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Copper-(II) and -(I) co-ordination by hexa-amine ligands of different rigidities. A thermodynamic, structural and electrochemical investigation†

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Two new polyamine ligands 2,9-bis(2-methylaminoethylaminomethyl)phenanthroline (**L3**) and 6,6′-bis(2-methylaminoethylaminomethyl)-2,2′-bipyridyl (**L4**) have been synthesized. **L3** and **L4** contain respectively a phenanthroline and a bipyridyl unit bearing two *N*-methylethylenediamine side-arms. Their co-ordination properties toward Cu^{II} were studied by means of potentiometric, calorimetric, UV-vis spectroscopic and electrochemical measurements and compared with those of macrocyclic ligands with similar molecular architecture (**L1** and **L2**). The macrocyclic ligands give only mononuclear complexes, while the acyclic ligands form mono- and bi-nuclear complexes in aqueous solution, due to their higher flexibility. Considering the mononuclear complexes, the analysis of the thermodynamic parameters for copper(II) co-ordination shows that the complexes with the acyclic ligands are mainly stabilized by the entropic change. On the contrary, the enthalpic term gives a more favourable contribution to the formation of the complexes with the macrocyclic ligands. This different behaviour is discussed in terms of ligand rigidity and ligand and metal desolvation. The crystal structure of the $[CuL3]^{2+}$ complex shows the metal to be six-co-ordinated, with a rather unusual geometry, enveloped inside the ligand cleft and almost co-ordinatively saturated and shielded from solvent molecules. At the same time the two heteroaromatic nitrogens are weakly bound to the metal.

Introduction

The development of highly preorganized macrocyclic or acyclic polyamine ligands has enhanced the success in molecular recognition promoting selective binding, transformation and transfer of a large variety of substrates such as inorganic or organic cations,[1–18] anionic species,[19] and neutral molecules.[20,21] Structural factors have been shown to play significant roles in determining the strength of the interactions between the polyaza receptor and the guest molecule. Therefore, introduction in the molecular framework of structural features that impart high selectivity in the recognition of different guests is one of the goals in the design of synthetic receptors. Aromatic subunits are often introduced as integral parts of the host molecules. In particular, several macrocycles containing 2,2′-bipyridyl or 1,10-phenanthroline moieties have recently been synthesized.[22–24] These units provide two aromatic nitrogens whose unshared electron pairs may act co-operatively in binding cations. Incorporation of such moieties into macrocyclic structure allows one to combine within the same ligand the special complexation features of macrocycles with the photophysical and photochemical properties displayed by the metal complexes of these heterocycles.[25,26]

Recently, we reported the synthesis of a new series of polyamine macrocycles, such as **L1**, containing a polyamine chain linking the 2,9 positions of phenanthroline.[27,28] A previous investigation on the zinc(II) co-ordination properties of these ligands revealed that the insertion of phenanthroline within a macrocyclic framework leads to stiffening of the macrocyclic backbone and precludes the simultaneous participation of the heteroaromatic donors and the benzylic amine groups in metal binding.[29,30] The metal is co-ordinated to the phenanthroline nitrogens and weakly bound to the benzylic nitrogens. It seems likely that the co-ordination properties of these ligands are strongly affected by the rigidity of the macrocyclic structure as well as by the different complexant ability of aromatic and aliphatic nitrogen donors. In order further to investigate the role of molecular rigidity in metal binding, we have now synthesized the macrocycle **L2**, where a less rigid heteroaromatic moiety, bipyridyl, replaces the phenanthroline one, and the open-chain ligands **L3** and **L4**, which are composed of two ethylenediamine chains connected by a phenanthroline or a bipyridyl unit. **L3** and **L4** contain respectively the same set of donors as the macrocycles **L1** and **L2** and, therefore, can be considered their acyclic counterparts. In this paper we report the results of a thermodynamic and structural study on copper(II) co-ordination by these cyclic and acyclic ligands. The electrochemical reduction of the complexes, through the copper(I) oxidation state, has been also analysed.

Experimental

Synthesis

1,4,7,10-Tetratosyl-1,4,7,10-tetraazadecane **1**,[31] 1-methyl-1,4-di(*p*-tolylsulfonyl)-1,4-diazabutane **2**,[32] 2,9-bis(bromomethyl)-

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† Electronic supplementary information (ESI) available: thermodynamic parameters for protonation of **L1**, **L3** and **L4**. See http://www.rsc.org/suppdata/dt/b0/b002102o/

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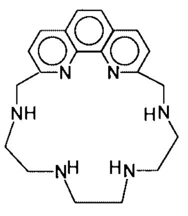
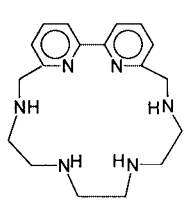


L1



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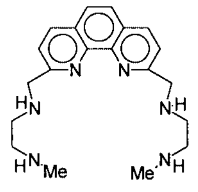

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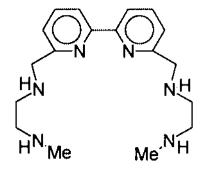

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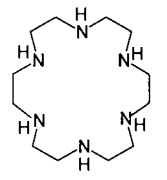
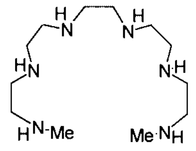


L5



L6

1,10-phenanthroline **3**,[33] 6,6′-bis(bromomethyl)-2,2′-bipyridyl **4**,[34] and **L1**[30] were prepared as previously described.

2,5,8,11-Tetratosyl-2,5,8,11-tetraaza[12](6,6′)-bipyridinophane 5. A solution of sodium (0.6 g, 26 mmol) in dry ethanol (50 cm^3) was added to a suspension of compound **1** (4.46 g, 5.8 mmol) in dry ethanol (150 cm^3). The resulting mixture was refluxed for *ca.* 30 min, and the solvent removed under reduced pressure. The solid residue was dissolved in dry DMF (400 cm^3) and K_2CO_3 (6 g, 43 mmol) added. To the resulting suspension heated at 115 °C was added a solution of **4** (2.0 g, 5.8 mmol) in dry DMF (300 cm^3) over a period of *ca.* 6 hours. The reaction mixture was kept at 115 °C for 2 h. After cooling at room temperature, the suspension was filtered and the solvent evaporated to dryness. The crude oil residue was purified by chromatography on neutral alumina eluting with CH_2Cl_2–ethyl acetate 100:3. The eluted fractions were collected and evaporated to dryness affording **5** as a white solid, mp 124–126 °C. Yield 4.24 g (76%). Calc. for $C_{23}H_{25}N_3O_4S_2$: C, 58.58; H, 5.34; N, 8.91. Found: C, 58.5; H, 5.4; N, 8.80%.

2,5,8,11-Tetraaza[12](6,6′)-bipyridinophane tetrahydrobromide (L2·4HBr). Compound **5** (2.12 g, 2.25 mmol) and phenol (26 g, 0.276 mol) were dissolved in 33% HBr–CH_3CO_2H (210 cm^3). The reaction mixture was stirred at 90 °C for 22 hours until a precipitate was formed. The solid was filtered off and washed several times with CH_2Cl_2. The tetrahydrobromide salt was recrystallized from EtOH–water 2:1. Yield 1.24 g (85%). Calc. for $C_9H_{15}Br_2N_3$: C, 33.26; H, 4.65; N, 12.93. Found: C, 33.3; H, 4.6; N, 12.8%.

