\beta 1mn}[Zn^{2+}]_i[X^-]_i^m[\text{bipy}]_i^n - V_{i-1}\Sigma\Sigma\beta_{1mn}\Delta H^\circ_{\beta 1mn}[Zn^{2+}]_{i-1}[X^-]_{i-1}^m[\text{bipy}]_{i-1}^n) \quad (3)$$

$$c_{M,i} = [Zn^{2+}]_i + \Sigma\Sigma\beta_{1mn}[Zn^{2+}]_i[X^-]_i^m[\text{bipy}]_i^n \quad (4)$$

$$c_{X,i} = [X^-]_i + \Sigma\Sigma m\beta_{1mn}[Zn^{2+}]_i[X^-]_i^m[\text{bipy}]_i^n \quad (5)$$

$$c_{L,i} = [\text{bipy}]_i + \Sigma\Sigma n\beta_{1mn}[Zn^{2+}]_i[X^-]_i^m[\text{bipy}]_i^n \quad (6)$$

Formation constants and enthalpies were simultaneously determined by minimizing $U = \Sigma(q_{i,obs.} - q_{i,calc.})^2$ by using a non-linear least-squares program, with an algorithm proposed by Marquardt.[18]

Results

Typical calorimetric titration curves obtained in the Zn^{II}–I^-–bipy system are depicted in Figures 1 and 2. The heat of reaction q_i measured at each titration point is normalized with the volume of the titrant added δv_i and the concentration of halide ions (or 2,2′-bipyridine) in the titrant $c_{X,tit}$ (or $c_{L,tit}$), and the term $-q_i/\delta v_i c_{X,tit}$ (or $-q_i/\delta v_i c_{L,tit}$) is plotted against $c_{X,i}/c_{M,i}$ (or $c_{L,i}/c_{M,i}$) in solution (i is omitted in the Figures). These titration curves are simultaneously analysed by assuming various sets of complexes, the most plausible set of which is explored, and their formation constants and enthalpies obtained. The solid lines in Figures 1 and 2, calculated by using the constants of a final set of complexes, reproduce well the experimental points. A similar procedure was applied to the systems Zn^{II}–Br^-–bipy and Zn^{II}–SCN^-–bipy.

The non-linear least-squares analysis of data for the binary Zn^{II}–Br^- and Zn^{II}–I^- systems indicated that the formation of $[ZnX_4]^{2-}$ (X = Br or I) can be rejected, and set (1,2,3) assuming the formation of $[ZnX]^+$, ZnX_2, and $[ZnX_3]^-$ and set (2,3) eliminating $[ZnX]^+$ from set (1,2,3) gave relatively small Hamilton R factors. These results are listed in Table 1. In the Zn^{II}–Br system the R value of set (1,2,3) is appreciably smaller than that of set (2,3), and thus set (1,2,3) is plausible. However, the formation of $[ZnBr]^+$ is very weak as in the case for the Zn^{II}–Cl system. In the Zn^{II}–I system the R values of sets (1,2,3) and (2,3) are similar (0.0126 and 0.0138, respectively), and the introduction of the $[ZnI]^+$ complex does not affect appreciably the β_2 and β_3 values, implying that the formation of the $[ZnI]^+$ complex is negligibly small. In the Zn^{II}–SCN^- system, as is also seen in Table 1, sets (1,2,3,4) and (1,3,4) gave relatively smaller R values, and the value for set (1,3,4) is slightly larger than that for set (1,2,3,4), but the difference is marginal. The log β_n (n = 1, 3, or 4) values hardly change even if the $Zn(NCS)_2$ complex is taken into account, and the standard deviations of the formation constants for set (1,3,4) are remarkably smaller than those for set (1,2,3,4). This indicates that the formation of $Zn(NCS)_2$ is very much suppressed. For the binary systems, as a consequence, we finally propose set (1,2,3) for Br, set (2,3) for I, and set (1,3,4) for SCN.

In the Zn^{II}–bipy system the titration curves can be well explained in terms of the formation of $[Zn(bipy)]^{2+}$, $[Zn(bipy)_2]^{2+}$, and $[Zn(bipy)_3]^{2+}$, and their overall formation constants and enthalpies were obtained. Final results are shown in Table 2. No appreciable dependence of these parameters on the ionic medium has been observed. These values were fixed in the course of the analysis of formation constants and enthalpies in the ternary systems.

