Oxatriaza Macrocyclic Ligands: Studies of Protonation and Metal Complexation

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Some 12- to 14-membered oxatriaza macrocyclic ligands and their methylated derivatives have been synthesised and their protonation studied by potentiometric and ^{1}H NMR techniques. The stability constants of the complexes formed by these ligands with several first-series transition-metal ions, Zn^{II}, Cd^{II} and Pb^{II}, were determined by automated potentiometry or by an 'out-of-cell' technique in the cases of slow equilibration of the reactions. All the ligands have two very basic nitrogen atoms. The third nitrogen atom is protonated at lower pH, the lower the value the shorter the distance between two protonated nitrogen atoms. Stability constants for complexes of the oxatriaza ligands are lower than those for tetraaza ligands of the same size, the differences being more pronounced for the 14-membered ligands. Larger ions, such as Cd^{II} and Pb^{II}, seem to prefer smaller rings, contrary to what might be expected if the metals were inserted in the ring. Curiously, the behaviour of the copper(II) and especially nickel(II) complexes is opposite in the two series. Stability constants of complexes of the methylated amines are lower than those of the complexes with the parent amines and the same metal ions, but the differences are smaller for the oxatriaza than for the tetraaza series. This suggests that in the former series both the amines and their methylated derivatives adopt similar conformations in their complexes.

A considerable amount of work has been done in the past two decades on the synthesis and characterization of metal complexes as well as solution studies of saturated macrocyclic amines, especially tetraamines, but also tri-, penta-amines and others.[1–4] Some thermodynamic properties of their metal complexes were unexpected when compared with those of similar linear amines, and the concept of the macrocyclic effect[5] was introduced to explain this behaviour. This matter has been reviewed recently.[6,7] The selectivity shown by some ligands, the very high values of some stability constants [for instance, 26.5 for the formation constant (log K) of the copper(II) complex with cyclam[8] or 25.5 for the mercury(II) complex of cyclen[9]] as well as the remarkable inertness of some of these metal complexes, even in very acidic media, are of great interest.

Nevertheless, a restrictive property of many of these ligands for practical applications is the slow kinetics of formation of their complexes. Illustrative of this is the time required for equilibration of Ni^{II} with cyclam (2 years),[10] the 6 months necessary for its reaction with cyclen and [13]aneN_4[11] or the 3–4 months necessary for the equilibration of the series of cyclic triamines ([9]–[12]aneN_3) with Cu^{II}, Ni^{II} and Zn^{II}.[12] To overcome some of these difficulties a large number of N-functionalized derivatives has been synthesised and studied. The majority has faster kinetics,[13] but also very different properties, especially in the case of substituents with ionizable groups or with additional donor atoms.[2–4,14]

Changes in the ring donors, *e.g.* by replacing nitrogen by oxygen or sulphur atoms, may also affect the kinetics, but the corresponding ligands have received less attention. Regardless of whether the metal complexes of this type of macrocycle are usually less stable than those of the full nitrogen derivatives, they have faster formation reactions[15–19] which may be important in many analytical, medical or other applications.

In the present work we decided to undertake the synthesis and a study of the protonation and of the metal complexation of some oxatriaza macrocycles, with 12- to 14-membered rings (L^1–L^5). Some tetraamines will also be referred to (L^6–L^{11}). Although some stability constants for the complexes of 12- and 13-membered rings have already been determined,[16,20] we have redetermined them to obtain a coherent series, under the same experimental conditions.

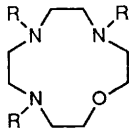
Experimental

Reagents.—All the ligands were synthesised and purified in our laboratories. 3,3′-Iminobis(propylamine) (98%) and *N*-(2-aminoethyl)propane-1,3-diamine (97%) were obtained from Aldrich. The chemicals used were of reagent grade and organic solvents were purified by standard methods.[21]

Synthesis and Characterization of the Ligands.—The cyclic amines L^1 and L^2 were synthesised following previously described procedures,[18,22] L^3 and L^4 by Richman–Atkins procedures.[23]

In a typical experiment, L^4 was prepared by condensation of the disodium salt of 3,3′-iminobis(propylamine) tritosylate (tosyl = toluene-*p*-sulphonyl) (0.05 mol) in dry dimethylformamide (dmf) (250 cm^3) and ditosylated diethylene glycol (0.05 mol) in dmf (250 cm^3) at 110–120 °C for 6 h. The disodium salt was obtained immediately before the reaction by addition of NaH (0.125 mol) in dry dmf (62 cm^3) to a solution of the tritosylated amine (0.05 mol), under nitrogen. The solution of the ditosylated diethylene glycol ($HOCH_2CH_2OCH_2CH_2OH$) was added slowly, dropwise, during a period of 3 h. The tritosylated cyclic amine obtained, after recrystallization from acetonitrile–methanol (yield: 50%), was refluxed with a mixture of glacial acetic acid, 48% hydrobromic acid (9:16 v/v) and phenol (5 g) for 5 h. Then the solution was concentrated and the required product, L^4, was precipitated with a mixture of methanol–diethyl ether, filtered off and washed with cold acetone. The pure product was obtained in 82% yield, after recrystallization from water–ethanol. M.p. 289–290 °C (decomp.). ^{1}H NMR (D_2O, pD 6.36): δ 1.938 (4 H, qtp), 2.875 (4 H, t), 3.286 (8 H, m) and 3.847 (4 H, t) (Found: C, 27.00; H, 5.90; N, 9.35. Calc. for $C_{10}H_{26}Br_3N_3O$: C, 27.05; H, 5.90; N, 9.45%).

