

Metal complexes of a tetraazacyclophane: solution and molecular modelling studies

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An alternative synthetic approach to yield the compound 2,3,5,6,8,9,11,14-octahydrobenzo[1][1,4,7,10]tetraazacyclotetradecine (bz[14]N₄) is presented. The protonation constants of bz[14]N₄ and the stability constants of its complexes with Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Pb²⁺ were determined in H₂O at 25 °C with ionic strength 0.10 mol dm⁻³ in KNO₃ and they were compared with structurally related macrocycles cyclam (1,4,8,11-tetraazacyclotetradecane) and cyclen (1,4,7,10-tetraazacyclododecane). These studies indicate that only 1 : 1 (M : L) species are formed in solution, and the ligand exhibits a high affinity for larger ions such as Cd²⁺ and Pb²⁺. The X-ray study of [bz[14]N₄H₃]³⁺ shows that an inclusion compound with a chloride counter-anion is formed through NH...Cl hydrogen bonds. Spectroscopic data in solution (electronic and NMR spectra) showed that the macrocycle adopts a planar arrangement upon metal complexation. Molecular mechanics calculations reveal that in spite of the presence of the benzene ring in the macrocyclic framework this ligand can encapsulate metal ions with different stereo-electronic sizes in square planar arrangements. Our results indicate that the presence of the benzene ring in the backbone of the bz[14]N₄ confers a coordination behaviour intermediate between that of cyclam and cyclen.

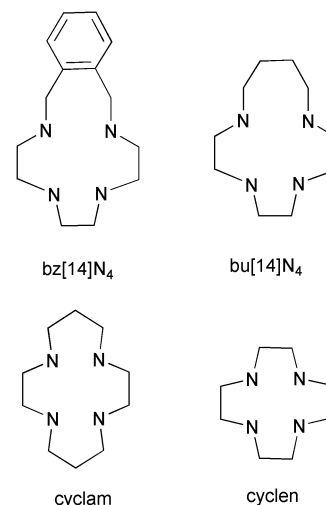
Introduction

Macrocyclic compounds have been extensively used to tune metal ion selectivity.^{1,2} The fit between the size of the cation and the cavity provided by the macrocycle is the crucial key for the design of the right hosts with the alkaline or alkaline earth metal ions, such as crown ethers, spherands or calixarenes.^{1,2} In the case of the transition metal ions, its stereo-electronic requirements must also be taken into account, and the design of specific tetraazamacrocycles for Ni²⁺ and Cu²⁺ have been undertaken.^{2,3} The 14-membered tetraazamacrocycle cyclam forms the thermodynamically and kinetically most stable complexes with copper and nickel, where the ligand is arranged in a strain-free conformation with the metal atom located in the plane defined by the four nitrogen atoms.³⁻⁵ The macrocycle adopts the *trans*-III (*RSRS*) conformation⁶ in these complexes with the two six-membered chains in chair configurations and the five-membered ones in *gauche* conformation with the hydrogen atoms of the nitrogen pointing up and down in a (+ + - -) pattern.³⁻⁶

When the macrocyclic cavity becomes smaller, as in the case of the 12-membered ligand, cyclen, the macrocycle tends to fold around the metal ion adopting a *cis* conformation.³⁻⁵ On the other hand, the increase of the ring size up to six become disadvantageous due to the enhanced ring strain and configurational energy for the arrangement of the donor atoms for the complexation.⁷

Other 14-membered tetraazamacrocycles have been studied, among them bu[14]N₄, which has the same number of atoms in the macrocyclic backbone but a different chelate ring sequence, 5,5,5,7 instead of the 5,6,5,6 of cyclam, see Scheme 1. It was verified that in spite of a decrease in the enthalpy of formation of the Cu²⁺ and Ni²⁺ complexes of the 5,5,5,7 arrangement when compared with that of the 5,6,5,6 ligand, an entropic gain was observed when compared with the linear ligand, triethylenetetraamine), reflecting an effective configurational entropy gain of the macrocyclic compound on complexation.⁸

The flexibility and the adopted conformation of cyclam, and other macrocycles, in complexation may be completely



Scheme 1

modified by incorporation of substituents at the amines or on the carbon backbone or by reinforcing the framework with rings or multiple bonds.⁹⁻¹² Knowing that an increase of the rigidity of the macrocycle usually leads to an increase of the selectivity we synthesized a tetraazacyclophane compound, bz[14]N₄ (2,3,5,6,8,9,11,14-octahydrobenzo[1][1,4,7,10]tetraazacyclotetradecine). In the present study we compare the properties of this ligand and its complexes with some divalent transition and post-transition metal ions with the behaviour of other tetraazamacrocycles, namely cyclam and cyclen.

Results and discussion

Synthesis of macrocycles

The protected compound, bz[14]N₄·(ts)₄, was synthesized by the Richman and Atkins method,¹³ through the condensation of *N,N',N'',N*-tetrakis-*p*-toluenesulfonyl-*N,N'*-bis(2-amino-

Table 1 Protonation ($\lg K_i^H$) constants of bz[14]N₄, cyclam, bu[14]N₄, and cyclen, and stability constants ($\lg K_{M,H,L}$) of their complexes with several divalent metal ions. $T = 25.0\text{ }^\circ\text{C}$; $I = 0.10\text{ mol dm}^{-3}$ in KNO₃

Ion	Equilibrium quotient	Bz[14]N ₄ ^a	Cyclam	Bu[14]N ₄	Cyclen
H ⁺	[HL]/[L] × [H]	9.87(3)	11.58, ^b 11.3 ^c	10.98, ^d 10.92 ^e	10.97 ^f
	[H ₂ L]/[HL] × [H]	8.99(3)	10.62, ^b 10.23 ^c	9.75, ^d 9.40 ^e	9.87 ^f
	[H ₃ L]/[H ₂ L] × [H]	3.38(5)	1.61, ^b 1.43 ^c	4.86, ^d 4.62 ^e	1.6 ^g
	[H ₄ L]/[H ₃ L] × [H]	< 2	2.42, ^b 2.27 ^c	2.00 ^e	0.8 ^g
	[H ₄ L]/[L] × [H] ⁴	< 24.24	26.23, ^b 25.23 ^c	27.59, ^d 26.94 ^e	23.24 ^{f,g}
Ni ²⁺	[ML]/[M] × [L]	14.64(5)	22.2, ^h 20.1 ⁱ	14.81, ^d 15.47 ^e	16.4 ^j
	[MHL]/[ML] × [H]	5.29(3)	—, 2.3 ⁱ	3.8 ^e	—
Cu ²⁺	[ML]/[M] × [L]	19.50(2)	26.5, ^c 27.2 ^k	22.36 ^d	23.29, ^c 24.8 ^k
	[MHL]/[ML] × [H]	2.85(3)	—	3.08 ^d	—
	[ML]/[MLOH] × [H]	6.24(9)	—	—	—
Zn ²⁺	[ML]/[M] × [L]	12.13(5)	15.5 ^l	12.90 ^e	16.2 ^l
	[ML]/[MLOH] × [H]	7.36(5)	3.99 ^m	—	5.74 ^m
Cd ²⁺	[ML]/[M] × [L]	11.42(1)	11.23 ^c	11.30 ^e	14.3 ^l
	[ML]/[MLOH] × [H]	9.55(3)	—	—	—
Pb ²⁺	[ML]/[M] × [L]	11.33(1)	10.83 ^c	11.59 ^e	15.9 ^l
	[ML]/[MLOH] × [H]	11.02(3)	—	—	—

