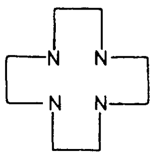
Co-ordinating Tendencies of a 14-Membered Tetra-aza Macrocycle which forms a Seven-membered Chelate Ring

By **Mauro Micheloni, Piero Paoletti,*** and **Antonio Poggi**, Istituto di Chimica Generale ed Inorganicà, Università di Firenze and Istituto CNR, Via J. Nardi, 39, 50132 Florence, Italy
Luigi Fabbrizzi,* Istituto di Chimica Generale ed Inorganicà Università di Pavia, Via Taramelli, 12, 27100 Pavia, Italy

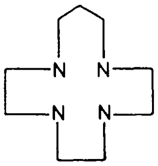
The basicity constant of 1,4,7,10-tetra-azacyclotetradecane (L^5) and the stability constants of the complexes $[CuL^5]^{2+}$ and $[Cu(HL^5)]^{3+}$ have been determined by potentiometry at 25 °C in 0.5 mol dm^{-3} $K[NO_3]$. The enthalpies of formation of the copper(II) and nickel(II) complexes of L^5 have been determined by flow and batch microcalorimetry respectively. The co-ordination of L^5 to copper(II) and nickel(II) to form a system with a (5,5,5,7) chelate ring sequence is remarkably less exothermic than that of 1,4,8,11-tetra-azacyclotetradecane (L^3) and 1,4,7,11-tetra-azacyclotetradecane (L^4) which form (5,6,5,6) and (5,5,6,6) chelate ring sequences respectively. The introduction of a hindered seven-membered chelate ring overrules completely the enthalpic advantage of the 14-membered cavity. The macrocyclic complex $[CuL^5]^{2+}$ is more stable than the corresponding complex with a non-cyclic polyamine $[Cu(trien)]^{2+}$ (trien = triethylenetetra-amine). This extra stability is due to a favourable entropy contribution, the enthalpy being slightly unfavourable. Finally, the stability of the monoprotonated complex $[Cu(HL^5)]^{3+}$ is compared with similar protonated complexes formed by other tetra-aza macrocycles.

TETRA-AZA macrocycles have attracted considerable interest among inorganic chemists in the past decade.[1] An intriguing feature of these systems is that the size of the ligand can be changed with relative ease by synthetic means which can have the effect that the enclosed metal ion behaves in quite different ways. In the case of 3*d* metal complexes with saturated unsubstituted ligands, the whole series of 12- to 16-membered tetra-aza macrocycles has been thoroughly investigated with respect to spectral,[1] magnetic,[2] thermodynamic,[3] kinetic,[4] and electrochemical aspects.[5]

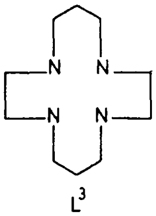
From these studies it has become evident that 14-membered macrocycles form the most stable complexes with bivalent copper and nickel ions. 14-Membered macrocyclic complexes are also exceptional from a kinetic point of view, exhibiting an unusual inertness: for instance $[NiL^3]^{2+}$ persists in strong acid solution for months.



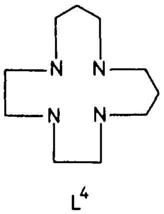
L^1



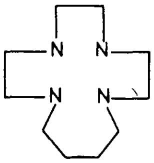
L^2



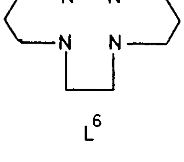
L^3



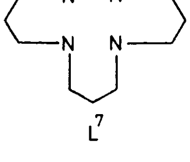
L^4



L^5



L^6



L^7

For ligands whose complexes contain only five- and/or six-membered chelate rings, the 14-membered species is unique, in that it may exist in two different forms which differ only in the sequence of the chelate rings, L^3 (5,6,5,6) † and L^4 (5,5,6,6). Although the number of atoms in the macrocyclic ring remains constant, the different arrangement of the fused rings causes appreciable differences in the bonding properties, as evidenced by investigations performed in this laboratory.[6]

