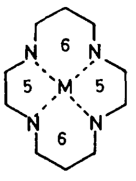
Encircling of Metal Ions by Tetra-aza Macrocycles. Enthalpies of Formation of High- and Low-spin Nickel(II) Complexes of 14-Membered Ligands

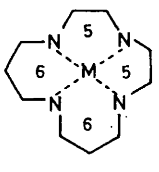
By **Luigi Fabbrizzi, Mauro Micheloni, and Piero Paoletti,*** Istituto di Chimica Generale ed Inorganica and Laboratorio C.N.R., Via J. Nardi 39, 50132 Florence, Italy

In aqueous solution, both the high- and low-spin forms of nickel(II) ions are encircled by the 14-membered macrocycle 1,4,7,11-tetra-azacyclotetradecane (chelate-ring sequence 5,5,6,6) less exothermically than by the isomeric 1,4,8,11-tetra-aza ligand (chelate-ring sequence 5,6,5,6), due to a decrease of the in-plane Ni–N interaction. Insertion of a pyridine ring into the ligand framework makes complexation much less exothermic.

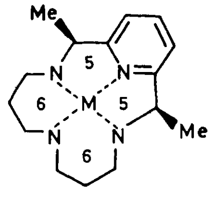
THE most important factor which governs the intensity of the co-ordinative interactions of d^0 or d^{10} metal complexes with macrocycles containing oxygen and/or sulphur as donor atoms is the relative matching of the size of the ligand aperture and the dimensions of the ion to be incorporated.[1] When transition-metal ions are involved (with polyaza macrocycles) a further term is expected to operate, *i.e.* the ligand's ability to satisfy the electronic and geometric preferences of the co-ordinated metal.[2] A typical example is that of the fully saturated tetra-aza macrocycles. In the case of 14-membered macrocycles two isomers have been studied: (*i*) the well known cyclam, L^1, which forms complexes having an alternating sequence of five- and six-membered chelate rings (5,6,5,6); (*ii*) the less well known [3] isocyclam, L^2, which forms similar complexes with a non-alternating sequence of five- and six-membered chelate rings (5,5,6,6). These two isomeric ligands should have apertures of comparable size, and differences in metal–ligand interactions should arise only from electronic effects on the metal. Thus it has been demonstrated, in the case of copper(II) (d^9), that L^1 gives stronger co-ordinative interactions than L^2 and this in turn influences the enthalpy of formation.[4]



L^1



L^2



L^3

(meso)

We have now directed our attention to the formation of nickel(II) (d^8) complexes. A special point of interest in these is that a nickel(II) ion, when encircled by a tetra-aza macrocycle, can be either high spin (paramagnetic) or low spin (diamagnetic). The low-spin ion is *ca.* 10% smaller than the high-spin one (Ni–N *ca.* 1.90 and *ca.* 2.10 Å, respectively). The nickel(II) ion is extremely inert towards the formation of macrocyclic complexes in aqueous solution and consequently it is impossible to follow this type of reaction calorimetrically. This problem has been overcome by studying the destruction of the complex by alkaline cyanide.[5] We report here the calorimetric determination of the enthalpies of formation of high- and low-spin nickel(II) complexes with isocyclam, for comparison with the corresponding enthalpy changes of cyclam complexes, previously reported.[5]

This calorimetric investigation has been extended to complexes of the ligand L^3 which is analogous to isocyclam in that it has the same sequence of chelate rings (5,5,6,6), but differs in the presence of one pyridine nitrogen instead of an amine nitrogen as donor atom. This comparison offers the possibility of evaluating the difference between the enthalpies of Ni–N(sp^3) and Ni–N(sp^2) co-ordinative bonds, in a macrocyclic environment. In this connection, it should be remembered that naturally occurring tetra-aza macrocyclic complexes, incorporating transition-metal ions, contain wholly sp^2 (pyrrole) nitrogen atoms.

