

ENCIRCLING OF 3d-METAL IONS BY POLYAZAMACROCYCLES: THERMODYNAMIC ASPECTS

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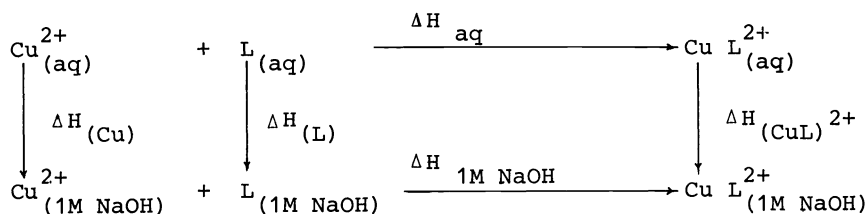
Abstract - We report and discuss the enthalpy values for the formation of copper(II) and nickel(II) complexes with a series of tetraaza-macrocycles, from [12]aneN₄ to [16]aneN₄, and three pentaazomacrocycles from [15]aneN₅ to [17]aneN₅.

Since their first appearance in the early sixties, tetra-aza macrocyclic complexes have attracted the attention of the inorganic chemists for some unusual properties. They show some properties, which have not been encountered with the corresponding complexes formed by the open-chain analogues: an extreme kinetic stability, the possibility to attain unusual oxidation states of the encircled metal ion, an extremely high thermodynamic stability. The last aspect was pointed out by Cabbines and Margerum in a pioneering paper in which the equilibrium constant for the formation of the copper(II) complex with the saturated macrocycle, [14]aneN₄, having six methyl substituents on the aliphatic backbone was reported and compared with that of the most stable complex among those with open chain tetramine, i.e., 2,3,2-tet. (Ref. 1). The remarkable extra-stability of the complex with the closed tetramine (about 3-4 log units) was named macrocyclic effect, and is considered to be a sort of additional contribution to the well known chelate effect due to the cyclisation of the multidentate ligand. The interpretation of the thermodynamic nature of the macrocyclic effect was only tentative, in the absence of reliable, experimentally obtained, enthalpy and entropy data. The determination of the enthalpy change associated with the complexation of a macrocycle was crucial. As a matter of fact, heat changes obtained in different laboratories by the temperature dependence of equilibrium data led to conflicting results and interpretation (Ref. 2&3).

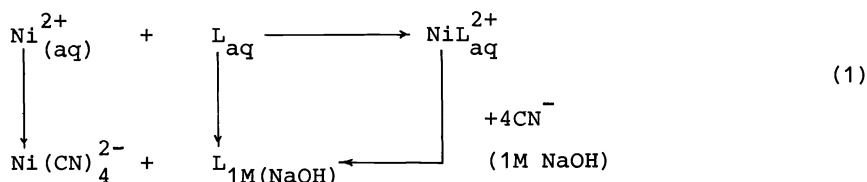
The extreme inertness of macrocyclic complexes both towards the metal plus ligand reaction and towards destruction of the preformed complexes (for instance in strong acid solution) prevented the use of the calorimetric techniques that has been tested in the study of complexation with non-cyclic (and labile) systems. These difficulties were circumvented in our laboratory through: 1) the design of appropriate experiments; 2) the use of special calorimetric apparatus, able to detect small amounts of heat, even if evolved in a comparatively long period (on the time scale of the calorimetric measurements).

In the case of the copper(II) complexes we carried out the complexation reaction in 1M NaOH, where the copper exists as hydroxo species and the strongly basic tetramine is not protonated (Ref. 4). In these conditions the incorporation of the metal into the macrocycle is instantaneous so that the associated heat effect can be determined. Due to the high dilution of the

