Inorganica Chimica Acta, 22 (1977) L25–L27

Ring Size Effect on the Enthalpies of Formation of Copper(II) and Zinc(II) Complexes with 1,4,7,10-tetra-aza-cyclododecane and 1,5,9,12-tetra-aza-cyclopentadodecane

A. ANICHINI, L. FABBRIZZI, P. PAOLETTI

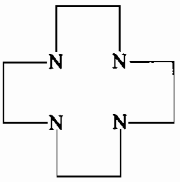
Istituto di Chimica Generale ed Inorganica dell'Università and Laboratorio C.N.R., Via I. Nardi 39, Florence, Italy

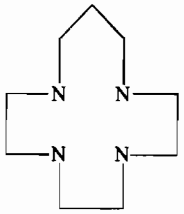
R. M. CLAY

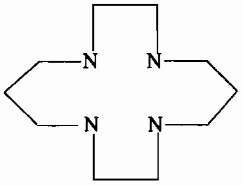
Chemistry Department, University of Stirling, Stirling, Scotland.

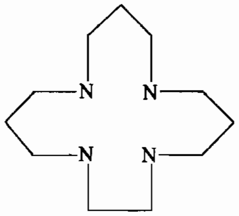
Received February 12, 1977

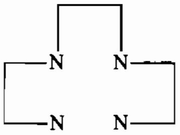
Aqueous metal complexes with cyclic tetramines are several orders of magnitude more stable than the corresponding complexes with linear counterparts (the Macrocyclic Effect) [1]. Until recently, the thermodynamic reasons for the macrocyclic effect have been unclear, some authors attributing enthalpy as the dominant term [2], others entropy [3]. This uncertainty in the thermodynamic interpretation has probably arisen because different investigators have used different metal ions, ligands of different ring size and most importantly because of the inherent uncertainty in determining reliable enthalpy values from other than direct calorimetric measurements. However, the calorimetric study of the formation of macrocyclic complexes is made very difficult by the following factors: i) many of the cyclic ligands are only slightly soluble in water necessitating very dilute concentrations of reactants ($<10^{-2}$ *M*); ii) the rate of the reactions, particularly at pH < 8–9 is normally very slow [4]; iii) all known cyclic tetramines have a great affinity for protons for the first two protonation steps [2], accurate equilibrium constants not being available. None of the above difficulties apply to the linear tetramines where complex formation in buffer solutions can be followed in widely used isoperibolic calorimeters [5], but this

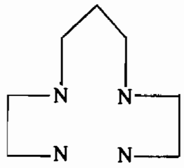

[12]ane N_4

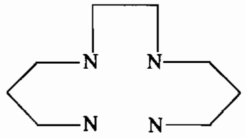

[13]ane N_4


[14]ane N_4


[15]ane N_4


2,2,2 tet


2,3,2 tet


3,2,3 tet

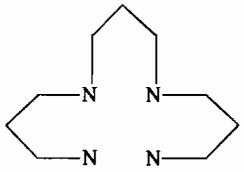

3,3,3 tet

TABLE I. Calorimetric Data.

Ligand	Cu(II) Complexes		Zn(II) Complexes	
	ΔH° kcal mol^{-1}	ΔS° cal K^{-1} mol^{-1}	ΔH° kcal mol^{-1}	ΔS° cal K^{-1} mol^{-1}
[12]ane N_4	–22.7[f]	+36.2[d]	–14.5[f]	
[13]ane N_4	–29.2[b]	+33.7[b]		
[14]ane N_4	–32.4[a]		–14.8[f]	
[15]ane N_4	–26.5[f]	+22.7[c]	–16.5[f]	
2,2,2 tet	–21.6[e]	+19.5[e]	– 8.9[e]	+25.0[e]
2,3,2 tet	–27.7[e]	+16.5[e]	–11.9[e]	+18.8[e]
3,2,3 tet	–25.9[e]	+13.1[e]	–10.6[e]	+15.9[e]
3,3,3 tet	–19.5[e]	+12.8[e]	– 7.4[e]	+18.0[e]

[a] Ref. 6. [b] Ref. 7 [c] Ref. 8. [d] Calculated using ΔH° from this work. [e] Taken from Ref. 9 and references therein. [f] This work.

well proven method is totally unsuitable for macrocyclic ligands. We have therefore devised a new experimental method which overcomes these difficulties as follows; i) the much lower thermal output from these very dilute solutions is measured by sensitive microcalorimeters of both FLOW and BATCH types; ii) the reactions are carried out in strongly alkaline solutions (pH 14) resulting in both faster rates of reactions and the effective elimination of any protonated forms of the ligand.

