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A new dipyridine-containing cryptand for both proton and Cu(II) encapsulation. A solution and solid state study

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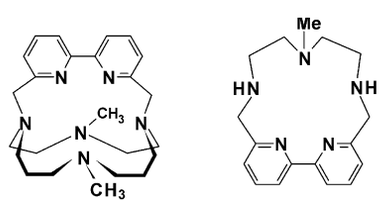
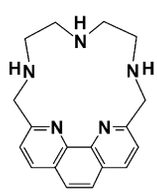
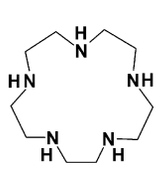
Synthesis and characterization of the new polyamine cryptand 2,5,8-triaza-5-methyl-2,8-(*N*-methyldipropylamino)[9]-2,2′-dipyridinophane (**L**) and its macrocyclic precursor 2,5,8-triaza-5-methyl[9]-2,2′-dipyridinophane (**L1**) are reported. Ligand **L1** contains a diethylenetriamine chain linking the 6,6′ positions of a 2,2′-dipyridine moiety; in **L** an *N*-methyldipropylamine bridge links the two benzylic nitrogens of **L1**. Protonation and Cu(II) coordination have been studied in aqueous solution by means of potentiometric and UV-vis spectrophotometric measurements. Considering proton binding, cryptand **L** behaves as a proton sponge, *i.e.*, the first protonation constant is too high to be measured in aqueous solution. Both ligands form 1 : 1 Cu(II) complexes in aqueous solutions. The crystal structure of $[Cu\mathbf{L1}]^{2+}$ reveals that the metal is coordinated by the five ligand donors in a strongly distorted square pyramidal geometry. Almost the same coordination environment is found in the protonated complex with **L**, $[Cu\mathbf{L}H]^{3+}$, while the nitrogen of the *N*-methyldipropylamine bridge is protonated. In marked contrast, in the $[Cu\mathbf{L}]^{2+}$ complex this nitrogen is involved in metal coordination. Both the solution and structural results account for the high rigidity of the macrocyclic moiety of **L** defined by the dipyridine unit and the diethylenetriamine chain, while coordination of the more flexible *N*-methyldipropylamine unit is modulated by complex protonation.

Introduction

There is much current interest in the development of new polyamine macrobicyclic receptors. Macropolycyclic polyamines containing appropriate binding sites and cavities of a suitable size and shape may be designed to form selective inclusion complexes in aqueous solution. Actually, the molecular topology of the host molecule can be synthetically modulated in order to bind many different chemical species from inorganic or organic cations,[1–10] to anionic species.[10–17] Structural factors, such as ligand rigidity, type of donor atoms and their disposition, have been shown to play significant roles in determining the binding features of macrocycles toward metal cations.[1–13] Heteroaromatic subunits, such as 2,2′-dipyridine or 1,10-phenanthroline, are often introduced as integral parts of the host molecules.[17–20] These units are rather rigid, and, at the same time, provide two aromatic nitrogens whose unshared electron pairs may act cooperatively in binding cations. Furthermore, incorporation of these moieties into macrocyclic structures may allow the combination, within the same species, of the special complexation features of macrocycles with the photophysical and photochemical properties displayed by the metal complexes of these heterocycles.[20] In the course of our investigation of the cation binding capabilities of phenanthroline-[21] and dipyridine-containing[22] polyazamacrocycles, we have synthesized the new cryptand **L**, which contains two different polyamine chains linked by a 2,2′-dipyridine moiety. In this paper we report on the synthesis, basicity and Cu(II) binding by cryptand **L** and by its synthetic precursor **L1**.







Results and discussion

Ligand synthesis

Cryptand **L** and its macrocyclic precursor **L1** were obtained by following the synthetic procedure depicted in Scheme 1. The disodium salt of the tosylated amine **1**,[23] was obtained according to the general procedure of Richman and Atkins.[24] Reaction of 6,6′-bis(bromomethyl)-2,2′-dipyridine[25] **2** with **1**, carried out in anhydrous DMF, afforded, after separation by column chromatography, the tosylated macrocycles **3** and, in a lower yield, **4**. (**3**, 29%; **4**, 10%).

The tosylated compounds **3** and **4** were finally deprotected in a 33% HBr/CH_3CO_2H mixture, according to a previously

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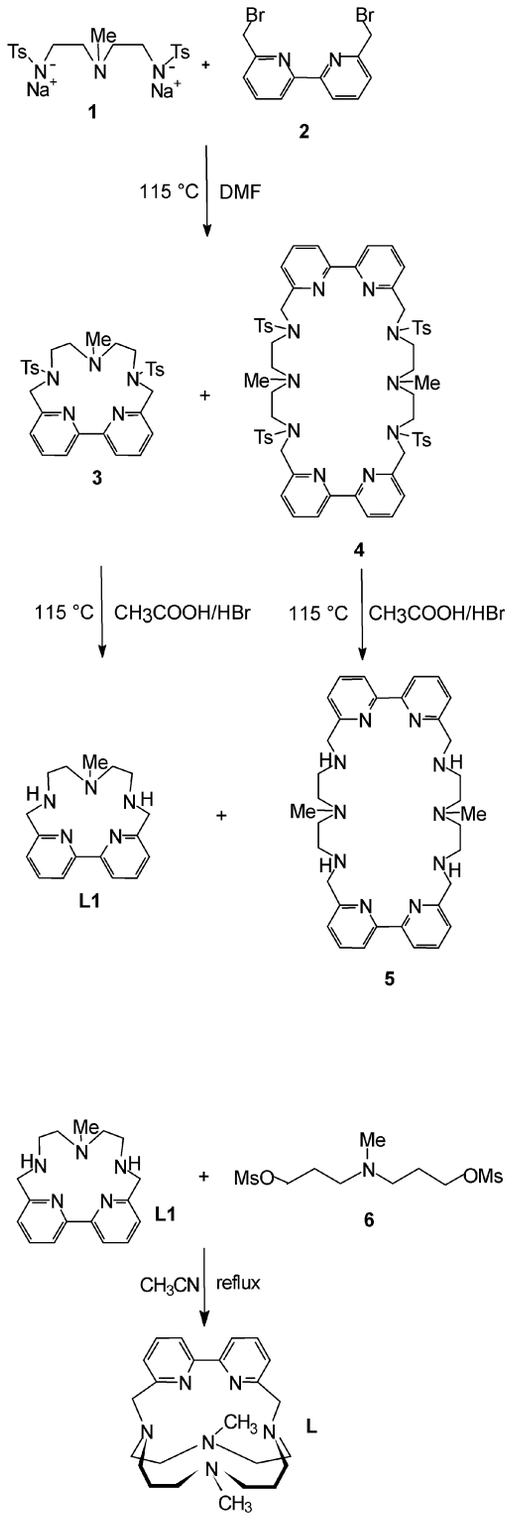

Scheme 1

reported procedure,[22d] to afford ligands **L1** and **5** as hydrobromide salts.