^a Values in parentheses are standard deviations in the last significant figures. ^b $I = 0.5\text{ mol dm}^{-3}$ KNO₃, ref. 16. ^c $I = 0.1\text{ mol dm}^{-3}$ NaNO₃, ref. 17. ^d $I = 0.5\text{ mol dm}^{-3}$ KNO₃, ref. 8. ^e $I = 0.1\text{ mol dm}^{-3}$ NaNO₃, ref. 18. ^f $I = 0.5\text{ mol dm}^{-3}$ KNO₃, ref. 19. ^g $I = 0.2\text{ mol dm}^{-3}$ NaClO₄, ref. 20. ^h $I = 0.1\text{ mol dm}^{-3}$ NaOH, ref. 21. ⁱ $I = 0.5\text{ mol dm}^{-3}$ NaCl, ref. 22. ^j $I = 0.1\text{ mol dm}^{-3}$ NaNO₃, ref. 23. ^k $I = 0.2\text{ mol dm}^{-3}$, ref. 24. ^l $I = 0.2\text{ mol dm}^{-3}$ NaClO₄, ref. 25. ^m $I = 0.2\text{ mol dm}^{-3}$, ref. 26.

ethyl)-1,2-ethanediamine (*p*-toluenesulfonyl or tosyl = ts groups) with 1,2-bis(bromomethyl)benzene at 40 °C, using K₂CO₃ as base, in dry dimethylformamide (DMF). Then the ts arms were removed by a reductive alkaline cleavage (Na/Hg) in buffered solution.¹⁴ The tosylated compound was obtained in high yield, but no satisfactory deprotection technique was found, as by-products of benzene derivatives were also obtained. The best procedure, using Na/Hg amalgam, led to 12% yield. Another approach to obtain the same macrocycle in 30% yield was described, by the reaction of 1,2-bis(bromomethyl)benzene and the bis(aminal) of ethylenetetramine (prepared by condensation of the linear tetraamine with biacetyl), followed by hydrolysis in aqueous HCl.¹⁵ Unfortunately, in our hands this procedure did not lead to better results.

Acid–base behaviour

Compound bz[14]N₄ has four basic centres, but only three protonation constants have been determined, see Table 1. As usual for tetraazamacrocycles of similar size,³ bz[14]N₄ presents two high and two small values of protonation constants. The first two occur in opposite positions, the values being of the order of those found for linear amines. The third protonation constant is very sensitive to the size of the macrocycle, the longer the chain between two adjacent amine centres the more basic is the third amine, due to the weaker electrostatic repulsion between positive charges of the existing ammonium centre and the one to be formed by protonation. Therefore, cyclam has a lower K_3 value^{16,17} while bu[14]N₄ presents a higher one.^{8,18} The comparison with bu[14]N₄ emphasises the enhancement of rigidity of bz[14]N₄ due to the presence of the aromatic ring, which causes the contiguous amines to approach, thus increasing the repulsion between charged nitrogen atoms and so leading to a more acidic third amine. The sequence of protonation of our ligand is then straightforward: the first two equivalents of acid added to the completely deprotonated macrocycle will protonate two amine centres in opposite positions, the third one will protonate the other amine contiguous to the benzene ring, and the last one will protonate the centre which is separated from the others already protonated by the ethane chain. Therefore the benzene ring causes mainly a strain effect then an electronic one, as is expected due to the CH₂ bridging the aromatic and the amine centre.

On the other hand, the first two protonation constants of bz[14]N₄ are lower than the corresponding values for all the other tetraazamacrocycles collected in Table 1.^{16–20} The higher

values of the first two constants of these ligands are ascribed to the presence of hydrogen bonding of the type ⁺N–H ⋯ N, which stabilizes the protonated form.³ This would imply that the hydrogen bonds in the case of bz[14]N₄ could not be formed or would be weaker. The X-ray structure of [bz[14]N₄H₃]³⁺ · 3Cl[−] clearly reveals that hydrogen bonds exist and are strong, however their formation is facilitated by the presence of the chlorine bridge between two adjacent nitrogen atoms (see below).

Crystal structure of bz[14]N₄

The X-ray study of bz[14]N₄ shows that its crystal structure is built up from an asymmetric unit composed of one [bz[14]N₄H₃]³⁺, three chloride anions and two water molecules leading to the molecular formula (bz[14]N₄H₃)Cl₃ · 3H₂O. The charge balance of the molecular formula of bz[14]N₄ requires the protonation of three nitrogen donor atoms, in agreement with the pH of the solution in which the crystals were grown. An ORTEP diagram of [bz[14]N₄H₃]³⁺ with the labeling scheme adopted and showing the three protonation sites is presented in Fig. 1a while Fig. 1b illustrates the adopted conformation.

In the crystal structure, as would be expected, the water molecules and the chloride anions are involved in hydrogen bonding interactions with nitrogen donor atoms of bz[14]N₄. Distances and angles of all intra and intermolecular hydrogen bonding interactions found are given in Table 2. The [bz[14]N₄H₃]³⁺ interacts with a chloride counter-anion through NH ⋯ Cl hydrogen bonds forming an inclusion compound. This Cl(1) is out of the macrocyclic cavity and makes three intermolecular hydrogen bonds with protonated nitrogen leading to NH ⋯ Cl distances of 2.24, 2.39 and 2.33 Å. The protonated nitrogen atoms N(11) and N(17), *trans* to each other, are also involved in intramolecular interactions with the non-protonated nitrogen N(14) *via* NH ⋯ N hydrogen bonds of 2.41 and 2.51 Å. The inclusion compounds are aggregated in the crystal structure by an extensive 2D network of hydrogen bonds comprising OH ⋯ Cl, NH ⋯ Cl and OH ⋯ N interactions. Furthermore a CH₂ group of bz[14]N₄ interacts with two independent chloride anions *via* short charge assisted C–H^{δ+} ⋯ Cl^{δ−} intermolecular contacts of 2.79 and 2.78 Å, and C–H ⋯ Cl angles of 168 and 150°. An intermolecular interaction between another CH₂ group and a water molecule also occurs *via* a short C–H^{δ+} ⋯ O^{δ−} hydrogen bond of 2.32 Å and a C–H ⋯ O angle of 157°.