We are now reporting enthalpy data for the reactions of Cu(II) and Zn(II) ions with the macrocyclic ligands [12]ane N_4 and [15]ane N_4 in aqueous solution at 25 °C. Comparison with similar calorimetric data for [14]ane N_4 [6] and indirect enthalpy data for Cu(II) with [12], [13] and [15]-ane N_4 [3, 7, 8] allows us to compare the two methods of obtaining enthalpy values and to consider the effect of the chelate ring sequence and the size of the macrocyclic hole on the enthalpies of formation. The data are assembled in Table I.

Experimental

[12]ane $N_4 \cdot 4HCl$ was supplied pure by Kimura. [15]ane N_4 was purified by preparing the tetrahydrochloride from the commercially available amine (Strem Chemicals) and recrystallising it from aqueous ethanol. Cu(II) and Zn(II) complexes of [15]-ane N_4 were prepared as perchlorates by mixing equimolar amounts of ligand and metal perchlorate in n-butanol. Elemental analysis on these compounds gave satisfactory agreement with calculated values. Calorimetric measurements were carried out using both FLOW (LKB 10700-1) and BATCH (LKB 10700-2) microcalorimeters. The reaction scheme used is outlined below, together with experimental values:

$$\begin{tikzcd}
M^{2+}(aq) + L(aq) \arrow[r, "\Delta H^\circ_1"] \arrow[d, "\Delta H^\circ_4"'] & ML^{2+}(aq) \arrow[d, "\Delta H^\circ_2\ \text{batch}"] \\
M^{2+}(1M\ NaOH) + L(1M\ NaOH) \arrow[r, "\Delta H^\circ_3", "\text{flow}"'] & ML^{2+}\ (1M\ NaOH)
\end{tikzcd}$$

Reactions	Experimental values (kcal mol^{-1}) ΔH°_2	ΔH°_3	ΔH°_4	ΔH°_1 (kcal mol^{-1})
Cu/[12]ane N_4	0	−11.8	−10.9	−22.7
Cu/[15]ane N_4	0	−15.6	−10.9	−26.5
Zn/[12]ane N_4	−1.2	− 8.2	− 7.5	−14.5
Zn/[15]ane N_4	−0.3	− 9.3	− 7.5	−16.5

ΔH°_2 had previously been determined [6]. The most critical measurement is the determination of ΔH°_3, and the values given are the mean values of reactions carried out using at least four different flow rates, within a range of ± 0.2 kcal mol^{-1}. Checks were made for both internal consistency and absolute accuracy, and full details of the experimental method and reaction conditions will appear elsewhere.

Discussion

Kodama and Kimura have previously reported values for the enthalpies of formation of the Cu(II) complexes of [12] and [15]ane N_4 of −18.3 and −26.5 kcal mol^{-1} respectively [2, 8], obtained by temperature dependent stability constant studies. The latter value is in excellent agreement with our own (−26.5) but the former is considerably less than our own value of −22.7 kcal mol^{-1}. Two points must be made. In our calorimetric study of the reaction of [12]ane N_4 with both Cu(II) and Zn(II) we found a marked dependence of ΔH° on the [L]/[M] ratio above unity, suggesting that at high ligand concentrations further complexation beyond 1:1 takes place. Below [L]/[M] = 1 the enthalpy is independent of concentration and our values are taken from this range. We found no equivalent behaviour for [15]ane N_4. Secondly, Kodama and Kimura, in calculating the stability constants at different temperatures made allowance for the temperature dependence of pK_1 and pK_2 for the complex with [15]ane N_4 but not [12]ane N_4. We believe that our value for [12]ane N_4 is more reliable and a recalculation of the entropy change on complex formation using this ΔH° value and the $\log K_{ML}$ value obtained by Kodama and Kimura gives a value of $\Delta S = 36.2$ cal K^{-1} mol^{-1}. This seems much more reasonable than the previous value of 51.4 cal K^{-1} mol^{-1} and the ΔS values now diminish steadily as the macrocyclic ligand becomes larger and consequently less rigid.

The enthaplies of formation for Cu(II) complexes follow the sequence [14] > [13] > [15] > [12] reflecting the relative strengths of the Cu–N interactions. The most exothermic complex contains alternating five and six membered chelate rings following the pattern already established for the linear tetramine complexes [9].

The lower exothermicity of the other complexes must, in part, be due to their less favourable configurations. Previously, a linear relationship has been demonstrated between the enthalpy of formation and the energy of the (d–d) band in Cu(II) complexes of both uni- and multidentate amine ligands [10]. The explanation of this relationship depends on the assumption that the complexes exhibit a distorted octahedral *trans*-diaquo configuration and it is significant that the few tetradentate ligands which do not obey the relationship are tripod-like ligands such as tren (tris(aminoethyl)amine) in which the nitrogen donors cannot co-ordinate *trans*. We have found that the Cu(II) complex with [14]ane N_4 obeys this relationship well [6], but the complexes with [12] and [15]ane N_4 do not,

	ν(d–d) (kK)	ΔH°_{calc} (kcal mol^{-1})	ΔH°_{exp} (kcal mol^{-1})
$[Cu([12]ane\ N_4)]^{2+}$	16.81	−18.4	−22.7
$[Cu([15]ane\ N_4)]^{2+}$	17.61	−21.8	−26.5

strongly suggesting a departure from the *trans*-diaquo configuration in these two complexes. For $[Cu([12]ane\ N_4)]^{2+}$, the use of the indirectly determined ΔH° value leads to the opposite conclusion [10].