EXPERIMENTAL

Materials.—Isocyclam was synthesized by the published procedure,[3] based on condensation of the appropriate tosylated segments.[6] The ligand L^3 was obtained by the method of Karn and Busch.[7] Nickel(II) complexes were obtained as perchlorates, from the reaction of $Ni[ClO_4]_2\cdot6H_2O$ and ligand in hot ethanol, and were recrystallized from methanol. The analyses were satisfactory.

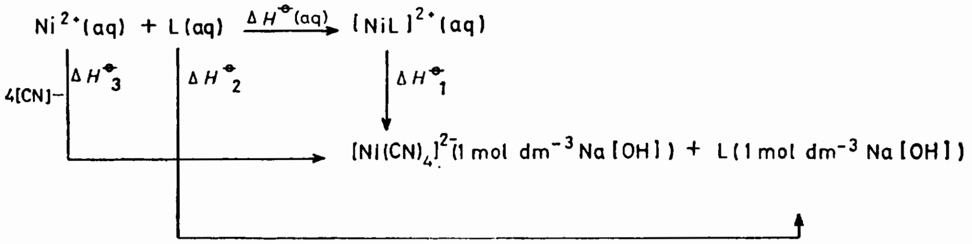
Calorimetric Procedure.—Calorimetric measurements of the heat of reaction between aqueous solutions of the nickel complexes and excess of sodium cyanide, in strong alkaline solution, were carried out in a LKB BATCH model 10700–2 microcalorimeter. The reaction can be represented as in (1) where L = L^2 or L^3; for L = $(OH_2)_6$ or L^1, $\Delta H^\ominus$ has

$$[NiL]^{2+} + 4[CN]^- \rightleftharpoons [Ni(CN)_4]^{2-} + L \qquad (1)$$

already been reported.[5] The calorimetric procedure has been fully described previously.[5] In a typical calorimetric measurement, the nickel complex solution (0.4 cm^3, 0.01—0.02 mol dm^{-3}) was introduced by weight into one side of the calorimetric cell compartment; the Na[OH]–Na[CN] solution (2.5 cm^3, 0.9 mol dm^{-3} Na[OH], 0.1 mol dm^{-3} Na[CN]) was introduced into the other side by a precision pipette (Pipetman). Different ligands have different kinetic inertness and the times (in hours) required for apparently complete reaction were as follows: Ni^{2+}(aq), 0.5; $[NiL^1]^{2+}$, 5; $[NiL^2]^{2+}$, 0.6; and $[NiL^3]^{2+}$, 0.6.

In order to confirm that the destruction of the complex with ligand L^2 was complete the concentration of [Ni-

$(CN)_4]^{2-}$ in the reaction mixture was determined spectrophotometrically immediately after completion of the calorimetric run, using a Varian model 17 spectrophotometer equipped with 1-mm quartz cell and the absorption band at 268 nm in the spectrum of $[Ni(CN)_4]^{2-}$ ($\varepsilon = 1.21 \times 10^4$ dm^3 cm^{-1} mol^{-1}). The concentration of $[Ni(CN)_4]^{2-}$ was found to be in good agreement with that expected for complete reaction. In the case of ligand L^3, because of its absorption in the u.v. region, the *d–d* visible absorption band of the low-spin complex $[NiL^3]^{2+}$ (maximum at 460 nm) was monitored using the same spectrophotometer, but equipped with 1-cm cells. No visible *d–d* band was detectable, even at the highest instrumental sensitivity, indicating complete destruction of the complex in the reaction mixture. The enthalpy of reaction (1) can be related to the enthalpy of complex formation through the thermochemical cycle shown in the Scheme.



SCHEME $\Delta H^{\ominus}(aq) = \Delta H^{\ominus}_1 - \Delta H^{\ominus}_3 - \Delta H^{\ominus}_2$, where $\Delta H^{\ominus}_3 = -42.8$ kcal mol^{-1},[5] and $\Delta H^{\ominus}_2$ is assumed to be zero.[8] Values for $\Delta H^{\ominus}_1$ and the enthalpies of formation for each species are reported in Table 2