Calorimetric data obtained for the ternary Zn^{II}–X^-–bipy systems were analysed by assuming various sets of ternary $[ZnX_m(\text{bipy})_n]^{(2-m)+}$ (denoted as [$1mn$]) complexes. In both

Table 1. Least-squares refinement of overall formation constants $\log(\beta_n/\mathrm{dm}^{3n}\ \mathrm{mol}^{-n})$ and enthalpies $\Delta H^{\ominus}_{\beta n}/\mathrm{kJ\ mol}^{-1}$ in the binary zinc(II) bromide, iodide, and thiocyanate systems in dimethylformamide at 25 °C

	X = Br[a]		I[b]	SCN[c]	
	(1,2,3)	(2,3)	(2,3)	(1,3,4)	(1,2,3,4)
$\log \beta_1$	3.1 (0.3)[d]			3.33 (0.05)	3.1 (0.5)
$\log \beta_2$	8.7 (0.2)	8.4 (0.4)	4.17 (0.03)		6.1 (0.4)
$\log \beta_3$	12.3 (0.3)	11.9 (0.5)	5.79 (0.06)	10.23 (0.06)	10.1 (0.3)
$\log \beta_4$				13.31 (0.07)	13.3 (0.4)
$\Delta H^{\ominus}_{\beta 1}$	33 (9)			4.9 (0.3)	6.1 (0.9)
$\Delta H^{\ominus}_{\beta 2}$	37.0 (0.2)	37.3 (0.4)	57.9 (1.4)		5 (16)
$\Delta H^{\ominus}_{\beta 3}$	31.4 (0.1)	31.1 (0.4)	67.3 (1.1)	9.5 (0.4)	10.4 (1.6)
$\Delta H^{\ominus}_{\beta 4}$				−7.9 (0.1)	−7.9 (0.1)
N[e]	142	142	92	115	115
R[f]	0.0124	0.0315	0.0138	0.0280	0.0226

[a] 0.16 mol dm^{-3} NEt_4ClO_4 ionic medium. [b] 0.10 mol dm^{-3} NEt_4ClO_4. [c] 0.4 mol dm^{-3} NEt_4ClO_4. [d] Values in parentheses refer to 3σ. [e] Total number of data points. [f] The Hamilton R factor; the value for set (1,2,3) in the Zn^{II}–I^- system is 0.0126.

Table 2. Least-squares refinement of overall formation constants $\log(\beta_n/\mathrm{dm}^{3n}\ \mathrm{mol}^{-n})$ and enthalpies $\Delta H^{\ominus}_{\beta n}/\mathrm{kJ\ mol}^{-1}$ in the binary zinc(II)–2,2′-bipyridine system in dimethylformamide at 25 °C

	I/mol dm^{-3}		
	0.1	0.16	0.4[a]
$\log \beta_1$	3.9 (0.2)[b]	3.7 (0.3)	3.9
$\log \beta_2$	6.9 (0.2)	6.9 (0.3)	6.9
$\log \beta_3$	8.8 (0.3)	8.9 (0.3)	8.7
$\Delta H^{\ominus}_{\beta 1}$	−18.1 (0.2)	−17.4 (0.3)	−18.2
$\Delta H^{\ominus}_{\beta 2}$	−38.5 (0.5)	−36.6 (0.5)	−39.1
$\Delta H^{\ominus}_{\beta 3}$	−55.2 (0.6)	−54.0 (0.7)	−55.9
N	73	58	
R	0.009 68	0.0108	

[a] Ref. 15. [b] Values in parentheses refer to 3σ.

Table 3. Least-squares refinement of overall formation constants $\log(\beta_{1mn}/\mathrm{dm}^{3(m+n)}\ \mathrm{mol}^{-(m+n)})$ and enthalpies, $\Delta H^{\ominus}_{\beta 1mn}/\mathrm{kJ\ mol}^{-1}$ for the formation of $[ZnX_m(bipy)_n]^{(2-m)+}$ (X = Br, I, or SCN) in dimethylformamide at 25 °C[a]

	Br	I	SCN[b]
$\log \beta_{110}$	2.9 (0.4)		3.33
$\log \beta_{120}$	8.48 (0.04)	4.21 (0.05)	
$\log \beta_{130}$	11.98 (0.08)	5.86 (0.08)	10.23
$\log \beta_{140}$			13.31
$\log \beta_{111}$	7.6 (0.2)	5.6 (0.14)	7.3 (0.4)
$\log \beta_{112}$	10.19 (0.10)	8.19 (0.07)	9.8 (0.2)
$\log \beta_{121}$	11.17 (0.06)	6.88 (0.15)	10.6 (0.1)
$\log \beta_{122}$			12.3 (0.06)
$\Delta H^{\ominus}_{\beta 110}$	38 (19)		4.9
$\Delta H^{\ominus}_{\beta 120}$	37.2 (0.2)	55 (2)	
$\Delta H^{\ominus}_{\beta 130}$	31.5 (0.2)	69 (2)	9.5
$\Delta H^{\ominus}_{\beta 140}$			−7.9
$\Delta H^{\ominus}_{\beta 111}$	0.6 (1)	3 (4)	−13.0 (3)
$\Delta H^{\ominus}_{\beta 112}$	−25 (2)	−32 (4)	−42.9 (2)
$\Delta H^{\ominus}_{\beta 121}$	15.7 (1.2)	50 (16)	−17.5 (1)
$\Delta H^{\ominus}_{\beta 122}$			−40.9 (2)
R	0.0176	0.0161	0.0376
N	287	247	131

