

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

