# Co-ordination Tendency of [3*k*]aneN$_k$ Polyazacycloalkanes. Thermodynamic Study of Solution Equilibria†

**Andrea Bencini,**[a] **Antonio Bianchi,***[,a] **Mauro Micheloni,***[,a] **Piero Paoletti,***[,a]
**Enrique Garcia-España***[,b] **and Miguel Angel Niño**[a]
[a] *Department of Chemistry, University of Florence, Via Maragliano 75/77, 50144-Florence, Italy*
[b] *Department of Inorganic Chemistry, University of Valencia, C/Dr. Moliner 50, 46100-Burjassot (Valencia), Spain*

---

Equilibria between polyazacycloalkanes of the series [3*k*]aneN$_k$ ($k$ = 3–11) and the bivalent metal ions of Mn through Zn have been studied. The stability constants (log *K*) for the complexes of $Mn^{2+}$, $Cu^{2+}$ and $Fe^{2+}$ with 1,4,7,10,13,16-hexaazacyclooctadecane ($L^4$), 1,4,7,10,13,16,19-heptaazacyclohenicosane ($L^5$) and 1,4,7,10,13,16,19,22-octaazacyclotetracosane ($L^6$) have been determined potentiometrically in 0.15 mol dm$^{-3}$ $NaClO_4$ at 25 °C: $[MnL^4]^{2+}$, 10.50; $[MnL^6]^{2+}$, 6.27; $[CuL^4]^{2+}$, 24.40; $[CuL^5]^{2+}$, 19.48; $[Cu_2L^5]^{4+}$, 30.49; $[Cu_2L^6]^{4+}$, 35.25; and $[FeL^5]^{2+}$, 12.09. The enthalpy changes ($-\Delta H^\circ$/kcal mol$^{-1}$) for the formation of $[CuL^4]^{2+}$ (23.9), $[CuL^5]^{2+}$ (19.7) and $[NiL^5]^{2+}$ (11.7) have been measured by means of microcalorimetric techniques. The results are discussed in terms of the increasing number of donor atoms and size of the macrocycles. As the size increases the co-ordination features of the metal complexes largely depend on the metal ion.

---

In the last few years some attention has been devoted to the co-ordination chemistry of large polyazacycloalkanes of the series [3*k*]aneN$_k$. This series, which up to date includes ligands containing from 3 to 12 nitrogen-donor atoms, has provided a wide variety of metal complexes.[1–12] The smallest terms of this series are rather rigid ligands, which impose upon the co-ordinated metal ion a preformed arrangement of binding sites.[13–15] On the other hand, as the size of these macrocycles increases, also their flexibility increases and the co-ordination features of their metal complexes largely depend on the metal ion.[1–12] The molecular structures of some complexes formed by the heptadentate macrocycle [21]aneN$_7$ ($L^5$) clearly support these considerations.[10–12] In $[NiL^5][ClO_4]_2$ the $Ni^{2+}$ ion binds six donor atoms of $L^5$, leaving an unco-ordinated nitrogen in a eight-membered chelate ring,[10] while in the isomorphic complex $[MnL^5][ClO_4]_2$ the $Mn^{2+}$ uses all seven nitrogen atoms of $L^5$ to achieve seven-co-ordination.[11] Furthermore, three $Pd^{2+}$ ions, in the presence of $Cl^-$ ions, bind one $L^5$ molecule forming a surprising complex $[Pd_3(L^5 - H)Cl_3][ClO_4]_2 \cdot H_2O$ in which the metal ions have induced deprotonation of an amino group of the ligand, giving rise to a charged donor atom which bridges two $Pd^{2+}$ ions.[12]

In this paper we present further results concerning the equilibria of $L^5$ and the two ligands [18]aneN$_6$ ($L^4$) and [24]aneN$_8$ ($L^6$) with the bivalent metal ions of the second half of the first transition row and analyse how the differences in size and in the number of nitrogen donors affect their chemical behaviour.

## Experimental

*Materials.*—Ligand $L^4$ was purchased from Fluka and purified as $L^4 \cdot 6HCl$. The other polyazacycloalkanes and their hydrochloride salts employed were obtained following previously reported procedures.[1–5] Satisfactory elemental analyses were obtained for all the compounds.

