Zinc Complexes of Four Tetra-aza Macrocycles: Enthalpies of Formation in Acetonitrile Solution

By **Douglas P. Graddon, Mauro Micheloni,** and **Piero Paoletti,** Istituto di Chimica Generale ed Inorganica, Università di Firenze and Laboratorio C.N.R., Via J. Nardi 39, 50132 Firenze, Italy

The reactions of four tetra-aza macrocycles, 1,4,8,12-tetra-azacyclotetradecane, 1,4,8,12-tetra-azacyclopentadecane, 1,5,9,13-tetra-azacyclohexadecane, and *NN'N''N'''*-tetramethyl-1,4,8,11-tetra-azacyclotetradecane, with $ZnBr_2$ and $[ZnBr_2(py)_2]$ (py = pyridine) in acetonitrile solution have been studied conductimetrically and calorimetrically and a variety of complexes isolated. With equivalent amounts of base and $ZnBr_2$ or $[ZnBr_2(py)_2]$ the reaction product is an equilibrium mixture of $[ZnBr_2(base)]$ and $[ZnBr(base)]Br$, but is completely ionised when the four N atoms of the base are methylated. In the presence of an excess of $ZnBr_2$ all the bases form $[ZnBr(base)]$-$[ZnBr_3]$. Enthalpies of formation of the complexes are smaller for the 14-membered macrocycle (' cyclam ') than for the 15- and 16-membered and are similar for methylated and unmethylated cyclam. The results support five-co-ordinated structures for the complex ions, in which the size of the macrocyclic cavity is not critical. Thermodynamic data are also reported for the formation of $ZnBr_3^-$ and $ZnBr_4^{2-}$ from $ZnBr_2$ and Br^- in acetonitrile solution.

CALORIMETRIC methods of determining thermodynamic data for metal–ligand systems are particularly useful in non-aqueous solution where highly refined competitive techniques, such as pH titration, are not readily available. They can also be used in systems where spectroscopic methods are not applicable, such as many of those involving Zn^{2+}, Cd^{2+}, or Hg^{2+}. Furthermore, these techniques can usually be expected to give more reliable enthalpy data than can be obtained from the variation of free energy with temperature. This paper reports a study by calorimetric and conductimetric methods of the reaction of zinc halides with nitrogen macrocycles in acetonitrile solution. Thermochemical studies are being made on the reactions of these macrocycles with zinc ion in aqueous solution.

There has recently been considerable interest in macrocyclic ligands, in which several donor atoms form part of a cyclic system; such ligands confer additional stability on their complexes as a result of particular enthalpy and/or entropy effects.[1-3] Thus, while the copper(II) complexes of 12—15-membered tetra-aza macrocycles are all more stable in aqueous solution than those of corresponding open-chain tetra-amines,[2] their stability reaches a maximum with the 14-membered macrocycle; this maximum is attributable to a much more negative enthalpy of complex formation, which is in turn associated with ligand-field spectra indicating stronger Cu–N interactions.[3] Similar observations have been made for the nickel(II) complexes.[4]

For zinc(II) in aqueous solution the results are rather different: the stabilities [5] and enthalpies [3] of formation of the tetra-aza macrocycle complexes are again greater than those of complexes with open-chain tetra-amines,† but the maximum with the 14-membered macrocycle is no longer observed; instead the stabilities fall very slightly from 12-membered ($\log K = 16.2$) to 15-membered (15.0), while the enthalpies become slightly more negative ($-\Delta H = 14.5$ to 16.5 kcal mol^{-1}),‡ so that there is a marked increase in entropy resistance to complex formation as the size of the macrocyclic ring increases. Small decreases in stability with increasing ring size have also been found for tri-and penta-aza macrocycles.[6]

In aqueous solution a major contribution to entropy changes on complex formation arises from the reorganisation of the hydration envelopes of the species involved and this also contributes to a lesser extent to the enthalpy change. These effects are much smaller in non-associated solvents and we have therefore obtained data for the formation of complexes of zinc(II) with tetra-aza macrocycles in non-aqueous solution; acetonitrile was selected as solvent because data have already been reported for the reaction of zinc halides with heterocyclic bases in this solvent.[7] Data are now reported for the reaction in acetonitrile solution of zinc(II) bromide with tetrabutylammonium bromide, 1,4,8,11-tetra-azacyclotetradecane (' cyclam ', L^1), 1,4,8,12-tetra-azacyclopentadecane (L^2), 1,5,9,13-tetra-azacyclohexadecane (L^3), and *NN'N''N'''*-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (L^4) and also for the reaction of dibromodipyridinezinc(II) with each base.