We have now prepared a further 14-membered tetra-aza macrocycle, 1,4,7,10-tetra-azacyclotetradecane (L^5), which is able to form on complexation a (5,5,5,7) sequence of chelate rings, and we have isolated its copper(II) and nickel(II) complexes. We report here a thermodynamic investigation on complexes of L^5 in solution covering the enthalpies of formation of the nickel(II) complexes (high- and low-spin forms), the enthalpy and entropy of formation of the copper(II) complex, and log*K* values for the protonation of the free unco-ordinated macrocycle and for its copper complex. The aim of this work is to evaluate to what extent the bonding properties in complexes of ligands with the same overall number of atoms in the cyclic framework are influenced by the relative positions of the donor atoms. Furthermore, seven-membered chelate rings are not encountered very often in co-ordination chemistry, and their low stability has been ascribed by Schwarzenbach [7,8] to an unfavourable entropy contribution. Incorporation of the unstable seven-membered ring within a closed framework in these studies allows a direct evaluation of the thermodynamic factors which govern its formation.

EXPERIMENTAL

Preparation of 1,4,7,10-*Tetra-azacyclotetradecane*.—OO′-*Bis*(*toluene*-p-*sulphonyl*)*butane*-1,4-*diol*, (I). A solution of

---

† The numbers in parentheses indicate the number of atoms in each chelate ring in the metal complex.

butane-1,4-diol (47.2 g) in triethylamine (400 cm^3) was added, dropwise over *ca.* 6 h, to a vigorously stirred solution containing toluene-*p*-sulphonyl chloride (200 g) (Erba RPE-ACS grade) in diethyl ether (1 dm^3). The reaction mixture was then stirred overnight at room temperature. The white crude product was filtered off, washed with water, and then with ethanol. The product was recrystallized from hot ethanol (Found: C, 54.5; H, 5.50. Calc. for $C_{18}H_{22}O_6S_2$: C, 54.25; H, 5.55%).

NN′N″N‴-*Tetrakis(toluene*-p-*sulphonyl)*-1,4,7,10-*tetra-azadecane*, (II). A solution of 1,4,7,10-tetra-azadecane (19.20 g) and Na[OH] (20.9 g) in water (200 cm^3) was added, dropwise over *ca.* 6 h, to a vigorously stirred solution containing toluene-*p*-sulphonyl chloride (100 g) in diethyl ether (500 cm^3). The reaction mixture was then stirred for 1 h at room temperature. The white powder precipitated was filtered off, and washed with water and ethanol. The dry crude material was recrystallized from hot ethanol (Found: C, 53.1; H, 5.40; N, 7.10. Calc. for $C_{34}H_{42}N_4O_8S_4$: C, 53.6; H, 5.55; N, 7.35%).

The disodium salt of (II) was prepared by the addition of sodium hydride (6 g) in small portions under nitrogen to a stirred solution of (II) (43 g) in anhydrous dimethylformamide (dmf) (1 dm^3). After the evolution of hydrogen had ceased, the excess of sodium hydride was filtered off.

1,4,7,10-Tetrakis(toluene-*p*-sulphonyl)-1,4,7,10-tetra-azacyclotetradecane, (III), was obtained by adding dropwise with stirring to the above filtrate heated to 110 °C a solution of the ditosylate of butane-1,4-diol (I) (22.5 g) dissolved in anhydrous dmf (500 cm^3). The reaction mixture was refluxed for a few hours. The volume was reduced to 150 cm^3 by vacuum distillation and water (1 dm^3) was slowly added. The white precipitate was filtered off and washed with water. The product was recrystallized from chloroform–ethanol (1 : 1) (Found: C, 55.6; H, 5.90; N, 7.10. Calc. for $C_{38}H_{48}N_4O_8S_4$: C, 55.85; H, 5.90; N, 6.85%). Infrared spectra demonstrated that cyclization had occurred since no bands in the N–H region (3 060—3 500 cm^{-1}) were observed. The free ligand was obtained by hydrolysis of the tetratosylate derivative, (III), with concentrated H_2SO_4 solution, following the procedure already described.[9] The crude solid product was isolated as the tetrahydrochloride.

1,4,7,10-*Tetra-azacyclotetradecane–hydrogen chloride* (1/4), (IV). Gaseous hydrogen chloride was bubbled through a diethyl ether solution of the ligand. The white crystals of (IV) were filtered off, washed with diethyl ether, and recrystallized from ethanol (Found: C, 34.5; H, 8.00; N, 15.9. Calc. for $C_{10}H_{28}Cl_4N_4$: C, 34.7; H, 8.15; N, 16.2%).