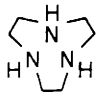
*Electromotive Force Measurements.*—The potentiometric titrations were carried out in 0.15 mol dm$^{-3}$ $NaClO_4$ solution at 25 °C, by using equipment (potentiometer, cell, burette, stirrer, microcomputer, *etc.*) that has been fully described.[16] The reference electrode was Ag–AgCl in saturated KCl solution. The glass electrode (Orion model 91–01) was calibrated as a hydrogen-ion concentration probe by titration of well known amounts of HCl with $CO_2$-free NaOH solutions and determining the equivalence point by the Gran method,[17] which gives the standard potential of the cell, $E^\circ$, and the ionic product of water ($pK_w = 13.73 \pm 0.01$). The computer program SUPERQUAD[18] was used to calculate the stability constants. Solutions of oxidizable metal salts were prepared in $O_2$-free water and handled under argon. The iron(II) stock solution was maintained in the reduced form by bubbling hydrogen gas in the presence of a small quantity of black palladium as catalyst. The concentrations of metal-ion solutions were determined by standard methods. All solutions were deaerated by an argon flow prior and during the electromotive force measurements. The protonation constants of the ligands studied here, under the experimental conditions employed, had already been reported in the case of $L^5$ and $L^6$;[7] for $L^4$ they are $pK_1 = 10.15$, $pK_2 = 9.48$, $pK_3 = 8.89$, $pK_4 = 4.27$, $pK_5 = 2.21$, and $pK_6 = 1.0$.

*Microcalorimetry.*—The enthalpy changes for the reaction of $L^5$ with copper(II) and nickel(II) and of $L^4$ with copper(II) to produce the corresponding mononuclear complexes have been determined by means of fully automatized equipment including a Model 2277 Thermal Activity Monitor (Termometric AB) microcalorimeter. The system was programmed to follow calorimetric titrations. Solutions of the metal ions (0.01 mol dm$^{-3}$, addition volumes ranging from 20 to 50 μl) were added to solutions (2.5 cm$^3$) of the free ligand (0.002 mol dm$^{-3}$). Corrections for the heats of dilution of the reacting solutions were applied.

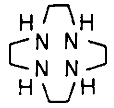
*Spectrophotometric Measurements.*—Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer equipped with 1 cm cells thermostatted at 25 °C.

---

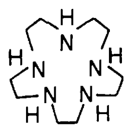
† *Non-SI unit employed:* cal = 4.184 J.