EXPERIMENTAL

Materials.—Anhydrous zinc bromide and tetrabutylammonium bromide were obtained from Fluka AG. The bases L^1, L^2, and L^4 were obtained from Strem Chemicals and purified by crystallisation from ethanol or acetonitrile; L^3 was prepared by the method described by Raymond and co-workers.[8]

The compound $[ZnBr_2(py)_2]$ (py = pyridine) was prepared as follows. Zinc carbonate (15 g) was added to 50% aqueous hydrobromic acid (30 g) and the mixture warmed until evolution of carbon dioxide ceased. After cooling, ethanol (100 cm^3) was added, the mixture was heated to boiling, and a small amount of undissolved zinc carbonate filtered off. Pyridine (30 cm^3) was then added to the filtrate which was again heated to boiling and enough ethanol added to complete solution of the precipitate. Dibromodipyridinezinc(II) was obtained as white crystals on cooling. Yield 28 g (80% calculated on HBr). A further crop can be obtained by evaporation of the mother-liquor. The compound $[ZnCl_2(py)_2]$ was prepared in the same way using hydrochloric acid. Acetonitrile for use as solvent was either Carlo Erba RPE or

---

† Based on the calorimetric enthalpy values (ref. 3), which are quite different.

‡ Throughout this paper: 1 cal = 4.184 J.

Merck zür Analyse, dried over a molecular sieve. All solutions used in quantitative work were prepared and handled under nitrogen.

Isolation of Complexes.—[$ZnCl_2L^1$] was prepared by dissolving equivalent amounts of L^1 and [$ZnCl_2(py)_2$] in the minimum volume of ethanol, adding about four times the volume of acetone, heating to dissolve the precipitated complex, and allowing to stand, when the complex slowly crystallised as white needles, which were filtered off, washed with acetone, and air dried (Found: C, 35.9; H, 7.3; N, 16.4. $C_{10}H_{24}Cl_2N_4Zn$ requires C, 35.7; H, 7.2; N, 16.6%).

Under similar conditions reactions of [$ZnBr_2(py)_2$] with various bases gave the following products: [$ZnBr_2L^1$] (Found: C, 28.45; H, 6.0; N, 13.3. $C_{10}H_{24}Br_2N_4Zn$ requires C, 28.2; H, 5.7; N, 13.2%); [$ZnBr_2L^2$] (Found: C, 30.6; H, 5.9; N, 12.8. $C_{11}H_{26}Br_2N_4Zn$ requires C, 30.0; H, 6.0; N, 12.7%); [$ZnBr_2L^3$] (Found: C, 31.5; H, 6.4; N, 11.7. $C_{12}H_{28}Br_2N_4Zn$ requires C, 31.7; H, 6.2; N, 12.3%); [$Zn(py)L^4$][$ZnBr_4$] (Found: C, 29.6; H, 4.9; N, 8.9. $C_{19}H_{37}Br_4N_5Zn_2$ requires C, 29.0; H, 4.7; N, 8.9%). Reaction of L^1 with two equivalents of [$ZnBr_2(py)_2$] gave [$ZnBr(py)L^1$]$_2$[$ZnBr_4$] (Found: C, 29.1; H, 4.9; N, 11.7. $C_{30}H_{58}Br_6N_{10}Zn_3$ requires C, 29.1; H, 4.7; N, 11.3%). Reaction of L^4 with one equivalent of $ZnBr_2$ gave [$ZnBr_2L^4$] (Found: C, 34.3; H, 7.0; N, 11.6. $C_{14}H_{32}Br_2N_4Zn$ requires C, 34.8; H, 6.6; N, 11.6%). Reaction of L^4 with two equivalents of $ZnBr_2$ gave [$ZnBr(C_2H_5OH)L^4$]$_2$[$ZnBr_4$] (Found: C, 29.5; H, 5.6; N, 8.7. $C_{32}H_{76}Br_6N_8O_2Zn_3$ requires C, 30.0; H, 6.0; N, 8.7%).

Conductivity Data.—These were obtained in acetonitrile solution on a Siemens model LRB/B conductivity meter at 20 ± 1 °C.

