Prediction and Observation of the Structure of the Zinc(II) Complex of 1,5,9,13-Tetraazacyclohexadecane. A Crystallographic and Molecular Mechanics Study of the Conformations assumed by the Macrocycle when complexed with Metal Ions†

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The complex of the macrocycle 1,5,9,13-tetraazacyclohexadecane ([16]aneN_4) with Zn^{II}, $[Zn([16]aneN_4)][ClO_4]_2$, has been synthesized and its crystal structure determined [monoclinic, space group $P2_1/n$, a = 8.558(3), b = 13.997(4), c = 16.738(3) Å, β = 92.48(2)°, Z = 4; R = 0.0826]. The Zn^{II} ion shows a somewhat distorted tetrahedral co-ordination geometry with N–Zn–N angles ranging from 101.9(5) to 105.4(5)° within the chelate rings of the complex, and 122.8(5) and 123.4(4)° for the N–Zn–N angles outside of the chelate rings. The Zn–N bond lengths ranged from 1.97(1) to 2.03(1) Å. A molecular mechanics analysis of [16]aneN_4 complexes shows that three types of conformers occur over the range of M–N bond lengths. At M–N bond lengths less than about 2.15 Å a novel previously predicted conformer is of low energy with small tetrahedral metal ions, and is the predicted conformer observed here for the Zn^{II} ion. At longer M–N bond lengths, and for metal ions which do not readily assume tetrahedral co-ordination geometry, no low energy conformations exist, accounting for the fact that [16]aneN_4 complexes are generally of low thermodynamic stability. At intermediate M–N bond lengths a variety of conformers containing twist-boat conformation chelate rings are the most stable, while at longer M–N bond lengths the conformer actually observed in the Cd^{II}, Hg^{II} and Pb^{II} structures, which has a large cavity such that large metal ions with M–N bond lengths of 2.4 Å fit best, becomes the most stable.

The cavities of macrocycles have been of interest in relation to understanding their selectivities for metal ions.[1] In a classical study of the sizes of macrocyclic cavities, Busch *et al.*[2] used molecular mechanics (MM) to calculate the best-fit M–N bond lengths for co-ordinating to the macrocycle in a minimum strain energy fashion, seen in Fig. 1. In these calculations, the geometry of the metal ion within the macrocyclic cavity was constrained to be square planar. It has become apparent that the situation is more complex than suggested in these early studies. For complexes of the macrocycles [12]aneN_4 to [14]aneN_4, MM calculations showed[3–5] that the idea of a central cavity in the macrocycle which was able to select metal ions based on the match between the size of the cavity in the macrocycle, and the size of the metal ion, was too simple. Instead of the complexes of these tetraaza macrocycles being constrained to square-planar geometry with a + + − − conformation (see Fig. 2 for the key to conformations of tetraaza macrocycles), the picture that emerged was that [14]aneN_4, for example, could assume at least three conformations which allowed for complexation of a range of metal-ion sizes and geometries. In two of these conformations the metal ions did not lie in the plane of the donor atoms of the ligand, so that the steric factors that controlled selectivity were the same as those that controlled the selectivity for metal ions in open-chain ligands, namely the size of the chelate ring. Chelate rings control selectivity for metal ions in that five-membered chelate rings promote selectivity for larger metal ions, while six-membered chelate rings promote selectivity for smaller metal ions.[7]