The nickel(II) complex of L^5 was prepared by mixing hot ethanol solutions of ligand and $Ni[ClO_4]_2 \cdot 6H_2O$ in equimolar proportions. The yellow complex which precipitated on cooling was filtered off (Found: C, 26.0; H, 5.30; N, 12.2. Calc. for $[NiL^5][ClO_4]_2$: C, 26.2; H, 5.30; N, 12.25%).

Reagents.—Carbon dioxide-free solutions of Na[OH], used for e.m.f. measurements, were prepared, stored, and standardized as described elsewhere.[10] A potassium nitrate solution (0.5 mol dm^{-3}) was prepared from solid potassium nitrate (C. Erba ACS grade) and used as the ionic medium for potentiometric measurements. A stock solution containing copper(II) was prepared from solid copper chloride (C. Erba ACS grade) and standardized by standard gravimetric methods.

E.M.F. Measurements.—A full description of the potentiometric apparatus and its standardization has already been given.[10] For the determination of the basicity constants of L^5 the cell was filled with $K[NO_3]$ (*ca.* 100 cm^3, 0.5 mol dm^{-3}) containing ligand (0.2—0.3 mmol) and hydrochloric acid in excess. For the complex-formation experiments, the solution also contained various amounts of copper(II) chloride. The Na[OH] solution was dispensed from a Mettler DV10 piston burette. Equilibrium was reached almost instantaneously in the pH range investigated. The computer program Miniquad [11] was used to calculate the equilibrium constants; the criteria adopted for selecting the species formed at equilibrium in the systems studied have already been reported.[12]

In the case of the nickel(II)–L^5 system, complex formation is too slow to use the potentiometric technique to determine the stability constant.

Calorimetric Procedure.—For the calorimetric measurements, the LKB BATCH model 10700-2 and LKB FLOW model 10700-1 microcalorimeters were used. The flow technique was employed to determine the enthalpy of formation of $[CuL^5]^{2+}$. A full description of the apparatus and its calibrations has already been reported.[13]

In aqueous solutions of the macrocycles, which are strong bases, the main species present is the diprotonated form $[H_2L]^{2+}$; the presence of two positive charges causes the insertion of the metal ion into the ligand cavity to be rather slow. This problem can be avoided by working in strongly alkaline solution where the ligand remains uncharged. We therefore studied macrocycle complexation in 1 mol dm^{-3} Na[OH]. The enthalpy change can be related to that in neutral solution through appropriate dilution experiments (see ref. 14).

Solutions were injected into the calorimeter by high-precision piston burettes (Mettler DV 10). In a typical experiment a solution of Cu^{II} (1.4×10^{-4} mol dm^{-3}) in Na[OH] (1 mol dm^{-3}) (burette A) and a solution of the ligand hydrochloride (1.5×10^{-4} mol dm^{-3}) in Na[OH] (1 mol dm^{-3}) were injected into the flow apparatus; the flow rates were manipulated in such a way as to have a metal-to-ligand ratio ranging from 1 : 1 to 1 : 1.7. In the range investigated, only the $[CuL^5]^{2+}$ complex was found, since the heat flow per number of moles of Cu^{II} was constant.

The batch technique was used to determine the enthalpy of formation of $[NiL^5]^{2+}$; a description of this apparatus and its mode of operation for slow reactions has already been given in detail.[15] Ultraviolet spectral measurements were made on a Varian–Cary 17 spectrophotometer equipped with 1-mm path length quartz cells.

The reactions for which $\Delta H^\ominus$ has been determined can be represented by equation (1) where L = 1,4,7,10-tetra-azacyclotetradecane; values of $\Delta H^\ominus$ for L = $(H_2O)_6$ have been reported previously.[15]