Calorimetric Data.—These were obtained on a LKB 10 700 flow microcalorimeter, served by Mettler DV10 motor driven burettes. Calorimetric titrations were made by placing an acetonitrile solution of $ZnBr_2$ or [$ZnBr_2(py)_2$] in one burette and a solution of base in the other; the ratio of concentrations after mixing in the calorimeter cell was varied by adjusting the two flow rates, keeping the total flow rate as nearly constant as possible. In typical titrations with about equal concentrations of the two reactants *ca.* 20 points on the enthalpogram were obtained by varying the ratio of flow rates from 0.2 : 1 to 2.0 : 1. All titrations were carried out at 25.00 ± 0.01 °C. The calibration constant of the calorimeter was obtained by sending a known current through the calibration heater. Control titration with reactant solution in one burette and solvent in the other showed that none of the reactant solutions had measurable heats of dilution. Enthalpograms were constructed by plotting the molar heat of reaction against the ratio base: zinc (Figures 1 and 4).

In titrations of $ZnBr_2$ with [NBu_4]Br the analytical concentrations of each species after mixing were calculated from the solution concentrations (c) and flow rates (f)

$$[\mathrm{ZnBr_2}] = c(\mathrm{ZnBr_2}) \left(\frac{f_{\mathrm{Zn}}}{f_{\mathrm{Zn}} + f_{\mathrm{Br}}}\right) \qquad (1)$$

$$[\mathrm{Br^-}] = c([\mathrm{NBu_4}]\mathrm{Br}) \left(\frac{f_{\mathrm{Br}}}{f_{\mathrm{Zn}} + f_{\mathrm{Br}}}\right) \qquad (2)$$

according to equations (1) and (2) where $c(ZnBr_2)$ and $c([NBu_4]Br)$ refer to the analytical concentrations of $ZnBr_2$ and [NBu_4]Br before mixing. For calculation of the equilibrium constant of reaction (3) the enthalpy change

$$\mathrm{ZnBr_3^-} + \mathrm{Br^-} \rightleftharpoons \mathrm{ZnBr_4^{2-}} \qquad (3)$$

corresponding to no reaction (Q_0) was taken as the observed enthalpy change for the quantitative formation of $ZnBr_3^-$ and the enthalpy change for complete reaction (Q_∞) was obtained approximately by extrapolation of the enthalpogram; equilibrium concentrations of each of the species $ZnBr_3^-$, Br^-, and $ZnBr_4^{2-}$ were then calculated from the observed enthalpy change (Q) at each point in the enthalpogram, assuming equation (4) holds.

$$[\mathrm{ZnBr_4^{2-}}] = ([\mathrm{ZnBr_3^-}] + [\mathrm{ZnBr_4^{2-}}]) \left(\frac{Q - Q_0}{Q_\infty - Q_0}\right) \qquad (4)$$

Equilibrium constants, $K = [ZnBr_4^{2-}]/[ZnBr_3^-][Br^-]$, were then calculated at each point. The values of Q_0 and Q_∞ were then refined iteratively to the nearest 0.05 kcal mol^{-1} until constant values of K were obtained throughout the titration.

RESULTS AND DISCUSSION

Conductivity Studies.—Zinc(II) bromide is almost a non-electrolyte in dry acetonitrile solution (Figure 1) and is probably present as the tetrahedral, molecular species [$ZnBr_2(NCCH_3)_2$].[9] The conductivity rose sharply on addition of a macrocyclic base, but different bases led to different behaviours as the base : zinc ratio increased.

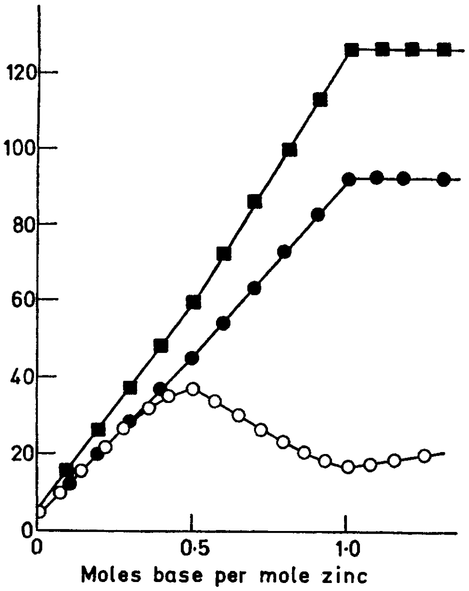

FIGURE 1 Conductimetric titration in acetonitrile solution of L^4 into 2.8 × 10^{-3} mol dm^{-3} [$ZnBr_2(py)_2$] (●), 1.0 × 10^{-2} mol dm^{-3} $ZnBr_2$ (■), and L^2 into 1 × 10^{-2} mol dm^{-3} $ZnBr_2$ (○)