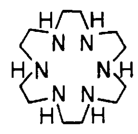
$L^1$



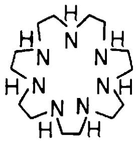
$L^2$



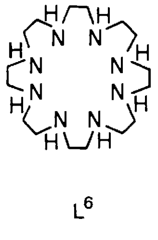
$L^3$



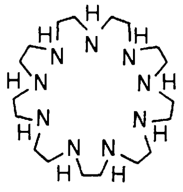
$L^4$



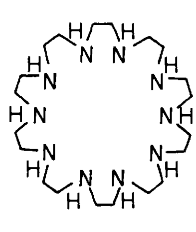
$L^5$



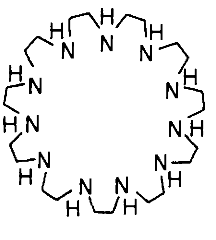
$L^6$



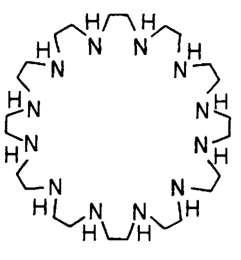
$L^7$



$L^8$



$L^9$



$L^{10}$

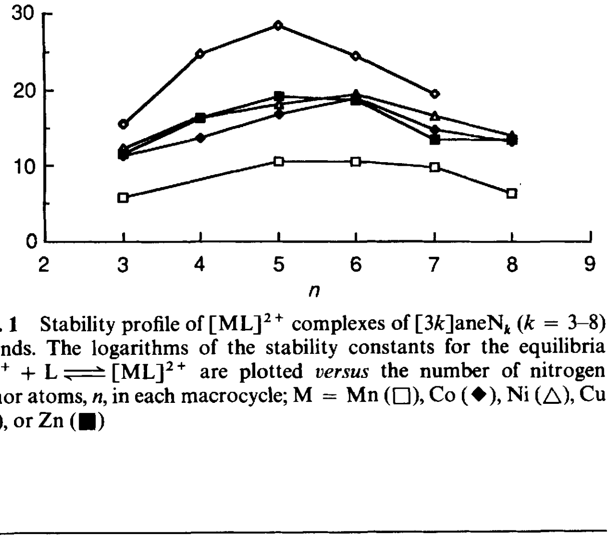


**Fig. 1** Stability profile of $[ML]^{2+}$ complexes of $[3k]aneN_k$ ($k$ = 3–8) ligands. The logarithms of the stability constants for the equilibria $M^{2+} + L \rightleftharpoons [ML]^{2+}$ are plotted *versus* the number of nitrogen donor atoms, $n$, in each macrocycle; M = Mn (□), Co (◆), Ni (△), Cu (◇), or Zn (■)

**Table 1** Logarithms of the formation constants of manganese(II) complexes[a] of macrocycles $[3k]aneN_k$ ($k$ = 6–8) in 0.15 mol dm$^{-3}$ $NaClO_4$ at 25 °C

| | log $K^b$ | | |
|---|---|---|---|
| | $[18]aneN_6$ | $[21]aneN_7$ | $[24]aneN_8$ |
| $Mn + L \rightleftharpoons [MnL]$ | 10.50(2) | 9.79(1) | 6.27(3) |
| $Mn + L + H \rightleftharpoons [Mn(HL)]$ | — | — | 14.51(4) |
| $MnL + H \rightleftharpoons [Mn(HL)]$ | — | — | 8.24 |
| $Mn + HL \rightleftharpoons [Mn(HL)]$ | — | — | 4.86 |

[a] Charges have been omitted for clarity. [b] Values in parentheses are standard deviations in the last significant figure.

## Results and Discussion

In Fig. 1 the logarithms of the equilibrium constants for the formation of $[ML]^{2+}$ complexes of $[3k]aneN_k$ ($k = 3-8$) ligands with the metal ions $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$ and $Zn^{2+}$ are plotted *versus* the number of nitrogen-donor atoms in each macrocycle. These plots have been constructed by means of the experimental results obtained in this work for $Mn^{2+}$ and $Cu^{2+}$, and reported in Tables 1 and 2, respectively, together with some of our previous results[7,9–11] and stability constants from different laboratories.[19–27] The equilibria between $Cu^{2+}$ and $L^4$, $L^5$ and $L^6$ had already been studied under experimental conditions different from those employed here.[1,2,25]

For all the metal ions considered there is a clear trend showing increasing stability of the mononuclear complexes from the smaller tridentate ligand $[9]aneN_3$ ($L^1$) to those of the pentadentate $[15]aneN_5$ ($L^3$), in the case of $Mn^{2+}$, $Cu^{2+}$ and $Zn^{2+}$, and to those of the hexadentate $L^4$ with $Co^{2+}$ and $Ni^{2+}$. Then, a general decrease is observed with larger macrocycles.

In the case of manganese(II) complexes this decrease is very small for $L^4$ and $L^5$, while it is markedly greater with the octadentate $L^6$. In a recent paper[11] we have reported the crystal and molecular structure of the complex $[MnL^5][ClO_4]_2$ in which $Mn^{2+}$ is seven-co-ordinated by $L^5$ which diposes its seven donor atoms at the vertices of an irregular polyhedron. However, as shown by the long Mn–N bond distances and by the distorted bond angles, this is achieved at the expense of severe intramolecular strain. In solution the absence of protonated complexes of $L^3$, $L^4$ and $L^5$ seems to indicate that all the nitrogen atoms of these ligands are involved in the co-ordination to $Mn^{2+}$, even though, as noted above, this does not involve an increase in stability. Also the thermodynamic parameters for the formation of $[MnL^5]^{2+}$ in solution (Table 3) are consistent with seven-co-ordination of the ligand. The entropy change, which is the main contribution to the stability