Table 2 Molecular dimensions of the hydrogen bonds

	H ... A/Å ^a	D ... A/Å ^a	D-H ... A/°
<i>Intramolecular</i>			
N(11)–H(11A) ... N(14)	2.41	2.819(7)	108
N(17)–H(17A) ... N(14)	2.51	2.892(7)	106
<i>Intermolecular</i>			
N(8)–H(8A) ... Cl(3)	2.22	3.082(6)	160
N(8)–H(8B) ... Cl(1)	2.24	3.128(6)	171
N(11)–H(11A) ... Cl(1)	2.39	3.234(5)	156
N(11)–H(11B) ... O(100)	1.84	2.735(7)	174
N(17)–H(17A) ... Cl(1)	2.33	3.185(5)	159
N(17)–H(17B) ... Cl(2)	2.24	3.116(5)	166
O(100)–H(101) ... Cl(3)	2.35(5)	3.147(6)	166(5)
O(100)–H(102) ... Cl(2)	2.43(6)	3.149(6)	147(6)
O(200)–H(201) ... Cl(2)	2.41(4)	3.223(7)	170(7)
O(200)–H(202) ... Cl(3)	2.38(6)	3.182(6)	167(6)
C(7)–H(7A) ... Cl(3)	2.66	3.593(7)	163
C(10)–H(10A) ... Cl(1)	2.79	3.748(7)	168
C(10)–H(10B) ... Cl(2)	2.78	3.660(7)	150
C(12)–H(12B) ... O(200)	2.32	3.232(8)	157

^a A and D denote the acceptors and donors of hydrogen atoms, respectively.

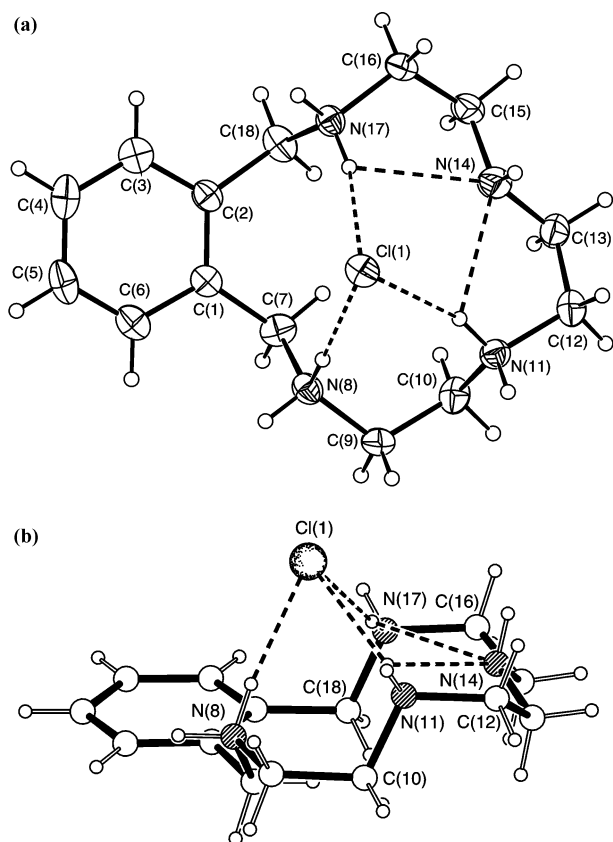


Fig. 1 Two perspective views showing the inclusion compound formed by [bz[14]N₄H₃]³⁺ and Cl[−] via hydrogen bonds: (a) ORTEP diagram with the ellipsoids drawn at 30% of probability level showing the labelling scheme adopted; (b) molecular diagram showing the position of chlorine relatively to the macrocycle and the ladder type conformation adopted.

The conformation found in the solid state for the macrocycle is of the ladder type, Fig. 1b, with the plane of benzene ring intercepting the planes [N(11),N(17),C(10),C(18)] and [N(11),C(12),C(16),N(17)] at dihedral angles of 63.9(2) and 12.5(3)°, respectively. These latter two planes make a dihedral angle of 65.7(2)°. The hydrogen bonds described contribute for the stabilization of the conformation adopted by bz[14]N₄ in the solid state. In fact this conformation is markedly different of the lowest energy conformation found in gas phase for this ligand, see below.

Table 3 pM values calculated^a at pH = 7.0 of aqueous 1 : 1 solutions of ligands and metal ions C_M = C_L = 1.0 × 10^{−2} mol dm^{−3}, T = 25.0 °C

Ion	Bz[14]N ₄	Cyclam ^b	Bu[14]N ₄	Cyclen
Ni ²⁺	5.81	7.99, 6.94	5.04, ^c 5.57 ^d	5.78
Cu ²⁺	9.11	10.19, 10.54	8.86 ^c	9.27, 10.02
Zn ²⁺	4.71	4.65	4.29 ^d	5.68
Cd ²⁺	4.28	2.57	3.49 ^d	4.73
Pb ²⁺	4.23	2.42	3.64 ^d	5.53

^a Values calculated using the Hyss program²⁷ and the values of Table 1.

^b Using the protonation values of ref. 16. ^c Using values of ref. 8.

^d Using values of ref. 18.

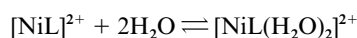
Metal complex studies

The stability constants of bz[14]N₄ with Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ were determined in water by potentiometric technique at 25 °C and 0.1 M ionic strength in KNO₃. The values are collected also in Table 1 together with the values for complexes of the same metal ions with other 14-membered macrocycles^{8,17,18,21,22,24–26} and also cyclen.^{17,23–26} Only 1 : 1 complexes were found. In certain cases protonated MHL species or hydroxocomplexes of the type ML(OH) were also obtained. The Cu²⁺ complex exhibits the highest thermodynamic stability and a remarkable peak of selectivity was observed in the studied series as the values of stability constant for the Ni²⁺ and Zn²⁺ complexes fall sharply by 5 and 7 lg units, respectively.