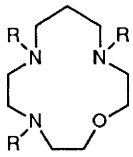
Ligand L^3 was prepared similarly by condensation of the disodium salt of *N*-(2-aminoethyl)propane-1,3-diamine tri-



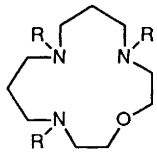
R

L^1 H 1–oxa–4, 7, 10– triazacyclododecane ([12]aneN$_3$O)

L^2 CH_3 4, 7, 10– trimethyl– 1– oxa– 4, 7, 10– triazacyclododecane (Me_3[12]aneN$_3$O)

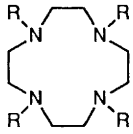


L^3 H 1–oxa–4, 7, 11– triazacyclotridecane ([13]aneN$_3$O)



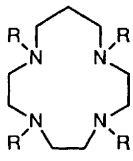
L^4 H 1–oxa–4, 8, 12– triazacyclotetradecane ([14]aneN$_3$O)

L^5 CH_3 4, 8, 12– trimethyl– 1– oxa– 4, 8, 12– triazacyclotetradecane (Me_3[14]aneN$_3$O)

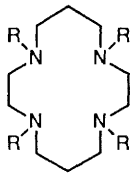


L^6 H 1, 4, 7, 10– tetraazacyclododecane (cyclen, [12]aneN$_4$)

L^7 CH_3 1, 4, 7, 10– tetramethyl– 1, 4, 7, 10– tetraazacyclododecane (Me_4[12]aneN$_4$)

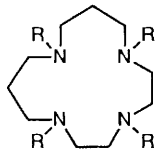


L^8 H 1, 4, 7, 10– tetraazacyclotridecane ([13]aneN$_4$)



L^9 H 1, 4, 8, 11– tetraazacyclotetradecane (cyclam, [14]aneN$_4$)

L^{10} CH_3 1, 4, 8, 11– tetramethyl– 1, 4, 8, 11– tetraazacyclotetradecane (tmc, Me_4[14]aneN$_4$)



L^{11} H 1, 4, 7, 11– tetraazacyclotetradecane (isocyclam)

tosylate (0.05 mol) and ditosylated diethylene glycol (0.05 mol) at 110–120 °C in dry dmf (550 cm^3) for 6 h. The toluene-*p*-sulphonyl groups were removed by reductive cleavage with a mixture of glacial acetic acid, 48% hydrobromic acid and phenol for 5 h (yield: 64%). M.p. 270–275 °C (decomp.). ^{1}H NMR (D_2O): δ 2.216 (2 H, qtp), 3.271–3.569 (12 H, m) and 3.916 (4 H, t) (Found: C, 24.25; H, 5.55; N, 9.65. Calc. for $C_9H_{24}Br_3N_3O{\cdot}H_2O$: C, 24.15; H, 5.85; N, 9.40%).

Ligand L^5 was obtained by refluxing $L^4{\cdot}3HBr$ (0.0225 mol) with formic acid (4.8 cm^3), formaldehyde (40%, 4.0 cm^3) and water (0.5 cm^3) for 24 h.[24] After addition of NaOH, the basic solution was extracted with chloroform and the pure methylated amine obtained by vacuum distillation as an oil, in 62% yield. ^{1}H NMR (D_2O, pD 6.12): δ 2.163 (4 H, qtp), 2.729 (3 H, s), 2.944 (6 H, s), 3.139 (4 H, t), 3.452 (8 H, m) and 3.925 (4 H, t). The molecular weight was confirmed by potentiometric titration.

Other Reagents and Standard Solutions.—Metal nitrates of analytical grade were used and solutions prepared in demineralized water (obtained from a Millipore/Milli-Q system) and standardized by ethylenediaminetetraacetate titrations. Carbonate-free solutions of the titrant, KOH, were prepared by treating freshly prepared silver oxide with KI solution, under nitrogen as described.[18] The solutions were standardized by titration with hydrochloric acid and discarded when the concentration of carbonate reached 0.5% of the hydroxide concentration. Solutions of the ligands for NMR measurements (≈0.01 mol dm^{-3}) were made up in D_2O (99.8 atom% deuterium, Merck) and the pD was adjusted by adding DCl or CO_2-free KOD. In all cases sodium 3-(trimethylsilyl)-propane-1-sulphonate was used as internal reference.

Equipment.—For the potentiometric titrations an Orion 720 instrument was used together with a 91–01 glass electrode and a 90–05 Ag–AgCl reference electrode, with a Wilhelm-type salt bridge containing 0.10 mol dm^{-3} KNO_3 solution. Titrations were carried out in a thermostatted cell kept at 25.0 ± 0.1 °C by circulating water through the jacketed titration cell from a Grant W6 thermostat, and the ionic strength of the solutions was kept at 0.10 mol dm^{-3} with KNO_3, as described previously.[18]

The adjustment in pD for the NMR measurements was made using a Crison Microph 2002 instrument fitted with a combined Ingold 405 M3 microelectrode. The electrode was calibrated with buffer aqueous solutions and the final pD calculated from pD = pH + 0.40.[25]

Proton NMR spectra were recorded at 100 MHz and probe temperature in a JEOL JNM 100 PTF spectrometer coupled to a JEOL 980A computer.

Formation Constant Studies.—It was found that equilibration of the amines L^1 and L^3 with all the metal ions studied in the present work was fairly rapid, with the exception of Ni^{II} which needed about 2 weeks. However, the cobalt(II) complex of L^2 needed 1 d; the copper, cobalt and nickel hydroxo complexes formed with this ligand took longer (about 1 month), and the cobalt complex gave a slight precipitate in the region of formation of such complexes. In contrast, all the metal complex-formation reactions of the 14-membered ligands were slow, with the exception of those of Pb^{II} and Cd^{II} for both L^4 and L^5 and also of Zn^{II} with L^5 which equilibrates immediately; the reactions of Zn^{II}, Cu^{II} and Ni^{II} with L^4 needed about 1 week to equilibrate and its cobalt(II) hydroxo complexes about 2 months (a precipitate was also noticed in this case); with L^5 the copper(II) complex took about 1 week and those of Ni^{II} and Co^{II} needed about 2 months.