**Table 2** Logarithms of the formation constants of copper(II) complexes[a] of macrocycles [3*k*]aneN$_k$ ($k$ = 6–8) in 0.15 mol dm$^{-3}$ NaClO$_4$ at 25 °C

| | log $K$[b] | | |
|---|---|---|---|
| | [18]aneN$_6$ | [21]aneN$_7$ | [24]aneN$_8$ |
| $Cu + L \rightleftharpoons [CuL]$ | 24.40(2) | 19.48(2) | — |
| $Cu + L + H \rightleftharpoons [Cu(HL)]$ | 27.40(5) | 28.00(2) | — |
| $Cu + L + 2H \rightleftharpoons [Cu(H_2L)]$ | 30.88(4) | 32.88(2) | — |
| $2Cu + L \rightleftharpoons [Cu_2L]$ | — | 30.49(2) | 35.25(3) |
| $2Cu + L + H \rightleftharpoons [Cu_2(HL)]$ | — | — | 38.15(2) |
| $2Cu + L + H_2O \rightleftharpoons [Cu_2L(OH)] + H$ | — | 23.75(2) | 26.25(3) |
| $[CuL] + H \rightleftharpoons [Cu(HL)]$ | 3.00 | 8.52 | — |
| $[Cu(HL)] + H \rightleftharpoons [Cu(H_2L)]$ | 3.48 | 4.88 | — |
| $[Cu_2L] + OH \rightleftharpoons [Cu_2L(OH)]$ | — | 7.00 | 4.74 |
| $Cu + HL \rightleftharpoons [Cu(HL)]$ | 17.25 | 18.24 | — |
| $Cu + H_2L \rightleftharpoons [Cu(H_2L)]$ | 11.25 | 13.84 | — |
| $2Cu + HL \rightleftharpoons [Cu_2(HL)]$ | — | — | 28.50(2) |

[a] Charges have been omitted for clarity. [b] Values in parentheses are standard devations in the last significant figure.

**Table 3** Thermodynamic parameters[a] for the formation of some complexes of [3*k*]aneN$_k$ ($k$ = 5–7) polyazacycloalkanes at 25 °C in 0.15 mol dm$^{-3}$ NaClO$_4$ unless otherwise noted

| | | $-\Delta H°$ | $T\Delta S°$ |
|---|---|---|---|
| | log $K$ | kcal mol$^{-1}$ | |
| $Mn^{2+}$ + [21]aneN$_7$ | 9.79(1)[b] | 5.0(5)[b] | 8.2(5)[b] |
| $Ni^{2+}$ + [21]aneN$_7$ | 16.563(5)[c] | 11.7(1)[d] | 10.9(1)[d] |
| $Cu^{2+}$ + [21]aneN$_7$ | 19.48(2)[d] | 19.7(1)[d] | 6.9(1)[d] |
| $Cu^{2+}$ + [18]aneN$_6$ | 24.40(2)[d] | 23.9(1)[d] | 9.4(1)[d] |
| $Cu^{2+}$ + [15]aneN$_5$ | 28.3(2)[e] | 32.9(3)[e] | 5.7(5)[e] |

[a] Values in parentheses are standard deviations in the last significant figure. [b] From ref. 11. [c] From ref. 10. [d] This work. [e] From ref. 26, 0.2 mol dm$^{-3}$ NaClO$_4$ at 25 °C.

of this complex, can be attributed to the large desolvation effect of both ligand and metal ion occurring upon full co-ordination of the heptadentate ligand. On the other hand the low enthalpic contribution can be ascribed to a reduced overall interaction between $Mn^{2+}$ and $L^5$ due to the strained disposition of the ligand around the metal ion. Extending the above considerations to the complexes of $L^3$ and $L^4$ we can justify the small decrease in the stability with the large $Mn^{2+}$ ion by assuming that some intramolecular strain accumulates with the increasing size of the macrocycles. A similar effect was also observed with the cadmium complexes of $L^3$ and $L^4$.[8] For the next complex of the series, $[MnL^6]^{2+}$, in which at least one donor atom remains unco-ordinated, the stability constant decreases markedly owing to the formation of a large chelate ring. The monoprotonated species $[Mn(HL^6)]^{3+}$ is also formed.