The direct comparison of thermodynamic stability constants of complexes with ligands of different basicities (as those listed in Table 1) is not appropriate, as the different proton competition for the ligands is not taking into account. The pM values (−lg [M]), determined at a given pH,²⁷ are the right values for the correct comparison, as the higher the pM the stronger the affinity for the ligand is. In Table 3 are collected the determined pM values for the studied complexes, which indicate that: (1) all the tetraaza macrocycles present higher pM values for Ni²⁺ and Cu²⁺ complexes in aqueous solutions, as expected for amine ligands, cyclam presenting the highest values for both metal complexes due to the strain-free conformation adopted by the ligand in these complexes, and cyclen the largest difference between Ni²⁺ and Cu²⁺ complexes; (2) the pM values decrease sharply for the Zn²⁺ complexes, the fall being more significant for cyclam and bu[14]N₄ complexes, and of comparable magnitude for cyclen and bz[14]N₄; (3) the metal ions of larger radii, which are simultaneously those which impose less geometric and electronic requirements on complex-

ation, Cd^{2+} and Pb^{2+} , present the lowest pM values with cyclam, and the highest ones with cyclen and bz[14] N_4 . It is interesting to emphasize that both ligands have the most rigid backbones of the series, cyclen due to its small cavity size and bz[14] N_4 due to the presence of the benzene ring. The above remarks confer to bz[14] N_4 the interesting place of intermediate metal complexing behaviour between cyclen and cyclam.

Spectroscopic studies. At room temperature the aqueous solution of the Ni^{2+} complex with bz[14] N_4 is pale green and exhibits a UV-vis-near IR spectrum typical of a mixture of high spin diaquo pseudo-octahedral (paramagnetic) and low spin square planar (diamagnetic) geometries, as happens with many other tetraazamacrocycles or linear amines:^{3,28,29}



This equilibrium is dependent upon the temperature and ionic strength. In the case of $[\text{Ni}(\text{bz}[14]\text{N}_4)]^{2+}/[\text{Ni}(\text{bz}[14]\text{N}_4)(\text{H}_2\text{O})_2]^{2+}$ the increase of the temperature increases the intensity of the band at 442 nm corresponding to the low spin species (the yellow form) and decreases the bands of the octahedral species (933, 570, 362 nm), the blue one. At 60 °C the interconversion is practically complete. As known, the visible spectrum of the yellow form exhibits a single absorption band, which envelops three d-d transitions. The energy of all these transitions is dependent of the value of the in-plane Dq . Therefore the band energy of the low spin Ni^{2+} complex, $\nu(\text{d-d})$, should reflect the Dq^{xy} value, and has been used as an empirical parameter to express the measure of the in-plane metal-donor interaction,²⁸ which is: 430 nm (23260 cm^{-1}) for cyclen,²⁹ 445 (22470) for cyclam,^{8,29} 463 (21600) for bu[14] N_4 ,⁸ and 442 nm (22624 cm^{-1}) for bz[14] N_4 . Since the Ni-N bond distances in a paramagnetic Ni^{2+} complex should be longer than those in the corresponding diamagnetic complex, macrocycles of larger cavity sizes are likely to facilitate the formation of paramagnetic complexes. This is confirmed by the high value of the in-plane Dq of the nickel complex of bz[14] N_4 , which is comparable of that of the cyclam complex.

The Cu^{2+} complex of bz[14] N_4 exhibits a broad band in the visible region at 570 nm with one shoulder at lower energies, due to the copper d-d transitions and an intense band in the UV region. The EPR spectrum of the complex was recorded at pH 7.0 in a DMSO : H_2O (1 : 1) solution at low temperature, showing the presence of only one species, see Fig. 2. Very broad bands are observed in water as a result of aggregation of the molecules, an effect that was not observed for the cyclam complex under identical experimental conditions, indicating possible π - π interaction between benzene rings of neighbouring $[\text{Cu}(\text{bz}[14]\text{N}_4)]^{2+}$ molecules. The spectrum shows three well resolved lines of the four expected at low field, due to the interaction of the unpaired electron spin with the copper nucleus, and no superhyperfine splitting due to the coupling with the nitrogen atoms of the macrocycle has been observed. The fourth copper line is overlapped by the strong band of the high field part of the spectrum but appears as a resolved band. The simulation of the spectrum³⁰ indicated three different values of g , revealing that the copper atom in this complex is in a rhombically-distorted ligand field. In Table 4 are compiled the hyperfine coupling constants (A) and g values, which are characteristic of rhombic symmetry with elongation of the axial bonds and $d_{x^2-y^2}$ ground state.³¹

The EPR spectra and the parameters (see Table 4) of the Cu^{2+} complexes with bz[14] N_4 and cyclam³² are very similar. In the copper complex of cyclam the macrocycle adopts a square planar arrangement around the metal centre in the crystal as well as in solution.^{4,5,33,34} On the other hand, it is also well established that according to the ligand field theory, the g values increase and the A_z value decreases as the planar ligand field becomes weaker, or as the axial ligand field becomes stronger

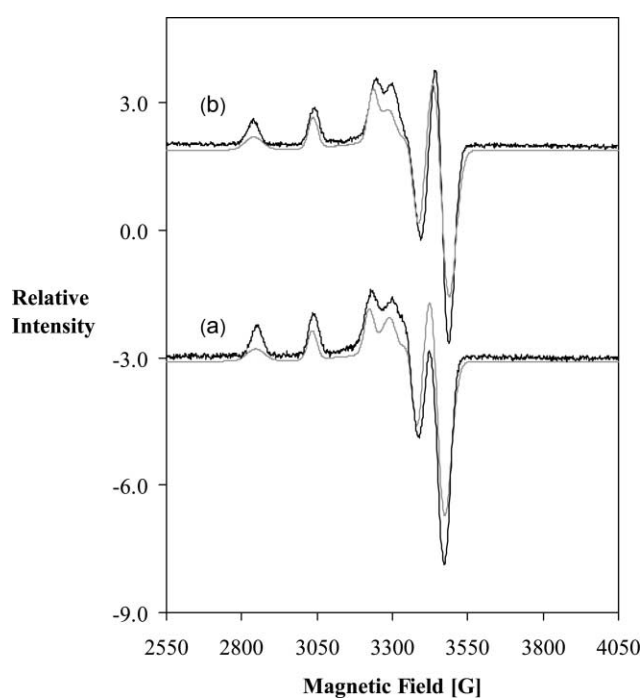


Fig. 2 EPR X-band spectra of the Cu^{2+} complexes of bz[14] N_4 (a) and cyclam (b) prepared in a 1 : 1 mixture of DMSO and the aqueous solution of copper complex $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ in 1.0 mol dm^{-3} NaClO_4 at pH = 7.0 and were recorded at 9.8 K, microwave power of 2.4 mW, modulation amplitude of 1.0 mT. The frequency (ν) was of 9.643 GHz in both cases.

and this occurs with the simultaneous red-shift of the d-d absorption bands in the electronic spectrum.^{35,36} Therefore, a comparison of the electronic spectra of the copper complexes of bz[14] N_4 and of cyclam suggests that the $[\text{Cu}(\text{bz}[14]\text{N}_4)]^{2+}$ complex either adopts a square planar geometry around the copper with a weaker equatorial ligand field than cyclam or a square pyramidal geometry with a weak axial interaction, in agreement with the determined thermodynamics stability constants of both complexes discussed before. For the same reasons the EPR parameters of the complex with cyclen³² are compatible with a square-pyramidal arrangement around the copper atom as determined by crystal X-ray diffraction³⁷ and in solution.³⁸

