

Enthalpy of Formation of Copper(II) Complexes with 14-Membered Tetra-aza Macrocycles

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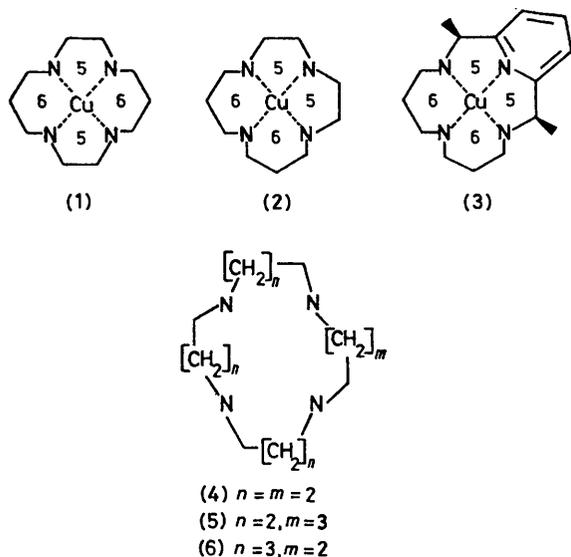
Summary Calorimetric studies show that the 14-membered macrocycle (1) incorporates copper(II) more exothermically than its less symmetric isomer (2), owing to stronger in-plane Cu-N interactions; introduction of a pyridine ring in the macrocyclic framework (3) further reduces the heat of complexation.

THE enthalpy of formation of tetra-aza-macrocyclic complexes, which significantly contributes to their comparatively high solution stability (the macrocyclic effect),¹ strictly depends upon the fitting of the metal ion

in the ligand cavity. Among 12- to 16-membered saturated macrocycles, the size of the 14-membered cyclam (1) is ideal² for incorporation of divalent 3d metal ions, such as copper(II) and high-spin nickel(II), forming a system of alternating five- and six-membered fused chelate rings (sequence 5,6,5,6) and in fact, co-ordinates the above ions more exothermically than the other ligands.^{3,4}

However, the 14-membered tetra-aza-system is unique among the 12- to 16-membered ligands, in that it may also exist in the isomeric form (2), forming complexes in which the five- and six-membered rings are separately

grouped (5,5,6,6). We have determined by calorimetry the enthalpy of formation of copper(II) complexes with the novel macrocycle (2) in water at 25 °C. Complexation, which is slow at acid or neutral pH values, was accelerated by making the solution basic (1M in NaOH). The heat effect, which is small owing to the limited solubility of Cu²⁺ at pH 14, was detected with accuracy by a flow microcalorimetric apparatus (LKB 8700-1), fed by high-precision electronic burettes (Mettler DV-10). The measured enthalpy was converted into a value for neutral solution through appropriate dilution experiments (see Table) as described for Cu(cyclam)^{2+,3}. The Table shows that (i) the less symmetric ligand (2) incorporates Cu^{II}

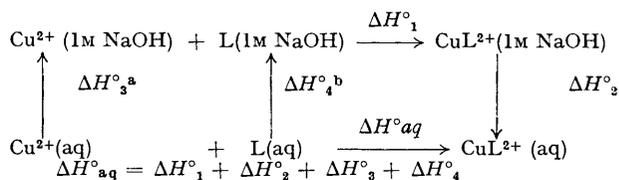


much less exothermically than (1); (ii) the heat effect for (1) and (2) is higher than that for smaller or larger macrocycles included in the Table, for comparison. The energy of the *d-d* band, which furnishes an approximate measure of the Cu-N in-plane interactions,⁵ is lower for the complex with (2) than that with (1) (18,200 and 19,900 cm⁻¹, respectively), suggesting that the smaller exothermicity originates from the formation of weaker co-ordinative bonds. An alternating sequence of five- and six-membered rings, present in the complex with (1), was also found to favour, through the enthalpy term, the formation of copper(II) complexes with open-chain tri- and tetra-amines,⁶ allowing the nitrogen atoms to occupy co-ordination sites close to the ideal requirements of the metal ion (*i.e.* the corners of a square). Moreover, the proximity of the two more hindering six-membered chelate rings in a *cis*-arrangement in the

complex with (2) would induce a deformation of the macrocyclic framework, causing a distortion of the co-ordination array. A less symmetrical arrangement of nitrogen atoms in the complex with (2) is also demonstrated by the much larger value for the molar absorptivity than that for the complex with (1) (172 and 100 l mol⁻¹ cm⁻¹, respectively).

These results show that copper(II) complex formation is more favourable, from an enthalpy point of view, for 14-membered systems than for other 12- to 15-membered macrocycles, the symmetrical (5,6,5,6) rather than the asymmetric (5,5,6,6) arrangement providing the most favourable system.

TABLE. Enthalpies of formation, ΔH°_{aq} , of copper(II) complexes with tetra-aza macrocycles, in water at 25 °C. Enthalpy values are calculated through the following cycle:



L	$\Delta H^\circ_{aq}^c$	$\Delta H^\circ_1^c$	$\Delta H^\circ_2^c$	Ref.
(2)	-27.8 ± 0.1	-17.71 ± 0.06	0.85 ± 0.06	This work
(3)	-23.9 ± 0.1	-13.14 ± 0.10	0.17 ± 0.05	This work
(1)	-32.4			3
(4)	-22.7			4
(5)	-25.6			This work
(6)	-26.5			4

^a $\Delta H^\circ_3 = -10.9$ kcal mol⁻¹, evaluated as described in ref. 3. ^b Process assumed athermic, see ref. 3. ^c In kcal mol⁻¹ (1 cal = 4.184 J).

We have also studied by the same technique the reaction of copper(II) with the macrocycle (3) in its *meso*-form, which has the same ring sequence as the ligand (2). Complexation of this macrocycle is much less exothermic than that of (2). The enthalpy difference (*ca.* 4 kcal mol⁻¹) is greater than expected for the substitution of an amine by a pyridine nitrogen [*e.g.* Cu(NH₃)⁺, $\Delta H^\circ -5$; Cu(py)⁺, $\Delta H^\circ -4$; Cu(en)²⁺, $\frac{1}{2} \Delta H^\circ -6$; Cu(py)₂²⁺, $\frac{1}{2} \Delta H^\circ -4$ kcal mol⁻¹];⁸ this is probably to be ascribed to the greater rigidity of (3), due to the presence of a pyridine ring in the macrocyclic backbone, compared with fully saturated and unsubstituted macrocycles, and to the consequent greater difficulty experienced by (3) in meeting the stereochemical requirements of the metal ion.

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