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

In a typical calorimetric experiment the $[NiL^5]^{2+}$ complex (0.4 cm^3) in solution (0.01—0.02 mol dm^{-3}) was introduced by weight into one side of the calorimetric cell compartment; the Na[OH]–Na[CN] (2.5 cm^3) solution (0.9 mol dm^{-3} Na[OH], 0.1 mol dm^{-3} Na[CN]) was introduced into the other by a precision pipette. The calorimeter was allowed to equilibrate until a steady baseline was obtained, then the measurement was started by mixing the reactants. The reaction was considered complete when no further heat change could be detected, after *ca.* 0.6 h. In order to confirm that the reaction was complete and that equilibrium had been reached, we determined the concentration of $[Ni(CN)_4]^{2-}$ spectrophotometrically in the reaction mixture, immediately following the collection of the thermal data. This was done by monitoring the sharp absorption band at 268 nm ($\varepsilon = 1.21 \times 10^4$ dm^3 mol^{-1} cm^{-1}).[15] The concentration of $[Ni(CN)_4]^{2-}$ was close to the value expected, 98%. A correction for the enthalpy of dilution of the Na[OH]–Na[CN] solution was made to each measurement by introducing Na[CN]–Na[OH] (2.5 cm^3) solution into one side of the calorimetric cell and pure water (0.4 cm^3) into the other. To prevent creeping, the reaction cell was coated with paraffin wax.

RESULTS AND DISCUSSION

Protonation.—In Table 1 are reported the protonation constants of the ligand L^5 determined at 25 °C in $K[NO_3]$ (0.5 mol dm^{-3}). The same parameters for the macrocycles L^3 and 1,4,8,12-tetra-azacyclopentadecane (L^6), together with those for the open-chain ligand triethylenetetra-amine (trien), are given for comparison. Ligand L^5 is a tetraprotic base for which the affinity towards protons is relatively high for the first and second steps of protonation, but much lower in the last two stepwise protonation processes. This behaviour is generally observed with cyclic tetra-amines.[16]

TABLE 1

Basicity constants at 25.0 °C and $I = 0.5$ mol dm^{-3}

log$K$	L^5 [a]	L^3 [b]	L^6 [b]	trien [c]
logK_1	10.98(1) [d]	11.58	11.08	10.02
logK_2	9.75(2)	10.62	10.38	9.39
logK_3	4.86(1)	1.61	5.28	7.00
logK_4	2.00(2)	2.42	3.60	4.00
logβ_4	27.59	26.23	30.34	30.41

[a] This work. [b] Ref. 16. [c] Ref. 17. [d] Values in parentheses are standard deviations in the last significant figure.

It is interesting to compare the protonation constants of L^5 with those of the open-chain polybasic trien;[17] in both molecules the amine groups are separated by ethylenic chains. The first two protonation steps of the macrocycle L^5 are favoured with respect to the noncyclic ligand trien. Several factors may be responsible for this behaviour: release of the lone-pair repulsion present in the macrocyclic framework, possible formation of intramolecular N–H · · · N hydrogen bonds, or an inductive effect due to the large number of methylene groups in the cyclic polybase. On the other hand, protonation of the macrocycle is progressively disfavoured in the last two steps. For L^5, the last two protons add to a system of positive charges which are structurally quite close and which are therefore expected to exert stronger repulsions than in the open-chain rigid polyammonium ion, where the charges are further apart.

Copper(II) *Complexes.*—In Table 2 the enthalpy changes for the formation of the $[Cu(macrocycle)]^{2+}$ complexes are reported for the three 14-membered ligands. It can be seen that the alternating sequence of five- and six-membered chelate rings is enthalpically preferred; the formation of the (5,5,6,6) system in which both the five- and the six-membered rings are adjacent is less exothermic (by *ca.* 19.2 kJ mol^{-1}) than the (5,6,5,6) system. However, the (5,5,5,7) arrangement causes a dramatic decrease in the enthalpy of formation, which is less than two thirds of that observed with ligand L^3.[14] Furthermore, the formation of the copper complex with ligand L^5 is less exothermic than that with the 12-, 13-, and 15-membered tetra-aza macrocycles;[18] that is the enthalpic advantage of the 14-membered cavity disappears with the introduction of a seven-membered chelate ring. It is well known that the enthalpy term for the formation of a metal complex in solution depends on the relative contributions of several factors including gas-phase bond enthalpy and solvation terms.[19]

TABLE 2

Enthalpy changes, $-\Delta H^{\ominus}$ (kJ mol^{-1}), for the reaction $M^{2+}(aq) + L(aq) \rightleftharpoons ML^{2+}(aq)$ in aqueous solution at 25 °C, $I = 0.5$ mol dm^{-3}