The most interesting finding is the formation, in the critical cyclization step, of compound **4**, derived from a 2 + 2 cyclization. The same synthetic procedure, carried out with tosylated tetra-, penta- or hexa-amines, allowed the obtention of only the 1 + 1 cyclization product, while the formation of the 2 : 2 macrocycles was not observed. Most likely, their longer more flexible chain allowed them to easily achieve a better conformation to react with the two bromo-methyl functions of **2**, which are instead separated by the rigid and smaller dipyridine moiety. In the present case, the short chain of **1** would be less suitable to give a 1 + 1 reaction with respect to "longer" polyamines, thus also giving rise to the 2 + 2 cyclization product.

L1 is a versatile precursor for the assembly of macropolycyclic structures, since it contains two secondary amine groups which can be connected by appropriate bridging moieties. Actually, reaction of **L1** with *N*,*N*-bis[3-(methanesulfonyloxy)-propyl]-*N*-methylamine **6**,[26] in the presence of K_2CO_3 as a base, gave the cryptand **L** (Scheme 1). Separation by column chromatography (neutral alumina, $CHCl_3$) afforded the macrobicycle **L** as its monochloride salt (**L**·HCl), which was characterized by means of elemental analysis, ^{1}H and ^{13}C NMR and ESI mass spectroscopy.

Table 1 Protonation constants (log *K*) of **L** and **L1** (Me_4NCl 0.1 M, 298.1 K)

Reaction	Log *K*	
	L1	**L**
$[\mathbf{L}] + H^+ = [H\mathbf{L}]^+$	9.59(1)	
$[H\mathbf{L}]^+ + H^+ = [H_2\mathbf{L}]^{2+}$	8.47(1)	10.42(1)
$[H_2\mathbf{L}]^{2+} + H^+ = [H_3\mathbf{L}]^{3+}$	2.64(1)	3.47(2)
$[H_3\mathbf{L}]^{3+} + H^+ = [H_4\mathbf{L}]^{4+}$		1.70(7)

Ligand protonation

The protonation equilibria of **L** and **L1** were studied in 0.1 mol dm^{-3} NMe_4Cl aqueous solution at 298.1 ± 0.1 K by means of potentiometric measurements in the pH range 2.5–12, and the results are reported in Table 1. Ligands **L** and **L1** bind up to four and three protons in aqueous solution, respectively. The first protonation constant of **L** is too high to be determined by means of potentiometric measurements (see below). In the case of **L1** a marked grouping of the first two protonation constants and a sharp decrease in basicity between the second and the third protonation step (more than six logarithm units) is observed. A marked drop between the second and the third protonation constant is also found in **L**. This behavior, common in polyamine compounds,[27] is generally explained in terms of minimization of the electrostatic repulsions between protonated amine groups. Dipyridine nitrogens, however, are characterized by far lower basicity than amine nitrogens and, therefore, it is expected that at least the first protonation steps take place on the aliphatic polyamine chains. Protonation of the heteroaromatic nitrogens can be easily monitored by using UV-vis spectrophotometric titrations, since protonation of dipyridine is accompanied by a marked red shift of the UV band of dipyridine at 290 nm with the appearance in the UV-vis spectra of a new red-shifted band at *ca.* 305 nm.[22e] The free amine **L1** displays a band in the UV-vis spectrum at 288 nm and these spectral features are not changed by ligand protonation in the pH range 11–2, indicating that protonation occurs on the aliphatic amine groups. Most likely, in the $[H_2\mathbf{L1}]^{2+}$ species the two acidic protons are localized on the two benzylic amine groups, separated by an unprotonated amine group and by the dipyridine spacer. The third protonation step would occur on the methylated nitrogen, adjacent to the two already protonated benzylic amines, with a consequent increase of the electrostatic repulsions, thus explaining the markedly lower log *K* value of the third protonation constant. Similar considerations can be made in the case of **L**, where a remarkable decrease of the log *K* values is found between the second and the third protonation step. The UV band at 290 nm of **L** does not bear significant change in the pH range 11–3, indicating that the first three protonation equilibria involve the aliphatic amine groups. Below pH 3, the formation of the tetraprotonated $[H_4\mathbf{L}]^{4+}$ species is accompanied by a red shift of the UV band of dipyridine (λ_{max} = 307 nm at pH 1.5) indicating that this protonation step occurs on the heteroaromatic moiety.

The most interesting finding in Table 1 is the remarkable higher basicity of cryptand **L** with respect to its macrocyclic precursor **L1**, at least in the first two protonation steps. The first protonation constant is too high to be determined by means of potentiometric measurements. However, in the $[H\mathbf{L}]^+$ species the proton cannot be removed even in more strongly alkaline solutions: the ^{1}H NMR spectrum recorded in aqueous solution at pH 13 does not show significant differences with respect to that of $[H\mathbf{L}]^+$. Extractions with chloroform of a 3 M NMe_4OH aqueous solution of the cryptand, in the presence of chloride, leads to the isolation of the [H**L**]Cl salt. All these experimental observations suggest that **L** displays a "proton sponge" behavior, *i.e.*, the acidic proton of the $[H\mathbf{L}]^+$ species cannot be removed by varying the pH in aqueous solutions. This behavior has been also observed in small aza-cryptands and was generally attributed to encapsulation of the acidic protons inside the cavity, allowing the formation of an intramolecular hydrogen bond network involving the protonated N–H^+ ammonium function and the other amine groups of the cryptand.[9] A similar assumption can also be made in the present case. Actually, the ^{1}H NMR spectrum of [H**L**]Cl in $CDCl_3$ shows the signal of a highly deshielded N–H^+ proton at 10.8 ppm, supporting the hypothesis that the acidic proton is encapsulated inside the cryptand cavity, deshielded by strong intramolecular hydrogen bonds.