The selectivity of [16]aneN_4 was not considered in detail.[4,5] The ligand has four six-membered chelate rings, so why is there a steep drop[8] in logK_1 in passing from [14]aneN_4 to [16]aneN_4 for nearly all metal ions, even with very small metal ions such as Cu^{II}? It is clear that, in fact, Cu^{II} is too large[3] for the 'cavity' in [16]aneN_4. The MM studies[3] showed that, if the tetraaza macrocycles were not constrained to square-planar co-ordination and a + + − − conformation, then the best-fit M–N bond lengths *decreased* from [12]aneN_4 to [16]aneN_4 (Fig. 1). The lowest energy conformation for [16]aneN_4 complexes was predicted to be that seen in Fig. 3 with a small tetrahedral metal ion with a M–N bond length of 1.81 Å, which will be referred to as the ch,ch,ch,ch + − + − conformer (ch = chair conformer, tw = twist-boat conformer). The stability of this conformation derives from the fact that it allows all of the six-membered chelate rings to assume the more stable chair conformation, and achieve angles to 109.5° for all N–M–N angles, which is only possible with a tetrahedral metal ion. This conformation is not present in any of the six structures reported[10–13] to date for [16]aneN_4 complexes. These structures are either of the ch,ch,tw,tw + + + − type (Ni^{II} [10]), the ch,tw,ch,tw + + − − type (Cr^{III} [13]), or the ch,ch,ch,ch + + + + type of conformer (Cd^{II},[11] Hg^{II} [11] and Pb^{II} [11]) seen in Fig. 3. The Ti^{IV} [12] complexes have some of the N–H hydrogens ionized to give co-ordinated amide groups, and are not considered further here, but effectively have mixtures of chair and twist-boat chelate rings. All of the metal ions for which structures with [16]aneN_4 have been reported[10–11] show octahedral geometry. Some may be too large to adopt the ch,ch,ch,ch + − + − conformation predicted, even when able to adopt tetrahedral co-ordination, as

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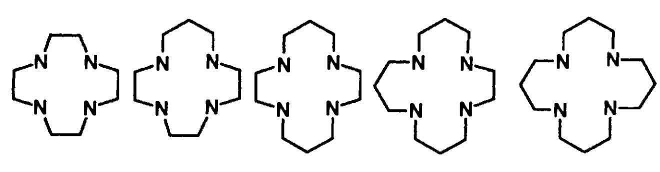
† *Supplementary data available* (SUP No. 57072, 2 pp.): coordinates for the energy minimized structure of $[Zn([16]aneN_4)]^{2+}$ generated by molecular mechanics calculations: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



	[12]aneN$_4$	[13]aneN$_4$	[14]aneN$_4$	[15]aneN$_4$	[16]aneN$_4$
(*a*) Early analysis: Best-fit M—N (Å):	1.83	1.92	2.07	2.22	2.38
(*b*) Present analysis: Best-fit M—N (Å):	2.21	-	2.07	-	1.81
Metal-ion geometry:	Square pyramidal		Square planar		Tetrahedral
Macrocycle conformation:	+ + + +		+ + − −		+ − + −

Fig. 1 The best-fit M–N bond lengths for co-ordinating in the cavity of tetraaza macrocycles, calculated (*a*) by MM by Busch *et al.*[2], assuming the + + − − conformer (see Fig. 2) for each complex, and square-planar co-ordination of the metal ion, and (*b*) finding the conformer and metal-ion geometry indicated which gives the global minimum strain energy for each complex[3]

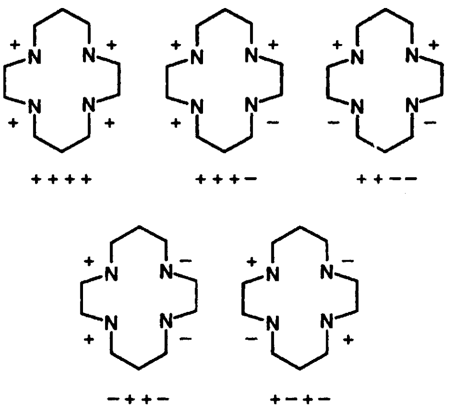


Fig. 2 The convention for indicating the N–H hydrogens in different conformers of [14]aneN$_4$.[6] A '+' indicates that the N–H hydrogen is above the plane of the macrocycle, while a '−' indicates that it is below