2,9-Bis[*N*,*N*′-bis(*p*-tolylsulfonyl)-2-methylaminoethylamino-methyl]phenanthroline 6. Compound **2** (5 g, 13 mmol) and K_2CO_3 (18 g, 130 mmol) were suspended in refluxing CH_3CN (200 ml). To this mixture a solution of **3** (2.4 g, 6.5 mmol) in CH_3CN (400 ml) was added dropwise in 6 h. After the addition was completed, the suspension was refluxed for 2 h and then filtered. The solution was vacuum evaporated to yield the crude product which was chromatographed on neutral alumina (CH_2Cl_2–ethyl acetate 100:4). The eluted fractions were collected and evaporated to dryness to afford **6** as a colourless solid. Yield 2.1 g, 33.6%, mp 45–48 °C. Calc. for $C_{24}H_{26}N_3O_4S_2$: C, 59.48; H, 5.41; N, 8.67. Found: C, 58.5; H, 5.5; N, 8.6%.

2,9-Bis(2-methylaminoethylaminomethyl)phenanthroline tetrahydrobromide L3·4HBr. Compound **6** (2.1 g, 2.2 mmol) and phenol (29 g, 308 mmol) were dissolved in a 33% HBr solution in acetic acid (240 ml). The solution was stirred at 90 °C for 22 h. The resulting suspension was filtered and the solid washed with CH_2Cl_2 several times. The yellowish solid was recrystallized from a water–ethanol mixture to give **L3** as its tetrahydrobromide salt (1.4 g, 96.5%). Calc. for $C_{10}H_{16}Br_2N_3$: C, 35.53; H, 4.77; N, 12.43. Found: C, 35.4; H, 4.7; N, 12.3%.

6,6′-Bis[*N*,*N*′-bis(*p*-tolylsulfonyl)-2-methylaminoethylamino-methyl]-2,2′-bipyridyl 7. A solution of sodium (0.6 g, 26 mmol) in dry ethanol (50 cm^3) was added to a suspension of compound **2** (5 g, 13 mmol) in dry ethanol (150 cm^3). The resulting mixture was refluxed for *ca.* 30 min, and the solvent removed by distillation under reduced pressure. The solid residue was dissolved in dry DMF (400 cm^3) and K_2CO_3 (6 g, 43 mmol) added. To the resulting suspension, heated at 115 °C, was added a solution of **4** (2.23 g, 6.5 mmol) in dried DMF (300 cm^3) over a period of *ca.* 6 hours. The reaction mixture was kept at 115 °C for 2 h. After cooling at room temperature, the suspension was filtered and the solvent evaporated to dryness. The crude oil was purified by chromatography on neutral alumina eluting with CH_2Cl_2–ethyl acetate (100:3). The eluted fractions were collected and evaporated to dryness affording **7** as a white solid. Yield 2.15 g (35%), mp 156–158 °C. Calc. for $C_{23}H_{26}N_3O_4S_2$: C, 58.45; H, 5.55; N, 8.90. Found: C, 58.5; H, 5.7; N, 8.8%.

6,6′-Bis(2-methylaminoethylaminomethyl)-2,2′-bipyridyl tetrahydrobromide L4·4HBr. Compound **7** (2.15 g, 2.3 mmol) and phenol (26.1 g, 0.277 mol) were dissolved in 33% HBr–CH_3CO_2H (230 cm^3). The reaction mixture was stirred at 90 °C for 22 h until a precipitate formed. The solid was filtered off and washed several times with CH_2Cl_2. The tetrahydrobromide salt was recrystallized from EtOH–water 2:1. Yield 1.3 g (88%). Calc. for $C_9H_{16}Br_2N_3$: C, 33.15; H, 4.95; N, 12.89. Found: C, 33.0; H, 4.9; N, 12.7%.

$[CuL3][ClO_4]_2$. A solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (3.7 mg, 0.01 mmol) in water (5 ml) was slowly added to an aqueous solution (15 ml) containing **L3**·4HBr (6.7 mg, 0.01 mmol). The pH was adjusted to 6.0 with 0.01 M NaOH. A blue powder was obtained by slow evaporation of this solution. Yield: 3.7 mg (60%). Calc. for $C_{20}H_{28}Cl_2CuN_6O_8$: C, 39.06; H, 4.59; N, 13.67. Found: C, 39.0; H, 4.6; N, 13.7%.

$[Cu_2(HL3)(\mu\text{-}OH)(ClO_4)_2Br]ClO_4{\cdot}0.5H_2O$. A solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (7.4 mg, 0.02 mmol) in water (5 ml) was slowly added to an aqueous solution (15 ml) containing **L3**·4HBr (6.7 mg, 0.01 mmol). The pH was adjusted to 5.0 with 0.01 M NaOH and the resulting solution stirred for 2 h at room temperature. Blue crystals of the complex suitable for X-ray analysis were obtained by slow evaporation at room temperature. Yield: 5.7 mg (65%). Calc. for $C_{20}H_{31}BrCl_3Cu_2N_6O_{13.5}$: C, 27.15; H, 3.53; N, 9.50. Found: C, 27.3; H, 3.4; N, 9.5%).

$[CuL4][ClO_4]_2$. A solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (3.7 mg, 0.01 mmol) in water (5 ml) was slowly added to an aqueous solution (15 ml) containing **L4**·4HBr (6.5 mg, 0.01 mmol). The pH was adjusted to 5.0 with 0.01 M NaOH and the resulting solution was stirred for 2 h at room temperature. By slow evaporation of the solution, blue crystals, suitable for X-ray analysis, were formed. Yield: 3.8 mg (65%). Calc. for $C_{18}H_{28}Cl_2CuN_6O_8$: C, 36.59; H, 4.78; N, 14.22. Found: C, 36.5; H, 4.8; N, 14.1%.

Single crystal X-ray diffraction analysis

Analyses on prismatic blue single crystals of [CuL4][ClO$_4$]$_2$ (a) and [Cu$_2$(HL3)(μ-OH)(ClO$_4$)$_2$Br]ClO$_4$·0.5H$_2$O (b) were carried out respectively on an Enraf-Nonius CAD4 and on a Siemens P4 diffractometer. A summary of the crystallographic data is reported in Table 1. No loss of intensity was observed during data collections. Both structures were solved by direct methods (SIR 92).[35] The DIFABS[36] method for absorption correction was applied once the structures were solved. Refinements were performed by means of full-matrix least squares using the SHELXL 93 program.[37,38]

The crystals of both compounds were weakly diffracting and, consequently, the data obtained were of rather low quality, resulting in high values for the final agreement factors and for e.s.d.s of bond lengths and angles.

(a) [CuL4][ClO$_4$]$_2$. All the non-hydrogen atoms were anisotropically refined. All the hydrogen atoms were introduced in calculated positions, with an overall fixed thermal parameter $U = 0.05$ Å^2. High anisotropic displacement parameters were found for the oxygen atoms belonging to the perchlorate anions, due to disorder and/or thermal motion. The Cl(2)–O bond distances were restrained (SADI) to be approximately equal to each other.

(b) [Cu$_2$(HL3)(μ-OH)(ClO$_4$)$_2$Br]ClO$_4$·0.5H$_2$O. All the non-hydrogen atoms, with the exception of C(18), C(19), C(19′) and C(20), were anisotropically refined. All the hydrogen atoms, except those linked to C(18), C(19), C(19′) and C(20), were introduced in calculated positions, with an overall fixed $U = 0.05$ Å^2. Disorder affects the N(5)–C(18)–C(19)–N(6) chain. In particular a double position was found for C(19). C(19) and C(19′) were introduced with population parameter 0.5. The bond distances C(18)–C(19) and N(6)–C(19) were restrained (SADI) to be approximately equal to the C(18)–C(19′) and N(6)–C(19′) ones, respectively. High anisotropic displacement parameters were found for the oxygen atoms of the perchlorate anions, due to disorder and/or thermal motion. A disordered water solvent molecule was found in the asymmetric unit and introduced with population parameter of 0.5.

CCDC reference number 186/2021.

See http://www.rsc.org/suppdata/dt/b0/b002102o/ for crystallographic files in .cif format.