Crystal structure of $[CuL1](ClO_4)_2$

The crystal structure of $[Cu\mathbf{L1}](ClO_4)_2$ consists of $[Cu\mathbf{L1}]^{2+}$ cations and perchlorate anions. Fig. 1a shows an ORTEP[28] drawing of the complex cation with atom labelling and Table 2 lists selected bond angles and distances. The coordination

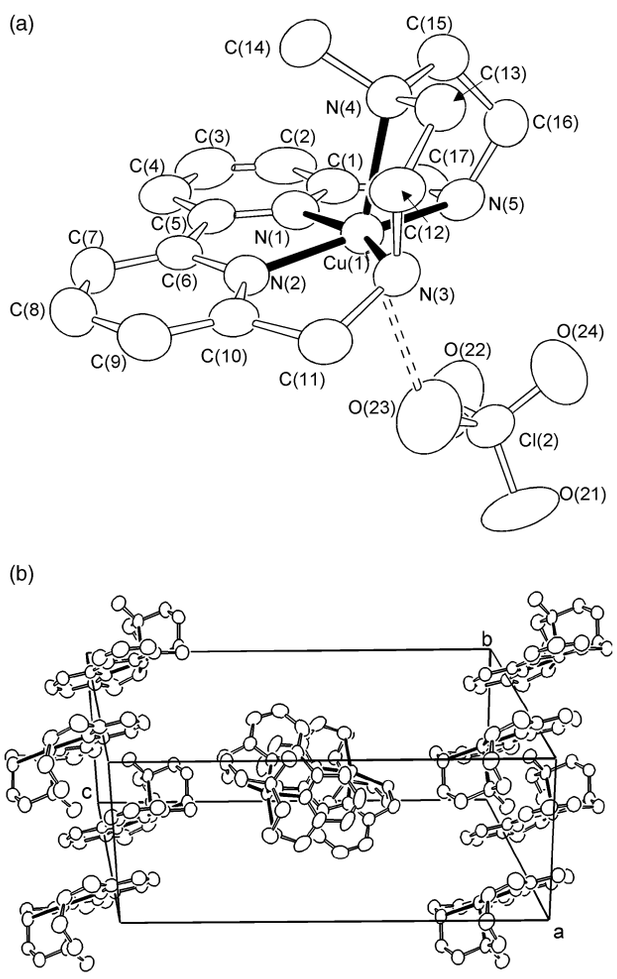

Fig. 1 ORTEP drawing of the $[Cu\mathbf{L1}]^{2+}$ complex (a) and crystal packing (b). The perchlorate anions are omitted for clarity.

Table 2 Selected bond lengths (Å) and angles (°) for $[Cu\mathbf{L1}](ClO_4)_2$

Cu(1)–N(2)	1.945(4)	Cu(1)–N(5)	2.122(5)
Cu(1)–N(1)	1.956(4)	Cu(1)–N(4)	2.226(5)
Cu(1)–N(3)	2.053(4)		
N(2)–Cu(1)–N(1)	79.57(18)	N(3)–Cu(1)–N(5)	118.4(2)
N(2)–Cu(1)–N(3)	80.92(18)	N(2)–Cu(1)–N(4)	110.60(18)
N(1)–Cu(1)–N(3)	160.5(2)	N(1)–Cu(1)–N(4)	102.27(17)
N(2)–Cu(1)–N(5)	158.9(2)	N(3)–Cu(1)–N(4)	83.78(17)
N(1)–Cu(1)–N(5)	81.1(2)	N(5)–Cu(1)–N(4)	81.7(2)

geometry for the Cu(II) ion can be best described as a distorted square pyramid. The aromatic N(1) and N(2) and the benzylic N(3) and N(5) nitrogens define the basal plane (max. deviation 0.081(6) Å for N(5)), while the methylated nitrogen N(4) occupies the apical position. The bond angles for the metal coordination geometry are significantly different from their theoretical values (Table 2). The metal atom lies 0.0772(8) Å apart from the basal plane shifted toward N(4), with the Cu(1)–N(4) bond forming an angle of 19.1(1)° with the normal to the basal plane.

The O(23) oxygen atom of a perchlorate anion gives rise to a weak interaction with the metal (Cu ··· O(23), 2.998(8) Å). Considering this interaction, the coordination environment could be described as a distorted octahedron, with the O(23) oxygen occupying the sixth position of the coordination polyhedron.

The planes defined by the two pyridine rings are almost coplanar (dihedral angle 5.7(2)°). The ligand assumes a folded conformation with a dihedral angle of 77.8(2)° between the mean plane defined by the two pyridine moieties and by the benzylic nitrogens (max. deviation 0.135(5) for N(3)) and that formed by the amine groups N(3), N(4) and N(5). The values of the C–C–N and C–N–C bond angles (mean value 111°) for the aliphatic chains indicate that this part of the ligand is rather strained. A similar bent conformation has already been found in the metal complexes with ligand **L2**, where a phenanthroline unit replaces the dipyridine moiety of **L1**. This suggests that the insertion of a phenanthroline or dipyridine unit as an integral part of a rather small cyclic framework leads to an increase in the rigidity of the macrocycle. Most likely, the ligand rigidity accounts for the observed distorted coordination polyhedron.

Finally, as far as the crystal packing is concerned (Fig. 1b), symmetry related macrocyclic complexes are coupled by π-stacking interactions between the dipyridine moieties. The aromatic systems are parallel, with a plane to plane distance of 3.4 Å.