[a] Ionic media of 0.16, 0.1, and 0.4 mol dm^{-3} NEt_4ClO_4 were used for the Br, I, and SCN systems, respectively. For all cases, the values for the binary 2,2′-bipyridine complexes are fixed (Table 2). Values in parentheses refer to 3σ. [b] The values for the binary complexes are fixed [set (1,3,4) in Table 1].

bromide and iodide systems, the formation of [111] and [121] was first assumed, as is the case for the Zn^{II}–Cl^-–bipy system. However, this gave large R values, and the [112] complex, which is rejected in the chloride system, was taken into account. The R value then considerably decreased, and thus the formation of the [112] complex in the bromide and iodide systems is obvious. Finally, thermodynamic parameters of both the binary and ternary complexes were simultaneously optimized. Particularly, in the iodide system, the $\log \beta_{121}$ and $\Delta H^{\ominus}_{\beta 121}$ values involve rather large uncertainties, indicating that the formation of the [121] complex is very weak. In the Zn^{II}–SCN^-–bipy system the ternary complexes [111], [112], [121], and [122] are evidently formed, because elimination of any one of them leads to appreciably large R values. As a consequence, we finally propose the formation of ternary complexes [111], [121], and [112] in the bromide and iodide systems, and [111], [121], [112], and [122] in the thiocyanate system. The thermodynamic parameters for the final sets are summarized in Table 3.

Discussion

Binary Zinc(II) *Halogeno Complexes.*—The distribution of species for the binary Zn^{II}–X^- (X = Cl, Br, or I) systems in dmf is depicted in Figure 3, along with that for the Zn^{II}–SCN^- system. In the binary Zn^{II}–Cl^- system the formation of a series of four mononuclear species, $[ZnCl]^+$, $ZnCl_2$, $[ZnCl_3]^-$, and $[ZnCl_4]^{2-}$, has been established.[16] In the Zn^{II}–Br^- and Zn^{II}–I^- systems the formation of the relevant $[ZnX_4]^{2-}$ complex is virtually negligible under the experimental conditions examined. The formation of $[ZnX]^+$ is suppressed in all the halide systems.

In Table 4 the $(\Delta S^{\ominus}_1 + \Delta S^{\ominus}_2)$ values, all large and positive, are practically the same among the halides, while the $\Delta S^{\ominus}_3$ values are very much smaller than the $(\Delta S^{\ominus}_1 + \Delta S^{\ominus}_2)$ values, suggesting that the number of liberated solvent molecules is large in the reaction $Zn^{2+} + 2X^- \longrightarrow ZnX_2$, but relatively small in the reaction $ZnX_2 + X^- \longrightarrow [ZnX_3]^-$. The $(\Delta H^{\ominus}_1 + \Delta H^{\ominus}_2)$ value is much larger than the $\Delta H^{\ominus}_3$ value in any halide system, which is consistent with the above consideration. Thus four-co-ordinate $[ZnX_2(dmf)_2]$ and $[ZnX_3(dmf)]^-$ complexes are formed in all halide systems, as in equations (7) and (8).

$$[Zn(dmf)_6]^{2+} + 2X^- \longrightarrow [ZnX_2(dmf)_2] + 4dmf \quad (7)$$

$$[ZnX_2(dmf)_2] + X^- \longrightarrow [ZnX_3(dmf)]^- + dmf \quad (8)$$

A similar conclusion regarding the changes in co-ordination geometry has been obtained in dimethyl sulphoxide (dmso) by Ahrland and Björk.[19] The suppressed formation of $[ZnX]^+$

Table 4. Stepwise formation constants log (K_n/dm^3 mol^{-1}), enthalpies ΔH_n°/kJ mol^{-1} and entropies ΔS_n°/J K^{-1} mol^{-1} for the reaction $[MX_{n-1}]^{(3-n)+} + X^- \longrightarrow [MX_n]^{(2-n)+}$ (X = Cl, Br, or I) of M [= Zn, Zn(bipy), or Zn(bipy)$_2$] in dimethylformamide at 25 °C