In the cases of slow equilibration it was not possible to perform automated titrations and an 'out-of-cell' titration was needed.[10–12] In this procedure, sets of solutions were prepared in individual vials (adding equimolar amounts of metal and ligand, sufficient potassium nitrate for a 0.1 mol dm^{-3} solution, water to the appropriate volume and an amount of base required to achieve a specific pH value), each solution corresponding to a single point in a normal automated titration.

Table 1 Protonation constants (K_i^H) of some oxatriaza macrocyclic compounds at 25.0 ± 0.1 °C and I = 0.10 mol dm^{-3} (KNO_3)

	L^1		L^2	L^3		L^4	L^5
log K_i^H [a]							
log K_1	10.109(3)	10.18[b]	10.973(4)	10.42(3)	10.34[b]	10.097(6)	10.098(3)
log K_2	8.525(4)	8.56[b]	8.286(9)	8.59(4)	8.64[b]	8.673(7)	8.121(4)
log K_3	1.56(4)	1.43[b]	1.67(3)	2.78(4)	2.79[b]	4.65(3)	5.370(5)

[a] log K_i^H = $[H_iL]/[H_{i-1}L][H^+]$, [b] 25 °C, I = 0.1 mol dm^{-3} ($NaNO_3$), ref. 20.

Table 2 Stability constants ($\beta_{M_mL_lH_h}$)[a] of metal complexes of some oxatriaza macrocyclic compounds at 25.0 ± 0.1 °C and I = 0.10 mol dm^{-3} (KNO_3)

Metal ion	Species	L^1		L^2	L^3		L^4	L^5
Mn^{2+}	ML	5.85(1)		—	3.96(9)		—	—
	MLH_{-1}	−4.60(4)		—	−5.93(6)		—	—
	ML_2	9.14(8)		—	—		—	—
Co^{2+}	ML	10.541(7)		10.30(3)	9.29(1)		8.87(4)	5.8(1)
	MHL	—		—	—		14.6(1)	—
	MLH_{-1}	2.84(8)		2.69(6)	−0.53(5)		—	—
	MLH_{-2}	—		—	—		−6.43(5)	−9.67(7)
Ni^{2+}	ML	12.36(3)	12.15[b]	11.42(4)	11.37(6)	11.90[b]	9.7(1)	6.41(7)
	MHL	—		—	—		16.67(7)	—
	MLH_{-1}	6.05(6)		—	—		—	—
	MLH_{-2}	—		−3.00(6)	−3.89(9)		−5.9(1)	−8.52(6)
Cu^{2+}	ML	15.63(1)	15.85[b]	14.98(4)	16.61(4)	16.92[c]	15.4(2)	13.60(3)
	MHL	—		—	19.6(1)		21.4(1)	—
	MLH_{-1}	6.90(4)		7.6(1)	6.12(9)		—	—
	MLH_{-2}	—		—	−4.62(7)		0.2(2)	−1.62(6)
Zn^{2+}	ML	10.43(7)	10.53[b]	10.006(8)	9.80(1)	9.94[c]	8.9(2)	6.36(2)
	MHL	—		—	—		16.0(1)	—
	MLH_{-1}	2.75(2)		2.54(3)	2.19(4)		—	−1.58(2)
	MLH_{-2}	—		—	−8.6(1)		−6.5(1)	−12.49(9)
Cd^{2+}	ML	10.69(1)	10.78[b]	10.23(1)	9.32(3)	9.09[b]	7.13(1)	4.7(3)
	MLH_{-1}	0.3(2)		0.12(3)	−0.29(9)		−2.06(6)	−4.95(6)
	ML_2	17.37(4)		—	—		—	—
Pb^{2+}	ML	11.54(1)	11.54[b]	10.53(1)	8.84(3)	8.68[b]	7.30(1)	6.61(2)
	MLH_{-1}	0.1(2)		0.20(4)	−0.5(1)		−1.6(1)	−2.22(7)
	ML_2	14.95(8)		—	—		—	—

[a] $\beta_{M_mL_lH_h}$ = $[M_mL_lH_h]/[M]^m[L]^l[H]^h$; $\beta_{MLH_{-i}}$ = $[ML(OH)_i][H]^i/[M][L]$. [b] 25 °C, I = 0.1 mol dm^{-3} ($NaNO_3$), ref. 20. [c] 25 °C, I = 0.1 mol dm^{-3} ($NaNO_3$), ref. 16.

The vials were sealed and the solution then allowed to equilibrate in a thermostatted bath (25 °C). The pH of each vial was measured periodically until no change was detectable.

Calculation of Protonation and Stability Constants.—The protonation and stability constants of the various species formed were obtained from the experimental titration data with the aid of the SUPERQUAD program.[26] The results were obtained from a minimum of two titrations for which the c_M:c_L ratios were 1:1 and 1:2 in the case of fast reactions when the titrations were performed by the usual automated system, but only the 1:1 ratio was used for the majority of the slower reactions when the titrations were performed by the 'out-of-cell' procedure.

The errors quoted are the standard deviations given directly by the program and do not represent the total experimental errors. In the case of the automated titrations the formation constants were obtained from about 50 readings in each set of titrations, but in the out-of-cell titrations, owing to difficulties in preparing and maintaining for a long time a larger number of vials, only 21–32 readings were possible. Obviously, in this last case, the experimental errors are larger, due to losses in the several readings and to eventual evaporation of the solvent with time.