Potentiometric measurements

Equilibrium constants for protonation and complexation reactions with **L1**, **L3** and **L4** were determined by pH-metric measurements at 298.1 K, by using equipment[39] and procedure[17] which have already been described. The low solubility of **L2** does not allow one to determine its protonation constants and the stability constants of the copper(II) complexes. The reference electrode was an Ag–AgCl electrode in saturated KCl solution. A glass electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO$_2$-free NaOH solutions and determining the equivalence point by Gran's method[40a] which yields the standard potential $E°$ and the ionic product of water. 1×10^{-3}–2×10^{-3} M ligand and metal ion concentrations were employed in the potentiometric measurements, performing three titration experiments (about 100 data points each) in the pH range 2.5–10. The ionic strength was 0.1 M NMe$_4$Cl (p$K_w = 13.83$ at 298.1 K). The computer program HYPERQUAD[40b] was used to calculate equilibrium constants from emf data. All titrations were treated either as single sets or as separate entities, for each system, without significant variation in the values of the determined constants.

Microcalorimetric measurements

The enthalpies of protonation and copper(II) complexation with **L1**, **L3** and **L4** were determined in 0.1 M NMe$_4$Cl aqueous solutions by using equipment and procedure which have already been described.[28] In the copper(II) complexation study, 1×10^{-3}–2×10^{-3} M ligand and metal ion concentrations were employed, performing at least three titration experiments. The corresponding enthalpies of reaction were determined from the calorimetric data by means of the KK88 program.[41]

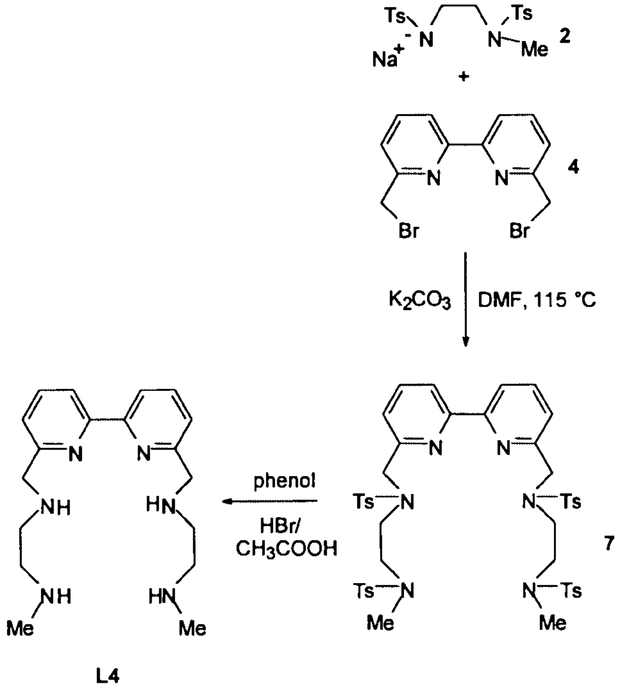
Electrochemical measurements

Electrochemical measurements were carried out using an EG&G Potentiostat/Galvanostat model 263. The working electrode was an EG&G parc model 303A HMDE (hanging mercury dropping electrode). The Ag–AgCl reference electrode in a KCl–AgCl solution was separated by a frit from the bulk solution. The electrode potential was 0.222 V *vs.* NHE (checked against the Cu$_{aq}^{II/0}$ couple as in ref. 42). The software used was EG&G model 270/250 Research Electrochemistry 4.00. The redox properties of the copper complexes were studied using cyclic and square wave voltammetry.

Results and discussion

Synthesis

The synthetic pathway for ligand **L4** is depicted in Scheme 1.



Scheme 1

Reaction of the sodium salt of the tosylated diamine **2** with the bipyridyl derivative **4** in the presence of K$_2$CO$_3$ in DMF at 115 °C, one of the most common modifications of the method of Richman and Atkins,[43] affords the expected product **7** in rather good yield. The same reaction conditions cannot be used for **L3**. Reaction of the dibromide derivative 2,9-bis(bromomethyl)-1,10-phenanthroline **3** with the sodium salt of **2** in DMF at 115 °C affords unchanged **2** and 2,9-bis(hydroxymethyl)-1,10-phenanthroline, as product of the hydrolysis of dibromide **3**. The tosylated ligand **6** can be obtained by using milder conditions, carrying out the reaction in refluxing CH$_3$CN in the presence of K$_2$CO$_3$. Both tosylated precursors **6** and **7** were deprotected in HBr–AcOH–PhOH to give ligands **L3** and **L4** as hydrobromide salts.

The synthesis of **L2** has previously been reported by reaction of the mesylated amine 1,4,7,10-tetra(methylsulfonyl)-1,4,7,10-tetraazadecane with 6,6′-bis(chloromethyl)-2,2′-bipyridyl,

Table 1 Crystal data and structure refinement details for $[\mathrm{Cu}\mathbf{L4}][\mathrm{ClO_4}]_2$ (a) and $[\mathrm{Cu_2(H}\mathbf{L3}\mathrm{)(\mu\text{-}OH)(ClO_4)_2Br]ClO_4\cdot 0.5H_2O}$ (b)

	$[\mathrm{Cu}\mathbf{L4}][\mathrm{ClO_4}]_2$	$[\mathrm{Cu_2(H}\mathbf{L3}\mathrm{)(\mu\text{-}OH)(ClO_4)_2Br]ClO_4\cdot 0.5H_2O}$
Empirical formula	$\mathrm{C_{18}H_{28}Cl_2CuN_6O_8}$	$\mathrm{C_{20}H_{31}BrCl_3Cu_2N_6O_{13.5}}$
Formula weight	590.90	884.85
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a/Å	12.309(9)	8.450(8)
b/Å	13.834(9)	22.613(4)
c/Å	14.528(7)	16.394(9)
β/°	97.74(5)	101.12(6)
U/Å^3	2451(3)	3074(3)
Z	4	4
λ/Å	0.71069	1.5418
μ/mm^{-1}	1.165	6.301
T/K	298	298
Measured reflections	4474	3341
Independent reflections	4290	3104
R_{int}	0.1231	0.1052
$R(F)$ ($I > 2\sigma(I)$)	0.0938	0.092
$wR(F^2)$	0.3969	0.2971

Table 2 Selected bond lengths (Å) and angles (°) for the $[\mathrm{Cu}\mathbf{L4}]^{2+}$ cation

Cu–N(1)	2.047(14)	Cu–N(4)	2.304(13)
Cu–N(2)	2.253(14)	Cu–N(5)	2.136(13)
Cu–N(3)	2.344(11)	Cu–N(6)	2.02(2)
N(6)–Cu–N(1)	162.9(6)	N(5)–Cu–N(4)	72.8(5)
N(6)–Cu–N(5)	85.7(7)	N(2)–Cu–N(4)	137.9(5)
N(1)–Cu–N(5)	93.4(6)	N(6)–Cu–N(3)	96.1(5)
N(6)–Cu–N(2)	90.9(6)	N(1)–Cu–N(3)	95.9(5)
N(1)–Cu–N(2)	80.9(6)	N(5)–Cu–N(3)	138.3(5)
N(5)–Cu–N(2)	148.3(6)	N(2)–Cu–N(3)	73.4(5)
N(6)–Cu–N(4)	105.6(6)	N(4)–Cu–N(3)	66.6(4)
N(1)–Cu–N(4)	90.4(5)		

followed by deprotection in concentrated $\mathrm{H_2SO_4}$.[44] We have carried out an alternative modified Richman and Aktins procedure, similar to that reported for **L4**, by using 1,4,7,10-tetratosyl-1,4,7,10-tetraazadecane and the dibromide **4** as starting materials. This leads to a higher yield in the cyclization, probably due to the better ability of bromide as leaving group than chloride.