On addition of L^4 the conductivity increased steadily to a base : zinc ratio of 1 : 1 and then remained constant (Figure 1). The conductivity was then that expected for a 1 : 1 electrolyte, so the reaction with base can be written as equation (5).

$$[\mathrm{ZnBr_2(NCCH_3)_2}] + \text{base} \longrightarrow [\mathrm{ZnBr(base)}]^+ + \mathrm{Br^-} + 2\mathrm{CH_3CN} \qquad (5)$$

Similar results were also obtained for the reaction of this base with [$ZnBr_2(py)_2$], [$ZnCl_2(py)_2$], and [$Zn(NCS)_2(py)_2$], a 1 : 1 electrolyte being formed, presumably with displacement of pyridine [equation (6)].

$$[\mathrm{ZnBr_2(py)_2}] + \text{base} \longrightarrow [\mathrm{ZnBr(base)}]^+ + \mathrm{Br^-} + 2\mathrm{py} \qquad (6)$$

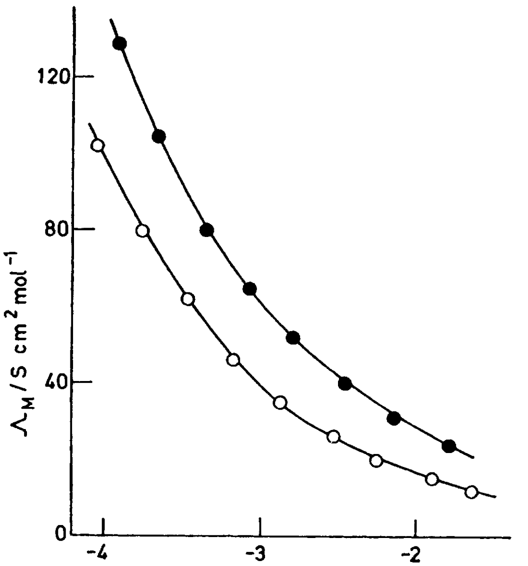

FIGURE 2 Conductivity at different concentrations of acetonitrile solutions of [ZnBr$_2$L^1] (●) and [ZnBr$_2$L^2] (○)

On addition of L^2 the conductivity rose until the base: zinc ratio reached 1 : 2, then fell to a minimum with a ratio of 1 : 1, after which addition of further base led to another increase (Figure 1). Similar results were obtained on addition of the macrocyclic base to solutions of [ZnBr$_2$(py)$_2$] or [ZnCl$_2$(py)$_2$]. The conductivity with base : zinc ratio of 1 : 1 is so low that the reaction product is mainly undissociated and the reactions can be written as equations (7) and (8).

$$[ZnBr_2(NCCH_3)_2] + base \rightleftharpoons [ZnBr_2(base)] + 2CH_3CN \quad (7)$$

$$[ZnBr_2(py)_2] + base \rightleftharpoons [ZnBr_2(base)] + 2py \quad (8)$$

Molar conductivities of the 1 : 1 solutions changed on dilution (Figure 2) from $\Lambda_M < 20$ S cm^2 mol^{-1} when the zinc concentration was 10^{-2} mol dm^{-3} to $\Lambda_M \sim 100$ when 10^{-4} mol dm^{-3}. A value of $\Lambda_M = 140$ is regarded as typical for 1 : 1 electrolytes in 10^{-3} mol dm^{-3} solution in acetonitrile[10] and control experiments gave $\Lambda_M = 154$ for 1×10^{-3} mol dm^{-3} Na[ClO$_4$] and $\Lambda_M = 90$ for 8×10^{-3} mol dm^{-3} [NBu$_4$]Br; the data for 1 : 1 solutions of L^2 : Zn thus represent *ca.* 20% ionisation in 10^{-2} mol dm^{-3} solution and *ca.* 70% in 10^{-4} mol dm^{-3} from which an approximate value of $K = 1 \times 10^{-4}$ mol dm^{-3} is obtained for the ionisation (9). In the same way a value of $K = 2 \times 10^{-5}$

$$[ZnBr_2L^2] \rightleftharpoons [ZnBrL^2]^+ + Br^- \quad (9)$$

mol dm^{-3} was obtained for the corresponding chloride.