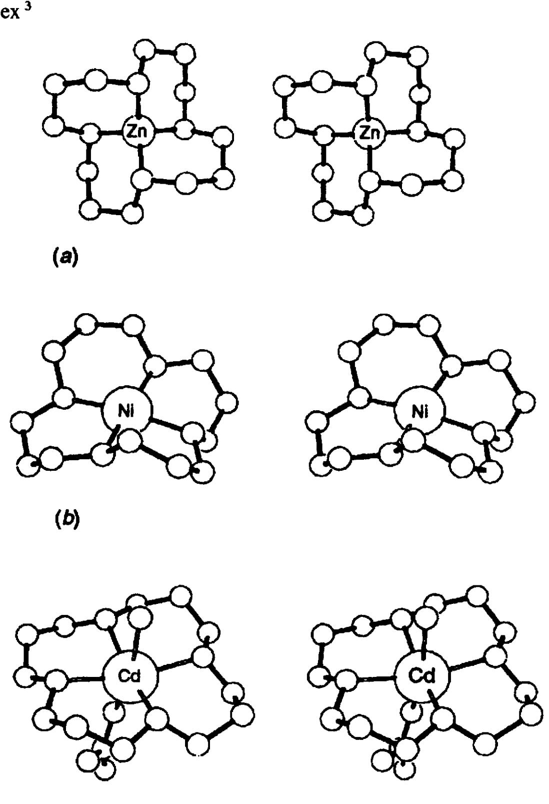


Fig. 3 Different types of conformer found in complexes of [16]aneN$_4$. At (*a*) is the ch,ch,ch,ch + − + − conformer predicted[3] for the small tetrahedral Zn^{II} ion (ionic radius[9] = 0.60 Å), (*b*) shows the ch,ch,tw,tw + + + − conformer of the complex of the larger Ni^{II} ion[10] which achieves the tetrahedral co-ordination geometry required by the + − + − conformer with great difficulty, and (*c*) the ch,ch,ch,ch + + + + conformer observed[11] with the large Cd^{II} ion (ionic radius[9] = 0.95 Å) and other large metal ions such as Pb^{II} and Hg^{II}

may be the case for Cd^{II}.[11] The best candidate for adopting the ch,ch,ch,ch conformation appeared to be the Zn^{II} ion. This ion readily adopts a tetrahedral geometry, where it has an ionic radius[9] of 0.60 Å, which is quite small. We therefore report herein the synthesis of [Zn([16]aneN$_4$)][ClO$_4$]$_2$, a crystallographic study of its structure, and MM analysis of the structure of [16]aneN$_4$ complexes in relation to metal-ion size and geometry.

Experimental

Synthesis of [Zn([16]aneN$_4$)][ClO$_4$]$_2$.—The ligand [16]aneN$_4$ was synthesized by the method of Barefield *et al.*[14] The complex [Zn([16]aneN$_4$)][ClO$_4$]$_2$ was synthesized by mixing Zn(ClO$_4$)$_2$·6H$_2$O (G. Frederick Smith Chemical) and the ligand in a 1:1 molar ratio in 50:50 water–ethanol. This deposited small colourless needles which were collected and dried (Found: C, 29.30; H, 5.50; N, 11.25. Calc. for $C_{12}H_{28}Cl_2N_4O_8Zn$: C, 29.25; H, 5.75; N, 11.35%).

X-Ray Crystallography.—A crystal was mounted on a glass fibre with epoxy cement and cooled to 163 K in a nitrogen gas cold stream. The crystal data and details of data collection and refinement are summarized in Table 1. Preliminary examination and data collection were performed on a Rigaku AFC5 rotating anode X-ray diffractometer (Mo-Kα, λ = 0.710 73 Å radiation, with oriented graphite monochromator). Cell parameters were calculated from a least-squares fit of setting angles for 50 reflections.