Crystal structure of $[CuLH](ClO_4)_3{\cdot}2H_2O$

The crystal structure of $[Cu\mathbf{L}H](ClO_4)_3{\cdot}2H_2O$ consists of a $[Cu\mathbf{L}H]^{3+}$ complex cation, perchlorate anions and water solvent molecules. The ORTEP[28] drawing of the cation (Fig. 2) shows the metal atom coordinated by five of the six donor atoms of the ligand, in a distorted square pyramidal coordination environment. The heteroaromatic and the bridgehead nitrogens N(1), N(2), N(3) and N(5), (max. deviation 0.026(5) Å for N(5)) define the basal plane, while N(4) occupies the apical position. Cu(II) is shifted toward the apical position, 0.2369(8) Å away from the basal plane. The apical bond gives rise to an angle of 20.7(1)° with the normal to the plane. Table 3 lists bond angles and distances.

The N(6) nitrogen is protonated and lies 4.688(5) Å away from Cu(1). This nitrogen atom, not involved in metal coordination, gives rise to an H-bond interaction with the O(100) oxygen of a water molecule (N(6)–H(100) ··· O(100) 2.14(5) Å).

The most interesting finding is the fact that the coordination geometry of the metal is very similar to that found in the **L1** complex (see above). In fact, the Cu(II) ion is coordinated by the smaller macrocyclic subunit defined by the dipyridine unit and the two ethylenic chains N(3)–C(12)–C(13)–N(4)

Table 3 Selected bond lengths (Å) and angles (°) for $[Cu\mathbf{L}H](ClO_4)_3 \cdot 2H_2O$

Cu(1)–N(2)	1.937(4)	Cu(1)–N(3)	2.107(5)
Cu(1)–N(1)	1.939(5)	Cu(1)–N(4)	2.183(5)
Cu(1)–N(5)	2.085(5)		
N(2)–Cu(1)–N(1)	80.6(2)	N(5)–Cu(1)–N(3)	112.15(19)
N(2)–Cu(1)–N(5)	160.4(2)	N(2)–Cu(1)–N(4)	110.5(2)
N(1)–Cu(1)–N(5)	82.5(2)	N(1)–Cu(1)–N(4)	114.2(2)
N(2)–Cu(1)–N(3)	81.59(19)	N(5)–Cu(1)–N(4)	85.65(19)
N(1)–Cu(1)–N(3)	158.0(2)	N(3)–Cu(1)–N(4)	84.1(2)

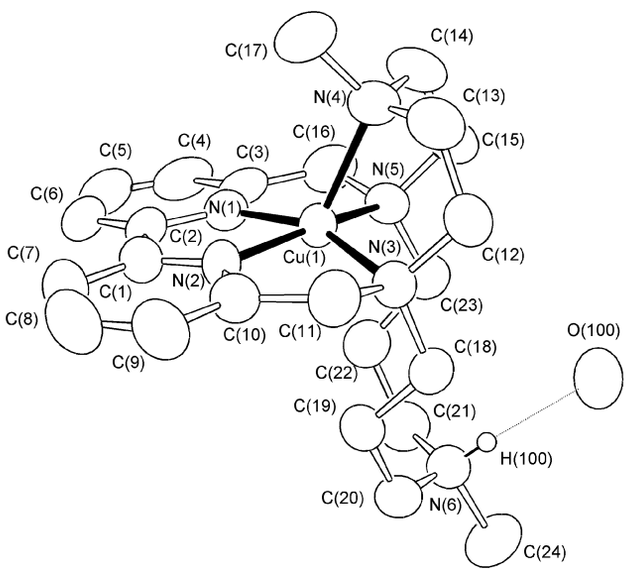

Fig. 2 ORTEP drawing of the $[Cu\mathbf{L}H]^{3+} \cdot H_2O$ complex.

and N(4)–C(14)–C(15)–N(5) The overall conformation of this cyclic moiety is similar to that found for **L1** in the $[Cu\mathbf{L1}]^{2+}$ complex, with the two pyridine units almost coplanar (dihedral angle 5.2(3)°) and an angle of 83.9(2)° between the mean plane defined by the heteroaromatic unit and the bridgehead amines and that formed by the N(3), N(4) and N(5) nitrogens. As in $[Cu\mathbf{L1}]^{2+}$, this part of the ligand is affected by a severe conformational strain, with large deviations of the C–C–N and C–N–C angles from their theoretical values (mean value 112°). These observations further confirm the high rigidity of this macrocyclic subunit.

The cryptand adopts a symmetrical conformation, with a non-crystallographic plane passing through the two methylated nitrogens and the metal ion and bisecting the C(1)–C(2) bond of the dipyridine unit. The tetraaza macrocyclic subunit defined by N(3), N(4), N(5) and N(6) is rather flat (max. deviation from the mean plane defined by N(3), N(4), N(5) and N(6) 0.123(6) Å for N(4)). The dipyridine unit bridges the two N(3) and N(5) nitrogens, defining a plane (max. deviation 0.001(7) Å for C(7)) almost perpendicular (84.5(2)°) to that of the tetraazamacrocycle.

Cu(II) coordination in aqueous solution

The formation of the Cu(II) complexes with **L** and **L1** has been investigated by means of potentiometric measurements in aqueous solution (NMe_4Cl 0.1 M, 298.1 K) and the determined stability constants of the complexes are reported in Table 4. On the basis of these equilibrium data, the distribution of individual metal complexes can be calculated as a function of pH and Fig. 3 displays the distribution diagrams for the systems Cu(II)/**L1** and Cu(II)/**L**. Unfortunately, the unavailability of a value for the first protonation constant of **L** did not allow us to determine the formation constant of the $[Cu\mathbf{L}]^{2+}$ complex. However, according to the potentiometric and NMR results we

Table 4 Stability constants (log K) of the Cu(II) complexes with **L** and **L1** (Me_4NCl 0.1 M, 298.1 K)