^1H NMR Cd^{2+} complex with bz[14] N_4 . The ^1H NMR spectrum of the diamagnetic cadmium complex at pD = 7.40 is shown in Fig. 3 together with the spectrum of the ligand at the same pD. All the resonances of the complex shift upfield, evidenced that all the donor atoms are involved on the coordination to the metal centre. All the geminal protons show chemical and magnetic equivalence, except the bz CH_2 geminal protons which form an AB spin system exhibiting two doublets at 4.12 and 3.77 ppm. The pattern of the spectrum is not compatible with a *cis* conformation where the macrocycle adopts a folded arrangement. The non-magnetic equivalence of the bz CH_2 geminal protons indicates that there is no symmetry plane passing through the prochiral carbons, and the magnetic equivalence observed for the other geminal protons can only be explained considering a dynamic process between the two energetically more favourable planar conformations ($++++$ and $+-+-$, see below). This process does not affect the bz CH_2 geminal protons due to the rigidity imposed by the benzo group. Then, the spectrum is consistent with a species where the macrocycle adopts a planar conformation. No coupling with $^{111/113}\text{Cd}$ has been observed.

Molecular modelling

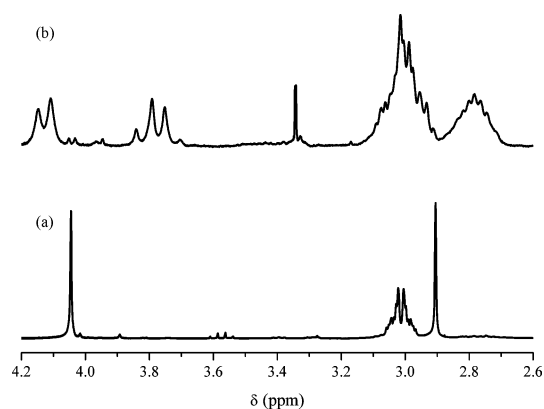
In order to ascertain the structural preferences and coordination behaviour of bz[14] N_4 relative to metal ions, molecular

Table 4 Spectroscopic vis and EPR data for the Cu²⁺ complexes of bz[14]N₄, cyclam and cyclen

Copper(II) complex	Visible band/nm ($\epsilon_{\text{molar}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	EPR parameters ($A/10^4 \text{ cm}^{-1}$)							
		g_x	g_{\perp}	g_y	g_z	A_x	A_{\perp}	A_y	A_z
[Cu([bz[14]N ₄])(ClO ₄) ₂] ^a	550 (150)	2.040	—	2.051	2.198	25.4	—	26.5	194.0
[Cu(cyclam)](ClO ₄) ₂ ^a	510 (125)	—	2.043	—	2.193	—	21.7	—	203.1
[Cu(cyclam)](Cl) ₂ ^b	513 (100)	—	2.049	—	2.186	—	38.7	—	205.0
[Cu(cyclen)(Cl)] ^{+b}	599 (220)	—	2.057	—	2.198	—	24.1	—	184.2

^a This work. ^b Ref. 32.**Table 5** Low energy conformations of bz[14]N₄ in gas phase

Conformer	Energy/ Kcal mol ⁻¹	Torsion angle ^{a/o}													
(a) ++ + -	65.49	1.9	-102.5	-168.3	-72.9	88.1	-173.7	90.0	70.8	179.2	68.2	53.8	-156.5	-179.8	-69.3
(b) + + + +	67.01	0.5	-123.1	-152.6	-66.2	-58.7	168.9	-79.3	-55.6	167.4	-165.9	65.4	88.6	-177.4	67.5
(c) + - + -	67.63	0.4	-102.8	-164.0	-67.3	91.4	-175.1	115.4	-64.8	176.6	-162.6	70.4	-136.4	175.4	-69.2
(d) + - + +	67.66	2.0	-103.2	-173.5	-160.9	80.8	-120.6	167.4	-84.8	89.9	-163.4	63.2	159.6	-177.7	56.6
(e) + + - -	68.15	-0.6	-80.4	166.6	-90.8	167.8	-88.6	-65.9	104.1	-162.2	95.6	62.8	-157.9	176.9	-67.2
(f) + - - +	68.98	-4.6	97.5	162.2	156.5	-87.7	143.5	-87.8	-60.6	-178.7	-125.9	69.2	-173.4	-174.0	-66.3

^a The endocyclic torsion angles are listed successively in clockwise direction starting at the torsion angle centred at the C–C aromatic bond.**Fig. 3** The upfield part of the ¹H NMR spectra of (a) bz[14]N₄ and (b) Cd²⁺ complex of bz[14]N₄ in D₂O at pH = 7.4 and 300 K, recorded using a 300 MHz spectrometer. In the downfield part of the spectra appears one resonance corresponding to the benzene protons at 7.42 (s) ppm for the free ligand and at 7.42–7.43 (m) ppm for the cadmium complex. The resonance at 3.33 ppm in (b) should be an impurity.

modelling studies comprising the conformational analysis of free ligand and molecular mechanics (MM) calculations on the [ML]ⁿ⁺ species were undertaken.

The conformational analysis on the free ligand was carried out *via* molecular dynamics using the universal force field,³⁹ within Cerius2 software, version 3.5.⁴⁰ The molecular structure of [bz[14]N₄H₃]³⁺ has retrieved from the crystal structure, and NH protons are removed and the structure was minimised by MM in order to create the starting model for the dynamics simulation. Atomic charges were calculated with the charge equilibration method implemented in Cerius2.⁴⁰ The optimised structure was heated at 3000 K with a step size of 1.0 fs for 500 ps. One thousand conformations were saved at 0.5 ps intervals and subsequently minimised through MM leading to a wider energy range between 65.5 and 94.5 kcal mol⁻¹, which indicates that the macrocycle is apparently flexible in the gas phase.