Results and Discussion

Three new oxatriaza macrocyclic ligands have been synthesised (L^2, L^4 and L^5) and their protonation and complexation reactions with several metal ions studied. Two other ligands (L^1 and L^3), already studied[16,20] in part, have been re-examined and the study extended to other metal ions, namely Co^{II} and Mn^{II}; the hydrolysis of the complexes formed was also studied. Now a complete series of macrocyclic ligands of this type is available and the stability constants of their metal complexes have been determined under the same conditions so that different effects can be monitored: (1) the replacement of a nitrogen by an oxygen atom in the ring, by comparison with similar tetraazamacrocyclic metal complexes; (2) the increase in size of the ring; and (3) the introduction of substituents in the nitrogen atoms of the ring, *i.e.* *N*-methyl groups.

Table 1 summarizes the protonation constants of the ligands studied in the present work and Table 2 the stability constants of the complexes formed by the same ligands with several first series transition-metal ions, Zn^{II}, Cd^{II} and Pb^{II}, calculated from potentiometric titrations, together with the corresponding values reported previously.

Protonation Constants.—All the values reported previously by Hancock and co-workers[16,20] for some of the ligands are close to ours although the ionic background salt used is different ($NaNO_3$ for Hancock's values and KNO_3 for ours). This was expected since these ligands do not form complexes with sodium or potassium ions of any appreciable stability.

All the ligands have two very basic nitrogen atoms; the third nitrogen atom is protonated at lower pH, the lower the value the shorter the distance between the two protonated nitrogen atoms due to the repulsions between closely neighbouring positive charges (log K_3 = 1.56 for L^1 and 1.67 for L^2 but 4.65 and 5.370 for L^4 and L^5, respectively; for L^3 an intermediate value is obtained, 2.78).

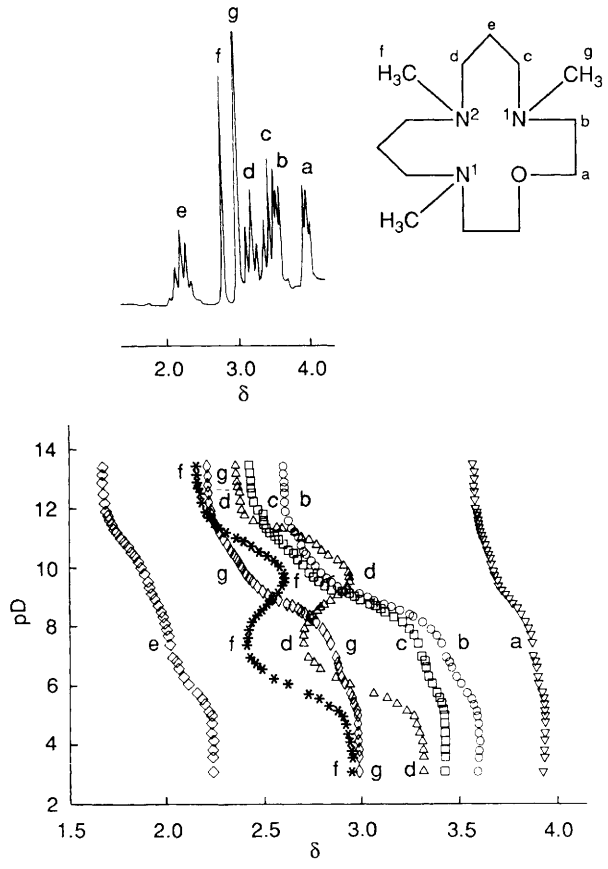


Fig. 1 Proton NMR spectrum of L^5 at pD 6.12 and titration curves

The introduction of methyl groups does not affect all the protonation constants of these ligands in a straightforward way; indeed the second protonation constants are always, in the cases studied, lower than the corresponding values for the parent amines and in the case of the 14-membered macrocycle the first protonation constants of both compounds have identical values.

The sequence of protonation for the two 12-membered macrocycles has been studied before.[22] It was found that for L^1 the first two protonations occur simultaneously at the three nitrogen atoms, but to a higher degree at the nitrogens in opposite positions; on further addition of acid the protonation proceeds until completed, which occurs only at very low pH. For L^2 a different and peculiar protonation sequence is observed: the first equivalent of acid added protonates the nitrogen opposite to the oxygen atom of the molecule (N^2); the second equivalent protonates the other two nitrogen (N^1) atoms while the first nitrogen is progressively deprotonated although on further addition of acid it protonates again and fully at very low values of pH.

The 14-membered ligands exhibit a protonation sequence that is very similar to that of the methylated amine of the 12-membered macrocycle (L^2). In Fig. 1 the titration curve of L^5 is presented with all its resonances together with a NMR spectra of the ligand at pD 6.12. The assignment of the resonances, similarly to that for L^2,[22] is straightforward taking into account the area ratio and the pattern of each absorption. The spectra exhibit seven resonances over the entire pD range: two singlets, readily assigned to the methyl protons (f and g), are distinguishable from one another by their relative area; four triplets are assigned to the methylenic protons a–d, and a quintuplet, at high field, is assigned to the four methylenic protons e.

The methylenic protons a, deshielded by the electronegative oxygen atom nearby, appear as a triplet at lower field. The assignment of the triplet corresponding to protons b was made by irradiation of the resonance of the protons a at pD 2.0, 5.4, 7.75, 10.48 and 13.99. Methylenic protons c and d were assigned by taking into account the profile of the titration curves: the d protons are only influenced by protonation of centre N^2 and their titration curve profile is very similar to that of protons f, while the c protons are influenced by the protonation of centre N^1 and have a titration profile very similar to those of protons b and g.