	$\log K_1K_2$	$\Delta H_1^\circ + \Delta H_2^\circ$	$\Delta S_1^\circ + \Delta S_2^\circ$
$Zn^{2+} + 2Cl \longrightarrow ZnCl_2$	11.8	16.1	283
$Zn^{2+} + 2Br^- \longrightarrow ZnBr_2$	8.5	37.2	287
$Zn^{2+} + 2I^- \longrightarrow ZnI_2$	4.2	57.9	274
$[Zn(bipy)]^{2+} + 2Cl^- \longrightarrow [ZnCl_2(bipy)]$	10.7	2.8	211
$[Zn(bipy)]^{2+} + 2Br^- \longrightarrow [ZnBr_2(bipy)]$	7.3	33.1	254
$[Zn(bipy)]^{2+} + 2I^- \longrightarrow [ZnI_2(bipy)]$	3.0		
	$\log K_1$	ΔH_1°	ΔS_1°
$[Zn(bipy)]^{2+} + Cl^- \longrightarrow [ZnCl(bipy)]^+$	5.4	11.4	141
$[Zn(bipy)]^{2+} + Br^- \longrightarrow [ZnBr(bipy)]^+$	3.8	18.0	133
$[Zn(bipy)_2]^{2+} + Br^- \longrightarrow [ZnBr(bipy)_2]^+$	3.2	11.7	100
$[Zn(bipy)_2]^{2+} + I^- \longrightarrow [ZnI(bipy)_2]^+$	1.4	9.8	59
	$\log K_2$	ΔH_2°	ΔS_2°
$[ZnCl(bipy)]^+ + Cl^- \longrightarrow [ZnCl_2(bipy)]$	5.3	−8.6	70
$[ZnBr(bipy)]^+ + Br^- \longrightarrow [ZnBr_2(bipy)]$	3.5	15.1	118
	$\log K_3$	ΔH_3°	ΔS_3°
$ZnCl_2 + Cl^- \longrightarrow [ZnCl_3]^-$	5.3	−17.6	42
$ZnBr_2 + Br^- \longrightarrow [ZnBr_3]^-$	3.5	−5.7	50
$ZnI_2 + I^- \longrightarrow [ZnI_3]^-$	1.6	9.4	63
	$\log K_4$	ΔH_4°	ΔS_4°
$[ZnCl_3]^- + Cl^- \longrightarrow [ZnCl_4]^{2-}$	2.2	−7.9	16

The formation of $[ZnX]^+$ (X = Cl, Br, or I), $[ZnI(bipy)]^+$, $[ZnCl(bipy)_2]^+$, and $[ZnX_2(bipy)_2]^+$ (X = Cl, Br, or I) is weak or practically negligible.

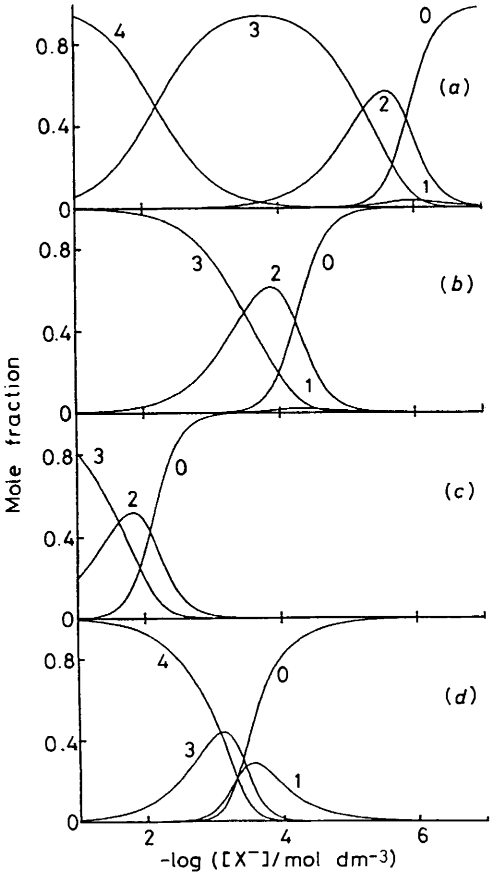

Figure 3. Species distribution in the binary zinc(II)–halide and -thiocyanate systems in dimethylformamide at 25 °C. The $[ZnX_n]^{(2-n)+}$ complexes are represented by their n values; X = Cl (*a*), Br (*b*), I (*c*), or SCN (*d*)

implies that a change from octahedral to tetrahedral geometry around the central metal ion may occur even at the first step of complexation. Note that the ΔH_3° value is negative for Cl and Br, implying that the Zn^{II}–dmf bonds within $[ZnX_2(dmf)_2]$ are very much weakened. Also that the ($\Delta H_1^\circ + \Delta H_2^\circ$) values increase in the order Cl < Br < I, *i.e.* increasing ionic radii of the anions. This trend is even more pronounced in dmf than in water. It is thus expected that Zn^{II} behaves as a hard ion in dmf as well as in water.