The conformations adopted by bz[14]N₄ are fully characterised using the fourteen endocyclic torsion angles of the macrocyclic framework. Alternatively, in a basic way the conformations can be described in terms of the positions of NH hydrogen atoms below (–) or above (+) the macrocyclic plane defined by the four nitrogen donor atoms. This nomenclature is particularly useful for metal complexes and it has been

used extensively in the structural studies involving tetraaza macrocycles.^{41,42}

All possible combinations of + and – signs, starting at one of the nitrogen atoms adjacent to the benzene ring, give rise to six unique conformers: + + + +, + + – –, + – + +, + + + –, + – + – and + – – +. When the bz[14]N₄ is coordinated the four nitrogen atoms become chiral and these conformations can then be described using the *RS* nomenclature: *SSSS* (+ + + +), *SSRR* (+ + – –), *SRSS* (+ – + +), *RRRS* (+ + + –), *SRSR* (+ – + –) and *RSSR* (+ – – +). The endocyclic torsion angles of the unique conformations found with lowest energies in the conformational analysis of bz[14]N₄ are given in Table 5 while their structures are presented in Fig. 4. There are other structures, not included in the Table 5, with higher energies and different endocyclic torsion angles, in which the four NH groups assume one of the six possible combinations of signs. The highest energy conformations of the macrocycle are unlikely to be found in the metal complex. By contrast the remaining ones, including those with slightly higher energies than those quoted in Table 5, converge to the same structure when one metal centre with a restrained coordination environment is added to the macrocycle and the structure subsequently minimised by MM calculations (see below). The + + + – conformer is the lowest energy structure listed in Table 5, while in the crystal structure the macrocycle in [bz[14]N₄H₃]³⁺ adopts a + + + + conformation. The MM minimization of bz[14]N₄ taken from the crystal structure leads to a different + + + + conformation with an energy of 73.2 kcal mol⁻¹. This result is understandable since in the solid state, as mentioned above, the macrocyclic conformation is stabilised by a complex system of hydrogen bonds.

In spite of our best efforts it was impossible to obtain suitable crystals of metal complexes for X-ray diffraction studies. Therefore, MM calculations were performed in order to find the structural preferences of bz[14]N₄ in four-coordinate environments. Six starting models corresponding to the six possible conformations for [ML]ⁿ⁺ species were constructed from the lowest conformations + + + +, + + – –, + – + +, + + + –, + – + – and + – – + given in Table 5, by addition of a square planar nickel centre. The steric energy profiles for bz[14]N₄ were calculated using our published method.^{41,42} The M–N distances were fixed at specific values (by including a large force constant for the M–N bond-stretch term), and the remainder of the structure was minimised to the lowest possible energy, pro-

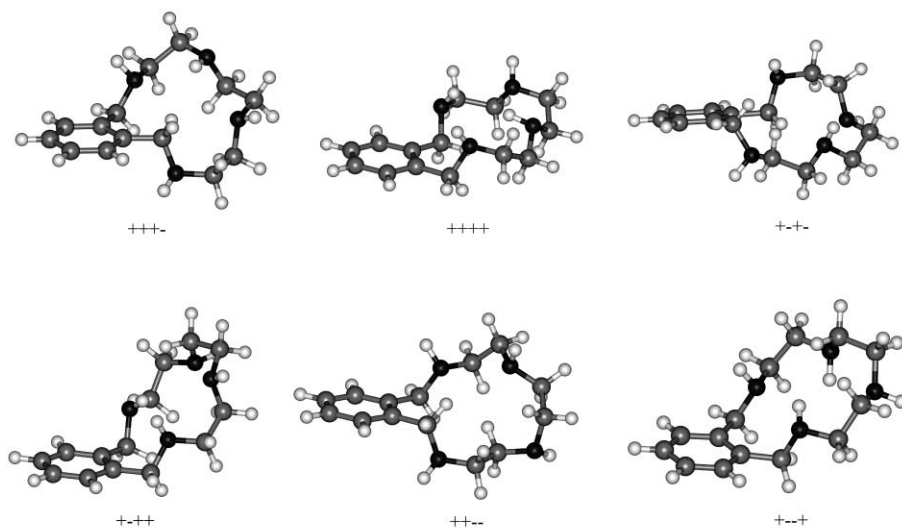


Fig. 4 Sketches of the low energy conformations for bz[14]N₄.

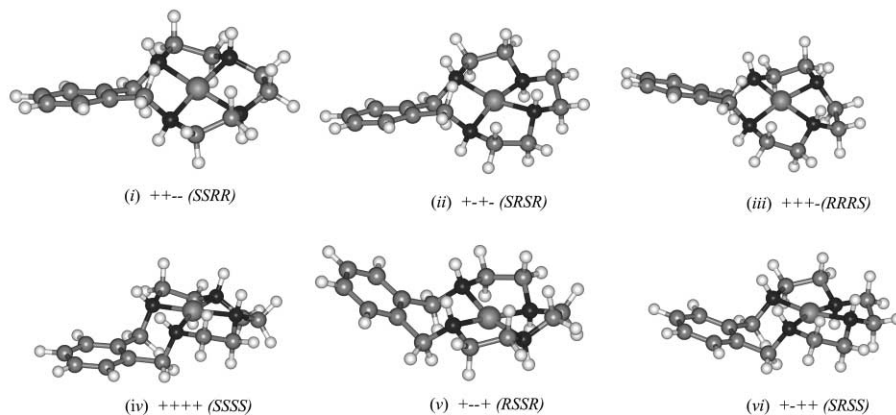
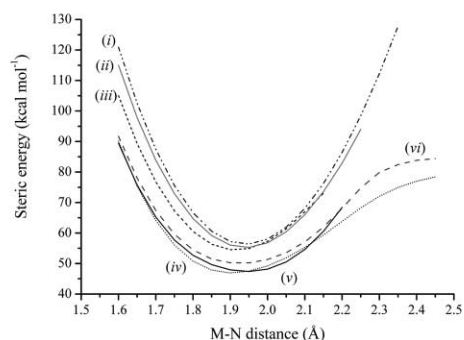


Fig. 5 Plot of the steric energy versus the M–L distance for the [ML]ⁿ⁺ species and the sketches of the six relevant conformations.

viding a plot of energy versus M–N distance. The resulting energy represents the steric strain in the macrocycle when complexing a particular metal centre in a specific coordination environment. This method is often used for the calculation of the macrocycle hole sizes.⁴³ Plots for all six possible conformations together with their sketches are shown in Fig. 5. The bending terms of the angles centred at the metal were described using a cosine periodic written as follows:

$$E_{\theta} = C(1 - B(-1)^n \cos[n\theta])$$

with B , C and n equal to 1, 100 kcal mol⁻¹ rad⁻² and 4 respectively.

This function allows that these angles take more than one ideal value, e.g. 90, 180 or 270°. Thus, it is possible to determine the M–N distance at which the macrocycle folds, losing the planar conformation. This happens with conformations

+-+-+ and +-+- at longer distances e.g. 2.15 and 2.25 Å, respectively. All conformations show broad energy profiles suggesting that bz[14]N₄, in spite of the presence of one aromatic ring in the macrocyclic framework, has enough flexibility to accommodate metal ions with different ionic sizes. The conformations ++++ and +-+- are the most stable forms at distances less than 2.20 Å, at which distance the +-+- conformer has equal energy to the ++++ conformation. Furthermore, the first two conformations show similar energy curves with the ++++ conformer having lower energy for M–N distances between 1.7 and 1.95 Å, and the +-+- conformer between 1.95 and 2.15 Å. Above 2.15 Å the ++++ conformer becomes the preferred one. Thus, this conformation is particularly suitable to accommodate large ions at M–N distances above 2.05 Å the metal centre can lie above the N₄ coordination plane in the direction of the four NH groups. By contrast, up to M–N distances of 1.95 Å the metal ion is in the square planar cavity provided by the macrocycle.