Crystal structure of $[\mathrm{Cu}\mathbf{L4}][\mathrm{ClO_4}]_2$

The crystal structure consists of $[\mathrm{Cu}\mathbf{L4}]^{2+}$ complex cations and perchlorate anions. Fig. 1(a) shows an ORTEP[45] drawing of $[\mathrm{Cu}\mathbf{L4}]^{2+}$ and Table 2 reports selected angles and distances. The metal ion is enveloped by the ligand, six-co-ordinated by the four aliphatic amine groups N(1), N(2), N(5) and N(6) and by two heteroaromatic nitrogens N(3) and N(4). The copper(II) co-ordination geometry is rather unusual (Fig. 1b); it can best be described as pseudo-square-pyramidal, with the basal plane defined by the aliphatic nitrogens N(1), N(2), N(5) and N(6) and the η^2-bipyridyl unit at the apical position. The metal ion lies 0.452(2) Å above the mean plane defined by the aliphatic nitrogens, shifted toward the bipyridyl nitrogens. The latter are co-ordinated at rather long distances (Cu–N(3) 2.34(1) and Cu–N(4) 2.30(1) Å) and give a small N(3)–Cu–N(4) angle (66.6(4)°). The Cu–N(3) and Cu–N(4) bonds form almost equal angles (*ca.* 33°) with the normal to the mean plane formed by the four aliphatic amine groups. These features are unusual for $\mathrm{CuN_6}$ chromophores. To our knowledge, only one example of a similar co-ordination geometry has previously been reported.[46] It is also to be noted that the rather weak interaction of the bipyridyl nitrogens N(3) and N(4) with the metal is an unusual binding feature for ligands containing bipyridyl or phenanthroline moieties, which are generally strongly involved in co-ordination.[22–24,28–31]

Considering the ligand conformation (Fig. 1c), the two aromatic rings of bipyridyl are not coplanar, forming a dihedral angle of 9°. The two aliphatic polyamine chains point in opposite directions with respect to the mean plane defined by the bipyridyl unit. Furthermore, this plane is almost perpendicular to the mean plane defined by the aliphatic nitrogens N(1), N(2), N(5) and N(6). The resulting conformation allows the ligand to wrap around the metal cation.

Crystal structure of $[\mathrm{Cu_2(H}\mathbf{L3}\mathrm{)(\mu\text{-}OH)(ClO_4)_2Br]ClO_4\cdot 0.5H_2O}$

The crystal structure consists of $[\mathrm{Cu_2(H}\mathbf{L3}\mathrm{)(\mu\text{-}OH)(ClO_4)_2Br]^+}$ cations, perchlorate anions and water molecules. An ORTEP[45] drawing of the complex cation is shown in Fig. 2 and bond lengths and angles for metal co-ordination environments are listed in Table 3. In the binuclear complex the two metal ions lie 2.973(3) Å apart, bridged by an exogenous oxygen atom. Both show rather unsaturated co-ordination spheres. In principle, two different formulations can be proposed for this complex: $[\mathrm{Cu_2(H}\mathbf{L3}\mathrm{)(\mu\text{-}OH)(ClO_4)_2Br]ClO_4}$ where an $\mathrm{OH^-}$ bridges the two metals while the unco-ordinated nitrogen N1 is protonated, or $[\mathrm{Cu_2}\mathbf{L3}\mathrm{(\mu\text{-}H_2O)(ClO_4)_2Br]ClO_4}$, with a water molecule bridging the two Cu atoms. The short intermetallic distance leads us to propose the former formulation. In fact, several examples of hydroxide anion bridging two first row transition metals, such as $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$, $\mathrm{Cu^{II}}$ and $\mathrm{Zn^{II}}$, have been reported and the M···M distances range between 2.9 and 3.6 Å.[47] Water-bridged dimetal cores are less common and a larger M···M distance, *ca.* 4 Å, is found.[48] It is to be noted that the short N(1)···O(1) distance (2.74(1) Å) is indicative of a charge–charge and hydrogen bonding interaction between the ammonium group and the hydroxide. The $\mathrm{NH_2}^+\cdots\mathrm{OH}^-$ interaction may be responsible for the strained conformation of the N(1)–C(2)–C(3)–N(2) chain, as evidenced by the significant deviations of the N(1)–C(2)–C(3) and C(2)–C(3)–N(2) bond angles (116(2) and 120(2)°, respectively) from their ideal values.

As far as the co-ordination geometry of the two metals is concerned, Cu(1) is five-co-ordinated by the two heteroaromatic nitrogens N(3) and N(4), a benzylic amine group (N(2)), an oxygen atom (O(14)) of a perchlorate anion and the hydroxide anion O(1). The co-ordination geometry can be best described as a distorted square pyramid, the basal plane being defined by N(2), N(3), N(4) and O(1) (maximum deviation 0.21(1) Å for N(2)). The perchlorate oxygen O(14) occupies the apical position. A further weak interaction with the bromide anion co-ordinated to Cu(2) is also observed (Cu(1)···Br 2.944(3) Å). Atom Cu(2) is five-co-ordinated by the aliphatic nitrogens of a similar polyamine chain (N(5) and N(6)), a bromide anion, an oxygen (O(32)) of a second perchlorate

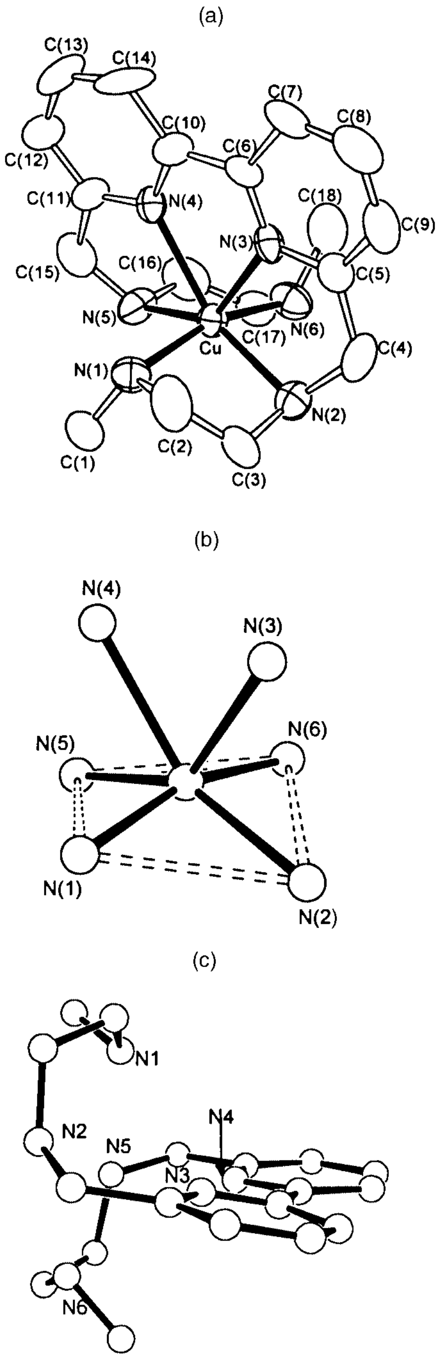


Fig. 1 An ORTEP drawing (a), co-ordination polyhedron for Cu^{2+} (b) and ligand conformation (c) of the $[Cu\mathbf{L4}]^{2+}$ cation.

anion and the bridging hydroxide, with a distorted square pyramidal geometry. The N(5) and N(6) nitrogens, the bromide anion and the oxygen O(1) define the basal plane (maximum deviation 0.41(2) Å for N(6)). Cu(2) lies above this plane, shifted 0.269(2) Å toward the perchlorate oxygen O(32), which occupies the apical position.