The titration curve for this compound (Fig. 1) shows the peculiar effects mentioned before due to the effect of charge repulsion on the competition between nitrogen atoms N^1 and N^2 for the proton. The first equivalent of acid added (pD 12–10) protonates the basic centre N^2 since only resonances d–f shift appreciably downfield; the second equivalent of acid (pD 10–7) protonates nitrogen atoms N^1 (resonances b, c and g move downfield) while N^2 is progressively deprotonated (resonances d and f move in the opposite direction; protons e do not show this behaviour perhaps because they are also influenced by the protonation of centre N^1). Centre N^2 starts to be protonated again at pD <7 and at pD 4.5 the protonation of this centre is completed. This titration curve allows the determination of the protonation constants in D_2O, as described before.[25]

Stability Constants.—The values obtained by us and by Hancock and co-workers[16,20] are very similar in spite of the different ionic media used. The only case where a larger difference was found (0.5 log units) is that of the nickel(II) complex of L^3 which took several days to equilibrate in our case; Thöm and Hancock[16] do not report this fact.

In the majority of the cases only 1:1 complexes are formed; however, for L^1, ML_2 species for the larger Cd^{II} and Pb^{II} and also for Mn^{II} may be formed according to the best set of stability constants calculated by the SUPERQUAD program. We have also checked the possibility of M_2L species but they do not appear to be formed under the conditions used. In certain cases protonated species of the type MHL were found and in all cases hydroxo complexes of the type ML(OH) or/and $ML(OH)_2$ were formed and their (apparent) constants determined. Although the formation of polymeric species is possible and likely, no attempt was made to study these species due to the extreme slowness of some of the reactions. The (apparent) formation constants corresponding to equilibria (1)–(3) are shown in Table 3, but the values may not correspond

$$ML(H_2O)_x + OH^- \rightleftharpoons ML(OH)(H_2O)_{x-1} + H_2O \quad K_{ML(OH)} \quad (1)$$

$$ML(OH)(H_2O)_{x-1} + OH^- \rightleftharpoons ML(OH)_2(H_2O)_{x-2} + H_2O \quad K_{ML(OH)_2} \quad (2)$$

$$ML(H_2O)_x + 2OH^- \rightleftharpoons ML(OH)_2(H_2O)_{x-2} + 2H_2O \quad \beta_{ML(OH)_2} \quad (3)$$

exactly to the equilibria shown due to the possibility of occurrence of polymeric species.

The acid–base behaviour of the complexes of Cd^{II} and Pb^{II} of all the ligands is identical, *i.e.* their titration curves show a sharp inflection at $a = 3$ (the moles of base added per mol of ligand) and hydrolysis is negligible. The same is found for the complexes of Cu^{II} and Co^{II} of L^3. The titration curves of the zinc(II) complexes have an inflection point at $a = 4$ in all cases except that of the complex formed with L^4 for which the inflection point is found at $a = 5$. In the cases of Cu^{II}, Ni^{II} and Co^{II}, with the methylated ligands L^2 and L^5, and the cobalt(II) complex of L^4 no inflection point is found for $a = 5$ and formation of polymeric species is likely. In the case of the lead(II) complexes formed by the 14-membered ligands precipitation occurs at pH >8.

On comparing the values in Tables 1 and 2 for the oxatriaza macrocycles with those in Table 4 for the corresponding

Table 3 Hydrolysis constants* for the oxatriaza macrocyclic compounds studied (in brackets are the pK_{ai}^{H} values)

Metal ion	Constant (log)	L^1	L^2	L^3	L^4	L^5
Mn^{2+}	$K_{ML(OH)}$	3.37 (10.45)	—	3.93 (9.89)	—	—
Co^{2+}	$K_{ML(OH)}$	6.12 (7.70)	6.21 (7.61)	4.0 (9.8)	—	—
	$\beta_{ML(OH)_2}$	—	—	—	12.34	12.17
Ni^{2+}	$K_{ML(OH)}$	7.51 (6.31)	—	—	—	—
	$\beta_{ML(OH)_2}$	—	13.22	12.38	12.04	12.71
Cu^{2+}	$K_{ML(OH)}$	5.09 (8.73)	6.44 (7.38)	3.33 (10.5)	—	—
	$K_{ML(OH)_2}$	—	—	3.09 (10.73)	—	—
	$\beta_{ML(OH)_2}$	—	—	6.41	12.44	12.42
Zn^{2+}	$K_{ML(OH)}$	6.14 (7.68)	6.35 (7.47)	6.21 (7.61)	—	5.88 (7.94)
	$K_{ML(OH)_2}$	—	—	3.03 (10.8)	—	2.91 (10.9)
	$\beta_{ML(OH)_2}$	—	—	9.24	12.24	8.79
Cd^{2+}	$K_{ML(OH)}$	3.43 (10.39)	3.71 (10.11)	4.21 (9.61)	4.63 (9.19)	4.17 (9.65)
Pb^{2+}	$K_{ML(OH)}$	2.38 (11.4)	3.49 (10.33)	4.48 (9.34)	4.92 (8.9)	4.99 (8.83)

* Defined as in equations (1)–(3); pK_a values in parentheses, corresponding to the equilibrium $ML(H_2O)_x \rightleftharpoons ML(OH)(H_2O)_{x-1} + H^+$.

Table 4 Protonation and stability constants[a] of some tetraaza macrocyclic compounds