		M		
Ligand	Chelate ring sequence	Cu^{II}	Ni^{II} (high spin)	Ni^{II} (low spin)
L^1	(5,5,5,5)	94.98 [a]	47.79 [b]	
L^2	(5,5,5,6)	107.11 [c]	83.68 [b]	52.3
L^5	(5,5,5,7)	87.5(7) [d]	53.6(4) [d]	36.4(8)
L^4	(5.5,6,6)	116.32 [c]	84.42 [e]	60.25
L^3	(5,6,5,6)	135.56 [a]	100.83 [f]	78.24
L^6	(5,6,6,6)	110.88 [a]	74.89 [b]	
L^7	(6,6,6,6)	83.68 [g]	40.58 [g]	

[a] Ref. 18. [b] Ref. 21. [c] Ref. 14. [d] This work, values in parentheses are standard deviations in the last significant figure. [e] Ref. 6. [f] Ref. 15. [g] Ref. 23.

Interestingly, the trend of $\Delta H^{\ominus}$(aq) for these 14-membered macrocyclic copper(II) complexes parallels that of the frequencies of the absorption maximum in the visible spectrum (see Table 3), $\nu(d\text{–}d)$. It has been shown that for copper(II) polyamine complexes, having a tetragonal stereochemistry, the empirical parameter $\nu(d\text{–}d)$ is proportional to the strength of the metal–nitrogen in-plane interactions.[20] Thus, it appears that the relative magnitude of the enthalpy of complex formation reflects the effectiveness of the bonding situation in these complexes.

TABLE 3

Frequency of the absorption maximum of copper(II) and low-spin nickel(II) 14-membered tetra-aza macrocyclic complexes [a]

		$\nu(d\text{–}d)$/cm^{-1}	
Ligand	Chelate ring sequence	Cu^{II}	Ni^{II}
L^5	(5,5,5,7)	17 600 (213) [b]	22 075 (181)
L^4	(5,5,6,6)	18 200 (172)	21 600 (116)
L^3	(5,6,5,6)	19 900 (100)	22 470 (67)

[a] Spectra of aqueous solutions. [b] Absorption coefficient, ε(dm^3 mol^{-1} cm^{-1}), in parentheses.

The most symmetric ligand, L^3, exhibits the strongest co-ordination bonds since it is able to dispose its donor atoms closest to the sites preferred by the metal ion, at the corners of the equatorial square in tetragonally distorted octahedral complexes. On the other hand, the location of the nitrogen atoms is much less symmetrical for the macrocycle L^5 and the formation of strong Cu–N bonds will be much less favoured.

It is interesting to compare the enthalpies of formation of copper(II) complexes with the L^5 ligand of chelate ring sequence (5,5,5,7) with that of other ligands containing the same sequence of three five-membered rings, L^1 (5,5,5,5),[18] L^2 (5,5,5,6), [21] and the open-chain tetra-amine trien (5,5,5).[22] Complexation of macrocycles L^1 and L^2 is more exothermic than that of the non-cyclic reference ligand, trien. This has been explained by the fact that macrocycles are ' synthetically pre-oriented ' for co-ordination, and therefore do not have to expend any configurational energy in folding themselves around the metal ion in the way that non-cyclic tetra-amines must do. The much greater $\Delta H^\ominus$ of formation of copper complexes with L^2 than with L^1 may be a consequence of the smaller cumulative ring strain present in the 5,5,5,6 system than in complexes with four fused five-membered rings. However, the macrocyclic enthalpic advantage disappears with L^5; the insertion of a seven-membered ring in the 5,5,5 system presumably induces a configurational strain large enough to more than compensate for the advantage due to the precyclization. Strictly speaking, comparison of the co-ordination behaviour in solution of open- and closed-chain ligands should be referred to the $\Delta G^\ominus$ values and the ' macrocyclic effect ', which was originally defined as a difference between the $\log K$ values for complexation [$\log K = \log K_{\text{closed}} - \log K_{\text{open}}$], or in other words the $\log K$ value for the metathetic equilibrium (2).

$$[\text{ML}_{\text{non-cyclic}}]^{2+} + \text{L}_{\text{cyclic}} \rightleftharpoons [\text{ML}_{\text{cyclic}}]^{2+} + \text{L}_{\text{non-cyclic}} \quad (2)$$