Reaction	Log K	
	L1	**L**
$\mathbf{L} + Cu^{2+} = [Cu\mathbf{L}]^{2+}$	19.8(1)	>20.6
$[H\mathbf{L}]^{+} + Cu^{2+} = [Cu\mathbf{L}H]^{3+}$		11.42(5)
$[Cu\mathbf{L}]^{2+} + H^{+} = [Cu\mathbf{L}H]^{3+}$	3.4(1)	2.82(2)
$[Cu\mathbf{L}]^{2+} + OH^{-} = [Cu\mathbf{L}OH]^{+}$	3.8(1)	

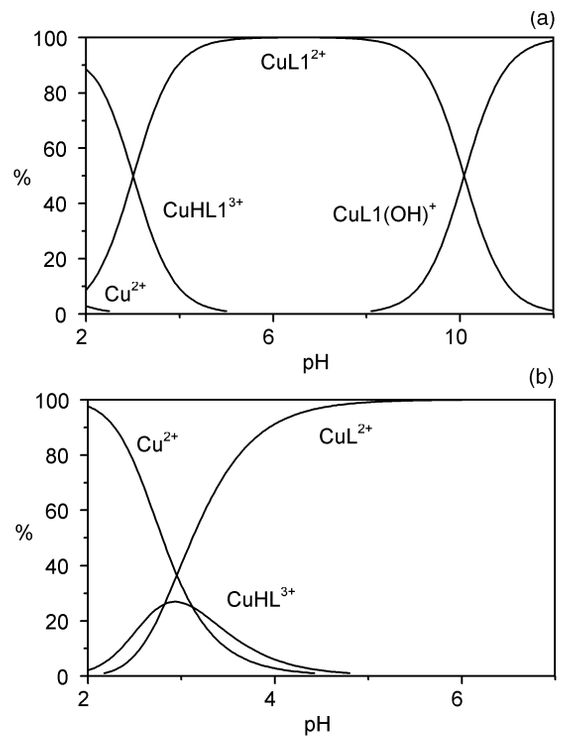

Fig. 3 Distribution diagrams of the species present in the systems: **L1**/Cu(II) (a) and **L**/Cu(II) (b) (NMe_4Cl 0.1 mol dm^{-3}, 298.1 K, [**L**] = [**L1**] = $[Cu^{2+}] = 1 \times 10^{-3}$ M).

can assume that the log K value for the equilibrium $\mathbf{L} + H^{+} = \mathbf{L}H^{+}$ is greater than 13 log. units. On this basis we can estimate log $K > 20.6$ for the formation of the $[Cu\mathbf{L}]^{2+}$ complex. Therefore, both ligands form rather stable 1 : 1 complexes with Cu(II).

Considering ligand **L1**, its Cu(II) complex forms a protonated complex at acidic pHs and a monohydroxo species $[M\mathbf{L1}(OH)]^{+}$ at alkaline pH values. It is to be noted, however, that the stability constants of the Cu(II) complexes with **L1** is remarkably lower than those found for the corresponding complexes with **L3**, where an ethylenediamine linkage replaces the dipyridine unit (log $K = 26.73$ for the equilibria $Cu^{2+} + \mathbf{L3} = [Cu\mathbf{L3}]^{2+}$).[29] At the same time, the $[Cu\mathbf{L3}]^{2+}$ complex does not form any hydroxylated complex at alkaline pHs and shows a very low tendency to protonate, giving rise to the $[Cu\mathbf{L3}H]^{3+}$ species only at strongly acidic pH values (log $K = 0.96$ for the equilibrium ($[Cu\mathbf{L3}]^{2+} + H^{+} = [Cu\mathbf{L3}H]^{3+}$). These observations suggested that in this complex the metal is "enveloped" by the ligand, achieving an almost saturated coordination sphere. The large drop in stability observed for the **L1** complex with respect to **L3** cannot be ascribed to a different binding ability of aliphatic secondary amine groups with respect to heteroaromatic ones, since 2,2′-dipyridine forms a $[CuL]^{2+}$ complex with an almost equal stability constant with respect to *N*,*N*′-dimethylethylenediamine (log $K = 9.0$ and 9.54 for the equilibrium $Cu^{2+} + L = [CuL]^{2+}$, where L = 2,2′-dipyridine and *N*,*N*′-dimethylethylenediamine, respectively).[30] The lower stability of the $[Cu\mathbf{L1}]^{2+}$ complex can be reasonably explained in terms of a lower overall interaction between the donor atoms of **L1** and the metal.

Actually, the UV-vis spectrum of the $[CuL1]^{2+}$ complex displays one band at 617 nm (ε = 109 mol^{-1} dm^3 cm^{-1}), *ca.* 30 nm red shifted with respect to that of $[CuL3]^{2+}$ (λ_{max} = 585 nm, ε = 181 mol^{-1} dm^3 cm^{-1}), indicating a weaker ligand field operating on the Cu^{2+} center in the **L1** complex. At the same time, the reflectance spectrum of the solid $[CuL1](ClO_4)_2$ complex shows similar spectral features (a band at 620 nm) to those found for $[CuL1]^{2+}$ in aqueous solution, suggesting a similar coordination for the Cu(II) ion both in solution and in the solid state.

Actually, the crystal structure of the $[CuL1]^{2+}$ cation shows the metal coordinated by the five nitrogens of **L1** in a strongly distorted square-planar coordination geometry, with two amine groups bound at a longer distance (Cu–N(4), 2.226 Å; Cu–N(5) 2.122(5) Å). These seem to be peculiar structural features of the first row transition metal complexes with phenanthroline and dipyridine-containing polyazamacrocycles,[21,22] due to the insertion of these heteroaromatic moieties which leads to a stiffening of the macrocyclic framework. Most likely, the rigidity of these large heteroaromatic units, together with the short ethylenic linkage connecting the aliphatic amine groups, does not allow a simultaneous optimal arrangement of the nitrogen donors around the metal ion. A weak interaction of the set of donors with the metal may also explain the different acid–base characteristics of the $[CuL1]^{2+}$ complex with respect to those of $[CuL3]^{2+}$. $[CuL1]^{2+}$ shows a higher tendency to form a monoprotonated $[CuHL1]^{3+}$ species, as expected considering that protonation can occur on weakly interacting amine groups. At the same time, the crystal structure of the $[CuL1]^{2+}$ cation displays a large zone on the metal not saturated by the ligand donors, occupied by a weakly bound oxygen atom of a perchlorate anion. Most likely, this anion is replaced by a water molecule in aqueous solution and deprotonation of the coordinated water takes place at alkaline pHs, giving the monohydroxo $[CuL1(OH)]^{+}$ complex.