It is to be noted that the ligand rigidity, imposed by the large heteroaromatic moiety, does not allow the simultaneous co-ordination of both benzylic nitrogens N(2) and N(5) and heteroaromatic ones to the same metal ion. Actually, while N(2) is bound to Cu(1), N(5) is co-ordinated to the Cu(2) metal cation.

As a consequence of the co-ordination of a binuclear assembly within the receptor cleft, the ligand assumes a more opened conformation than that found for the $[Cu\mathbf{L4}]^{2+}$ complex, with the two ethylenediamine side-arms on the same side with respect to the plane of the phenanthroline unit.

Table 3 Selected bond lengths (Å) and angles (°) for the $[Cu_2(H\mathbf{L3})(\mu\text{-}OH)(ClO_4)_2Br]^+$ cation

Cu(1)–O(1)	1.889(8)	Cu(2)–O(1)	1.949(10)
Cu(1)–N(2)	2.096(12)	Cu(2)–N(5)	1.979(14)
Cu(1)–N(3)	1.923(10)	Cu(2)–N(6)	1.975(14)
Cu(1)–N(4)	2.173(12)	Cu(2)–O(32)	2.39(2)
Cu(1)–O(14)	2.47(1)	Cu(2)–Br	2.411(4)
O(14)–Cu(1)–N(4)	94.2(4)	O(1)–Cu(2)–N(5)	89.7(5)
O(14)–Cu(1)–N(3)	106.2(4)	N(6)–Cu(2)–N(5)	85.6(7)
O(14)–Cu(1)–N(2)	84.6(5)	O(1)–Cu(2)–O(32)	89.6(5)
O(1)–Cu(1)–O(14)	85.5(4)	N(6)–Cu(2)–O(32)	91.2(7)
O(1)–Cu(1)–N(3)	168.3(5)	N(5)–Cu(2)–O(32)	105.4(8)
O(1)–Cu(1)–N(2)	101.2(5)	O(1)–Cu(2)–Br	86.3(3)
N(3)–Cu(1)–N(2)	80.8(5)	N(6)–Cu(2)–Br	98.2(6)
O(1)–Cu(1)–N(4)	98.7(4)	N(5)–Cu(2)–Br	158.0(4)
N(3)–Cu(1)–N(4)	80.3(5)	O(32)–Cu(2)–Br	96.2(7)
N(2)–Cu(1)–N(4)	159.9(5)	Cu(1)–O(1)–Cu(2)	101.5(4)
O(1)–Cu(2)–N(6)	175.3(7)		

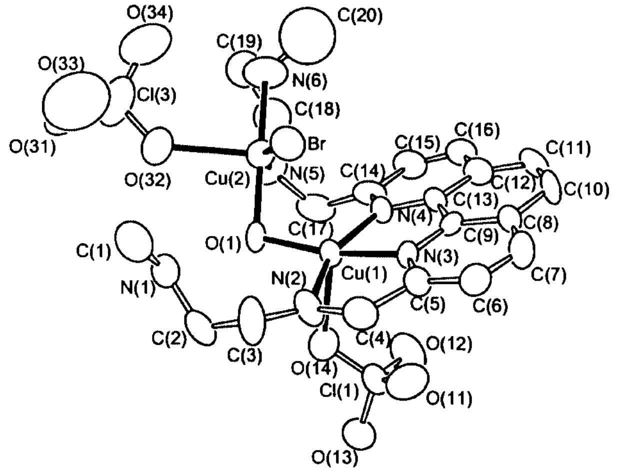


Fig. 2 An ORTEP drawing of the $[Cu_2H\mathbf{L3}(\mu\text{-}OH)(ClO_4)_2Br]^+$ cation.

Copper(II) co-ordination in aqueous solution

The co-ordination properties of ligands **L1**–**L4** have been studied by means of potentiometric, microcalorimetric and spectrophotometric UV-vis measurements in aqueous solution. Table 4 lists the thermodynamic parameters for copper(II) co-ordination with ligands **L1**, **L3** and **L4**.‡ The low solubility of **L2** does not allow one to determine the stability constants of its copper(II) complexes.

The data in Table 4 clearly show that the open-chain ligands **L3** and **L4** form both mono- and bi-nuclear metal complexes in aqueous solution, while the macrocycle **L1** gives only mononuclear complexes. In the case of **L2**, a Job plot of the molar absorbance of the d–d band at 641 nm as a function of the ligand to metal molar ratio (pH 8) showed the formation of only 1:1 complexes. The binucleating ability of the acyclic ligands can be ascribed to their higher flexibility, which allows them to accommodate two metal ions in their co-ordinative clefts.

Considering the mononuclear complexes, ligands **L1** and **L3** show an almost equal stability of their $[Cu\mathbf{L}]^{2+}$ species (log $K = 17.53$ and 17.30 for $[Cu\mathbf{L1}]^{2+}$ and $[Cu\mathbf{L3}]^{2+}$ respectively). These values, however, are by far lower than those reported for cyclic or acyclic hexa-amines, and even lower than those usually found for tetra-amine compounds.[1–4] For instance, formation constants of 24.40 and 21.58 log units were found for copper(II) binding with the hexa-aza ligands **L5**[49] and **L6**,[32] where two

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‡ The thermodynamic parameters for protonation of **L1**, **L3** and **L4** are similar to those found for analogous polyamine ligands.[30] Their values are reported within the supplementary material.

Table 4 Thermodynamic parameters for copper(II) complexation with **L1**, **L3** and **L4** (0.1 M $\mathrm{NMe_4Cl}$, 298.1 K)

Reaction	log *K*	$-\Delta G°$/kJ mol^{-1}	$-\Delta H°$/kJ mol^{-1}	$T\Delta S°$/kJ mol^{-1}
$\mathrm{Cu^{2+}} + \mathbf{L1} \rightleftharpoons \mathrm{Cu}\mathbf{L1}^{2+}$	17.53(3)[a]	100.0	64.8(2)	35.2
$\mathrm{Cu}\mathbf{L1}^{2+} + \mathrm{H^+} \rightleftharpoons \mathrm{CuH}\mathbf{L1}^{3+}$	5.94(4)[b]	33.8	33.0(2)	0.8
$\mathrm{Cu}\mathbf{L1}^{2+} + \mathrm{OH^-} \rightleftharpoons \mathrm{Cu}\mathbf{L1}\mathrm{(OH)^+}$	3.94(4)[c]	20.1	20.9(3)	−0.8
$\mathrm{Cu^{2+}} + \mathbf{L3} \rightleftharpoons \mathrm{Cu}\mathbf{L3}^{2+}$	17.30(2)[a]	98.6	44.7(2)	53.9
$\mathrm{Cu}\mathbf{L3}^{2+} + \mathrm{H^+} \rightleftharpoons \mathrm{CuH}\mathbf{L3}^{3+}$	5.41(2)[b]	30.8	26.3(2)	4.5
$\mathrm{CuH}\mathbf{L3}^{3+} + \mathrm{H^+} \rightleftharpoons \mathrm{CuH_2}\mathbf{L3}^{4+}$	4.08(3)[b]	23.2	30.5(2)	−7.3
$\mathrm{CuH_2}\mathbf{L3}^{4+} + \mathrm{H^+} \rightleftharpoons \mathrm{CuH_3}\mathbf{L3}^{5+}$	4.0(1)[b]	22.8	29.7(2)	−6.9
$\mathrm{Cu}\mathbf{L3}^{2+} + \mathrm{Cu^{2+}} \rightleftharpoons \mathrm{Cu_2}\mathbf{L3}^{4+}$	3.70(4)[d]	21.1	22.6(2)	−1.5
$\mathrm{Cu_2}\mathbf{L3}^{4+} + \mathrm{OH^-} \rightleftharpoons \mathrm{Cu_2}\mathbf{L3}\mathrm{(OH)^{3+}}$	8.03(4)[e]	45.8	23.4(3)	22.4
$\mathrm{Cu_2}\mathbf{L3}\mathrm{(OH)^{3+}} + \mathrm{OH^-} \rightleftharpoons \mathrm{Cu_2}\mathbf{L3}\mathrm{(OH)_2{}^{2+}}$	5.57(5)[f]	31.9	19.4(2)	12.5
$\mathrm{Cu^{2+}} + \mathbf{L4} \rightleftharpoons \mathrm{Cu}\mathbf{L4}^{2+}$	19.05(2)[a]	108.6	51.0(3)	57.6
$\mathrm{Cu}\mathbf{L4}^{2+} + \mathrm{H^+} \rightleftharpoons \mathrm{CuH}\mathbf{L4}^{3+}$	5.90(2)[b]	33.4	27.6(3)	5.8
$\mathrm{CuH}\mathbf{L4}^{3+} + \mathrm{H^+} \rightleftharpoons \mathrm{CuH_2}\mathbf{L4}^{4+}$	4.76(3)[b]	27.1	35.9(3)	−8.8
$\mathrm{CuH_2}\mathbf{L4}^{4+} + \mathrm{H^+} \rightleftharpoons \mathrm{CuH_3}\mathbf{L4}^{5+}$	2.49(3)[b]	14.2	5.4(2)	8.8
$\mathrm{Cu}\mathbf{L4}^{2+} + \mathrm{Cu^{2+}} \rightleftharpoons \mathrm{Cu_2}\mathbf{L4}^{4+}$	3.95(3)[d]	22.6	13.0(3)	9.6
$\mathrm{Cu_2}\mathbf{L4}^{4+} + \mathrm{OH^-} \rightleftharpoons \mathrm{Cu_2}\mathbf{L4}\mathrm{(OH)^{3+}}$	8.09(3)[e]	46.0	29.3(3)	16.7
$\mathrm{Cu_2}\mathbf{L4}\mathrm{(OH)^{3+}} + \mathrm{OH^-} \rightleftharpoons \mathrm{Cu_2}\mathbf{L4}\mathrm{(OH)_2{}^{2+}}$	6.11(3)[f]	34.7	28.0(3)	6.7