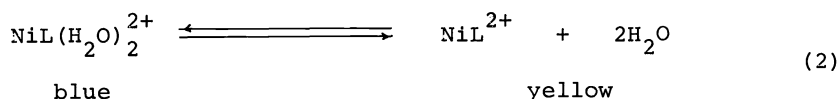
reagents (the limiting factor is the solubility of the copper(II) salt in 1M NaOH) the heat evolved during the reaction is very small and appropriately sensitive apparatuses (e.g. microcalorimeters) must be employed in order to perform precise measurements. Once the enthalpy of complexation in alkaline solution (pH = 14, ΔH 1M NaOH) is known, the heat change for the complexation reaction in neutral solution, ΔH_{aq} , is calculated through the cycle



This procedure cannot be employed in the case of Ni(II) complexes due to the insolubility of nickel salt in strongly alkaline solution. Therefore a different type of experiment was designed for the Ni(II) complexes. The key reaction of this method is the destruction by cyanide ion, in 1M NaOH, of the preformed Ni(II) macrocyclic complex (Ref. 5).



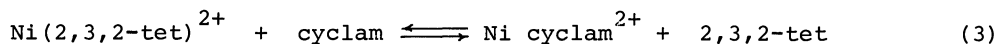
This reaction is not instantaneous, as it goes to completion in about 0.5 to 5 hours, depending on the structure of the ligand and on the ring size controlled kinetic inertness of the complex which is in turn largely determined by the size of the ring. The heat evolved during the destruction of the complex was measured by an integral microcalorimeter (Batch). Through the appropriate thermochemical cycle the enthalpy change for the complex formation in aqueous solution was then evaluated. Notably nickel complexes with some tetra-aza macrocycles (the 13-membered and the 14-membered saturated ligands) exist in solution as an equilibrium mixture of two species, the high-spin blue form and the low-spin yellow form, according to the following scheme: (Ref. 6 & 7)



Since the fractions of the two forms and the enthalpy change for the blue-to-yellow form conversion are known through variable-temperature spectrophotometric measurements, the heat effect obtained from the cycle(1), which refers to the equilibrium mixture, can be partitioned into the enthalpies of formation of the high-spin and low-spin forms.

The thermodynamic interpretation of the macrocyclic effect

The availability of sound enthalpy data on the complexation of tetra-aza macrocycles allowed us to reconsider the thermodynamic nature of the macrocyclic effect. Let us consider for instance nickel(II) complexes. The macrocyclic effect is expressed by the equilibrium constant of the following metathetic reaction, which involves the most stable complexes among those formed with cyclic and non cyclic tetramines:



A large macrocyclic effect exists for both high- and low-spin complexes (see table 1) and this is due to both remarkably favourable enthalpy and entropy contributions

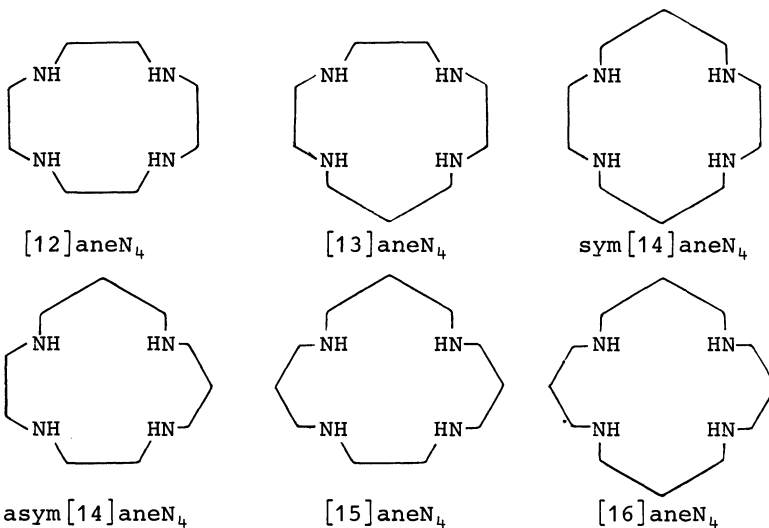
TABLE 1. $\log K$, ΔH° and $T\Delta S^\circ$ values for the metathetic reaction (3) in aqueous solution at 25°C