For the other metal ions here considered a clear maximum of stability is observed for the complex of a certain ligand of the series. Thus $Co^{2+}$ and $Ni^{2+}$ form complexes of highest stability with the hexadentate ligand $L^4$, while $Cu^{2+}$ and $Zn^{2+}$ reach the maximum with the pentadentate $L^3$. It was assumed[9,10,22,28,29] that all the nitrogen-donor atoms of $L^4$ are involved in the co-ordination to $Co^{2+}$ and $Ni^{2+}$, while just one nitrogen of this ligand is excluded from the co-ordination sphere of $Zn^{2+}$in its $[ZnL^4]^{2+}$ complex.[7] As far as the co-ordination of $Cu^{2+}$ is concerned, Kodama *et al.*[22] determined the equilibrium constants for the addition of $Cu^{2+}$ to $[HL^4]^+$ (log $K$ = 21.6) and to $[H_2L^4]^{2+}$ (log $K$ = 16.1), but failed to determine the formation constant of $[CuL^4]^{2+}$. This was attributed to an exceedingly large value of the last stability constant which caused failure of the potentiometric method. Otherwise, treatment of data from potentiometric titrations performed in our laboratories, by the computer program SUPERQUAD,[18] led to the determination of the stability constants of the species $[CuL^4]^{2+}$, $[Cu(HL^4)]^{3+}$ and $[Cu(H_2L^4)]^{4+}$ (Table 2). While the chemical model supposed by Kodama *et al.*[22] coincides with ours, the values of the equilibrium constants reported by these authors are quite higher than those we have obtained. These large differences cannot be justified on the basis of the slightly different experimental conditions employed (0.2 mol dm$^{-3}$ NaClO$_4$ and 25 °C by Kodama *et al.*[22]; 0.15 mol dm$^{-3}$ NaClO$_4$ and 25 °C by us), but they can be attributed to the treatment of the experimental data performed by Kodama *et al.*, which neglected the unprotonated species. The enthalpy change (Table 3) for the formation of $[CuL^4]^{2+}$, as well as for $[CuL^5]^{2+}$, has been measured by means of a microcalorimetric technique. The stability of both complexes is mainly enthalpic in nature, the difference between the stability of these two species being due to both enthalpic (4.2 kcal mol$^{-1}$) and entropic (2.5 cal K$^{-1}$ mol$^{-1}$) contributions. The thermodynamic parameters for the reaction of $Cu^{2+}$ with the pentadentate ligand $L^3$ (log $K$ = 28.3, $-\Delta H°$ = 32.9 kcal mol$^{-1}$, $T\Delta S°$ = 5.7 kcal mol$^{-1}$) were estimated by determining polarographically the variation of the equilibrium constant with temperature. The decrease in stability observed between $[CuL^3]^{2+}$ and $[CuL^4]^{2+}$ complexes seems to be due only to the enthalpy changes (Table 3). This trend could be explained if a maximum of five nitrogen-donor atoms of these ligands is involved in the co-ordination to $Cu^{2+}$. The decrease of the overall interaction between the ligand and the metal ion observed from $L^3$ to $L^5$ could be ascribed to the formation of large chelate rings. On the other hand, if the analysis of the protonation equilibria involving these copper(II) complexes is used to distinguish whether unco-ordinated donor atoms are present or not, we get contrasting conclusions. The stepwise protonation constants of $[CuL^4]^{2+}$ are very low (Table 2), even lower than that reported[26] for $[CuL^3]^{2+}$ (log $K$ = 4.4), in which all five donor atoms are co-ordinated. Furthermore the first protonation constant of $[CuL^5]^{2+}$, in which at least one nitrogen is not co-ordinated, is high and similar to the third stepwise protonation constant of the free ligand, while the second one is low again. The last considerations point to the involvement of six nitrogen-donor atoms of both $L^4$ and $L^5$ in the co-ordination to $Cu^{2+}$. Unfortunately structural information on these complexes is not available and also their electronic spectra cannot aid in removing these doubts. The complexes $[CuL^3]^{2+}$ and $[CuL^4]^{2+}$ exhibit in aqueous solution a single d–d band at 17 095 (ε 200)[26] and 15 200 cm$^{-1}$ (ε 85 dm$^3$ mol$^{-1}$ cm$^{-1}$), respectively, while $[CuL^5]^{2+}$ has a broad band at 15 720 cm$^{-1}$ (ε 193 dm$^3$ mol$^{-1}$ cm$^{-1}$) with a shoulder at lower energy. These spectral data can, at most, account for the overall strong interaction of $L^3$ with respect to $L^4$ and $L^5$.