Ternary Zn^{II}–X$^-$–bipy (X = Cl, Br, or I) *Systems*.—The distribution of species in the Zn^{II}–Br$^-$–bipy system is depicted in Figure 4. The [121] and [112] complexes occur in solution over a wide concentration ratio c_L/c_M between 2,2′-bipyridine and zinc(II) ion, while the [111] complex occurs at low c_L/c_M. At high bromide-ion concentration the $[ZnBr_3]^-$ complex predominates, and consequently the ternary species disappear. On the other hand, in the Zn^{II}–I$^-$–bipy system the $[Zn(bipy)_3]^{2+}$ complex predominates at high 2,2′-bipyridine concentration, as shown in Figure 5.

In Table 4, the ($\Delta S_1^\circ + \Delta S_2^\circ$) value for the formation of $[ZnCl_2(bipy)]$ is significantly smaller, and the corresponding ($\Delta H_1^\circ + \Delta H_2^\circ$) value less endothermic, than those for the formation of ZnCl$_2$. The same applies also for Br, though not so marked. This suggests that the number of solvent molecules liberated on formation of $[ZnX_2(bipy)]$ (X = Cl or Br) is less than that on formation of ZnX$_2$. This may be reasonably explained if the six-co-ordinate $[ZnX_2(bipy)(dmf)_2]$ complex is partly formed as a minor species, along with the main four-co-ordinate $[ZnX_2(bipy)]$ complex, as in equations (9) and (10).

$$[Zn(bipy)(dmf)_4]^{2+} + 2X^- \longrightarrow [ZnX_2(bipy)(dmf)_2] + 2dmf \quad (9)$$

$$[Zn(bipy)(dmf)_4]^{2+} + 2X^- \longrightarrow [ZnX_2(bipy)] + 4dmf \quad (10)$$

Evidently, the number of liberated solvent molecules is less for

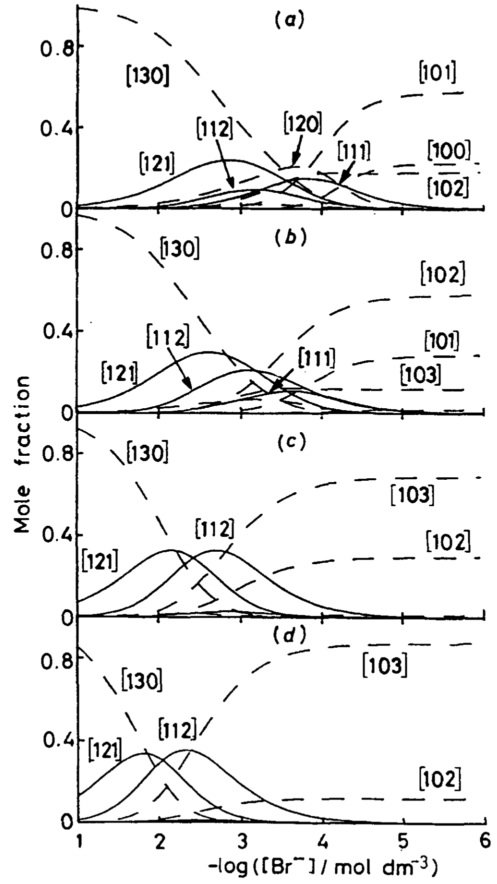

Figure 4. Species distribution in the Zn^{II}–Br^-–bipy system calculated at c_M/mol dm^{-3} and c_X/mol dm^{-3} = 0.01, 0.01 (*a*); 0.01, 0.02 (*b*); 0.01, 0.05 (*c*); and 0.01, 0.10 (*d*), in dimethylformamide at 25 °C. The $[ZnBr_m(bipy)_n]^{(2-m)+}$ complexes are represented by the symbols [1*mn*]

reaction (9), and thus the observed enthalpy and entropy values may be smaller than those expected for the case in which the four-co-ordinate complex $[ZnX_2(bipy)]$ is uniquely formed. The coexistence of both $[ZnX_2(bipy)(dmf)_2]$ (O_h) and $[ZnX_2(bipy)]$ (T_d) in solution implies that an octahedral–tetrahedral equilibrium (11) is established. The ($\Delta S^\circ_1 + \Delta S^\circ_2$) values for the formation of $[ZnCl_2(bipy)]$ is appreciably smaller than that for $[ZnBr_2(bipy)]$, in contrast to the similar values for ZnX_2 (X = Cl, Br, or I). This suggests that equilibrium (11) is