Spin-state	$\log K$	ΔH° (kcal.mol ⁻¹)	$T\Delta S^\circ$ (kcal.mol ⁻¹)
High-	5.9	-4.9	3.2
Low-	6.9	-2.9	6.2

The process of decomplexation of 2,3,2-tet involves the change from a situation in which the open chain ligand is constrained to a more or less fixed configuration, to an extremely free situation, in which it can assume a number of energetically favourable configurations. This process involves a gain in energy, both enthalpic and entropic in origin. This energy gain associated with the decomplexation of the open-chain tetra-amine cannot be compensated by the complexation of the macrocycle which is preoriented to the coordination even in its free form, since its donor atoms are already in the cyclic square arrangement, required for coordination.

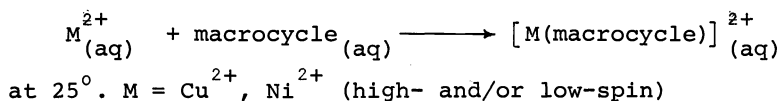
Ring size effect in the formation of tetra-aza macrocyclic complexes:
Copper(II)

A further point in which we were interested was the effect of the size of the macrocyclic cavity on the complexation exothermicity. In this connection we have considered a complete series of saturated 12- to 16-membered tetra-aza macrocycles



the enthalpy changes for the reactions with copper(II) ion are reported in table 2.

TABLE 2. Enthalpy changes, ΔH_{aq} , (kcal.mol⁻¹) associated to the reaction:



Ligand	Cu ²⁺	Ni ²⁺ (high-spin)	Ni ²⁺ (low-spin)
[12] ane N ₄	22.7 ^a	11.9 ^b	==
[13] ane N ₄	25.6 ^a	20.0 ^b	12.5 ^b
sym[14] ane N ₄	32.4 ^a	24.1 ^e	18.7 ^e
asym[14] ane N ₄	27.8 ^d	19.7 ^e	14.4 ^e
[15] ane N ₄	26.5 ^a	17.9 ^c	==
[16] ane N ₄	20.0 ^b	9.7 ^f	==

^a Ref. 4, ^b Ref. 9, ^c Ref. 5, ^d Ref. 8, ^e Ref. 10, ^f Ref. 11.

Expansion of the macrocyclic cavity does not necessarily involve a lengthening and a consequent weakening of the Cu-N bonds. However the macrocycle exceeding the right size must be forced to contract its aperture, so that steric strains are induced in its framework and its donor atoms attain a less favourable orientation. This is evident in the Cu [15] aneN₄ (ClO₄)₂ complex for which an X-ray investigation has been recently reported (Ref. 12). The Cu-N bond distance is in the range expected for copper polyamine complexes but the ligand is seriously constrained. For instance, the six-membered chelate ring trans to the five-membered one is in the disfavoured "sofa" conformation, rather than in the preferred chair one. On the other hand macrocycles of an atomicity lower than 14 have too small an aperture to incorporate copper and to establish strong in plane interactions; for instance, in the copper complex with the smallest macrocycle Cu [12] aneN₄ (NO₃)₂, the metal ion is displaced 0.4 Å above the plane of the four nitrogen atoms in a square pyramidal environment (the oxygen atom of a NO₃⁻ ion occupies the fifth coordination site) (Ref. 13). The 14-membered aperture is the most favoured one, but a substantially different thermochemical behaviour is observed depending on the sequence of the five and six-membered chelate rings. The strongest and most exothermic coordinative interactions are established by the more symmetric ligand having an alternating (5,6,5,6) sequence of the chelate rings. This is also confirmed by the higher energy of the electronic absorption band. Coordination appears to be less favoured for the (5,5,6,6) ligand, which is structurally forced to offer its nitrogen donor atoms according to a stereochemical arrangement which deviates from the preferred square planar one. Moreover the existence of two adjacent six-membered rings may cause some steric constraints in the ligand framework, which are not encountered in the 5,6,5,6 macrocycles where the two six-membered rings are trans.