The ligand $L^5$ is the smallest of the series able to form binuclear copper(II) complexes, while the octadentate ligand $L^6$ is required to form binuclear species of $Ni^{2+}$ (ref. 10) and $Zn^{2+}$,[7] and $L^7$ for $Co^{2+}$.[9] Apart from these ligands which can produce with the indicated metal ions both mono- and bi-nuclear

**Table 4** Logarithms of the formation constants of iron(II) complexes[a] of [21]aneN$_7$ in 0.15 mol dm$^{-3}$ NaClO$_4$ at 25 °C

| | log $K^b$ |
|---|---|
| Fe + L $\rightleftharpoons$ [FeL] | 12.09(1) |
| Fe + L + H $\rightleftharpoons$ [Fe(HL)] | 17.73(5) |
| [FeL] + H $\rightleftharpoons$ [Fe(HL)] | 5.64 |
| Fe + HL $\rightleftharpoons$ [Fe(HL)] | 7.97 |

[a] Charges have been omitted for clarity. [b] Values in parentheses are standard deviations in the last significant figure.

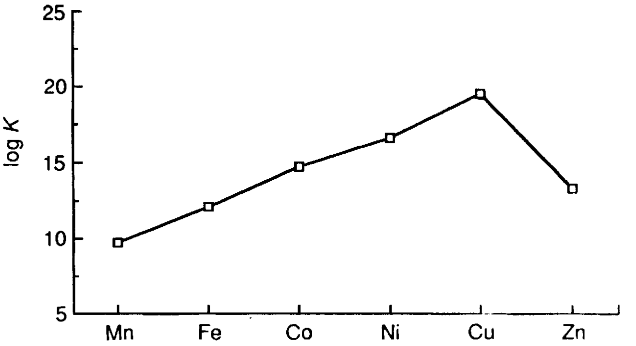


**Fig. 2** Stability order for the mononuclear complexes of [21]aneN$_7$ with the bivalent metal ions of Mn through Zn

complexes, larger [3$k$]aneN$_k$ macrocycles form only binuclear species.[1–10]

In order to complete the study of the co-ordinating ability of L$^5$ towards metal ions of the second half of the first transition row, equilibria with Fe$^{2+}$ have also been considered. In Table 4 the formation constants for the observed species [FeL$^5$]$^{2+}$ and [Fe(HL$^5$)]$^{3+}$ are given. The relatively high value for the protonation of [FeL$^5$]$^{2+}$ to produce [Fe(HL$^5$)]$^{3+}$, and the absence of a second protonation step, seems indicative for six-co-ordination of L$^5$ to Fe$^{2+}$. As shown in Fig. 2, the stability of the mononuclear complexes of L$^5$ increases from Mn$^{2+}$ to Cu$^{2+}$ and then decreases with Zn$^{2+}$, which forms a complex whose stability is intermediate between those of the analogous species with Fe$^{2+}$ (lower value) and Co$^{2+}$ (higher value). This order of stability is generally observed when ligands containing nitrogen-donor atoms are considered for co-ordination to the bivalent metal ions of Mn through Zn and analogous complexes are formed.[30] It has also been observed that this order is followed by the enthalpic contributions to the stability of the relevant complexes. In other words it means that, generally, the entropic contribution to the formation of similar complexes is almost the same, if similar co-ordination features are present. In the present case the entropic contribution to the formation of the complexes of L$^5$ with Mn$^{2+}$, Ni$^{2+}$ and Cu$^{2+}$ (Table 4) is largely variable with respect to the enthalpic one. In fact the thermodynamic parameters $T\Delta S°$ prevail over the enthalpy change in determining the stability of [MnL$^5$]$^{2+}$, while in the case of [NiL$^5$]$^{2+}$ similar enthalpic and entropic contributions have been observed and for [CuL$^5$]$^{2+}$ $\Delta H°$ is largely of main importance. However the stability respects the above order even if these metal ions (Mn$^{2+}$, Ni$^{2+}$, Cu$^{2+}$) form, with L$^5$, complexes in which the co-ordination spheres around the metal ions are quite different.

Indeed the main co-ordination feature of this heptadentate ligand, in spite of its cyclic topology, is its tendency to adapt to the stereochemical requirements of the metal ions. From this point of view L$^5$ resembles much more the largest ligands of the series [3$k$]aneN$_k$ than the smallest ones, which present a rigid assembly of binding sites. The last feature, which is particularly marked in tri-, tetra- and penta-azamacrocycles, is closely related to the so-called 'macrocyclic effect'. The ligational properties presented by L$^5$, as well as by L$^6$–L$^{10}$, bring into question the existence of a similar effect in large polyazacycloalkanes. Unfortunately further considerations on this point cannot be drawn as appropriate open-chain counterparts of large [3$k$]aneN$_k$ macrocyclic ligands are not known.