Metal ion	Species	L^6 (cyclen)	L^7	L^8	L^9 (cyclam)	L^{10} (tmc)
H^+	HL	10.6,[b] 10.97[c]	11.07[d]	11.02,[e] 11.2[c]	11.59,[f] 11.3[e]	9.34,[g] 9.70[f]
	H_2L	9.6,[b] 9.87[c]	8.95[d]	9.96,[e] 10.1[c]	10.62,[f] 10.23[e]	8.99,[g] 9.31[f]
	H_3L	1.7[h] —	—	1.96,[e] 1.6[c]	1.61,[f] 1.43[e]	2.58,[g] 3.09[f]
	H_4L	0.9[h] —	—	—	2.42,[f] 2.27[e]	2.25,[g] 2.64[f]
Co^{2+}	ML	13.8[i]	—	14.28[i]	12.71[i]	7.58,[j] 10.9[b]
	ML(OH)	—	—	—	—	5.76,[j] 5.28[k]
Ni^{2+}	ML	16.4,[l] 14.4[m]	—	17.98[l]	22.2,[n] 20.1[o]	8.65,[j] 11.8[b]
	ML(OH)	—	3.62[p]	—	—, 2.3[o]	3.72,[k] 3.12[q]
Cu^{2+}	ML	23.3,[e] 24.8[q]	18.37[d]	24.36,[e] 28.8[h]	26.5,[e] 27.2[q]	18.3,[j] 17.7[b]
	ML(OH)	—	1.82[r]	—	—	very small[j]
Zn^{2+}	ML	16.2[s]	14.04[d]	15.6[s]	15.5[s]	10.35,[j] 12.2[b]
	ML(OH)	5.74[t]	—	—	3.99[t]	5.44,[j] 5.4[u]
Cd^{2+}	ML	14.3[s]	13.06[d]	12.71[e]	11.23[e]	9.0[j]
	ML(OH)	—	—	—	—	5.60,[j] 4.4[u]
Pb^{2+}	ML	15.9[s]	13.91[d]	13.48[e]	10.83[e]	—

[a] 25 °C, $K_{ML} = [ML]/[M][L]$, $K_{ML(OH)} = [ML(OH)]/[ML][OH]$. [b] I = 0.5 mol dm^{-3}, ref. 27. [c] I = 0.5 mol dm^{-3}, ref. 28. [d] I = 0.1 mol dm^{-3}, ref. 29. [e] I = 0.1 mol dm^{-3}, ref. 8. [f] I = 0.5 mol dm^{-3}, ref. 30. [g] I = 0.1 mol dm^{-3}, ref. 31. [h] I = —, ref. 32. [i] I = 0.2 mol dm^{-3}, 35 °C, ref. 33. [j] I = 0.1 mol dm^{-3}, ref. 34. [k] I = 0.5 mol dm^{-3}, ref. 35. [l] I = 0.1 mol dm^{-3}, ref. 11. [m] I = 0.1 mol dm^{-3}, ref. 36. [n] I = 0.1 mol dm^{-3}, ref. 37. [o] I = 0.1 mol dm^{-3}, ref. 10. [p] I = 0.5 mol dm^{-3}, ref. 38. [q] I = 0.2 mol dm^{-3}, ref. 39. [r] I = 0.1 mol dm^{-3}, ref. 40. [s] I = 0.2 mol dm^{-3}, ref. 41. [t] I = 0.2 mol dm^{-3}, ref. 42. [u] I = 0.1 mol dm^{-3}, ref. 43.

tetraaza macrocycles several important differences can be perceived.

(*a*) *Replacement of one nitrogen by an oxygen atom in the ring.* All the values for the complexes of the oxatriaza ligands are lower than those for the tetraaza ligands of the same ring size; the difference is more pronounced for the 14-membered compounds, reaching more than ten log units for the complexes of Cu^{II} or Ni^{II}, although the series are not strictly comparable, see below. In general, the differences are larger for Cu^{II} and Ni^{II} and smaller for Cd^{II} and Pb^{II}, Zn^{II} being in an intermediate position. For the methylated amines the differences are smaller and similar for the various types of metal ions.

It must be emphasized that the two series of 14-membered ligands compared are not structurally equivalent; indeed, the oxatriaza ligands form complexes with the two six- and five-membered chelate rings in consecutive positions, while cyclam (L^9) forms alternating five- and six-membered chelate rings. It is known, even for the open-chain polyamines and also for macrocyclic compounds,[44] that the possibility of formation of alternating five- and six-membered chelate rings favours the formation of stronger co-ordinative interactions and hence more stable complexes. Unfortunately, only one value was found in the literature for the stability constants of the metal complexes of isocyclam (L^{11}) and a more direct comparison is not possible. The value is for the complex with Co^{2+} (10.9),[33] and is lower than that of the Co^{2+}–cyclam complex (12.71),[33] which is a confirmation of the above statement. The two 14-membered macrocycles have comparable ring sizes and the difference in behaviour must lie in the ligand configuration and resulting orientation of the lone pair of electrons of the donor atoms.

(*b*) *Increase in ring size.* The Irving–Williams order of stability is obeyed for all the ligands and the values of the stability constants decrease with increasing ring size, with the single exception of the copper complexes since the complex of L^3 is more stable than the others. The zinc and cobalt complexes decrease slightly in stability throughout the series, but the nickel, cadmium and lead complexes show a more pronounced decrease in stability with increasing ring size, particularly in the case of Pb^{II}.

Considering all the metal ions studied in the present work, the following sequences of decreasing stability constants are obtained: L^1, $Cu^{II} \gg Ni^{II} > Pb^{II} > Cd^{II} \approx Co^{II} \approx Zn^{II}$; L^3, $Cu^{II} \ggg Ni^{II} > Zn^{II} > Cd^{II} \approx Co^{II} > Pb^{II}$; L^4, $Cu^{II} \ggg Ni^{II} > Zn^{II} \approx Co^{II} > Pb^{II} \approx Cd^{II}$. Curiously, the macrocycle with smaller ring size, L^1, forms complexes with the two larger metal ions Cd^{II} and Pb^{II} which are more stable than that of Zn^{II}, but the situation is reversed with the larger ligands, contrarily to what might be expected if the metals were inserted in the ring.