Nickel(II) tetra-aza macrocyclic complexes

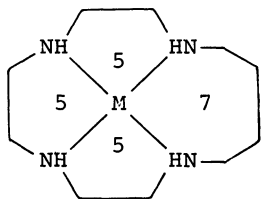
A quite similar ring-size dependent behaviour is observed for the nickel(II) complexes with the same macrocycles (see Table 2). Once again, the 14-membered cavity is privileged as far as the enthalpy changes of complexation are concerned and both decrease and increase of the ligand atomicity induce stereochemical changes and a reduction of the heat effect. As previously outlined the nickel(II) complexes with the considered macrocycles can be both of high- and of low-spin type. The low-spin complexes have a square planar stereo-

-chemistry, whereas the high-spin complexes are octahedral with the two remaining coordination sites being occupied by water molecules. Moreover, for the 13-membered and 14-membered macrocycles the two species coexist according to a temperature and ionic-strength dependent equilibrium (the blue-to-yellow conversion is pushed to the right by an increase of both temperature and concentration of an inert electrolyte.) (Ref. 14).

In the case of high-spin nickel(II) complexes a different coordinative arrangement occurs depending on the ligand atomicity: a) macrocycles having a 14-membered or larger cavity are coplanarly chelated to give a trans-octahedral stereochemistry, b) macrocycles with atomicity smaller than 14 have too small an aperture to encircle in a coplanar fashion the high-spin Ni(II) ion so that the ligand is folded according to a cis-octahedral geometry. It should be remembered that the spin-paired Ni(II) ion (Ni-N distance: $\sim 1.90 \text{ \AA}$) is about 10% smaller than the high-spin cation (Ni-N distance $\sim 2.10 \text{ \AA}$). As a consequence, the 13-membered macrocycle is able to coplanarly chelate the low-spin cation: in fact the yellow square-planar complex predominates in solution at 0.1 M ionic strength (87%). The $[12]aneN_4$ complex in aqueous solution is 100% in the blue high-spin cis-octahedral form; however also the smallest tetra-aza macrocycle can achieve the coplanar coordination under special conditions: as a matter of fact, addition of large amounts of $NaClO_4$ and heating cause the blue solution of the cis-octahedral high-spin complex to turn yellow due to the presence of a remarkable amount of the low-spin square planar complex (up to 50%) (Ref. 15).

The anomalous behaviour of a novel 14-membered macrocycle forming a (5,5,5,7) sequence of the chelate rings

It has been shown in the preceding paragraphs, that, as far as the formation of strong metal macrocycle interactions is concerned, the 14-membered cavity is especially privileged, only second order effects being observed, depending on the sequence of the chelate rings. However, we have very recently obtained in our laboratory a novel 14-membered macrocycle which forms upon coordination a system of fused chelate rings in a (5,5,5,7) membered sequence (Ref. 16). Copper and nickel complexes with this ligand have been isolated and they offer the quite unusual opportunity to study the effect of the formation of a seven-membered chelate ring on the coordinative properties. The enthalpy changes for the complexation of this novel ligand have been measured Cu(II): $\Delta H^\circ = -20.9 \text{ kcal.mol}^{-1}$; Ni(II), (high-spin): $\Delta H^\circ = -12.8$ low-spin: $\Delta H^\circ = -8.7 \text{ kcal.mol}^{-1}$.



Comparison with the other macrocycles shows that the presence of the seven-membered ring causes the disappearance of the advantages associated with the atomicity number 14: for instance, in the case of copper(II), the heat effect is even lower than that observed with the smallest macrocycle, $[12]aneN_4$. For nickel(II), the formation of the high-spin complex is less exothermic than has been observed for $[13]$ and $[15]$ membered ligand complexes. However, there is a property in which the (5,5,5,7) ligand resembles its homologues of the same atomicity: i.e. the formation in aqueous solution of a blue- and yellow-equilibrium mixture, in comparable concentrations, 50% and 50%; for the (5,5,6,6) ligand, 59% of the yellow form; for (5,6,5,6) 69%. It may be of some interest to compare the thermochemical behaviour of macrocyclic ligands which form on coordination three fused five-membered chelate rings (plus an additional ring) with the open-chain tetra-aza ligand, triethylenetetramine (trien) which gives the same (5,5,5) sequence Cu(II): $\Delta H^\circ = -21.6$ Ni(II) (h.s.): $\Delta H^\circ = -14.0 \text{ kcal.mol}^{-1}$. If, in a "gedanken" experiment, one inserts