The molar conductivity of a solution with L^2 : Zn ratio 1 : 2 was about half that expected for a 1 : 1 electrolyte, consistent with the formulation of the species in solution as [ZnBr(base)][ZnBr$_3$]; the formation in solution of a highly stable ZnBr$_3^-$ ion and much less stable ZnBr$_4^{2-}$ ion by reaction of ZnBr$_2$ with Br$^-$ was confirmed calorimetrically (see below) and it is thus clear that ZnBr$_2$, but not ZnBr$_3^-$, is a sufficently strong Lewis acid to accept a Br$^-$ ion by the bromide transfer reaction (10). The

$$[ZnBr_2(base)] + ZnBr_2 \longrightarrow [ZnBr(base)]^+ + [ZnBr_3]^- \quad (10)$$

conductivity data are not consistent with formulation of the reaction product as [ZnBr(base)]$_2$[ZnBr$_4$] or [Zn(base)][ZnBr$_4$].

Addition of L^1 or L^3 to acetonitrile solutions of ZnBr$_2$ or [ZnBr$_2$(py)$_2$] gave similar results to L^2, except that the maximum conductivity at base : zinc ratio 1 : 2 was not so high, nor the minimum at ratio 1 : 1 so low. While these bases apparently react similarly to L^2, the species [ZnBr$_2$(base)] are evidently more readily ionised. This was confirmed by the variation of conductivity with concentration for acetonitrile solutions of solid [ZnX$_2$L^1] (Figure 2), from which ionisation constants $K = 3 \times 10^{-4}$ (X = Br) and 1×10^{-4} mol dm^{-3} (X = Cl) were obtained.

Calorimetric Studies.—Zinc bromide with tetrabutylammonium bromide. Calorimetric titrations of zinc bromide with tetrabutylammonium bromide in acetonitrile solution showed a quantitative 1 : 1 reaction ($K > 10^5$ dm^3 mol^{-1}) when the Br$^-$: ZnBr$_2$ ratio was less than 1 : 1 and further reaction with an excess of bromide, still incomplete when the ratio reached 13 : 1. Data obtained with ratios greater than 1 : 1 gave consistent equilibrium constants when treated as representing a second 1 : 1 reaction. The successive reactions can thus be represented by equations (11) and (12) where (s) represents

$$ZnBr_2\,(s) + Br^-(s) \rightleftharpoons ZnBr_3^-(s) \quad (11)$$

$$ZnBr_3^-(s) + Br^-(s) \rightleftharpoons ZnBr_4^{2-}(s) \quad (12)$$

variable solvation. Thermodynamic data obtained for these reactions were as follows: $K_{11} > 10^5$ dm^3 mol^{-1}, $-\Delta H_{11}^{\ominus} = 5.0 \pm 0.1$ kcal (20.9 ± 0.4 kJ) mol^{-1} (11);

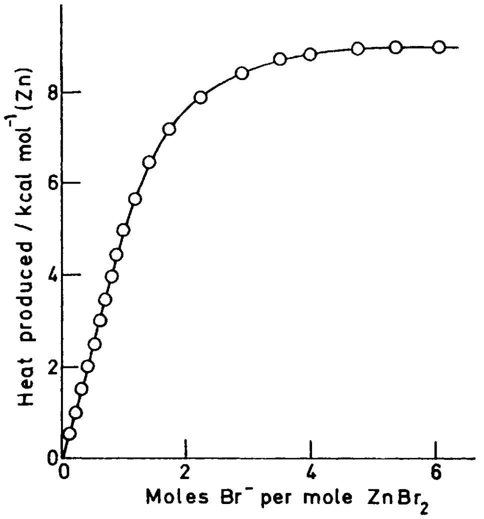

FIGURE 3 Calorimetric titration in acetonitrile solution of 1.02×10^{-2} mol dm^{-3} ZnBr$_2$ with 4.2×10^{-2} mol dm^{-3} [NBu$_4$]Br

$K_{12} = 528 \pm 30$ dm^3 mol^{-1}, $-\Delta H_{12}^{\ominus} = 4.3 \pm 0.1$ kcal (18.0 ± 0.4 kJ) mol^{-1} (14) where uncertainties are mean deviations from the average of the number of experimental measurements given in parentheses. A typical enthalpogram is shown in Figure 3.

The overall reaction of zinc bromide with excess of bromide most probably involves replacement of two solvent molecules in tetrahedral $[ZnBr_2(NCCH_3)_2]$ by two bromine atoms to give tetrahedral $ZnBr_4^{2-}$. It is not known whether the intermediate ion is three-co-ordinate $ZnBr_3^-$ or tetrahedral $[ZnBr_3(NCCH_3)]^-$, but the approximately equal enthalpies for the two steps argue for the latter and the difference in successive equilibrium constants would then be attributable to a statistical effect.