$$\underset{O_h}{[ZnX_2(bipy)(dmf)_2]} \rightleftharpoons \underset{T_d}{[ZnX_2(bipy)]} + 2dmf \quad (11)$$

more shifted toward the O_h side in the chloride system than in the bromide one. A similar O_h–T_d equilibrium has been suggested between $[CdX_2(bipy)(dmf)_2]$ and $[CdX_2(bipy)]$ in the ternary Cd^{II}–X^-–bipy systems.[20] This deduction leads to the conclusion that all the [111] complexes possess six-co-ordinate $[ZnX(bipy)(dmf)_3]^+$ geometry.*

Formation of the [112] complex occurs extensively in the iodide system, less so in the bromide, and practically not at all in the chloride system. This is surprising, because Zn^{II} is rather hard, and thus the Zn^{II}–X^- interaction is expected to be weaker in the order Cl > Br > I, as discussed in a previous section.

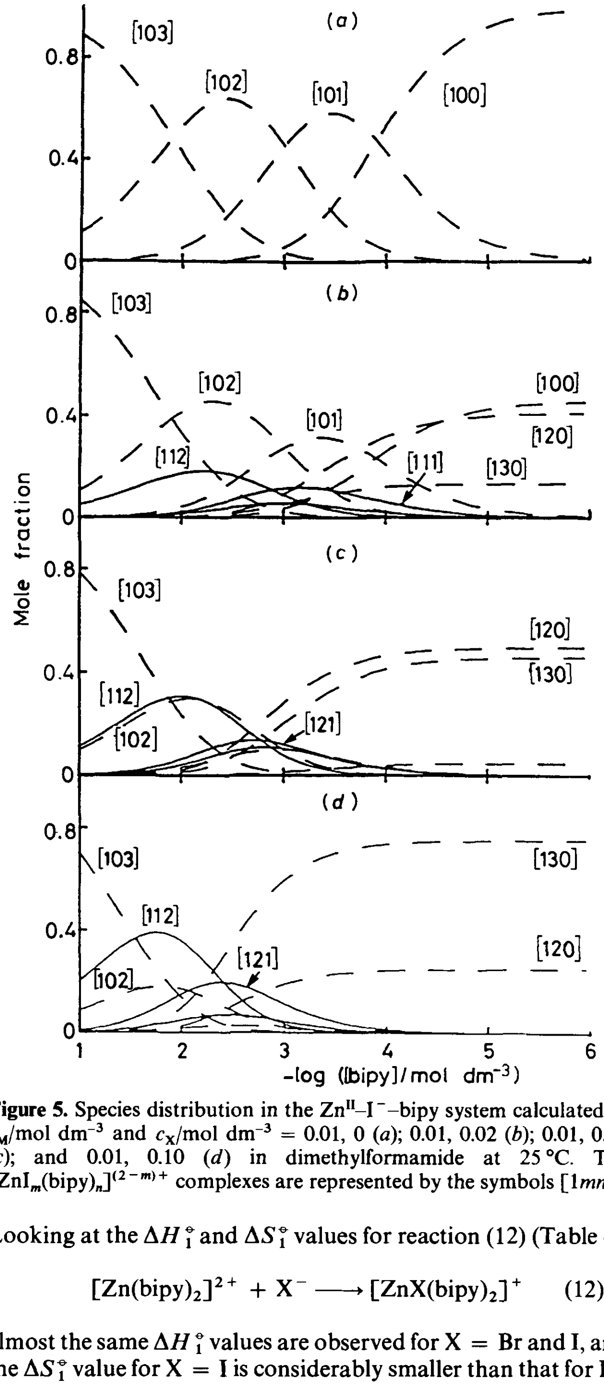

Figure 5. Species distribution in the Zn^{II}–I^-–bipy system calculated at c_M/mol dm^{-3} and c_X/mol dm^{-3} = 0.01, 0 (*a*); 0.01, 0.02 (*b*); 0.01, 0.05 (*c*); and 0.01, 0.10 (*d*) in dimethylformamide at 25 °C. The $[ZnI_m(bipy)_n]^{(2-m)+}$ complexes are represented by the symbols [1*mn*]