Unfortunately, there are no X-ray structures available for metal complexes of bz[14]N₄ to support the structural trends found. Indeed from the CSD⁴⁴ we retrieved only three structures of complexes of a 14-membered macrocycle having the same framework pattern, namely bu[14]N₄: [Ni(bu[14]N₄)Cl₂] (Refcode BOZZIZ), [Cu(bu[14]N₄)(ClO₄)₂] (Refcode CIFDEA) and [Ni(bu[14]N₄)(NCS)₂] (Refcode BINSEW). The first two complexes have a *trans*-octahedral geometry with the macrocycle adopting a *+-+-* planar conformation with average distances Ni–N of 2.068(3) Å and Cu–N of 1.95(3) Å, while the third one displays a *cis*-octahedral coordination environment with the macrocycle exhibiting a folded *++++* conformation with a mean Ni–N distance of 2.122(5) Å. The macrocycles bz[14]N₄ and bu[14]N₄ have different steric demands and their conformations cannot be compared directly. Finally, in the case of the copper(II) complex of bz[14]N₄ the EPR spectrum is consistent with a distorted square planar geometry with the four nitrogen atoms bonded to the metal centre. In addition our MM calculations suggest that the *++++* or *+-+-* conformations can be adopted by the copper and nickel complexes.

Conclusions

Our studies showed that the compound bz[14]N₄ forms complexes thermodynamically slightly less stable with Ni²⁺ and Cu²⁺ than those of cyclam. However, bz[14]N₄ is a better complexing agent than cyclam for larger metal ions, such as Cd²⁺ and Pb²⁺, presenting a behaviour comparable to that of cyclen. This macrocycle has a small cavity size and the metal centres are accommodated above the N₄ coordination plane in strongly distorted square pyramidal geometries. Otherwise, the encapsulation with a coordination number of five or higher requires the folding of the macrocycle.^{45,44}

Our MM calculations indicate that the *++++* or *+-+-* conformations should be adopted by [M(bz[14]N₄)]^{m+} species. On the other hand, MM calculations performed for the complexes of cyclam using the same force field, in the same theoretical conditions,⁴¹ showed that the *++++* (*RRRR*) conformation exhibits the lower strain energy till 2.00 Å followed by the *+-+-* (*RSRS*) conformation up to M–N distances of 2.35 Å. Above this distance the *++++* conformation definitively becomes the preferred one.

Therefore, this set of results suggest that the presence of the benzene ring in the backbone of the bz[14]N₄ affords a ligand with a steric flexibility which arise to a coordination behaviour intermediate between cyclam and cyclen.

Experimental

Microanalyses were carried out by the ITQB Microanalytical Service. IR spectra were recorded from KBr pellets on a UNICAM Mattson 7000 spectrometer.

Reagents

1,2-bis(bromomethyl)benzene and *N,N'*-bis(2-aminoethyl)-1,2-ethanediamine were obtained from Aldrich. All the chemicals were of reagent grade and used as supplied without further purification. Organic solvents were purified or dried by standard methods.⁴⁵ The reference used for the ¹H NMR measurements in D₂O was 3-(trimethylsilyl)-propanoic acid-d₄-sodium salt and in CDCl₃ the solvent itself. For ¹³C NMR spectra dioxane was used as the internal reference.

Synthesis and characterization of 2,3,5,6,8,9,11,14-octahydrobenzo[1][1,4,7,10]tetra-azacyclotetradecine (bz[14]N₄)

The cyclic compound was prepared by condensation of *N,N',N'',N*-tetrakis-*p*-toluenesulfonyl-*N,N'*-bis(2-aminoethyl)-1,2-ethanediamine [*p*-toluenesulfonyl or tosyl (ts) groups] with 1,2-bis(bromomethyl)benzene at 40 °C, in dry dimethylform-

amide (DMF) as solvent and using K₂CO₃ as base. The protection of the amine centres of the linear tetraamine with tosyl groups was done as described.⁴⁶ The protected groups of the cyclic compound formed were removed by a reductive alkaline cleavage (Na/Hg) in buffered solution.

The *N,N',N'',N*-tetrakis-*p*-toluenesulfonyl-*N,N'*-bis(2-aminoethyl)-1,2-ethanediamine (12 mmol, 10.90 g) was added to a flask containing K₂CO₃ (28.9 mmol, 4.025 g) in DMF (210 cm³), under nitrogen. The suspension formed was heated at 40 °C for 1 h. The solution of the 1,2-bis(bromomethyl)benzene (14.7 mmol, 4.060 g) in DMF (130 cm³) was added slowly, dropwise, for a period of 18 h, and left more 24 h at the same temperature (40 °C). Then the solvent was evaporated to 1/10 of its volume and after filtration the pale yellow powder formed was refluxed in ethanol (140 cm³) for 2 h. The white solid formed, which was the desired pure tosylated macrocycle, was filtered off and dried at 80 °C. Yield: 11.4 mmol (95%). ¹H-NMR (CDCl₃, ppm): 7.62–7.59 (4 H, d), 7.53–7.50 (4 H, d), 7.27–7.17 (12 H, m), 4.29 (4 H, br s), 3.15 (4 H, br s), 2.88 (8 H, s), 2.34 (6 H, s), 2.33 (6 H, s). ¹³C-NMR (CDCl₃, ppm): 143.79, 143.36, 135.18, 134.31, 133.91, 129.86, 129.73, 129.51, 128.47, 127.17, 127.06, 50.50, 48.99, 48.55, 21.29.

The tosyl groups were removed under reductive alkaline cleavage as follows: a 3% Na/Hg amalgam was prepared by the reaction of Na (3.6 g) with Hg (120 g) under nitrogen. After cooling, dry methanol (48 cm³), the tetratosylated macrocycle (6.5 mmol, 5.6 g) and NaH₂PO₄ (4.706 g) were added and the mixture was rapidly stirred and heated to reflux for 12 h. After that time, another portion of NaH₂PO₄ (4.706 g) was added, followed by more 12 h of reflux. The Hg was then decanted from the slurry and washed several times. To the methanolic solution was added the water solution resulting from the washing of the Hg, the solution filtered off and concentrated almost to dryness. The resulting solid was dissolved in H₂O (150 cm³) and extracted with CHCl₃ (4 × 100 cm³). The organic layer was dried with Na₂SO₄, filtered off, and evaporated till the precipitation of the required cyclic tetraamine as a white powder. Yield: 0.78 mmol (12%). ¹H-NMR (CDCl₃, ppm): 7.23–7.15 (4 H, m), 3.71 (4 H, s), 2.76–2.72 (8 H, m), 2.26 (4 H, s). ¹³C-NMR (CDCl₃, ppm): 137.78, 129.96, 126.58, 51.47, 48.07, 47.18, 46.92.