## References

1 A. Bianchi, S. Mangani, M. Micheloni, V. Nanini, P. Orioli, P. Paoletti and B. Seghi, *Inorg. Chem.*, 1985, **24**, 1182.
2 M. Micheloni, P. Paoletti and A. Bianchi, *Inorg. Chem.*, 1985, **24**, 3702.
3 A. Bencini, A. Bianchi, E. Garcia-España, M. Giusti, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1987, **26**, 681.
4 A. Bencini, A. Bianchi, E. Garcia-España, M. Giusti, S. Mangani, M. Micheloni, P. Orioli and P. Paoletti, *Inorg. Chem.*, 1987, **26**, 1243.
5 A. Bencini, A. Bianchi, E. Garcia-España, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1988, **27**, 176.
6 A. Bencini, A. Bianchi, E. Garcia-España, S. Mangani, M. Micheloni, P. Orioli and P. Paoletti, *Inorg. Chem.*, 1988, **27**, 1104.
7 A. Bencini, A. Bianchi, P. Dapporto, E. Garcia-España, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1989, **28**, 1188.
8 A. Bencini, A. Bianchi, M. Castello, M. Di Vaira, J. Faus, E. Garcia-España, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1989, **28**, 347.
9 A. Bencini, A. Bianchi, E. Garcia-España, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1989, **28**, 2480.
10 A. Bencini, A. Bianchi, M. Castello, P. Dapporto, J. Faus, E. Garcia-España, M. Micheloni, P. Paoletti and P. Paoli, *Inorg. Chem.*, 1989, **28**, 3175.
11 A. Bencini, A. Bianchi, P. Dapporto, E. Garcia-España, V. Marcelino, M. Micheloni, P. Paoletti and P. Paoli, *Inorg. Chem.*, 1990, **29**, 1716.
12 A. Bencini, A. Bianchi, P. Dapporto, E. Garcia-España, M. Micheloni, P. Paoletti and P. Paoli, *J. Chem. Soc., Chem. Commun.*, 1990, 1382.
13 P. Chaudhuri and K. Wieghardt, *Prog. Inorg. Chem.*, 1987, **35**, 329.
14 R. Bhula, P. Osvath and D. C. Weatheburn, *Coord. Chem. Rev.*, 1988, **91**, 89.
15 *Coordination Chemistry of Macrocyclic Compounds*, ed. G. A. Melson, Plenum, New York, 1979; *The Chemistry of Macrocyclic Ligand Complexes*, ed. L. F. Lindoy, Cambridge University Press, Cambridge, 1989.
16 A. Bianchi, L. Bologni, P. Dapporto, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1984, **23**, 1201.
17 G. Gran, *Analyst* (*London*), 1952, **77**, 661; F. J. Rossotti and H. Rossotti, *J. Chem. Educ.*, 1965, **42**, 375.
18 P. Gans, A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1985, 1195.
19 M. R. Squillante, Ph.D. Thesis, Tufts University, MA, 1980.
20 J. E. Newton and S. C. Jackels, *J. Coord. Chem.*, 1988, **19**, 265.
21 T. Arishima, K. Hamada and S. Takamoto, *Nippon Kagaku Kaishi*, 1973, 1119; M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 1980, 327; M. Kodama and E. Kimura, *Inorg. Chem.*, 1980, **19**, 1871.
22 M. Kodama, E. Kimura and S. Yamaguchi, *J. Chem. Soc., Dalton Trans.*, 1980, 2536.
23 R. M. Smith and A. E. Martell, *Critical Stability Constants*, Plenum, New York, 1975, vol. 5.
24 R. Yang and L. J. Zompa, *Inorg. Chem.*, 1976, **15**, 1499.
25 M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 1976, 116.
26 M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 1978, 104.
27 M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 1977, 2269.
28 R. W. Hay, B. Jaragh, S. F. Lincoln and G. H. Searle, *Inorg. Nucl. Chem. Lett.*, 1978, **14**, 435.
29 A. Bencini, L. Fabbrizzi and A. Poggi, *Inorg. Chem.*, 1981, **20**, 2544.
30 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn., Wiley, New York, 1988.

*Received* 13*th August* 1990; *Paper* 0/03698F