Comparison of $\log K$ values for copper(II) co-ordination with L^5 and trien shows that a macrocyclic effect still exists, in spite of the slightly unfavourable enthalpy contribution. In fact, the metathetic reaction (2) is entropy controlled and this reflects the large configurational entropy gain due to decomplexation and unfolding of the open-chain ligand (whereas the free precyclized macrocycle does not lose entropy on co-ordination). This behaviour is consistent with that found for all other macrocyclic amine systems of 3*d* metal ions so far investigated.[18,23,24] The formation of macrocyclic complexes with respect to the non-cyclic analogues is always strongly favoured by the entropy term; the enthalpy contribution may or may not be favourable according to the ligand's ability to adjust to the geometrical requirements of the metal ion.[18]

Protonated Copper Complexes.—The monoprotonated species $[\text{Cu(HL}^5)]^{3+}$ has been isolated and its stability constant measured potentiometrically at 25 °C in $\text{K[NO}_3]$ (0.5 mol dm^{-3}) (see Table 4). Formation of complexes with monoprotonated ligands is not unusual for macrocyclic tetra-amines or their open-chain analogues.

In Table 4 $\log K$ values for similar reactions of the 16-membered macrocycle, L^7 are reported for comparison. It can be seen that complexation of $[\text{HL}^5]^+$ to copper(II) ion is favoured with respect to the 16-membered tetra-aza macrocycles, HL^{7+}, by two log units. It is probable that, in the $[\text{Cu(HL}^5)]^{3+}$ complex, the hydrogen ion is bound to one of the two nitrogen atoms linked by the tetramethylenic chain; in this way the ligand can form a favourable system of two fused five-membered rings on co-ordination and the ammonium group is at the longest distance with the ligand adopting an out configuration. The larger value of $\log K$ for the $\text{Cu}^{2+} + \text{HL}^{5+}$ reaction relative to the corresponding one with HL^{7+} may then be ascribed to the fact that the latter protonated ligand forms a system with two adjacent six-membered rings which is less favoured.

TABLE 4

Stability constants of copper(II) complexes with ligands L^5 and L^7

Reaction	$\log K$	Ref.
$\text{Cu}^{2+} + \text{L}^5 \longrightarrow [\text{CuL}^5]^{2+}$	22.36(7) [a]	*b*
$\text{Cu}^{2+} + \text{H}^+ + \text{L}^5 \longrightarrow [\text{Cu(HL}^5)]^{3+}$	25.44(9)	*b*
$\text{Cu}^{2+} + [\text{HL}^5]^+ \longrightarrow [\text{Cu(HL}^5)]^{3+}$	14.47	*b*
$\text{Cu}^{2+} + [\text{HL}^7]^+ \longrightarrow [\text{Cu(HL}^7)]^{3+}$	12.6	23

[a] Values in parentheses are the standard deviations in the last significant figure. [b] This work.

Nickel(II) *Complexes.*—Nickel(II) complexes with both cyclic and non-cyclic tetra-amines normally exist in aqueous solution as a mixture of two species: the blue high-spin, diaquo-octahedral form and the yellow low-spin, square form, see equation (3). The relative stability of the two species is ring-size dependent: the blue

$$[\text{NiL(OH}_2)_2]^{2+} \rightleftharpoons [\text{NiL}]^{2+} + 2\,\text{H}_2\text{O} \qquad (3)$$

form is much more stable with 12-, 15-, and 16-membered macrocycles (>99%), whereas for other ligands both forms co-exist in appreciable concentrations although the yellow species normally predominates.[15,21]

The ligand L^5 shows a behaviour similar to the other 14-membered macrocycles, since the blue and the yellow complexes are formed in nearly equal concentrations in aqueous solution at 25 °C. Similarly, the thermodynamic data for the blue-to-yellow conversion ($\Delta H^\ominus = 17.2$ kJ mol^{-1}, $\Delta S^\ominus = 58.6$ J K^{-1} mol^{-1}) are very similar to those for the other 14-membered ligands.[6,15]

The enthalpy change obtained for the Ni–L^5 system (see Table 2), determined by the cyanide-destruction method,[14] refers to the blue and yellow equilibrium mixture. Using the thermodynamic parameters for the blue-to-yellow conversion, we have evaluated the enthalpies of formation at 25 °C of the blue and yellow forms. The pattern is similar to that in the copper(II) system; the complexation of Ni^{II}, to form both high- and low-spin species, is less exothermic than for the other 14-membered macrocycles, L^3 and L^4. For both copper(II) and high-spin nickel(II) complexes with the non-cyclic reference ligand trien,[22] formation is more exothermic than that for the corresponding macrocyclic complexes with L^5 where all nitrogen atoms involved in the M–N bonds are secondary.