Omega scans for several intense reflections indicated

Table 1 Crystal data and structure refinement details for $[Zn([16]aneN_4)][ClO_4]_2$

Empirical formula	$C_{12}H_{28}Cl_2N_4O_8Zn$
M	492.65
T/K	163(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	8.558(3)
b/Å	13.997(4)
c/Å	16.738(3)
β/°	92.48(2)
U/Å^3	2003(1)
Z	4
D_c/Mg m^{-3}	1.634
μ/mm^{-1}	1.540
F(000)	1024
Crystal size/mm	0.34 x 0.24 x 0.1
θ/°	2.63–25.08
Index ranges	$-10 \leqslant h \leqslant 10, 0 \leqslant k \leqslant 16, 0 \leqslant l \leqslant 19$
Reflections collected	3549
Independent reflections	3518
Absorption correction	Semi-empirical from psi-scans
Max. and min. transmission	0.999 and 0.882
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3495/214/245
Goodness-of-fit on F^2 (all data)	1.027
Final R indices [$I \geqslant 2\sigma(I)$]	$R(F) = 0.0826$, $wR(F^2) = 0.2172$
R indices (all data)	$R(F) = 0.2055$, $wR(F^2) = 0.3218$
Largest difference peak and hole/e Å^{-3}	1.078 and −0.562

acceptable quality. Data were collected for $4.0 < 2\theta < 50.0°$ at 163 K. The scan range, on ω, for the data collection was $1.575 + 0.3\tan(\theta)$, with a variable scan rate of 4.0–16.0° min^{-1}. Three control reflections collected every 97 reflections showed no significant trends. Background measurement by stationary crystal and counter technique was done at the beginning and end of each scan for the total scan time. Weak reflections were rescanned three times to improve their total counting statistics.

Lorentz and polarization corrections were applied to 3549 reflections. A semiempirical absorption correction[15] was applied to the data. The structure was solved by direct methods.[16] Examination of photographs and peak shapes indicated the presence of a possible crystallographic twin.[17,18] The sum of the calculated structure factors squared (F_c^2) of the individual twin domains (generated with the matrix 1,0,0, 0, −1,0, 0,0, −1) multiplied by their individual fraction component contribution factor (0.932 and 0.068) were fitted to the observed structure factors squared (F_o^2), which improved the residual factors from about 0.13 down to the value close to 0.08 reported in Table 1. Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms,[19] with the number of least-squares parameters = 245; quantity minimized $\Sigma w(F_o^2 - F_c^2)^2$; $w = \{\sigma^2(F^2) + [0.1248(F_o^2 + 2F_c^2)/3]^2 + 17.6044(F_o^2 + 2F_c^2)/3\}^{-1}$ yielded $R(F) = 0.0826$, $wR(F^2) = 0.2172$, $S(F^2) = 1.179$ for observed data [$I > 2\sigma(I)$], at convergence (largest $\Delta/\sigma = 0.118$; mean $\Delta/\sigma = 0.005$); largest positive peak in the final Fourier difference map was 1.078 e Å^{-3} [near Cl(1)]; the largest negative peak in the final Fourier difference map was −0.562 e Å^{-3}. Atoms closer than 1.7 Å were restrained with an effective standard deviation of 0.05 to have the same U_{ij} components. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08 Å^2. Neutral-atom scattering factors and anomalous scattering correction terms were taken from refs. 20 and 21.