[a] $K = [\mathrm{Cu}\mathbf{L}^{2+}]/[\mathrm{Cu^{2+}}][\mathbf{L}]$. [b] $K = [\mathrm{CuH}_n\mathbf{L}^{(n+2)+}]/[\mathrm{CuH}_{n-1}\mathbf{L}^{(n+1)+}][\mathrm{H^+}]$. [c] $K = [\mathrm{Cu}\mathbf{L}\mathrm{(OH)^+}]/[\mathrm{Cu}\mathbf{L}^{2+}][\mathrm{OH^-}]$. [d] $K = [\mathrm{Cu_2}\mathbf{L}^{4+}]/[\mathrm{Cu}\mathbf{L}^{2+}][\mathrm{Cu^{2+}}]$. [e] $K = [\mathrm{Cu_2}\mathbf{L}\mathrm{(OH)^{3+}}]/[\mathrm{Cu_2}\mathbf{L}^{4+}][\mathrm{OH^-}]$. [f] $K = [\mathrm{Cu_2}\mathbf{L}\mathrm{(OH)_2{}^{2+}}]/[\mathrm{Cu_2}\mathbf{L}\mathrm{(OH)^{3+}}][\mathrm{OH^-}]$.

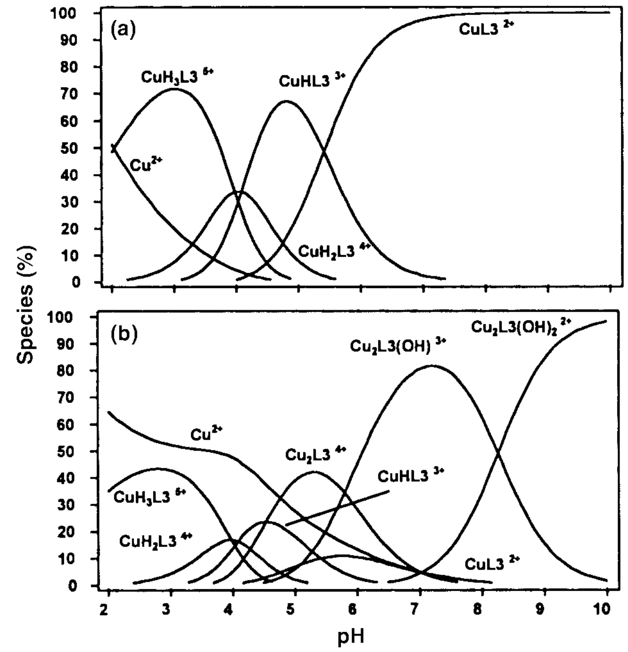

Fig. 3 Distribution diagram for the system **L3**/$\mathrm{Cu^{II}}$ at 298.1 K and $I = 0.1$ M. (a) $[\mathrm{Cu^{2+}}] = [\mathbf{L3}] = 1 \times 10^{-3}$ M. (b) $[\mathrm{Cu^{2+}}] = 2 \times 10^{-3}$ M, $[\mathbf{L3}] = 1 \times 10^{-3}$ M.

aliphatic amine groups replace the heteroaromatic donors. For these aliphatic polyamines it was suggested that five to six nitrogen donors are involved in metal co-ordination.

Furthermore, both **L1** and **L3** show a rather high tendency to give protonated complexes, and, as shown in Fig. 3(a) for the $[\mathrm{Cu}\mathbf{L3}]^{2+}$ complex, protonated species are formed in large amounts at slightly acidic pH. These observations strongly suggest that in both $[\mathrm{Cu}\mathbf{L1}]^{2+}$ and $[\mathrm{Cu}\mathbf{L3}]^{2+}$ some nitrogen donors are weakly bound, or not bound, to the metal. The analysis of the thermodynamic data in Table 4 also shows that the low stability of these complexes is mostly due to the unusually low enthalpy changes for copper(II) complexation with **L1** and **L3**. Actually, the hexa-aza ligands **L5**[49] and **L6**,[32] not containing the phenanthroline unit, show by far higher enthalpic contributions for the formation of their copper(II) complexes ($-\Delta H° = 100$ and 106.2 kJ mol^{-1} for the formation of $[\mathrm{Cu}\mathbf{L5}]^{2+}$ and $[\mathrm{Cu}\mathbf{L6}]^{2+}$, respectively). This observation indicates, once again, a weaker interaction of the set of donors in the $[\mathrm{Cu}\mathbf{L1}]^{2+}$ and $[\mathrm{Cu}\mathbf{L3}]^{2+}$ complexes with respect to the **L5** and **L6** ones. Similar considerations can be made for the mononuclear copper(II) complex with the acyclic ligand **L4**, where a bipyridyl unit replaces the phenanthroline moiety of **L3**. Although the $[\mathrm{Cu}\mathbf{L4}]^{2+}$ complex displays a higher stability than the **L3** one, both the free energy and enthalpy change are still much lower than those found for the copper(II) complex with the aliphatic hexa-amine **L6**. As far as the entropy changes are concerned, similar positive entropic contributions are found for copper(II) complexation with the cyclic ligands **L1** and **L5**, while the formation of the complexes with the acyclic ligands **L3** and **L4** is accompanied by favourable $\Delta S°$ values, higher than that found for the aliphatic linear amine **L6**. Therefore, the lower stability of the copper(II) complexes with **L1**, **L3** and **L4** derives from the rather low enthalpic contribution, indicating that the overall metal–ligand interaction decreases from **L5** to **L1** and from **L6** to **L3** and **L4**. These findings support the hypothesis that in the present ligands some nitrogen donors weakly interact with the metal. Such a difference between phenanthroline or bipyridyl-containing ligands and the two aliphatic hexa-amines **L5** and **L6** can be ascribed, in principle, to two main factors: first, to the stiffening of the ligands, due to the large and rigid phenanthroline or bipyridyl moieties, which can preclude the simultaneous involvement of all the donors in metal binding; secondly, to a different binding ability of aliphatic secondary amine groups with respect to heteroaromatic ones. On the other hand, 1,10-phenanthroline and 2,2′-bipyridyl form $[\mathrm{Cu}\mathbf{L}]^{2+}$ complexes with almost equal stability constants with respect to *N*,*N*′-dimethylethylenediamine (log $K = 9.25$, 9.0 and 9.54 for the equilibrium $\mathrm{Cu^{2+}} + \mathbf{L} \rightleftharpoons [\mathrm{Cu}\mathbf{L}]^{2+}$, where **L** = 1,10-phenanthroline,[50] 2,2′-bipyridyl[51] or *N*,*N*′-dimethylethylenediamine,[52] respectively). This consideration points out that the large difference in stability constants between the copper(II) complexes with aliphatic polyamines **L5** and **L6** and the phenanthroline and/or bipyridyl-containing ligands is mainly due to ligand stiffening. The fact that the copper(II) complex with **L4** is more stable than the **L3** one can be explained, once again, in terms of rigidity of the heteroaromatic moieties, since the possible rotation of the two aromatic rings of bipyridyl along the 2–2′ axis may allow a more suitable disposition of the ligand donors for metal binding. The crystal structure of $[\mathrm{Cu}\mathbf{L4}][\mathrm{ClO_4}]_2$ gives confidence to these hypotheses. First, in the $[\mathrm{Cu}\mathbf{L4}]^{2+}$ cation, some nitrogen donors interact with the metal at rather long distance (Table 2). In particular, both the heteroaromatic nitrogens are only weakly involved in co-ordination. Secondly, the two pyridine units are not coplanar, confirming the higher flexibility of this ligand than the phenanthroline-containing polyamine **L3**.