As far as cryptand **L** is concerned, the formation of a monoprotonated $[CuLH]^{3+}$ complex takes place at pH > 2.5, with almost simultaneous deprotonation of a nitrogen donor to give the $[CuL]^{2+}$ complex. As shown in Fig. 3b, only a minor amount of the protonated complex $[CuLH]^{3+}$ is formed in aqueous solution. However, the protonated $[CuLH](ClO_4)_3$ complex can be crystallized by slow evaporation of an aqueous solution containing $Cu(ClO_4)_2$ and **L** in equimolar ratios at pH 3. Crystallization from an aqueous solution at neutral pH, instead, leads to the isolation of the unprotonated $[CuL](ClO_4)_2$ complex. The potentiometric measurements also point out that no hydroxylated species are formed in the pH range investigated (2.5–12). This suggests a more saturated coordination environment for the metal with respect to the **L1** complex. Although the $[CuL](ClO_4)_2$ complex was not characterized by X-ray analysis, comparison of the UV-vis of the Cu(II) complexes with **L** and **L1** may allow us to gain further insight on the coordination environment of this complex. The reflectance spectrum of the protonated $[CuLH](ClO_4)_3$ solid complex displays a band at 615 nm, almost equal to that found for $[CuL1](ClO_4)_2$, as expected considering the similar coordination geometry of the metal displayed by the crystal structures of the two complexes. Interestingly, the deprotonated $[CuL](ClO_4)_2$ complex, both in aqueous solution and in the solid state, displays a 25 nm blue-shifted band (λ_{max} = 590 nm ε = 120 mol^{-1} dm^3 cm^{-1} at pH 7) with respect to the protonated $[CuLH](ClO_4)_3$ solid complex. The stronger ligand field experienced by Cu^{2+} in $[CuL]^{2+}$ can be reasonably ascribed to the involvement of the methylated nitrogen N(6) in metal coordination, confirming the hypothesis, made on the basis of the potentiometric results, of a more saturated coordination sphere for the Cu(II) ion.

Coordination of N(6) to the metal suggests a higher flexibility of the dipropylamine bridge with respect to the remaining pentaaza-macrocycle, due to the longer propylenic linkages connecting N(6) to the bridgehead nitrogen donors.

These observations point out that cryptand **L** is composed of a rigid cyclic pentaaza moiety, where the metal is lodged, and by a flexible dipropylamine bridge, whose involvement in metal coordination is modulated by complex protonation.

Concluding remarks

The particular cage-like molecular architecture of **L** strongly affects both its protonation and Cu(II) binding behavior. Cryptand **L** behaves as a proton sponge, *i.e.*, it has a very high basicity in the first protonation step, which is not measurable in aqueous solution. Most likely, the high stability of the monoprotonated species $[HL]^{+}$ is due to the involvement of the $N–H^{+}$ proton in a hydrogen bond network inside the tridimensional cavity, which stabilizes this cation. In the Cu(II) complexes with **L** the metal is enveloped inside the cryptand cavity. In the protonated $[CuLH]^{3+}$ complex the metal is coordinated by the pentaaza moiety defined by the dipyridine unit and by two short ethylenediamine linkages, with a coordination geometry almost equal to that found in the Cu(II) complex with the precursor macrocycle **L1**. The similar conformation of this binding unit in both $[CuL]^{2+}$ and $[CuLH]^{3+}$ accounts for the high rigidity of the monocyclic part of the cryptand. In $[CuLH]^{3+}$ the proton is localized on the N(6) nitrogen of the dipropylamine bridge. Deprotonation of the complex, however, takes place at acidic pHs and is accompanied by coordination of N(6) to the metal, indicating a higher flexibility of the dipropylamine linkage with respect to the remaining cyclic framework of the cryptand.

Experimental

General procedures

N-Methyl-2,2′-ditosylimino-bis(ethylamine) disodium salt (**1**),[23] 6,6′-bis(bromomethyl)-2,2′-dipyridine (**2**)[25] and *N*,*N*-bis[3-(methanesulfonyloxy)propyl]-*N*-methylamine (**6**)[26] were prepared as previously described. 200.0 MHz ^1H and 50.32 MHz ^{13}C NMR spectra in D_2O or $CDCl_3$ solutions were recorded at 298 K on a Bruker AC-200 spectrometer. In ^1H NMR spectra peak positions are reported relative to TMS ($CDCl_3$ solutions) or to HOD at 4.75 ppm (D_2O solutions). Dioxane was used as the reference standard in ^{13}C NMR spectra (δ = 67.4 ppm) in D_2O solutions. UV-vis spectra were recorded on a Shimadzu UV-2101PC spectrophotometer.

Synthesis of the ligands and their Cu(II) complexes

2,8-Ditosyl-2,5,8-triaza-5-methyl[9]-2,2′-dipyridinophane (3) and 2,8,23,29-tetratosyl-2,5,8,23,26,29-hexaaza-5,26-dimethyl-[24]-10,21,31,42-bis-dipyridinophane (4). A solution of sodium ethanolate, obtained by addition of small amounts (*ca.* 200 mg each) of sodium (1.5 g, 0.062 mol) in dry ethanol (100 cm^3), was added to a suspension of *N*-methyl-2,2′-ditosylimino-bis(ethylamine) (12.45 g, 0.029 mol) in ethanol (400 cm^3). The resulting mixture was refluxed for *ca.* 30 min and the solvent was then removed under reduced pressure. The solid residue **1** was dissolved in dry DMF (500 cm^3) and Na_2CO_3 (8 g, 0.075 mol) was added. To the resulting suspension, heated at 115 °C, was added **2** (10 g, 0.029 mol) in dry DMF (300 cm^3) over a period of *ca.* 6 h. The reaction mixture was kept at 115 °C for 2 h. After being cooled at room temperature, the suspension was filtered out and the solvent was evaporated to dryness. The crude oil was chromatographed on neutral alumina eluting with $CHCl_3$. The eluted fractions containing **3** (R_f = 0.3) and **4** (R_f = 0.6) were collected separately and evaporated to dryness affording **3** and **4** as white solid compounds. **3**: Yield 5.1 g (8.4 mmol, 29%). ^1H NMR ($CDCl_3$): δ 1.80 (s, 6H), 1.86 (s, 3H), 3.02 (t, 4H), 3.63 (t, 4H), 4.66 (s, 4H), 7.46 (d, 4H), 7.59 (d, 4H), 7.87 (m, 12H), 7.99 (t, 4H) ppm. ^{13}C NMR ($CDCl_3$): δ 21.9, 22.1, 43.7, 47.8,