a six-membered chelate ring in the (5,5,5) system of the trien complexes to form the 13-membered macrocyclic complex, a sharp exothermic effect results for both copper(II) (of $4.0 \text{ kcal.mol}^{-1}$) and high-spin nickel(II) (of $6.0 \text{ kcal.mol}^{-1}$). On the contrary, insertion of a seven-membered ring produces a clear endothermic effect (copper(II): $0.7 \text{ kcal.mol}^{-1}$; nickel(II): $1,2 \text{ kcal.mol}^{-1}$). In a memorable paper (Ref. 17) Gerold Schwarzenbach predicted that the formation of a seven-membered chelate ring should be disfavoured, on the basis of entropic considerations. Present results would suggest that also the enthalpy term may give a comparatively negative contribution to the formation of chelate rings of this size, which are rarely encountered in the chemistry of multidentate ligands

Nickel(II) complexes with penta-aza ligands

The nickel(II) complexes with three saturated penta-aza macrocycles of varying size have been obtained in our laboratory.

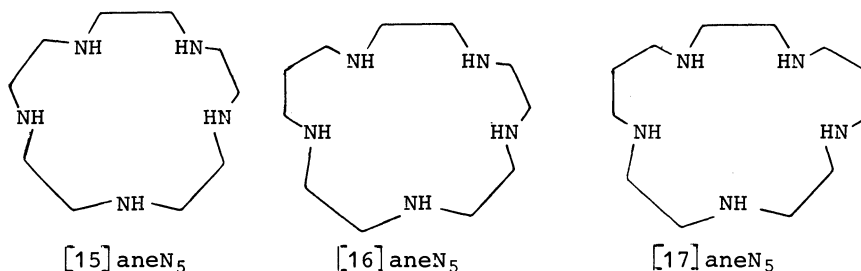
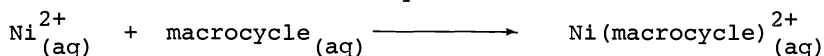


TABLE 3. Enthalpy changes $\Delta H_{\text{aq}}^{\circ}$ (kcal.mol^{-1}) associated to the reaction:



Ligand	$\Delta H_{\text{aq}}^{\circ}$
[15]aneN ₅	16.1
[16]aneN ₅	23.0
[17]aneN ₅	19.4

They are of the high-spin type and should have an octahedral stereochemistry, in which the ligand is folded to span five coordination sites, the sixth one being occupied by a counterion or, in solution, by a solvent molecule. Calorimetric investigations, performed using the cyanide destruction technique (Ref. 18), have shown that also for this series of ligand a ring-size dependent thermochemical behaviour exists (Table 3). In particular, the medium size 16-membered penta-aza macrocycle gives a more exothermic complexation than the upper and lower homologues. The ligand structure-enthalpy change correlation is not straightforward. In this case the 16-membered ligand is that which accomplishes the best compromise situation of strong equatorial (4 nitrogen atoms) and apical (1 nitrogen atom) interactions. It is worth noting that the most favourable complexation to Ni(II) by a penta-aza macrocycle (with [16]aneN₅) is less exothermic than that observed with the most favourable quadridentate macrocycle, sym [14]aneN₄, giving origin to the paradox that four nitrogen atoms bind a metal ion more exothermically than five nitrogen atoms. This apparently curious result emphasizes the striking importance and prominence of the structural features of the ligand on the formation of coordinative bonds.

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