Both of the perchlorate ions appeared to be disordered on the basis of the large anisotropic thermal parameters. An attempt to resolve the disorder was not successful, and the structure as refined was accepted, even though the disorder leads to a fairly high final conventional R factor of 0.0826. The atomic coordinates are given in Table 2, and selected bond angles and lengths in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Molecular Mechanics Calculations.—These were carried out using the program SYBYL.[22,23] All force-field parameters were as contained in the TAFF force field used in SYBYL, except that parameters for the M–N bond with force constants of 200 kcal mol^{-1} Å^{-1} (1 cal = 4.187 J) and an ideal M–N bond length of 2.00 Å were added for Zn^{II}, together with an angle bending constant of 0.008 kcal mol^{-1} deg^{-1} and ideal N–Zn–N and Zn–N–C angles of 109.5° to describe the co-ordination geometry of the tetrahedral Zn^{II} ion. For the scans of strain energy *versus* M–N bond length, where the value of the ideal M–N bond length was varied from 1.7 to 2.7 Å, all parameters apart from the ideal M–N bond length were kept at constant values, with the M–N force constant at a value of 200 kcal mol^{-1} Å^{-1}. The M–N–C force constant was kept constant at 0.005 kcal mol^{-1} deg^{-1}. However, the N–M–N angle force constants were set to zero so as to allow the complex to assume whichever metal-ion co-ordination geometry was dictated by the ligand at the particular ideal M–N bond length used. In an attempt to ensure that the structures and energies obtained represented true minima, these structures were subjected to repeated molecular dynamics runs along the DYNAMICS module of SYBYL. Lower energy structures occurring in the dynamics run were selected and subjected to energy reminimization, and dynamics runs repeated, until no structures of lower energy could be found. The metal ions were four-co-ordinate at all times, and where metal ions are approximately square planar, as is true for the ch,ch,ch,ch + + + + or ch,ch,tw,tw + + + − conformer, then the complex can also be octahedral with axially co-ordinated unidentate ligands, as is true for all the complexes with these conformations. The starting coordinates for the ch,ch,ch,ch + + + + conformer were those from the reported[11] structure of $[Cd([16]aneN_4)]^{2+}$, those for the ch,ch,tw,tw + + + − conformer were from the reported[11] structure of $[Ni([16]aneN_4)]^{2+}$, while the coordinates for the MM generated structure of the + − + − ch,ch,ch,ch conformer of $[Zn([16]aneN_4)]^{2+}$ are deposited as SUP 57072.

Results and Discussion

The structure of the $[Zn([16]aneN_4)]^{2+}$ complex cation is shown with its numbering scheme in Fig. 4. The conformation found for the complex cation is that predicted[3] by MM calculations. In their complexes with $[16]aneN_4$, the small Zn^{II} ion adopts the ch,ch,ch,ch + − + − conformer, while the larger Cd^{II} ion adopts the ch,ch,ch,ch + + + + conformer. The question of which conformation of a complex will have the minimum energy as the size of the metal ion varies can be examined by MM calculations using a technique discussed previously.[5] In this approach, the ideal M–N bond lengths of the complex are varied monotonically over the range of bond lengths of interest, typically with steps in M–N bond length of 0.1 Å. The strain energy for each conformer is calculated at each M–N bond length interval, keeping all the other parameters in the calculation constant. A plot of strain energy *versus* M–N bond length shows the length over which each of the conformers is of lowest energy. Such a plot is given for $[16]aneN_4$ complexes in Fig. 5. All were kept four-co-ordinate so as to make the energies comparable.

Fig. 5 shows that the ch,ch,ch,ch + + + + conformer is of lowest energy at M–N bond lengths above 2.3 Å, while the ch,ch,tw,tw + + + − conformer is of lowest energy in the range 2.15–2.3 Å. Below 2.15 Å, the + − + − conformer is of lowest

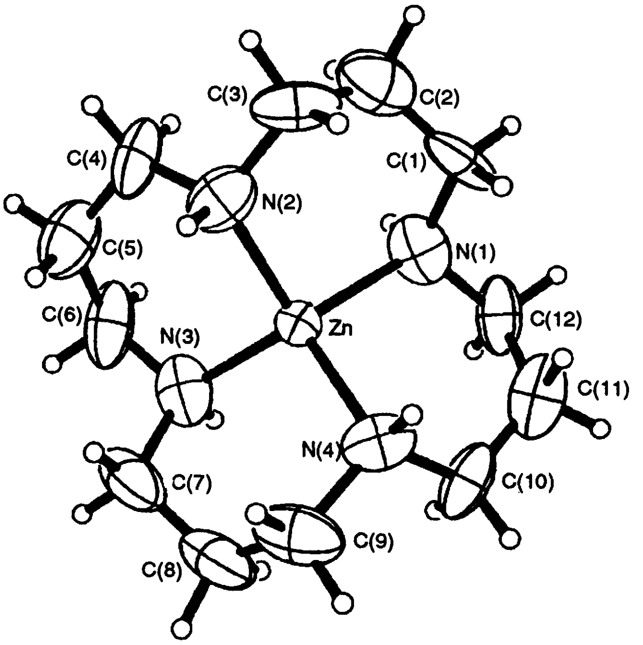


Fig. 4 Drawing of the $[Zn([16]aneN_4)]^{2+}$ cation showing the numbering scheme. Thermal ellipsoids drawn at the 50% probability level