To the cyclic amine prepared was added a solution of HCl 6 mol dm⁻³ (10 cm⁻³) for the formation of the hydrochloric compound. Mp 255 °C (decomp.). Found: C, 41.04; H, 8.06; N, 13.90. Calculated for C₁₄H₂₇Cl₃N₄·3H₂O (bz[14]N₄·3HCl·3H₂O): C, 40.83; H, 8.08; N, 13.61%. FAB MS, *m/z*: 249 ([M + H]⁺). ¹H-NMR (D₂O, ppm): 7.55–7.50 (4 H, m), 4.37 (4 H, s), 3.48–3.44 (4 H, m), 3.34–3.30 (4 H, m), 3.16 (4 H, s). IR (*v*_{max}/cm⁻¹): 3350.71–3465.37 (N–H), 2624.40–2955.75 (N–H), 2361.30 (N–H), 1653.65, 1596.57, 1449.35, 1366.18, 1068.53, 987.20, 898.41, 760.91, 597.20, 531.26, 478.6.

Potentiometric measurements. *Reagents and solutions.* Metal ion solutions were prepared at about 0.025 mol dm⁻³ from the nitrate salts of the metals, of analytical grade with demineralized water (obtained by a Millipore/Milli-Q system) and were standardised as described. Carbonate-free solutions of the titrant, KOH, were obtained, maintained and discarded as described.⁴⁷

Equipment and work conditions. The equipment used was described before.⁴⁷ The temperature was kept at 25.0 ± 0.1 °C; atmospheric CO₂ was excluded from the cell during the titration by passing purified nitrogen across the top of the experimental solution in the reaction cell. The ionic strength of the solutions was kept at 0.10 mol dm⁻³ with KNO₃.

Measurements. The [H⁺] of the solutions was determined by the measurement of the electromotive force of the cell, $E = E'^{\circ} + Q \lg [H^+] + E_j$, E'° , Q , E_j and $K_w = ([H^+][OH^-])$ were obtained as described previously.⁴⁶ The term pH is defined as $-\lg [H^+]$. The value of K_w was found equal to 10^{-13.80} mol² dm⁻⁶.

The equilibrium for the complex formation reactions was sufficiently fast to attain to work with automatic acquisition data, although the duration of each titration was 20 h in average. The same values of stability constants were obtained either using the direct or the back titration curves.

Calculation of equilibrium constants. Protonation and stability constants were calculated by the HYPERQUAD program.⁴⁸ Only mononuclear species, ML, MHL and M-HL (being $\beta_{\text{M-HL}} = \beta_{\text{MLOH}} \times K_w$) were found. Differences, in lg units, between the values β_{MHL} (or $\beta_{\text{M-HL}}$) and β_{ML} provide the stepwise protonation reaction constants, shown in Table 1. The errors quoted are the standard deviations of the overall stability constants given directly by the program for the input data that include all the experimental points of all titration curves.

Spectroscopic studies

¹H NMR spectra were recorded with a Bruker CXP-300 spectrometer at probe temperature. Electronic spectra were measured with a Shimadzu model UV-3100 spectrophotometer for UV-vis-near IR, using aqueous solutions of the complexes prepared by the addition of the metal ion (in the form of nitrate salt) to the ligand at the appropriate pH value. EPR spectroscopy measurements of the Cu²⁺ complexes were recorded with a Bruker ESP 380 spectrometer equipped with continuous-flow cryostats for liquid helium, operating in the X-band. The complexes were prepared by the 1 : 1 mixture of DMSO and the aqueous solution of copper complex 2.0×10^{-3} mol dm⁻³ in 1.0 mol dm⁻³ NaClO₄ at pH = 7.0 and were recorded at 9.8 K.

Crystallography

Suitable single crystals of (bz[14]N₄)·3HCl·2H₂O, **1**, for X-ray diffraction studies were grown from an aqueous solution kept at 0 °C over approximately one month.

C₁₄H₃₁Cl₃N₄O₂, *M_r* = 393.78, Monoclinic, space group *P*2₁/*c*, *a* = 10.264(11) Å, *b* = 16.020(17) Å, *c* = 12.105(13) Å, β = 94.14(1)°, *U* = 1985.2 Å³, *Z* = 4, ρ (calc) = 1.318 Mg m⁻³, μ (Mo-K α) = 0.475 mm⁻¹.

CCDC reference number 202378.

See <http://www.rsc.org/suppdata/dt/b3/b301033c/> for crystallographic data in CIF or other electronic format.

X-ray data were collected at room temperature on a MAR research plate system using graphite monochromatized Mo-K α radiation (λ = 0.71073 Å) at Reading University. The crystals were positioned at 70 mm from the image plate. 95 frames were taken at 2° intervals using an adequate counting time with the diffraction pattern observed. Data analysis was performed with the XDS program.⁴⁹ Intensities were not corrected for absorption effects.

6590 reflections measured were merged in the Laue symmetry 2/*m* to 3538 unique reflections with a *R*_{int} of 0.0515.

The structure was solved by direct methods and by subsequent difference Fourier syntheses using the SHELX-97 system programs.⁵⁰ The hydrogen atoms on the parent carbon and nitrogen atoms were included in calculated positions. In addition in the case of N-H groups all trial possible models comprising the protonation of three of the four nitrogen atoms were taken in account and the structure presented in Fig. 1 corresponds to the combination with slightly lower *R* values. This structure is consistent with the acid-base behaviour studies of bz[14]N₄. The hydrogen atoms of the water molecules were located from difference Fourier maps and refined with O-H distances and H-O-H angles constrained to 0.82 Å and 104.5°, respectively. Anisotropic thermal parameters were used for all non-hydrogen atoms while the thermal movement of hydrogen atoms was described using isotropic parameters equivalent 1.2 times those of the atom to which were attached. The structure was refined by full-matrix least-squares method against *F*² until convergence to be achieved leading to final

indices *R*₁ = 0.0739 and *wR*₂ = 0.1948 for 2338 reflections with *I* > 2σ(*I*) and *R*₁ = 0.1235 and *wR*₂ = 0.2297 for all data. The largest hole and peak in the final difference Fourier map were -0.420 and 0.500 e Å⁻³, respectively.

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