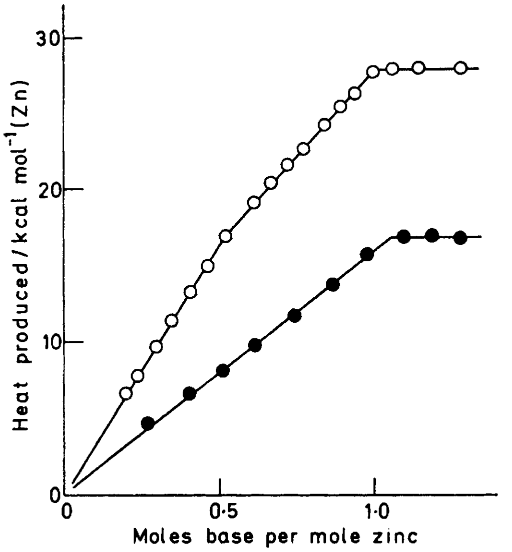

FIGURE 4 Calorimetric titrations in acetonitrile solution of 5.1×10^{-3} mol dm^{-3} $ZnBr_2$ with 4.0×10^{-3} mol dm^{-3} L^4 (○) and of 2.0×10^{-3} mol dm^{-3} $[ZnBr_2(py)_2]$ with 2.8×10^{-3} mol dm^{-3} L^4 (●)

Zinc bromide with tetra-aza macrocycles. Similar enthalpograms were obtained for titrations of zinc bromide with all four macrocyclic bases. A typical example is shown in Figure 4 and consists of three linear sections, reproducible over a wide range of concentrations.

The linear portion with ratio of base : $ZnBr_2$ less than 1 : 2 represents quantitative formation of a new species from two equivalents of $ZnBr_2$ and one of base; conductivity data show that the reaction should be formulated as equation (13) omitting solvent molecules.

$$2\,ZnBr_2 + \text{base} \longrightarrow [ZnBr(\text{base})]^+ + [ZnBr_3]^- \qquad (13)$$

The formation of $ZnBr_3^-$ rather than $ZnBr_4^{2-}$ in dilute solution is consistent with the lower stability of the $ZnBr_4^{2-}$ ion, though this appears to be present in solid complexes isolated from more concentrated solutions. The flow calorimeter gives independent enthalpy measurements for each pair of flow rates selected and enthalpies of reaction were therefore calculated for each system at each experimental point in each of several titrations, using reactant concentrations in the range 10^{-3}—10^{-2} mol dm^{-3} for L^2, L^3, and L^4 and 5×10^{-4}—10^{-3} mol dm^{-3} for the much less soluble L^1. Combination of the data obtained for reaction (13) with those for the formation of $ZnBr_3^-$, reaction (11), gave data for the formation of the ionised 1 : 1 species, [ZnBr(base)]Br, according to reaction (5). These results are summarised in Table 1, in which the uncertainties in $\Delta H^{\ominus}$ are mean deviations from the average of the number, *n*, of experimental measurements made.

TABLE 1

Enthalpies of formation of the complexes $[ZnBr(\text{base})][ZnBr_3]$ and [ZnBr(base)]Br from $ZnBr_2$ and base in acetonitrile solution at 25 °C

		$-\Delta H_{13}^{\ominus}$		$-\Delta H_5^{\ominus}$	
Base	*n*	kcal mol^{-1}	kJ mol^{-1}	kcal mol^{-1}	kJ mol^{-1}
L^4	10	32.4 ± 0.2	135.6 ± 0.8	27.4 ± 0.3	114.7 ± 1.2
L^1	18	32.0 ± 1.0	133.9 ± 4.2	27.0 ± 1.1	113.0 ± 4.6
L^2	7	36.3 ± 0.7	151.9 ± 2.9	31.3 ± 0.8	131.0 ± 3.1
L^3	8	36.5 ± 1.2	152.7 ± 5.0	31.5 ± 1.3	131.7 ± 5.4