Table 2 Atomic coordinates (× 10^4) for $[Zn([16]aneN_4)][ClO_4]_2$

Atom	*x*	*y*	*z*
Zn	2 640(2)	2 498(1)	9 042(1)
Cl(1)	−2 319(3)	2 497(3)	9 889(2)
Cl(2)	9 306(3)	39(3)	7 526(2)
O(1)	−3 305(12)	1 896(8)	10 308(8)
O(2)	−3 171(14)	3 142(9)	9 350(8)
O(3)	−1 192(13)	2 959(9)	10 333(7)
O(4)	−1 460(14)	1 926(10)	9 339(8)
O(5)	7 801(14)	63(14)	7 402(11)
O(6)	9 701(26)	966(1)	7 560(17)
O(7)	10 123(16)	−285(14)	6 874(8)
O(8)	9 980(18)	243(14)	8 264(8)
N(1)	2 346(12)	1 088(8)	9 275(8)
N(2)	3 884(13)	2 472(9)	8 053(7)
N(3)	903(12)	3 365(8)	8 737(8)
N(4)	3 502(13)	2 980(9)	10 083(7)
C(1)	3 717(17)	545(9)	9 103(11)
C(2)	4 211(20)	713(12)	8 227(12)
C(3)	4 926(16)	1 651(11)	7 991(10)
C(4)	2 874(19)	2 498(12)	7 328(8)
C(5)	1 719(18)	3 275(12)	7 340(9)
C(6)	390(17)	3 309(13)	7 929(10)
C(7)	1 327(21)	4 380(10)	8 948(11)
C(8)	1 805(20)	4 449(11)	9 834(1)
C(9)	3 401(19)	4 054(10)	10 131(11)
C(10)	2 753(16)	2 473(12)	10 753(7)
C(11)	2 908(17)	1 479(12)	10 731(10)
C(12)	1 948(16)	896(10)	10 085(9)

energy. Fig. 5 explains reasonably well the distribution of conformers in the known[10–13] structures of $[16]aneN_4$ complexes. The existence of the novel ch,ch,ch,ch $+ - + -$ conformer predicted previously,[3] and observed here for the Zn^{II} complex is to be understood in terms of the fact that Zn^{II} readily assumes the required tetrahedral co-ordination geometry, where it has suitable Zn–N bond lengths of approximately 2.0 Å. In contrast, Cd^{II}, which readily forms tetrahedral complexes,[24] is shown in Fig. 5 to have M–N bond lengths that are rather too long to yield a low energy ch,ch,ch,ch $+ - + -$ conformer, and instead the ch,ch,ch,ch $+ + + +$ conformer