For the tetraaza series, the sequence of stabilities for complexes of the various metal ions is as follows: L^6 (cyclen), $Cu^{II} \ggg Ni^{II} \approx Zn^{II} > Pb^{II} \gg Cd^{II}$; L^8, $Cu^{II} \ggg Ni^{II} > Zn^{II} > Pb^{II} > Cd^{II}$; L^9 (cyclam), $Cu^{II} \ggg Ni^{II} > Zn^{II} \gg Cd^{II} > Pb^{II}$. Now, the complexes formed with the larger ions Cd^{II} and Pb^{II} are the least stable in all cases but whereas the complexes of Cu^{II} and Ni^{II} increase in stability with increasing ring size, those of

Table 5 Effect of the introduction of *N*-methyl substituents in the 12- and 14-membered macrocycles ($\Delta = \log K_{ML} - \log L_{ML'}$)[a]

Metal ion	12-Membered macrocycle		14-Membered macrocycle	
	Oxatriaza	Tetraaza[b]	Oxatriaza	Tetraaza[b]
Co^{II}	0.24	—	3.07	—
Ni^{II}	0.94	—	3.29	13.55–8.3
Cu^{II}	0.65	4.92–6.43	1.8	9.5–8.2
Zn^{II}	0.42	2.16	2.54	5.2–3.3
Cd^{II}	0.49	1.24	2.43	2.23
Pb^{II}	1.01	1.99	0.69	—

[a] L = Parent amine, L′ = methylated amine. [b] Maximum and minimum difference between literature values (*cf.* Table 4).

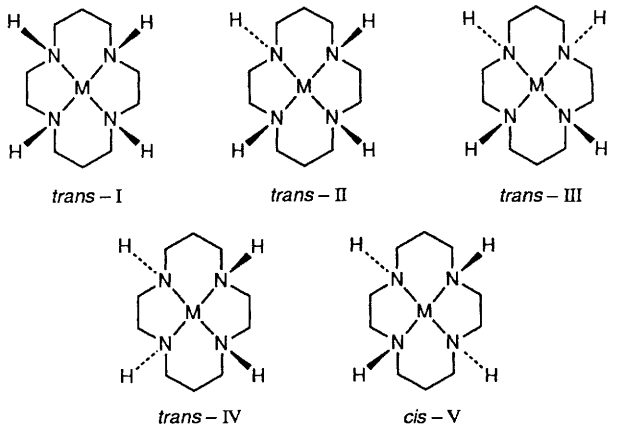


Fig. 2 Designations proposed by Bosnich *et al.*[45] for the different combinations of the chiral nitrogen donor groups possible for cyclam

Cd^{II} and Pb^{II} decrease in stability and the zinc(II) complexes do not appear to be affected by the size of these ligands. Hence, similarly to what happens in the oxatriaza series, the larger ions, like Cd^{II} and Pb^{II}, seem to prefer the smaller rings, contrarily to expectation, but the behaviour of Cu^{II} and especially Ni^{II} is opposite in the two series.

The behaviour of the metal complexes in the tetraaza series, studied by many researchers in the last two decades, is well known and explained by the different configurations adopted by the macrocycle in the various complexes: the ring size or cavity of the 12-membered ligand is too small to accommodate most metal ions in the plane formed by the four nitrogen atoms, so the metal ion is forced out of the ring and lies above this plane, while the macrocycle is in a *trans*-I (*R,S,R,S*) configuration (see Fig. 2, designations proposed by Bosnich *et al.*[45] for the different combinations of chiral nitrogen donor groups possible for cyclam), as in the case of $[CuL^6(NO_3)]NO_3$.[46] The macrocycle may also adopt a folded conformation of the type *cis*-V (*R,R,R,R*), as in the case of $[CoL^6(NO_2)_2]Cl{\cdot}H_2O$,[47] where the four nitrogen atoms of the macrocycle and two nitro groups are co-ordinated to the cobalt in *cis* position. Folded *cis*-octahedral complexes are also known for Co^{II} and Ni^{II}.[48] However, the 14-membered cyclam has a large enough ring to encircle a range of metal ions and their complexes generally adopt the strain-free, thermodynamically more stable *trans*-III (*R,S,S,R*) conformation, in which the metal ion is indeed inside the ring of the macrocycle in a square-planar structure, with two adjacent NH hydrogen atoms directed towards one side of the macrocycle plane and the other two in the opposite direction. The two six-membered chelate rings are in chair conformations and the two five-membered rings are in *gauche* conformations. Examples of this structure were found for Ni^{II}, Ni^{III}, Co^{II}, Cu^{II}, Tc^{V} and Ru^{III}.[49–51] Still, for the complexes of the large Pb^{II} or of metal ions which form kinetically inert complexes such as Co^{III}, Rh^{III} and Cr^{III}, cyclam is found in a folded octahedral *cis* geometry[52–54] and in a *trans*-I configuration in the cases of Cd^{II} and Hg^{II}.

Hancock and co-workers[8,11,55] explained the preference of the larger metal ions for the smallest macrocycle of the tetraaza series using molecular mechanics calculations: the most stable form of L^6 is the *trans*-I conformer, the hole size being such that complexes of metal ions with M–N bond lengths of 2.11 Å fit best; in the *trans*-III most stable conformer for cyclam the hole size is such that complexes of metal ions with M–N bond lengths of 2.05 Å fit best. On the other hand, the 12-membered ring is more flexible with respect to expansion and contraction than is the 14-membered ring, because six-membered chelate rings are less prone to expansion and contraction as their hydrogens lose the more favourable all-staggered position on deforming the ring.[11]

Now, it is clear from these results that ions whose radii is such that the M–N bond in their complexes is larger than 2.11 Å (*e.g.* Pb^{2+} which usually exhibits M–N bond lengths of 2.5–2.7 Å in its complexes depending on the co-ordination number) cannot fit into the cavity of these macrocyclic ligands and their complexes adopt a structure with the metal ion forced out of the ring.

Given their ionic radii, the larger ions studied in this work may therefore prefer to co-ordinate to the 12-membered ligands with least distortion in their normal configuration, hence giving more stable complexes since the basicity of the donor atoms is not very different from the others.