A second linear portion of the enthalpograms is observed when the ratio base : zinc lies between 1 : 2 and 1 : 1, representing formation of the 1 : 1 adduct from the species first formed, equation (14), but it is more convenient to combine this reaction with reaction (13) to obtain data for the formation of $[ZnBr_2(\text{base})]$ from $ZnBr_2$ and base [reaction (7)]. Enthalpies for reaction (14) were determined for each experimental point in each titration and combined with the data in Table 1 to give enthalpy data for reaction (7). Data for this reaction were also obtained independently from the third linear portion of the enthalpograms, which represents the limiting enthalpy change when the base : zinc ratio exceeds 1 : 1. This portion of the enthalpograms shows that no further heat is produced when the base is in excess and the titrant solutions are in the more highly concentrated range, near 10^{-2} mol dm^{-3}; data reported as ΔH^* in Table 2 are from these titrations. When more dilute solutions were titrated a small further evolution of heat was sometimes observed with excess of base and this further reaction was still incomplete even with base : zinc ratios as high as 10 : 1; since conductivity data also show a slightly rising conductivity in the presence of large excesses of base, it seems likely that this additional heat may arise from displacement of the second bromine atom as Br^-, but it was found not possible to suppress the reaction by addition of $[NBu_4]Br$ at concentrations up to 3×10^{-2} mol dm^{-3} and the origin of the additional heat production remains uncertain. This effect prevented the the observation of a limiting value of ΔH^* for reaction with L^1, which can only be used in concentrations less than 10^{-3} mol dm^{-3}. Enthalpy data for the formation of $[ZnBr_2(\text{base})]$ are summarised in Table 2.

$$[ZnBr(\text{base})]^+ + [ZnBr_3]^- + \text{base} \longrightarrow 2[ZnBr_2(\text{base})] \qquad (14)$$

TABLE 2

Enthalpies for formation of [$ZnBr_2$(base)] from base and $ZnBr_2$ in acetonitrile solution at 25 °C

Base	n	$-\Delta H_7^\ominus$		$-\Delta H_7^{\ominus *}$	
		kcal mol^{-1}	kJ mol^{-1}	kcal mol^{-1}	kJ mol^{-1}
L^4	11	28.2 ± 0.5	118.0 ± 2.1	28.0	117.2
L^1	25	28.3 ± 0.9	118.4 ± 3.8		
L^2	10	31.3 ± 0.4	131.0 ± 1.7	31.4	131.4
L^3	14	30.1 ± 0.3	125.9 ± 1.3	30.8	128.9

Conductivity data show that the 1 : 1 complex [$ZnBr_2L^4$] is completely ionised in solution, so that $\Delta H_5^\ominus$ and $\Delta H_7^\ominus$ should be equal, as they are, within experimental error. For the three other bases, however, conductivity data show that the 1 : 1 complexes are partly ionised in solutions; for these $\Delta H_5^\ominus$ represents the heat of formation of the fully ionised compounds and $\Delta H_7^\ominus$ that of the partly ionised, the extent of ionisation being only 20—30% in the more concentrated solutions. Nevertheless there is no significant difference between $\Delta H_5^\ominus$ and $\Delta H_7^\ominus$ for any of these systems, nor was any variation of $\Delta H_7^\ominus$ observed with changing concentration. We conclude that the enthalpy of ionisation, reaction (9), is very small for all three bases, an upper limit of about ± 1.5 kcal mol^{-1} (±6 kJ mol^{-1}) being possible for L^2 and ±4 kcal mol^{-1} (±17 kJ mol^{-1}) for L^1 or L^3, which give more highly ionised complexes.

Dibromodipyridinezinc(II) *with tetra-aza macrocycles.* Calorimetric titrations of [$ZnBr_2(py)_2$] with macrocycles gave simple enthalpograms (Figure 4) showing only quantitative formation of the 1 : 1 complex, presumably with displacement of pyridine; the complex formed, [$ZnBr_2$(base)], is completely ionised when the base is L^4, reaction (6), and predominantly non-ionised with the other bases, reaction (8). Enthalpies of reaction, determined at n points in several titrations with solutions in the concentration range 1×10^{-3}—3×10^{-3} mol dm^{-3}, are summarised in Table 3, in which all reactions are referred to as reaction (8); the Table also includes values $\Delta H_8^{\ominus *}$ for this reaction, calculated from the values of $\Delta H_7^\ominus$ in Table 2 and the published [7] enthalpy for reaction (15).

TABLE 3

Enthalpies of formation of [$ZnBr_2$(base)] from base and [$ZnBr_2(py)_2$] in acetonitrile solution at 25 °C

Base	n	$-\Delta H_8^\ominus$		$-\Delta H_8^{\ominus *}$/
		kcal mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
L^4	6	15.8 ± 0.2	66.3 ± 0.8	70.0 ± 4.1
L^1	13	15.5 ± 0.3	64.8 ± 1.0	70.4 ± 4.4
L^2	15	21.1 ± 0.3	88.4 ± 1.2	83.0 ± 5.7
L^3	4	20.6 ± 0.2	86.2 ± 0.6	77.9 ± 5.3

$$[ZnBr_2(NCCH_3)_2] + 2py \longrightarrow [ZnBr_2(py)_2] + 2\,CH_3CN \qquad -\Delta H^\ominus = 48 \pm 4 \text{ kJ mol}^{-1} \quad (15)$$

Agreement between the values of $\Delta H_8^\ominus$ and $\Delta H_8^{\ominus *}$ is as close as can be expected and confirms the displacement of pyridine from [$ZnBr_2(py)_2$] by the macrocyclic bases and hence, by implication, displacement of co-ordinated solvent. These results also confirm the two most notable features of the values of $\Delta H_5^\ominus$ and $\Delta H_7^\ominus$: (*a*) that the enthalpies of complex formation are significantly more negative with L^2 and L^3 than with L^1 and (*b*) that the enthalpies of complex formation with L^1 and L^4 are similar.