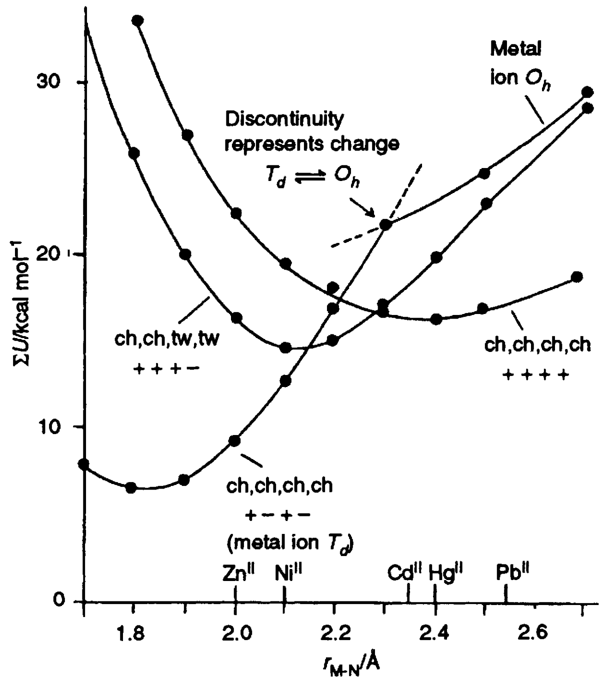


Fig. 5 A scan[5] of the strain energy of different conformers of $[M([16]aneN_4)]^{2+}$ as a function of initial strain-free M–N bond length. The geometry of the metal ion was optimized as well as the structure of the ligand. At short M–N bond lengths the $+ - + -$ conformer favours the small tetrahedral Zn^{II} ion. At longer bond lengths the $+ + + +$ conformer has a best-fit cavity corresponding to a M–N bond length of 2.4 Å. The discontinuity for the $+ - + -$ conformers at 2.3 Å corresponds to a change from tetrahedral to *cis*-octahedral co-ordination. At intermediate M–N bond lengths square-planar co-ordination of the metal ion in the $+ + - -$ conformer, with various twist-boat forms of chelate rings present, is favoured

Table 3 Selected bond lengths (Å) and angles (°) for $[Zn([16]aneN_4)]$-$[ClO_4]_2$

Zn–N(1)	2.03(1)	Zn–N(2)	2.01(1)	Zn–N(3)	1.97(1)
Zn–N(4)	1.98(1)	N(2)–C(3)	1.46(2)	N(1)–C(1)	1.44(2)
C(1)–C(2)	1.56(2)	C(2)–C(3)	1.51(2)	Cl(1)–O(2)	1.45(1)
Cl(2)–O(5)	1.30(1)	Cl(2)–O(8)	1.40(1)	Cl(2)–O(6)	1.34(2)

N(1)–Zn–N(2)	102.4(5)	N(1)–Zn–N(3)	123.4(4)
N(1)–Zn–N(4)	101.9(5)	N(2)–Zn–N(3)	102.6(5)
N(2)–Zn–N(4)	122.8(5)	N(3)–Zn–N(4)	105.4(5)
Zn–N(1)–C(1)	111.5(9)	Zn–N(1)–C(12)	113.9(5)
Zn–N(2)–C(3)	114.8(9)	Zn–N(2)–C(4)	111.6(9)
N(1)–C(1)–C(2)	111.5(13)	C(1)–C(2)–C(3)	120.4(13)

is of lower energy. This conformer is found for Cd^{II}, and also Hg^{II} and Pb^{II},[11] which all have M–N bond lengths in the appropriate range.

The discontinuity in the strain energy *versus* bond length curve seen for the ch,ch,ch,ch $+ - + -$ conformation in Fig. 5 represents a change in geometry from the metal ion being approximately tetrahedral to having the nitrogens of the $[16]aneN_4$ ligand co-ordinated to the metal ion in a *cis*-octahedral fashion. This conformation is unlikely to be observed, since it is higher in energy than the ch,ch,ch,ch $+ + + +$ conformation, which also allows for octahedral co-ordination. However, co-ordination of a bidentate ligand to the metal ion, such as oxalate or ethylenediamine, would stabilize the *cis*-octahedral arrangement of the ch,ch,ch,ch $+ - + -$ conformer of the $[16]aneN_4$ complex at longer M–N bond lengths.