Ample X-ray evidence shows that [14]ane N_4 and its derivatives prefer to co-ordinate *trans* [11–13] although a few *cis* complexes are known [14, 15]. For [12]ane N_4 no evidence exists for *trans*-configurations.

Whether or not Cu(II) with its strong preference for tetragonally distorted octahedral co-ordination, adopts a *cis* configuration with [12]ane N_4 is open to question. It is clear, however, that we should not expect the structure of $[Cu([12]ane\ N_4)]^{2+}$ to contain a CuN_4 plane. No structural studies have been made on complexes with [15]ane N_4, but a recent study of the paramagnetic–diamagnetic interconversion of $[Ni([15]ane\ N_4)]^{2+}$ has demonstrated the difficulty that this ligand experiences in arranging its donor atoms at the corners of a square plane [16]. It seems that each ligand, because of the restraining influence of its particular cyclic structure, will experience a varying degree of difficulty in accommodating a particular metal ion at the same time maintaining an MN_4 plane resulting, on complexation, in distortions from this planarity. The size of the metal ion will also be important in determining the extent of such distortions.

For the Zn(II) complexes, the enthalpies of formation are all very close together, the most exothermic complex being formed with [15]ane N_4. This suggests that for these complexes, the size of the macrocyclic hole is not a significant factor and that their structures should be very similar. The ionic radius of Zn^{2+} is larger than that of Cu^{2+} and the zinc ion probably sits most comfortably in the largest hole; it is dangerous, however, to draw any firm conclusions in view of the known preference of zinc to form tetrahedral complexes.

The macrocyclic enthalpy can be determined for the metathetic reactions

$$ML^{2+}_{linear} + L_{cyclic} \longrightarrow ML^{2+}_{cyclic} + L_{linear}$$

using known values of the enthalpies of formation of the complexes with linear tetramine ligands [9]. As a reference an attempt can be made to assign for each macrocyclic ligand the most appropriate linear ligand in terms of ring sequence (*e.g.* [12]ane N_4 would be compared with 2,2,2 tet). For Cu(II) and Zn(II) the macrocyclic enthalpy makes a significant contribution to the extra stability of the macrocyclic complexes; the extent of the contribution is, however, much less than previously reported for $[Ni([14]ane\ N_4)]^{2+}$, where the macrocyclic enthalpy was solely responsible for the extra stability [2]. In contrast, the entropy term had previously been thought to be solely responsible for the extra stability of $[Cu([12]ane\ N_4)]^{2+}$ [3] and our results demonstrate that while the entropy contribution is more dominant, it is not solely responsible for the extra stability.

Acknowledgements

We thank Professor Kimura for the gift of the ligand [12]ane N_4, together with the Italian C.N.R. for financial support and the Royal Society for the award of a European fellowship to R.M.C.

References

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

2 F. P. Hinz and D. W. Margerum, *Inorg. Chem., 13,* 2941 (1974).

3 M. Kodama and E. Kimura, *J. Chem. Soc. Dalton,* 116 (1976).

4 C. Lin, D. B. Rorabacher, G. C. Cayley and D. W. Margerum, *Inorg. Chem., 14,* 919 (1975).

5 I. Wadso, *Science Tools, 13,* 1 (1966).

6 A. Anichini, L. Fabbrizzi, P. Paoletti and R. Clay, submitted for publication.

7 M. Kodama and E. Kimura, *Chem. Comm.,* 891 (1975).

8 M. Kodama and E. Kimura, *J. Chem. Soc. Dalton,* 2341 (1976).

9 P. Paoletti, L. Fabbrizzi and R. Barbucci, *Inorg. Chim. Acta Rev., 7,* 43 (1973).

10 L. Fabbrizzi, P. Paoletti and A. B. P. Lever, *Inorg. Chem., 15,* 1502 (1976).

11 N. F. Curtis, D. A. Swann and T. N. Waters, *J. Chem. Soc. Dalton,* 1963 (1973).

12 B. Bosnich, R. Mason, P. J. Pauling, G. B. Robertson and M. L. Tobe, *Chem. Comm.,* 97 (1965).

13 R. M. Clay, J. Murray-Rust and P. Murray-Rust, unpublished results.

14 P. O. Whimp, M. F. Bailey and N. F. Curtis, *J. Chem. Soc. A,* 1956 (1970).

15 C. K. Poon and M. L. Tobe, *J. Chem. Soc. A,* 1549 (1968).

16 L. Fabbrizzi, unpublished results.