The more negative enthalpy of complex formation observed with L^2 compared to L^1 is paralleled by the enthalpies of formation of the corresponding complex ions [Zn(base)]$^{2+}$ in aqueous solution, −16.5 and −14.8 kcal mol^{-1} respectively; [3] this contrasts with the much larger enthalpies of complex formation with L^1 when the cations are Cu^{2+} or Ni^{2+}. The large difference between the enthalpies of formation of [Zn(base)]$^{2+}$ in aqueous solution and those obtained in non-aqueous solution is noteworthy. The preference of Zn^{2+} for L^2 may simply reflect the better fit of the slightly larger Zn^{2+} ion in the cavity of the larger macrocycle; alternatively it may arise from a change in stereochemistry with the zinc atom lying out of the N_4 plane in a five-co-ordinate arrangement, since there is no crystal-field term to stabilise the in-plane configuration. Zinc has been shown by *X*-ray analysis to be five-co-ordinate in [$ZnClL^4$][ClO_4], in which all four methyl groups lie on the same side of the N_4 plane as the zinc atom and the co-ordinated Cl^- ' rests ' on the four methyl groups; [11] in the crystal the Zn atom lies 57 pm above the N_4 plane, but ^{13}C n.m.r. spectra show that in solution there is a dynamic equilibrium with other configurations. A similar five-co-ordinate structure has been found for crystalline [$Ni(N_3)L^4$][ClO_4], but in this case the Ni atom lies only 33 pm out of the N_4 plane [12] and it was shown by the use of space-filling models that co-ordination of a sixth ligand cannot be achieved without causing steric interference of the four methyl groups with the co-ordinated azide ion.

In the systems discussed here the conductivity data suggest that the complex with L^4 is always five-co-ordinate, but that further co-ordination of a second Br^- ion is possible with the unmethylated macrocycles, leading to the low conductivities of the 1 : 1 complexes; the least dissociation of this Br^- is observed with L^2, suggesting that the five-co-ordinate ion [$ZnBrL^2$]$^+$ is the one in which co-ordinate extension by addition of a second Br^- most readily occurs, but the differences between the 14-, 15-, and 16-membered macrocycles are only slight, not critical as they are with Cu^{2+} and Ni^{2+}.[5,13]

[9/1961 *Received*, 10*th December*, 1979]

REFERENCES

[1] D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, 1969, **91**, 6540.

[2] M. Kodama and E. Kimura, *J.C.S. Dalton*, 1976, 116, 1720, 2341; 1977, 1473.

[3] A. Anichini, L. Fabbrizzi, P. Paoletti, and R. M. Clay, *J.C.S. Dalton*, 1978, 577.

[4] L. Fabbrizzi, P. Paoletti, and R. M. Clay, *Inorg. Chem.*, 1978, **17**, 1042.

[5] M. Kodama and E. Kimura, *J.C.S. Dalton*, 1977, 2269.

[6] M. Kodama and E. Kimura, *J.C.S. Dalton*, 1978, 1081.

[7] L. T. Ang and D. P. Graddon, *J. Inorg. Nuclear Chem.*, 1976, **38**, 2279.

[8] W. L. Smith, J. Ekstrand, and K. N. Raymond, *J. Amer. Chem. Soc.*, 1978, **100**, 3539.

[9] I. V. Isakov and Z. V. Zvonkava, *Doklady Akad. Nauk S.S.S.R.*, 1962, **145**, 81.

[10] W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81.

[11] N. W. Alcock, N. Herron, and P. Moore, *J.C.S. Dalton*, 1978, 1282.

[12] M. J. D'Aniello, jun., M. T. Mocella, F. Wagner, E. K. Baresfield, and I. C. Paul, *J. Amer. Chem. Soc.*, 1975, **97**, 192.

[13] J. Fabbrizzi, M. Micheloni, and P. Paoletti, *Inorg. Chem.*, 1980, **19**, 535.