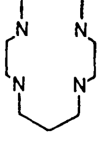
Calorimetric Determination of Macrocyclic Enthalpy. Copper(II) and Zinc(II) Complexes with 1,4,8,11-Tetra-azacyclotetradecane

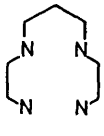
By Andrea Anichini, Luigi Fabbrizzi, and Piero Paoletti*
(*Istituto di Chimica Generale ed Inorganica, Università di Firenze and Laboratorio C.N.R., Via I. Nardi* 39,
50132 *Firenze, Italy*)
and Robert Clay
(*Department of Chemistry, University of Stirling, Stirling* FK9 4LA, *Scotland*)

Summary The first direct calorimetric values for the enthalpies of formation of macrocyclic complexes in aqueous solution show for the title systems the existence of a macrocyclic enthalpy (Cu^{II} 4·7 and Zn^{II} 3 kcal mol^{-1});† for the Cu^{II} complex the enthalpy of formation fits the linear correlation with spectral energy as previously described for noncyclic nitrogen ligands.

The thermodynamic interpretation of greater stability of aqueous complexes of metals with tetra-aza cyclic ligands compared to that of complexes with analogous linear ligands (the macrocyclic effect)[1] is controversial since the reported enthalpy data are conflicting and all have so far been determined indirectly.[2] We report a direct calorimetric determination of the enthalpies of formation of the Cu^{II} and Zn^{II} complexes of 1,4,8,11-tetra-azacyclotetradecane, [14]aneN_4, (**1**) in aqueous solution at 25 °C. Both



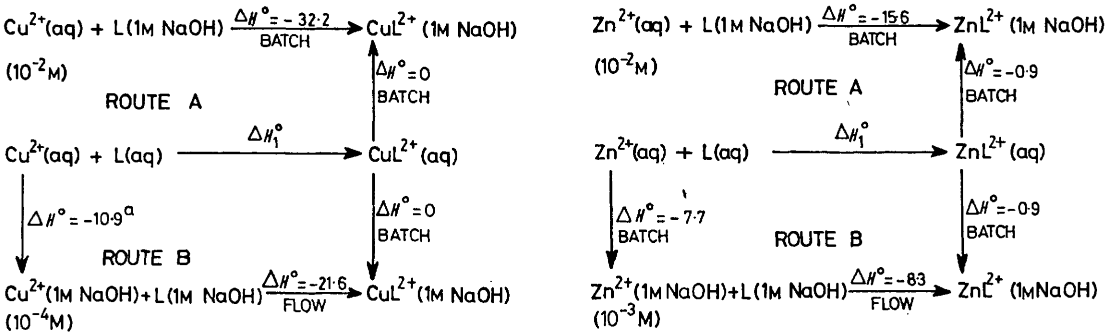
(1)



(2)

---

† 1 kcal = 4·184 kJ.



SCHEME. $\Delta H_1{}^0$ values: Cu^{II}, −32·2 and −32·5 (mean, −32·4 ± 0·4); Zn^{II}, −14·7 and −14·9 (mean, −14·8 ± 0·3) kcal mol^{-1}, respectively, for Route A (based on BATCH measurements) and Route B (based on BATCH/FLOW measurements). [a] Determined *via* an identical cycle using (**2**) as ligand and the known value of $\Delta H_1{}^0$ of the copper complex. L = Ligand (**1**).

BATCH (LKB 10700-2) and FLOW (LKB 10700-1) microcalorimeters were used to measure the ΔH° values (Scheme). The extreme conditions (pH 14) were necessary to avoid interference from the protonation of the ligand ($\log_{10}K_1$ = 11·5)[2b] and to ensure that the reaction proceeded rapidly, the rate being strongly pH dependent.[3]

For both copper(II) and zinc(II) complexes, the enthalpy of formation exceeds that of the most stable analogous linear system[4] (**2**) by 4·7 and 3·0 kcal mol^{-1}, respectively.† These values are much lower than the value of 11·6 kcal mol^{-1} reported[2b] for the analogous nickel(II) system which has been attributed to the difference in the solvation enthalpies of cyclic and linear ligands.

The reported linear relationship between the enthalpy of formation and the energy of the visible band [ΔH (kcal mol^{-1}) = − 54·43 + 0·00433 $\nu(d\text{–}d)$ cm^{-1}] was found to be valid for about thirty copper(II) complexes with linear polyamines.[5] A good correlation also exists for the Cu^{II} complex of (**1**) [$\nu(d\text{–}d)$ = 19,880 cm^{-1}, ΔH_{calc} = − 31·7, ΔH_{obs} = − 32·4 kcal mol^{-1}]. The energy of the (d–d) band has been associated[5] with the energy of the in-plane interaction, for copper(II) complexes showing tetragonally distorted geometry with the 4 nitrogen atoms in the equatorial sites. This correlation suggests that, for the Cu^{II} complex of (**1**) in which the chelate rings are arranged in the most favourable 5,6,5,6-sequence, the formation of strong Cu–N bonds takes place within a CuN$_4$ plane, the geometry assumed for complexes with linear ligands. Thus the solvation term (the difference between the enthalpy of hydration of the complex and that of the ligand) must be the same for the Cu([14]aneN$_4$) complex and complexes with linear ligands, indicating that this term cannot play any discriminating role in the co-ordinating ability of different ligands, in contrast to the previous interpretation for nickel(II) compounds.[2b] For zinc(II) which forms tetrahedral complexes much more readily, it is very difficult to draw meaningful conclusions without further structural or entropy data. However, in this case the macrocyclic enthalpy does contribute to the overall stability of the complex.

We thank the Italian C.N.R. for financial support and the Royal Society for the award of a European Fellowship (to R.M.C.).

(*Received*, 25*th January* 1977; *Com.* 061.)

---

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

[2] (a) M. Kodama and E. Kimura, *J.C.S. Chem. Comm.*, 1975, 891; *J.C.S. Dalton*, 1976, 116, 2335, and 2341; (b) F. P. Hinz and D. W. Margerum, *Inorg. Chem.*, 1974, **13**, 2941.

[3] C. Lin, D. B. Rorabacher, G. C. Cayley, and D. W. Margerum, *Inorg. Chem.*, 1975, **14**, 919.

[4] L. Fabbrizzi, R. Barbucci, and P. Paoletti, *J.C.S. Dalton*, 1972, 1529.

[5] L. Fabbrizzi, P. Paoletti, and A. B. P. Lever, *Inorg. Chem.*, 1976, **15**, 1502.