54.7, 56.5, 121.3, 124.1, 127.5, 130.1, 137.3, 138.3, 143.6, 156.0, 157.4 ppm. Anal. calc. for $C_{31}H_{35}N_5S_2O_4$: C, 61.46; H, 5.82; N, 11.56. Found: C, 61.42; H, 5.70; N, 11.5%. **4**: Yield 1.8 g (1.5 mmol, 10%). ^{1}H NMR ($CDCl_3$): δ 1.74 (s, 12H), 1.77 (s, 6H), 2.55 (m, 16H), 4.76 (s, 8H), 7.41 (d, 8H), 7.61 (d, 4H), 7.74 (d, 8H), 7.87 (m, 8H) ppm. ^{13}C NMR ($CDCl_3$): δ 21.8, 22.0, 46.9, 56.7, 65.1, 120.8, 126.1, 129.1, 129.9, 135.9, 137.7, 145.0, 148.9, 155.5 ppm. Anal. calc. for $C_{62}H_{70}N_{10}S_4O_8$: C, 61.46; H, 5.82; N, 11.56. Found: C, 61.32; H, 5.79; N, 11.60%.

2,5,8-Triaza-5-methyl[9]-2,2′-dipyridinophane trihydrobromide (L1·3HBr). Compound **3** (5.1 g, 0.0082 mol) and phenol (40.0 g, 0.41 mol) were dissolved in 33% HBr/CH_3CO_2H (300 cm^3). The reaction mixture was continuously stirred at 90 °C for 22 h until a precipitate was formed. The solid was filtered out and washed several times with CH_2Cl_2. The trihydrobromide salt was recrystallized from an EtOH–water 2 : 1 mixture. Yield 3.0 g (0.0055 mol, 67%). ^{1}H NMR (D_2O, pH = 11): δ 2.28 (3H, s), 3.66 (4H, t), 3.78 (4H, t), 4.78 (4H, s), 7.68 (4H, d), 8.21 (4H, t), 8.32 (4H, d) ppm.^{13}C NMR (D_2O pH = 11): δ 43.5, 45.6, 52.2, 56.3, 125.8, 127.1, 143.5, 154.0, 155.8 ppm. MS *m*/*z* 298 ([M + H]$^+$). Anal. calc. for $C_{17}H_{26}N_5Br_3$: C, 37.80; H, 4.85; N, 12.97. Found: C, 37.6; H, 4.8; N, 13.0%.

2,5,8,23,26,29-Hexaaza-5,26-dimethyl[24]-10,21,31,42-bis-dipyridinophane octahydrobromide (5·8HBr). This compound was synthesized from **4** (2.28 g, 2 mmol) following the procedure reported for **L1** obtaining pure **5**·8HBr as a colorless solid. Yield: 1.1 g (0.9 mmol, 44%). ^{1}H NMR (D_2O, pH = 11): δ 2.47 (s, 6H), 3.11 (t, 8H), 3.52 (t, 8H), 4.47 (s, 8H), 7.29 (d, 8H), 7.66 (t, 8H), 7.90 (d, 8H) ppm. ^{13}C NMR (D_2O, pH = 11): δ 41.4, 43.0, 51.1, 52.8, 122.6, 125.0, 140.7, 150.4, 153.8 ppm. MS *m*/*z* 5.95 ([M + H]$^+$). Anal. calc. for $C_{34}H_{54}N_{10}Br_8$: C, 32.87; H, 4.38; N, 11.28. Found: C, 32.7; H, 4.4; N, 11.1%.

2,5,8-Triaza-5-methyl-2,8-(*N*-methyldipropylamino)[9]-2,2′-dipyridinophane monohydrochloride (L·HCl). A solution of **6**·HCl (1.25 g, 3.7 mmol) in dry CH_3CN (100 cm^3) was added over a period of 64 h to a refluxing and vigorously stirred suspension of **L1**·3HBr (2 g, 3.7 mmol) and Na_2CO_3 (3.8 g, 37 mmol) in CH_3CN (300 cm^3). After the addition was completed, the solution was refluxed for additional 48 h. The resulting suspension was filtered out and the solution was vacuum evaporated to give a crude solid. The product was chromatographed on neutral alumina ($CHCl_3$). The eluted fractions were collected and vacuum evaporated to afford **L**·HCl as a colorless solid, which was recrystallized from a $CHCl_3$–cyclohexane 1 : 1 mixture. Yield: 0.9 g (2 mmol, 55%). ^{1}H NMR ($CDCl_3$): δ 1.43 (m, 4H), 1.58 (m, 4H), 2.11 (s, 3H), 2.24 (s, 3H), 2.45 (t, 4H), 2.60 (m, 4H), 3.26 (t, 4H), 3.77 (s, 4H), 7.12 (d, 2H), 7.65 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$): δ 27.2, 40.8, 41.1, 52.1, 53.0, 55.5, 56.4, 60.2, 119.8, 121.2, 157.0, 161.4 ppm. MS *m*/*z* 446 ([M + H]$^+$). Anal. calc. for $C_{24}H_{37}N_6Cl$: C, 64.77; H, 8.38; N, 18.88; Cl, 7.97. Found: C, 64.6; H, 8.5; N, 18.70; Cl, 8.1%.