Table 5 UV-vis data, λ/nm (ε/M^{-1} cm^{-1}), of ligands **L1**, **L2**, **L3** and **L4** and their copper(II) complexes

L1	L2	L3	L4
272 (42900)	289 (11400)	271 (44500)	290 (12400)
$[\mathrm{Cu}\mathbf{L1}]^{2+}$	$[\mathrm{Cu}\mathbf{L2}]^{2+}$	$[\mathrm{Cu}\mathbf{L3}]^{2+}$	$[\mathrm{Cu}\mathbf{L4}]^{2+}$
274 (36100)	304 (9500)	270 (44600)	294 (12200)
670 (64)	641 (82)	760 (83)	690 (82)
		$[\mathrm{Cu_2}\mathbf{L3}]^{4+}$	$[\mathrm{Cu_2}\mathbf{L4}]^{4+}$
		271 (42400)	299 (10880)
		709 (128)	679 (140)

The different molecular topologies of ligands **L1**, **L3** and **L4** can also explain the trend observed for the enthalpy changes, which increase in the order **L3** < **L4** < **L1**. The higher enthalpic contribution for copper(II) complexation with **L1** can reasonably be ascribed to the macrocyclic structure of this ligand, which may offer a preformed co-ordination environment to the metal. In the case of the open-chain ligands **L3** and **L4**, the very low values of the enthalpic contribution are probably due to the enthalpic cost due to the rearrangement of the ligands in order to "wrap" around the metal cation. Furthermore, polyamine macrocycles are usually less solvated than linear ones. The consequent lower enthalpic cost for ligand desolvation in the process of complex formation can further contribute to the enthalpic stabilization of the $[\mathrm{Cu}\mathbf{L1}]^{2+}$ complex. On the contrary, the entropic contribution to the stabilization of copper(II) complexes decreases from the open-chain ligands to the macrocyclic ones. Although several factors may contribute to determine the entropic change in the process of metal complexation, the change of translational entropy usually gives the main contribution to this term.[2,11] Therefore, the higher $T\Delta S^\circ$ values found for **L3** and **L4** can be ascribed to a larger desolvation of the copper(II) ion and of the acyclic ligands with respect to the macrocyclic one. The crystal structure of the $[\mathrm{Cu}\mathbf{L4}]^{2+}$ cation, which shows the metal deeply embedded into the ligand cleft and shielded from the solvent, may support this hypothesis.

In order to get further information on the co-ordination properties of these ligands, copper(II) binding was also studied by means of spectrophotometric UV-vis measurements and the results are reported in Table 5. Ligands **L3** and **L4** display a rather sharp band at 271 (ε = 44500) and at 290 nm (ε = 12400 M cm^{-1}), respectively. As shown in Table 5, these spectral features are only slightly affected by the formation of the mononuclear complexes. On the contrary, the UV spectra of **L1** and **L2** show a marked decrease of the molar absorbance upon metal co-ordination. These data suggest that in the case of the acyclic ligands **L3** and **L4** the heteroaromatic nitrogens are involved more weakly in metal co-ordination, as actually shown by the crystal structure of the $[\mathrm{Cu}\mathbf{L4}]^{2+}$ cation. It is of interest that the reflectance spectra of both $[\mathrm{Cu}\mathbf{L3}][\mathrm{ClO_4}]_2$ and $[\mathrm{Cu}\mathbf{L4}][\mathrm{ClO_4}]_2$ show similar features (a broad band with $\lambda_{\mathrm{max}} = 770$ and 695 nm, respectively) with respect to those recorded in aqueous solution, suggesting that the co-ordination environment of the metal shown by the crystal structure of $[\mathrm{Cu}\mathbf{L4}][\mathrm{ClO_4}]_2$ is also retained in solution. In the case of the complexes with the macrocyclic ligands **L1** and **L2**, the UV data account for the strong involvement of the heteroaromatic nitrogens in metal co-ordination. On the other hand, the rigidity of the heteroaromatic units does not allow simultaneous metal binding to the aromatic nitrogens and the benzylic amine groups. On the basis of these considerations, it can be suggested that at least one of the benzylic nitrogens is not co-ordinated, as sketched in Fig. 4. Considering the visible spectral region, of interest is the red shift of the d–d bands in the order $[\mathrm{Cu}\mathbf{L1}]^{2+} < [\mathrm{Cu}\mathbf{L4}]^{2+} \ll [\mathrm{Cu}\mathbf{L3}]^{2+}$, that is the same trend observed for the $-\Delta H^\circ$ values. A similar correlation between the ν_{max} and the enthalpy change was also found for several aliphatic polyamines.[53] Moreover, the red shift observed for the complexes with **L1** and **L2** with respect to their acyclic counterparts, **L3** and **L4**, suggests a larger crystal field splitting in the macrocyclic complexes.

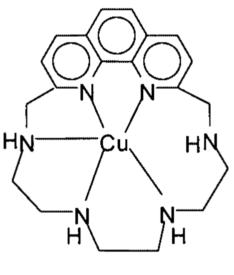

Fig. 4 Proposed co-ordination mode of $\mathrm{Cu^{2+}}$ in the $[\mathrm{Cu}\mathbf{L1}]^{2+}$ complex. The structure drawn is only partial, and eventual additional water molecules bound to $\mathrm{Cu^{2+}}$ are not specified.