Looking at the ΔH°_1 and ΔS°_1 values for reaction (12) (Table 4),

$$[Zn(bipy)_2]^{2+} + X^- \longrightarrow [ZnX(bipy)_2]^+ \quad (12)$$

almost the same ΔH°_1 values are observed for X = Br and I, and the ΔS°_1 value for X = I is considerably smaller than that for Br. This is unusual, because if the $[ZnBr(bipy)_2]^+$ and $[ZnI(bipy)_2]^+$ complexes possess the same co-ordination number, either five or six, similar ΔS°_1 values for both Br and I may result. A different co-ordination number might occur, *e.g.* five for $[ZnI(bipy)_2]^+$ and six for $[ZnBr(bipy)_2(dmf)]^+$, as iodide ion is larger than bromide. In this case, the number of solvent molecules liberated upon complexation may be larger for I than for Br, leading to a larger ΔS°_1 value for I. However, ΔS°_1 is in fact smaller for I. Such behaviour cannot be explained without considering a specific interaction within the $[ZnI(bipy)_2]^+$ complex. An interligand interaction through the zinc(II) ion is hardly acceptable as the d_π donor property of zinc(II) is generally weak and not essentially changed by the co-ordination of 2,2′-bipyridine molecules.[5–7] Indeed, unusual behaviour is not observed for the $[ZnX(bipy)]^+$ and $[ZnX_2(bipy)]$ complexes. Thus, the specific interaction in the $[ZnX(bipy)_2]^+$

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* In ref. 15 we derived a wrong conclusion that both $[ZnCl(bipy)]^+$ and $[ZnCl_2(bipy)]$ possess a tetrahedral, four-co-ordinate geometry, by simply considering the larger ΔS°_1 value for $[ZnCl(bipy)]^+$ than the ΔS°_2 value for $[ZnCl_2(bipy)]$

Table 5. Stepwise formation constants log (K_n/dm^3 mol^{-1}), enthalpies ΔH°_n/kJ mol^{-1}, and entropies ΔS°_n/kJ mol^{-1} for the reaction of $[M(NCS)_{n-1}]^{(3-n)+} + SCN^- \longrightarrow [M(NCS)_n]^{(2-n)+}$ [M = Zn, Zn(bipy), or Zn(bipy)$_2$] in dimethylformamide at 25 °C

	log K_1	ΔH°_1	ΔS°_1
$Zn^{2+} + SCN^- \longrightarrow [Zn(NCS)]^+$	3.3	4.9	80
$[Zn(bipy)]^{2+} + SCN^- \longrightarrow [Zn(NCS)(bipy)]^+$	3.4	5.2	83
$[Zn(bipy)_2]^{2+} + SCN^- \longrightarrow [Zn(NCS)(bipy)_2]^+$	3.0	−3.8	44
	log K_2	ΔH°_2	ΔS°_2
$[Zn(NCS)(bipy)]^+ + SCN^- \longrightarrow [Zn(NCS)_2(bipy)]$	3.3	−4.5	48
$[Zn(NCS)(bipy)_2]^+ + SCN^- \longrightarrow [Zn(NCS)_2(bipy)_2]$	2.5	2.0	55
	log K_2K_3	$\Delta H^{\circ}_2 + \Delta H^{\circ}_3$	$\Delta S^{\circ}_2 + \Delta S^{\circ}_3$
$[Zn(NCS)]^+ + 2SCN^- \longrightarrow [Zn(NCS)_3]^-$	6.9	4.6	147
	log K_4	ΔH°_4	ΔS°_4
$[Zn(NCS)_3]^- + SCN^- \longrightarrow [Zn(NCS)_4]^{2-}$	3.2	−17.4	3

The formation of Zn(NCS)$_2$ is weak and practically negligible.

complex might arise from a through-space interaction between a halide ion and 2,2′-bipyridine molecules with a *cis* arrangement in the vicinity of the zinc(II) ion.

The Binary Zn^{II}–SCN$^-$ *and Ternary* Zn^{II}–SCN$^-$–bipy *Complexes*.—In the binary Zn^{II}–SCN$^-$ system the formation of the $[Zn(NCS)]^+$, $[Zn(NCS)_3]^-$, and $[Zn(NCS)_4]^{2-}$ complex is favourable, but that of Zn(NCS)$_2$ is negligibly small. The thermodynamic parameters for stepwise formation of the complexes are summarized in Table 5, along with those for the ternary complexes. The ($\Delta S^{\circ}_2 + S^{\circ}_3$) value is large and positive, while ΔS°_4 is close to zero. This indicates that the number of solvent molecules liberated on formation of $[Zn(NCS)_3]^-$ is large, but very small on the formation of $[Zn(NCS)_4]^{2-}$, and thus following reactions (13) and (14) are proposed. As a

$$[Zn(NCS)(dmf)_5]^+ + 2SCN^- \longrightarrow [Zn(NCS)_3(dmf)]^- + 4dmf \quad (13)$$