RESULTS AND DISCUSSION

Although the reaction of cyclam with nickel(II) ion in aqueous solution is more exothermic than that of isocyclam, this comparison is not straightforward since complexes with these two ligands exist in solution as an equilibrium mixture of two species [equation (2)]: a

$$[Ni(macrocycle)(OH_2)_2]^{2+} \rightleftharpoons [Ni(macrocycle)]^{2+} + 2H_2O \quad (2)$$

tetragonally distorted octahedral high-spin complex, $[Ni(macrocycle)(OH_2)_2]^{2+}$, in which water molecules occupy axial positions, and a planar low-spin $[Ni(macrocycle)]^{2+}$ species.[3,5] For both ligands L^1 and L^2 the low-spin form predominates under the conditions of the calorimetric measurements and the relative percentages of the high- and low-spin forms are shown in Table 1, where the enthalpies of interconversion of the high- to low-spin forms are also given. Combination of these values with the calorimetrically determined heat changes, referring to the mixture, gives the enthalpies of formation of each individual species of different spin multiplicity (see Table 2). Both high- and low-spin complexes of cyclam are formed more exothermically than those of isocyclam and this energy difference is nearly the same (*ca.* 5 kcal mol^{-1}) * for each spin state.

TABLE 1

Enthalpy changes associated with the interconversion of the blue high-spin to the yellow low-spin species and the percentages of each species in aqueous solution at 25 °C

L	$\Delta H^{\ominus}$/ kcal mol^{-1}	Percentage of species high-spin	low-spin	Ref.
L^1	5.4	29	71	5
L^2	5.3	39	61	3
L^3	4.4	39	61	7

TABLE 2

Enthalpies of formation (kcal mol^{-1}) in aqueous solution at 25 °C of nickel(II) complexes with 14-membered tetraaza macrocycles in their high- and low-spin forms

Complex	Reaction mixture	High-spin form	Low-spin form	Ref.
$[NiL^1]^{2+}$	-20.3 ± 0.2	-24.1	-18.7	5
$[NiL^2]^{2+}$	-16.5 ± 0.3	-19.7	-14.4	This work
$[NiL^3]^{2+}$	-9.3 ± 0.2	-12.0	-7.6	This work

The enthalpy of formation of a metal complex in aqueous solution results from the balance of a series of different contributions: dehydration of both ligand and metal ions, hydration of the complex formed, formation of co-ordinative bonds, and conformational changes experienced by the ligand during complexation. Thus, the difference between the enthalpies of formation of cyclam and isocyclam complexes could be potentially ascribed to different contributions from any of the above processes. More direct information on the significance of one of these contributions can be obtained from spectroscopic parameters. In the case of the high-spin complexes, the Dq^{xy} value, which expresses the energy of the Ni–N in-plane interaction, is higher for the cyclam than for the isocyclam complexes {10 Dq^{xy} = 14 750 (ref. 8) and 13 700 cm^{-1} (ref. 3) for $[NiL]Cl_2$ complexes}. For low-spin complexes the electronic spectra will not allow the determination of the Dq^{xy} value, but they present a unique band at *ca.* 22 000—23 000 cm^{-1} which is the envelope of three transitions and it has been shown that, in the case of complexes with ligands having nitrogen donor atoms (tetramines [9] or tetrapeptides [10,11]), the energy of this band may be correlated quite well with the intensity of the in-plane interactions. Once again, the frequency of the absorption band is higher for the cyclam than for the isocyclam complex (22 470 and 21 600 cm^{-1}, respectively). Interestingly, the spectroscopically evaluated differences between the energies of the Ni–N interactions are the same for both high- and low-spin complexes (*ca.* 1 000 cm^{-1} ≡ 3 kcal mol^{-1}) and of the same order of magnitude as the enthalpy differences measured calorimetrically (*ca.* 5 kcal mol^{-1}). This

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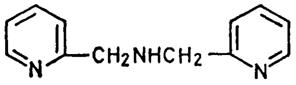
* Throughout this paper: 1 cal = 4.184 J.