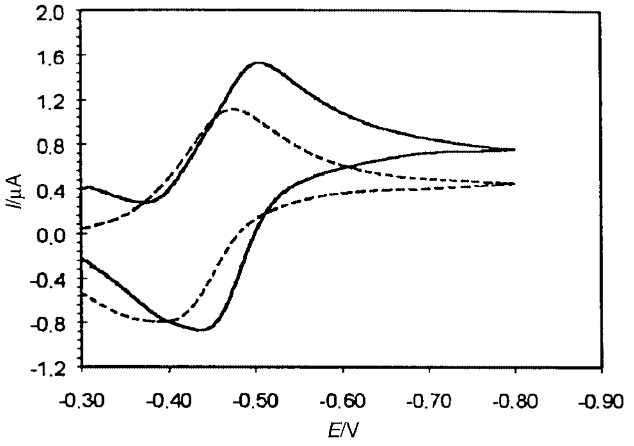

Fig. 5 Cyclic voltammograms (HMDE *vs.* Ag–AgCl) for the mononuclear (---, scan rate = 100 mV s^{-1}, $[\mathrm{Cu^{2+}}] = [\mathbf{L}] = 2.3 \times 10^{-4}$, pH 8.4) and for the binuclear (——, scan rate = 100 mV s^{-1}, $[\mathrm{Cu^{2+}}] = 4.6 \times 10^{-4}$ M, $[\mathbf{L}] = 2.3 \times 10^{-4}$, pH 11) complexes of $\mathrm{Cu^{2+}}$ with **L4** at 298 K and $I = 0.1$ M.

The redox properties of these complexes were also studied by means of cyclic and square wave voltammetry. The cyclic voltammogram of $[\mathrm{Cu}\mathbf{L1}]^{2+}$ shows a broad irreversible wave, which reveals two single-electron processes at *ca.* −0.16 and −0.2 V *vs.* NHE. The reduction of the $[\mathrm{Cu}\mathbf{L3}]^{2+}$ complex is more defined, with two single-electron consecutive waves at −0.164 and −0.294 V *vs.* NHE. The observed stabilization of $\mathrm{Cu^{II}}$ is mainly due to co-ordination by the secondary amine groups, since complexation by phenanthroline does not shift the redox potential of the $\mathrm{Cu^{II}}$–$\mathrm{Cu^{I}}$ couple[54] in aqueous solutions. At the same time, it is well known that phenanthroline gives stable copper(I) complexes in aqueous solutions, while copper(I) stabilization in complexes with secondary amines is usually not observed. The observation of the $\mathrm{Cu^{I}}$–$\mathrm{Cu^{0}}$ couple may indicate that this ligand stabilizes the copper(I) complex in aqueous solution, suggesting that $\mathrm{Cu^{I}}$ is bound to the phenanthroline nitrogens. An alternative explanation is a kinetic stabilization of the copper(I) complex, as often found in copper complexes with rigid ligands, due to a slow enough rate of ligand loss which inhibits the disproportionation reaction $2\mathrm{Cu^{I}} \rightleftharpoons \mathrm{Cu^{0}} + \mathrm{Cu^{II}}$. The copper(II) complex with the bipyridyl-containing ligand **L4** is reduced directly to $\mathrm{Cu^{0}}$ in a single two-electron process at −0.228 V *vs.* NHE, as shown in Fig. 5. Such a different behaviour with respect to the **L3** complex may stem from the higher flexibility of **L4**, which does not allow the copper(I) complex to be kinetically stabilized and enables the reduction of the copper(II) centre directly to $\mathrm{Cu^{0}}$.

As previously anticipated, both the acyclic ligands **L3** and **L4** can add a second copper(II) ion in aqueous solution, giving binuclear complexes. Both **L3** and **L4**, however, show a low tendency to form binuclear complexes. Both the free energy and enthalpy changes for the equilibrium $CuL^{2+} + Cu^{2+} \rightleftharpoons Cu_2L^{4+}$ are remarkably lower than those found for the formation of the mononuclear complexes (Table 4), in accord with the presence of only six nitrogen donors available for the co-ordination of two copper(II) ions. Furthermore, the addition of a second copper(II) ion to the mononuclear complexes leads to a marked change in ligand conformation, with a consequent enthalpic cost. As a consequence of the low stability of the $[Cu_2\mathbf{L}]^{4+}$ complexes, both mono- and bi-nuclear species are present in aqueous solution even with a 1:2 ligand to metal molar ratio (Fig. 3b). The data in Table 5 clearly show that the formation of the binuclear complexes is accompanied by a marked decrease of the molar absorbance of the UV bands at 270 and 290 nm for **L3** and **L4**, respectively, indicating that the heteroaromatic nitrogens are involved in co-ordination, as actually shown by the crystal structure of the $[Cu_2(H\mathbf{L3})(\mu\text{-}OH)(ClO_4)_2Br]^+$ cation. The most interesting finding is the high log *K* values for the addition of hydroxide anions to $[Cu_2\mathbf{L3}]^{4+}$ and $[Cu_2\mathbf{L4}]^{4+}$ to give mono- and di-hydroxo-species. As a consequence, hydroxo-complexes are present in aqueous solution even at slight acidic pH (Fig. 3b). Actually, the six donors of the ligands cannot complete the co-ordination spheres of two copper(II) ions. At the same time the two metals are kept at close distance by the ligand frameworks. These characteristics make these binuclear complexes potential receptors for bridging substrate molecules. The hydroxide anion can be considered one of the simplest examples of a bridge between two metal centres. Indeed, the remarkably high log *K* and $-\Delta H^\circ$ values for the addition of the first hydroxide to the $[Cu_2\mathbf{L}]^{4+}$ complex indicate a strong interaction of OH^- with the dimetallic core, and suggest a bridging co-ordination of this anion. This feature is, once again, confirmed by the crystal structure of $[Cu_2(H\mathbf{L3})(\mu\text{-}OH)(ClO_4)_2Br]^+$, which shows the $Cu_2(\mu\text{-}OH)$ cluster lodged within the ligand cleft.

The electrochemical reduction of the binuclear copper(II) complex with **L3** at pH 9.2 shows two waves at −0.168 and −0.288 V *vs.* NHE. These results may account for two different electron processes, *i.e.* the reduction may take place either through two consecutive two-electron processes ($Cu^{II} \longrightarrow Cu^0$), involving two copper(II) ions with different co-ordination geometries or two single-electron processes ($Cu^{II} \longrightarrow Cu^I \longrightarrow Cu^0$) at two metal centres with equal co-ordination environments. The similarity of the reduction potentials with respect to those found for the mononuclear **L3** complex makes the latter hypothesis more reasonable. The binuclear **L4** complex instead is directly reduced to Cu^0 through a single two-electron process at −0.248 V *vs.* NHE (Fig. 5). As previously observed for the mononuclear $[Cu\mathbf{L4}]^{2+}$ complex, such different behaviour may be due to the more flexible structure of ligand **L4**.

Concluding remarks

The open-chain molecular architecture of ligands **L3** and **L4** remarkably affects the co-ordination properties toward Cu^{II} with respect to those of their cyclic counterparts **L1** and **L2**. The latter form only mononuclear copper(II) complexes. On the contrary, **L3** and **L4** can give also binuclear species in aqueous solutions, due to the higher flexibility which allows the ligands to assume a suitable conformation for lodging bimetallic assemblies. Besides that, the mononuclear complexes with the acyclic ligands are mainly stabilized by a marked favourable entropic change, due to a large desolvation effect. In these complexes the ligands "wrap" around the metal, which as a result is almost co-ordinatively saturated and shielded from the solvent. At the same time, the formation of the $[Cu\mathbf{L3}]^{2+}$ and $[Cu\mathbf{L4}]^{2+}$ complexes is characterized by a rather low enthalpic contribution. This stems mainly from the enthalpic cost of ligand rearrangement in the process of metal co-ordination. Furthermore, in the resulting complexes the heteroaromatic donors are weakly bound to the metal. This feature, which may also contribute to the low enthalpy change, represents a further significant difference with respect to the macrocyclic ligands **L1** and **L2**, where the heteroaromatic units are strongly involved in co-ordination.

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