The complexes of $[16]aneN_4$ which have chelate rings with the twist conformation, such as the ch,ch,tw,tw $+ + + -$ conformer found[10] in the complex of Ni^{II}, occupy the range of intermediate bond lengths 2.15–2.3 Å. The Ni^{II} complex adopts this conformation, even though high-spin Ni^{II} has an ideal M–N bond length of 2.1 Å, a little below the range which Fig. 5 indicates should be in the region of stability for this complex. This is because Ni^{II} is the most reluctant of the divalent ions of the first-row transition metals to adopt a tetrahedral co-ordination geometry.[24] It was found that several conformations of the [16]aneN$_4$ complex containing both chair and twist rings were of similar energy, and these often switched from one to another during the course of dynamics runs on the complexes. The similarity in energy of these conformations probably accounts for the disorder found in the structures of the Ni^{II} and Cr^{III} complexes, where both twist and chair chelate rings are present. To keep Fig. 5 reasonably simple, a curve for only the ch,ch,tw,tw + + + − conformation observed in the Ni^{II} complex was calculated, but it should be borne in mind that other conformations with twist conformation chelate rings should be stable in this intermediate range.

The Cu^{II} ion, like tetrahedral Zn^{II}, has an ideal M–N bond length[5] of about 2.0 Å, and so Cu^{II} is of the right length to adopt the ch,ch,ch,ch + − + − conformation. However, Cu^{II} is more reluctant than Zn^{II} to adopt a tetrahedral co-ordination geometry, so that it will be interesting to see whether the [16]aneN$_4$ complex of Cu^{II} has the ch,ch,ch,ch + − + − conformation, or one like the ch,ch,tw,tw + + + − found in Ni^{II}.

Fig. 5 also indicates why the complexes of most metal ions with [16]aneN$_4$ are generally of much lower thermodynamic stability[8] than those of other metal ions. One cannot strictly compare the strain energies of different complexes, but in general strain energies of complexes of tetraaza macrocycles of high stability tend to be less than 10 kcal mol^{-1}, while the strain energies of the conformers of complexes of [16]aneN$_4$ available to large metal ions are all considerably higher than that. Only the ch,ch,ch,ch + − + − conformer forms complexes of low strain energy, but in order to achieve this stability the metal ions should be small and readily form a tetrahedral complex. The log K_1 values for [16]aneN$_4$ and [12]aneN$_4$ complexes are compared below (logK_1 values from refs. 8, 25 and 26).

Metal ion	Cu^{II}	Ni^{II}	Zn^{II}	Cd^{II}	Pb^{II}
Ionic radius/Å	0.57	0.69	0.74	0.95	1.18
logK_1					
[16]aneN$_4$	21.2	13.2	13.0	12.65	9.3
[12]aneN$_4$	23.4	16.4	16.2	14.3	15.9
ΔlogK_1	−2.2	−3.2	−3.2	−1.6	−6.6

It appears that overall, smaller metal ions show smaller decreases in logK_1 in passing from [12]aneN$_4$, which forms all five-membered chelate rings, to [16]aneN$_4$, which forms all six-membered chelate rings. This is a complex situation, with changes in co-ordination number and geometry occurring in passing from the one set of complexes to the other, but in spite of this, this is much as would be expected from the rules[7] regarding chelate ring size, metal-ion size, and complex stability. A surprise is the high stability of the complex of Cd^{II} with [16]aneN$_4$. Before commencing this study, we had thought that it might show tetrahedral co-ordination geometry in solution, even if it did not do so in the solid state.[11] Fig. 5 suggests that the high stability of the Cd^{II} complex of [16]aneN$_4$ is unlikely to be due to the adoption of a tetrahedral co-ordination geometry, since Cd^{II} is too large. At this stage the most plausible explanation may simply be (Fig. 5) that Cd^{II} fits the ch,ch,ch,ch + + + + conformer best.

This work has shown how MM can be used to gain insight into the steric factors that control selectivity in macrocycles. The picture for the complexes of [16]aneN$_4$ is very similar to that for the complexes of other tetraaza macrocycles[4] such as [12]aneN$_4$ to [14]aneN$_4$. For all of these macrocycles there is a conformation of the complex that is of lower energy than the others (the + + + + in [12]aneN$_4$, the + + − − in [14]aneN$_4$, and the + − + − conformer in [16]aneN$_4$ complexes). However, size selectivity in the tetraaza macrocycles is not sharp, because other conformers of the complexes exist that are not too much higher in energy than the lowest energy conformers, and these accommodate metal ions of other sizes.

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