suggests that the term which is most responsible for the differences in the enthalpy of formation of the nickel(II) complexes with the two 14-membered macrocycles is that due to bond formation. The reason for this must lie in the structures of the two ligands. The strongest interactions to both high- and low-spin nickel(II) ion are expected when donor atoms are placed, at the right distances, at the corners of a square. The more symmetrical arrangement of chelate rings in cyclam complexes (5,6,5,6) would probably allow a closer approach to this ideal geometrical situation; moreover, in the isocyclam complexes, the two six-membered chelate rings are adjacent and steric repulsions would probably induce a further distortion from that ideally required by the encircled metal. Likewise, for copper(II), the reaction of cyclam has been found to be 5 kcal mol^{-1} more exothermic than that of isocyclam and once again this energy difference parallels the spectroscopically evaluated difference between the in-plane Cu–N interactions.[4]

Comparison of the enthalpy data for isocyclam and ligand L^3, which have the same sequence of chelate rings, allows an evaluation of the effect of the insertion of a pyridine ring into a macrocyclic framework; L^3 also has two methyl groups pointing out from the aliphatic chain, but it has been shown that alkyl substitution on carbon atoms has only a very small influence on the enthalpy of formation of nickel(II) polyamine complexes.[12] Changing from isocyclam to L^3, the decrease in enthalpy of formation is large (8 and 7 kcal mol^{-1} for high- and low-spin complexes, respectively). While the Ni–N bond enthalpy is typically lower for a pyridine than for an amine nitrogen atom, the difference is usually very moderate {compare, for instance, the enthalpies of formation of nickel(II) complexes with pyridine and amines: $[Ni(py)]^{2+}$, $\Delta H^{\ominus} = -2.6$; $[Ni(NH_3)]^{2+}$, $\Delta H^{\ominus} = -3.5$; $[Ni(en)]^{2+}$ (en = ethylenediamine), $\frac{1}{2}\Delta H^{\ominus} = -4.5$ kcal mol^{-1}}.[13] The difference is also small for complexes with ligands in which the pyridine ring is inserted in an open-chain polyamine framework [see, for instance, complexes with the two ligands L^4 and L^5 for which $\Delta H^{\ominus}(NiL^{2+}) = -11.1$ and -11.8 kcal mol^{-1} respectively].[14,15] Therefore we believe that the very low exothermicity of L^3 complexation does not depend upon a large difference in the energy of Ni–N co-ordinative bonds.



L^4

$H_2NCH_2CH_2NHCH_2CH_2NH_2$

L^5

However, the introduction of a pyridine ring into the macrocycle makes the ligand much less flexible and serious constraints on the macrocyclic framework may be expected to arise during complexation. Thus the crystal structure of low-spin $[Ni(DL\text{-}L^3)]^{2+}$ has been reported[16] and the Ni–N(sp^2) bond length has a value of 1.80 Å (normal value, 1.90 Å).[17] We therefore suggest that the comparatively low enthalpies of formation of *meso*-L^3 complexes should be ascribed to the strain experienced by this comparatively rigid macrocycle in its efforts to satisfy the geometrical requirements of the encircled metal ion.

Similar behaviour was noticed in the case of copper(II), but the enthalpy difference was less pronounced: $[Cu(isocyclam)]^{2+}$, $\Delta H^{\ominus} = -27.8$; $[Cu(meso\text{-}L^3)]^{2+}$, $\Delta H^{\ominus} = -23.9$ kcal mol^{-1}.[4] We ascribe this difference between Cu and Ni to the nature of the two ions: copper(II) is more ' plastic ',[18] in the sense that it can assume a greater range of stereochemistries, each of which is slightly different. So, in the case of the *meso*-L^3 complex, a moderate change from a purely tetragonal stereochemistry, such as a small elevation of the copper(II) ion from the N_4 plane, would relieve most of the steric constraints on the macrocyclic framework. Conversely, nickel(II) ions offer only two well defined stereochemical arrangements (octahedral or planar), each having quite different electronic structures, and in both of which the nickel(II) ion and donor atoms must be strictly coplanar. In other words, nickel(II) cannot alleviate, for electronic reasons, the unfavourable configurational situation of co-ordinated *meso*-L^3, and this is reflected in the enthalpy of formation.

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