The oxatriaza complexes of Zn^{II}, Cd^{II} and Pb^{II} seem to have a behaviour similar to that of the tetraaza complexes and similar structures will probably be adopted. However, for the copper complexes, X-ray diffraction studies showed differences between the two series: the L^1 complex formed with this metal ion adopts a folded structure where the four donor atoms do not form a plane and the three hydrogen atoms bonded to the nitrogen donor atoms are on the same side of the molecule where the copper atom is co-ordinated;[56] the L^3 complex of the same metal adopts a *trans*-I configuration with the Cu atom raised 0.467 Å above the macrocyclic plane defined by the three nitrogen and one oxygen atom[51] and the L^5 complex has a configuration with all the hydrogens bonded to the nitrogen on the same side of the macrocycle, opposed to the Cu atom, which stays on the other side in a position slightly out of the plane.[56] The *trans*-III configuration was not adopted in this case, contrarily to what happens in the tetraaza series, probably due to the greater strain of the two consecutive six-membered chelate rings. This results in a displacement of the donor atoms from square co-ordination, giving a less favourable orientation, and hence leading to less-stable complexes.

(*c*) *Introduction of* N-*methyl substituents.* The difference in stability of the complexes formed with the *N*-methyl derivatives and the corresponding parent amines are more pronounced for the tetraaza macrocycles than for the oxatriaza series. The complexes formed with the methylated amines are always weaker than those of the secondary amines, the differences being smaller for the complexes of the 12-membered ligands.

For the 12-membered oxatriaza complexes the differences are small (*cf.* Table 5), the largest (1.01 log units) being found for the lead(II) complexes. For the tetraaza counterparts the differences are much larger: 4.92–6.43 log units for Cu^{II}, 2.16 for Zn^{II}, 1.99 for Pb^{II} and 1.24 for Cd^{II}. For the 14-membered macrocycles the differences are larger for both series, except in the case of Pb^{II} with the oxatriaza macrocycle. Methylation of the nitrogen donors has a much more pronounced effect in the tetraaza series and in the larger ligands.

On the other hand, the orders of stability of the different complexes are as follows: L^2, $Cu^{II} \gg Ni^{II} > Pb^{II} > Co^{II} \approx Cd^{II} > Zn^{II}$; L^5, $Cu^{II} \gg Pb^{II} > Ni^{II} > Zn^{II} > Co^{II} > Cd^{II}$; L^7, $Cu^{II} \gg Zn^{II} \approx Pb^{II} > Cd^{II}$; L^{10} (tmc), $Cu^{II} \gg Zn^{II} \gg Cd^{II}$. The sequence for the complexes of L^2 is similar to that of the

respective parent amine and the same is true with the tetraaza ligands. However for L^5 the position of the lead(II) complex is different since it is now more stable than that of Ni^{II}. There are no comparable data for the tetraaza ligands.

For the methylated tetraaza macrocycles only one structure for the 12-membered compound has been reported, that of the complex $[NiL^7][ClO_4]_2 \cdot 2H_2O$,[38] in which the macrocycle is in the *trans*-I configuration (see Fig. 2), very similar to that of $[CuL^6(NO_3)]^+$.[48]

However, complexes of the methylated 14-membered compound (tmc) were extensively studied by NMR and electronic spectroscopy and several solid-state structures have been reported. In the majority of cases the macrocycle adopts the arrangement with all methyl groups disposed on the same side of the molecule which is also that of the metal ion, *i.e.* that of the isomer *trans*-I. For example, $[Ni(tmc)(N_3)]^+$,[57] $[Zn(tmc)Cl]^+$,[58] $[Fe(tmc)(NO)][BF_4]_2$[59] and $[Cd(tmc)][NO_3]_2$[54] all have square-pyramidal structures with the four nitrogen donor atoms of the macrocycle forming a perfect plane and the metal ion out of this plane on the same side as the unidentate ligand bound in the axial position. (In solution, however, ^{13}C NMR spectra of the complexes of Ni^{II} and Zn^{II} indicate fluxional behaviour, possibly involving trigonal-bipyramidal structures.[58,60])

With these data it is possible to understand the large difference in stability between the complexes of Cu^{II} and Ni^{II} with cyclam and tmc. The cyclam complexes adopt the strain-free configuration *trans*-III, while the tmc-complexes are forced to adopt the *trans*-I configuration in five-co-ordinate complexes, hence are less stable. When the size of the metal ion increases the cyclam complex tends to adopt the *cis*-V or, even, the *trans*-I configuration similar to that observed for the same complexes with tmc.

For the 12-membered macrocycles there is less information, but the smaller difference in stability observed for the cyclen and the corresponding *N*-methyl cyclen complexes may be due to the fact that the smaller size of the cyclen ring forces the complexes to adopt more strained structures, possibly similar to those adopted by the methylated amine, *cf.* the cases of $[CuL^6(NO_3)]^+$ and $[NiL^7]^{2+}$ mentioned above.

Now, the differences in stability of the complexes formed by the amines and their methylated forms in the oxatriaza series is smaller in both cases studied in this work, being practically insignificant for the 12-membered case. By analogy we may assume that both the amines and their methylated derivatives in this series (and especially in the 12-membered rings) adopt similar conformations in their complexes. This hypothesis is supported by our results for the copper complexes of the two 14-membered macrocycles, L^4 and L^5, for which X-ray diffraction study showed very similar structures in the solid state for both complexes.[56] A possible reason for the difference in behaviour between the tetraaza and the oxatriaza ligands is the steric interactions between the methyl groups, which probably are less important in the latter series due to the presence of only three groups (four in the tetraaza case). It must also be mentioned that the six-membered chelate rings in the 14-membered compound must be in the chair conformation, since the methyl groups are constrained to approximate axial positions; the boat conformation would lead to important steric interactions between the methyl groups and the α-hydrogens.[24]

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