[CuL1](ClO$_4$)$_2$. A solution of $Cu(ClO_4)_2·6H_2O$ (7 mg, 0.019 mmol) in water (5 cm^3) was slowly added to an aqueous solution (10 cm^3) containing **L1**·3HBr (10 mg, 0.019 mmol). The pH was adjusted to 7 with 0.01 M NaOH and then $NaClO_4$ (30 mg) was added. Blue crystals of the complex suitable for X-ray analysis were obtained by slow evaporation at room temperature. Yield: 7 mg (66%). Anal. calc. for $C_{17}H_{23}Cl_2CuN_5O_8$: C, 36.47; H, 4.14; N, 12.50. Found: C, 36.3; H, 4.2; N, 12.3%.

CAUTION! Perchlorate salts of organic ligands and their metal complexes are potentially explosive; these compounds must be handled with great care.

[CuLH](ClO$_4$)$_3$·2H$_2$O. A sample of $Cu(ClO_4)_2·6H_2O$ (9 mg, 0.025 mmol) in water (5 cm^3) was slowly added to an aqueous solution (10 cm^3) containing **L**·HCl (11 mg, 0.025 mmol). The pH was adjusted to 3 with 0.01 M $HClO_4$. $NaClO_4·H_2O$ (70 mg) was added and the resulting solution was stirred for 5 h at room temperature. Blue crystals of the complex suitable for X-ray analysis were obtained by slow evaporation of this solution. Yield: 10 mg (50%). Anal. calc. for $C_{24}H_{41}Cl_3CuN_6O_{14}$: C, 35.70; H, 5.12; N, 10.41. Found: C, 35.6; H, 5.2; N, 10.3%.

[CuL](ClO$_4$)$_2$. This complex was synthesized following the procedure reported for [Cu**L**H]$(ClO_4)_3·2H_2O$, adjusting the solution pH to 7. Yield: 14 mg (84%). Anal. calc. for $C_{24}H_{36}Cl_2CuN_6O_8$: C, 42.96; H, 5.41; N, 12.52. Found: C, 42.8; H, 5.4; N, 12.5%.

Table 5 Crystal data and structure refinement for [Cu**L1**]$(ClO_4)_2$ (a) and [Cu**L**H]$(ClO_4)_3·2H_2O$ (b)

	[Cu**L1**]$(ClO_4)_2$	[Cu**L**H]$(ClO_4)_3·2H_2O$
Empirical formula	$C_{17}H_{23}Cl_2CuN_5O_8$	$C_{24}H_{41}Cl_3CuN_6O_{14}$
Formula weight	559.84	807.52
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a/Å	12.1570(10)	29.500(7)
b/Å	8.8210(10)	17.825(7)
c/Å	20.685(3)	13.781(3)
β/°	100.973(9)	104.193(10)
U/Å^3	2177.6(4)	7025(4)
Z	4	8
λ/Å	1.54180	1.54180
μ/mm^{-1}	4.186	3.606
T/K	298	298
Reflections collected	4100	11338
Independent reflections	3034	4936
R(int)	0.0743	0.0105
$R(F)^a$ ($I > 2\sigma(I)$)	0.0684	0.078
$WR(F2)^a$	0.2012	0.2302

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

X-Ray crystallography

Analyses on prismatic blue single crystals of [Cu**L1**]$(ClO_4)_2$ (a) and [Cu**L**H]$(ClO_4)_3·2H_2O$ (b) were carried out on a Siemens P4 X-ray diffractometer. A summary of the crystallographic data is reported in Table 5. No loss of intensity was observed during data collections. Empirical absorption corrections (ψ-scan method) were applied. Both structures were solved by direct methods (SIR-97).[31] Refinements were performed by means of full-matrix least-squares using the SHELXL-97 program.[32]

In both structures all non-hydrogen atoms were anisotropically refined while the hydrogen atoms were introduced in calculated position and their coordinates and thermal factors were refined according to the linked atom.

In [Cu**L1**]$(ClO_4)_2$, the H(1)–N(3) and H(1)–N(5) hydrogen atoms, bound to the benzylic secondary nitrogens, were localized in the ΔF map, introduced in the calculation and isotropically refined.

In [Cu**L**H]$(ClO_4)_3·2H_2O$, the ΔF map carried out in the last refinement step allowed us to locate the H100 acidic proton which was then introduced in the calculation and isotropically refined. Two perchlorate anions (Cl(1) and Cl(2) are located in special position on C_2 crystallographic axes (symmetry operation: $-x + 1, y, -z + 0.5$ for Cl(1) and $-x + 1, y, -z + 1.5$ for Cl(2)). In particular, in the Cl(1) perchlorate the crystallographic axis passes along the Cl(1)–O(11) bond. This is due to the rotational disorder affecting this perchlorate. Actually, two different tetrahedrons, sharing the Cl(1)–O(11) bond and related by the C_2 axis, have been used to resolve such disorder.

CCDC reference numbers 177616 and 177617.

See http://www.rsc.org/suppdata/dt/b2/b200486k/ for crystallographic data in CIF or other electronic format.

Potentiometric measurements

All the pH metric measurements (pH = $-\log [H^+]$) were carried out in degassed 0.1 mol dm^{-3} NMe_4Cl solutions, at 298.1 K, by using previously reported equipment and procedures.[33] The combinated Ingold 405 S7/120 electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO_2-free NMe_4OH solutions and determining the equivalent point by the Gran's method[34] which allows determination of the standard potential $E°$, and the ionic product of water (pK_w = 13.83(1) at 298.1 K in 0.1 mol dm^{-3} NMe_4Cl). At least three potentiometric titrations were performed for each system in the pH range 2.5–11. A ligand concentration of [L] = 1×10^{-3} mol dm^{-3} and a metal concentration of [M] = 0.8[L] were adopted in the complexation experiments (L = **L** or **L1**). Due to the high stability of the Cu(II) complexes with **L1**, competition between protonation of the free ligands and complex formation is not significant enough to derive the values of the stability constants, and the use of EDTA as an auxiliary ligand was necessary. The relevant emf data were treated by means of the computer program HYPERQUAD[35] which furnished the equilibrium constants reported in Tables 1 and 4.

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