$$[Zn(NCS)_3(dmf)]^- + SCN^- \longrightarrow [Zn(NCS)_4]^{2-} + dmf \quad (14)$$

consequence, the $[Zn(NCS)(dmf)_5]^+$ complex may possess octahedral geometry like $[Zn(dmf)_6]^{2+}$, while $[Zn(NCS)_3(dmf)]^-$ and $[Zn(NCS)_4]^{2-}$ may be tetrahedral. The tetrahedral geometry of $[Zn(NCS)_4]^{2-}$ has been established by solution *X*-ray diffraction in water[21] and dmso.[22] The ΔH°_4 value is negative in contrast to the positive ($\Delta H^{\circ}_2 + \Delta H^{\circ}_3$), implying that the Zn^{II}–dmf interaction in the $[Zn(NCS)_3(dmf)]^-$ is much weakened.

In the ternary Zn^{II}–SCN$^-$–bipy system the formation of four complexes, [111], [121], [112], and [122], is established, and the distribution of species is depicted in Figure 6. Among the ternary complexes, the formation of [121] and [122] is of particular interest, as the formation of Zn(NCS)$_2$ is practically negligible. As seen in Table 5, the log K_1, ΔH°_1, and ΔS°_1 values for the formation of [111] are similar to those for the formation of $[Zn(NCS)]^+$, implying that the former complex possesses six-co-ordinate $[Zn(NCS)(bipy)(dmf)_3]^+$ geometry, like $[Zn(NCS)(dmf)_5]^+$. On the other hand, the ΔH°_1 value for the formation of [112] is negative and the corresponding ΔS°_1 value is significantly small, in contrast to the values for the formation of the $[Zn(NCS)]^+$ and [111] complexes. A specific interaction as observed in the $[ZnX(bipy)_2]^+$ complex might operate also in the $[Zn(NCS)(bipy)_2]^+$ complex. It is interesting that the negative ΔH° and relatively small ΔS° values, similar to those found for the formation of the [112] complex, are also found in

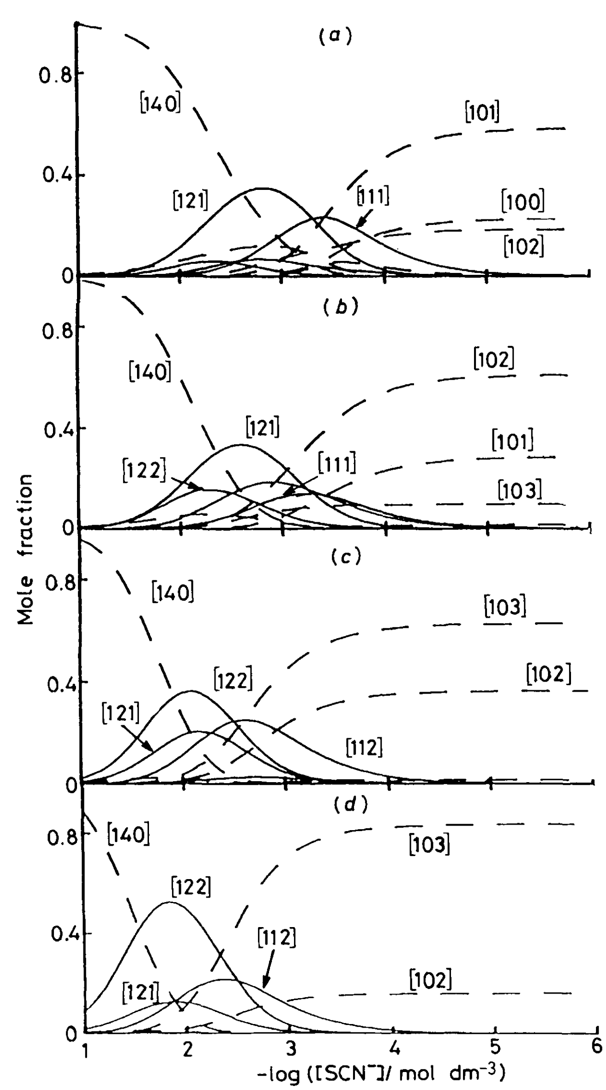

Figure 6. Species distribution in the Zn^{II}–SCN$^-$–bipy system calculated at c_M/mol dm^{-3} and c_X/mol dm^{-3} = 0.01, 0.01 (*a*); 0.01, 0.02 (*b*); 0.01, 0.05 (*c*); and 0.01, 0.10 (*d*) in dimethylformamide at 25 °C. The $[Zn(NCS)_m(bipy)_n]^{(2-m)+}$ complexes are represented by the symbols [1*mn*]

the reaction $[Zn(NCS)(bipy)]^+ + SCN^- \longrightarrow [Zn(NCS)_2(bipy)]$.

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