As far as low-spin nickel(II) complexes are concerned, it has been observed that the energy of the absorption band in the visible region is an empirical measure of the magnitude of the Ni–N in-plane interactions.[5] However, the $\nu(d\text{–}d)$ values do not follow the $\Delta H^\ominus$ values; in particular, the formation of $[\text{NiL}^5]^{2+}$ is less exothermic than that of $[\text{NiL}^4]^{2+}$, but the $[\text{NiL}^5]^{2+}$ complex exhibits a considerably higher-energy absorption band. It is probable that the low-spin nickel(II) ion has a 10% smaller radius than the high-spin cation; the 14-membered macrocycle must therefore contract which may involve serious configurational constraints resulting in the observed decrease in its internal energy. This unfavourable energy contribution probably varies according to the structure of the macrocycle and could be especially high for the ligand forming the seven-membered chelate ring. In the $[NiL^5]^{2+}$ complex it is possible that the donor atoms are in positions favouring the formation of strong bonds, but this situation has already required an endothermic rearrangement.

[1/470 *Received, 23rd March,* 1981]

REFERENCES

[1] L. Y. Martin, L. J. Dehayes, L. J. Zompa, and D. H. Busch, *J. Am. Chem. Soc.*, 1974, **96**, 4046.

[2] L. Fabbrizzi, *J. Chem. Soc., Dalton Trans.*, 1979, 1857.

[3] F. P. Hinz and D. W. Margerum, *Inorg. Chem.*, 1974, **13**, 2941; M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 1976, 116; L. Fabbrizzi, M. Micheloni, and P. Paoletti, *ibid.*, 1979, 1581.

[4] W. Steinmann and T. Kaden, *Helv. Chim. Acta*, 1975, **58**, 1358.

[5] F. V. Lovecchio, E. S. Gore, and D. H. Busch, *J. Am. Chem. Soc.*, 1974, **96**, 3109.

[6] L. Fabbrizzi, M. Micheloni, and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 1980, 134.

[7] G. Schwarzenbach, *Helv. Chim. Acta*, 1952, **35**, 2344.

[8] G. Schwarzenbach, Proceedings of the Summer School on Stability Constants, Bivigliano, Florence, Edizioni Scuola Universitaria, Florence, 1974, p. 151.

[9] W. L. Smith, J. D. Ekstrand, and K. N. Raymond, *J. Am. Chem. Soc.*, 1978, **100**, 3539.

[10] M. Micheloni, A. Sabatini, and A. Vacca, *Inorg. Chim. Acta*, 1977, **25**, 41.

[11] A. Sabatini, A. Vacca, and P. Gans, *Talanta*, 1974, **21**, 53.

[12] A. Sabatini and A. Vacca, *Coord. Chem. Rev.*, 1975, **16**, 161.

[13] C. Bianchini, L. Fabbrizzi, and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 1975, 1036.

[14] L. Fabbrizzi, M. Micheloni, and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 1979, 1581.

[15] L. Fabbrizzi, P. Paoletti, and R. M. Clay, *Inorg. Chem.*, 1978, **17**, 1042.

[16] M. Micheloni, A. Sabatini, and P. Paoletti, *J. Chem. Soc., Perkin Trans. 2*, 1978, 828.

[17] R. M. Smith and A. E. Martell, ' Critical Stability Constants,' Plenum Press, New York, 1975, vol. 2.

[18] A. Anichini, L. Fabbrizzi, P. Paoletti, and R. M. Clay, *J. Chem. Soc., Dalton Trans.*, 1978, 577.

[19] P. Paoletti, *Adv. Mol. Relaxation Processes*, 1980, **18**, 73.

[20] L. Y. Martin, C. R. Sperati, and D. H. Busch, *J. Am. Chem. Soc.*, 1977, **99**, 2968.

[21] L. Fabbrizzi, M. Micheloni, and P. Paoletti, *Inorg. Chem.*, 1980, **19**, 535.

[22] L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Chem. Soc.*, 1961, 1013.

[23] E. Gallori, E. Martini, M. Micheloni, and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 1980, 1722.

[24] M. Kodama and E. Kimura, *J. Chem. Soc., Chem. Commun.*, 1975, 891.