

Cu(II) and Ni(II) complexes with dipyrindine-containing polyamines with different binding units †

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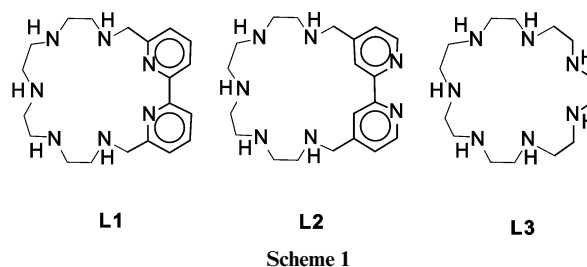
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The coordination features of the two dipyrindine-containing polyamine macrocycles 2,5,8,11,14-pentaaza[15]-[15](2,2')[1,15]-bipyridylophane (**L1**) and 4,4'-(2,5,8,11,14-pentaaza[15]-[15](2,2'))-bipyridylophane (**L2**) toward Cu(II) and Ni(II) have been studied by means of potentiometric and spectrophotometric UV-vis titrations in aqueous solutions. While in **L1** all the nitrogen donor atoms are convergent inside the macrocyclic cavity, in **L2** the heteroaromatic nitrogen atoms are located outside. Ligands **L1** and **L2** form stable mono- and dinuclear complexes with Cu(II). In the case of Ni(II) coordination, only **L1** gives dinuclear complexes, while **L2** can form only mononuclear species. In the Cu(II) or Ni(II) complexes with **L1** the metal(s) are lodged inside the macrocyclic cavity, coordinated to the heteroaromatic nitrogens. As shown by the crystal structure of the [Cu**L1**]²⁺ and [Ni**L1**]²⁺ cations, at least one of the two benzylic nitrogens is not coordinated and facile protonation of the complex takes place at neutral or slightly acidic pH values. The particular molecular architecture of **L2**, which displays two well-separated binding moieties, strongly affects its coordination behavior. In the mononuclear [Cu**L2**]²⁺ complex, the metal is encapsulated inside the cavity, not coordinated by the dipyrindine unit. Protonation of the complex, however, occurs on the aliphatic polyamine chain and gives rise to translocation of the metal outside the cavity, bound to the heteroaromatic nitrogens. In the [Ni**L2**]²⁺ complex the metal is coordinated by the dipyrindine nitrogens, outside the macrocyclic cavity. Thermodynamic and/or kinetic considerations may explain the different behavior with respect to the corresponding Cu(II) complex.

There is a continuing interest in the chemistry of polyaza-macrocycles because of their ability to interact with both metal cations^{1–12} and anionic species.^{12–19} In particular, cyclic polyamines containing six or more nitrogen donors are able to form very stable metal complexes, containing one or more metal ions, due to their large number of nitrogens.^{1,2,6,7} Structural factors, such as ligand rigidity, electron-donor properties of the nitrogens and their disposition, have been shown to play significant roles in determining the binding features of macrocycles toward metal cations.^{1–12} Heteroaromatic subunits, such as 2,2'-dipyridine or 1,10-phenanthroline, are often introduced as integral parts of the host molecules.^{20–26} These units are rigid, and provide two aromatic nitrogens whose unshared electron pairs are beautifully placed to act cooperatively in binding cations. At the same time, incorporation of these moieties into macrocyclic structures allows 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.²⁴

Earlier we reported the synthesis of a series of macrocyclic polyamine ligands containing a dipyrindine unit.^{25,26} Among these, **L1** and **L2** are two isomeric ligands containing different binding sites for metal cations (Scheme 1).²⁷

In **L1** the disposition of the heteroaromatic and aliphatic nitrogen donors is convergent toward the macrocyclic cavity, where the metal cations can be conveniently hosted. The particular molecular architecture of **L2**, instead, defines two



well-separated binding zones, the macrocyclic cavity and the external dipyrindine unit. Actually, a previous study on Zn(II), Cd(II) and Pb(II) binding by **L2** showed that both these units may act as metal binding sites.²⁷ It was shown that in the [Zn**L2**]²⁺ and [Cd**L2**]²⁺ complexes the metal is coordinated to the polyamine chain, inside the cavity. Protonation of this complex occurs on the aliphatic amine groups and gives rise to translocation of the metal outside the macrocyclic cavity. This pH-induced movement does not occur in the [Pb**L2**]²⁺ complex, where the metal is encapsulated into the cavity also in the protonated forms of the complex. Therefore, the binding site for the metal is not only determined by complex protonation, but also by the different characteristics of the metal. For these metal ions, however, the macrocyclic cavity seems to be the preferred binding site in their unprotonated [ML]²⁺ complexes.

It is of interest, therefore, to extend this study to transition metals, such as Cu(II) and Ni(II), with stricter stereochemical requirements than Zn(II), Cd(II) and Pb(II). In this paper we report on Cu(II) and Ni(II) binding by **L1** and **L2**. Aiming to elucidate the relationship between the structural features of these ligands and their coordination properties toward Cu(II) and Ni(II), we have carried out a potentiometric and spectro-

† Electronic supplementary information (ESI) available: selected bond lengths [Å] and angles [°] for [Cu**L1**](ClO₄)₂ (Table S1) and for [Ni**L1**](ClO₄)₂ (Table S2); absorption spectra of **L2** in the presence of Cu(II) (1 : 1 molar ratio) at different pH values (Fig. S1). See <http://www.rsc.org/suppdata/dt/b211904h/>

photometric (UV-vis) study on the interaction with these metals in aqueous solutions. The results are compared with those previously obtained with the saturated polyazacycloalkane 1,4,7,10,13,16,19-heptaazacycloheptacosane (**L3**),²⁸ which contains seven secondary amine groups linked by ethylenic chains (Scheme 1).

Results and discussion

Cu(II) complexation

Crystal structure of [CuL1](ClO₄)₂. The molecular structure consists of complexed cations [CuL1]²⁺ and perchlorate anions. The asymmetric unit contains two independent molecules. The ORTEP drawings of the [CuL1]²⁺ cations in the two molecules (herein indicated A and B) are shown in Fig. 1a and b, respectively. Selected bond distances and angles for the coordination sphere of Cu(II) are reported within the ESI (Table S1). † The Cu(II) ions in A and B display slightly different coordination geometries. In both cases the coordination environments can be best described as octahedral with a strongly tetragonal distortion, as often observed in hexa-coordinated Cu(II) complexes. In complex A the N(1), N(3), N(4) and N(5) nitrogen donors define the equatorial plane (max deviation 0.1473(2) Å for N(4)), the Cu(1)–N bond distances spanning in the range 1.98–2.11 Å. The benzylic amine group N(2) and the heteroaromatic nitrogen N(7) occupy the apical positions, bound at

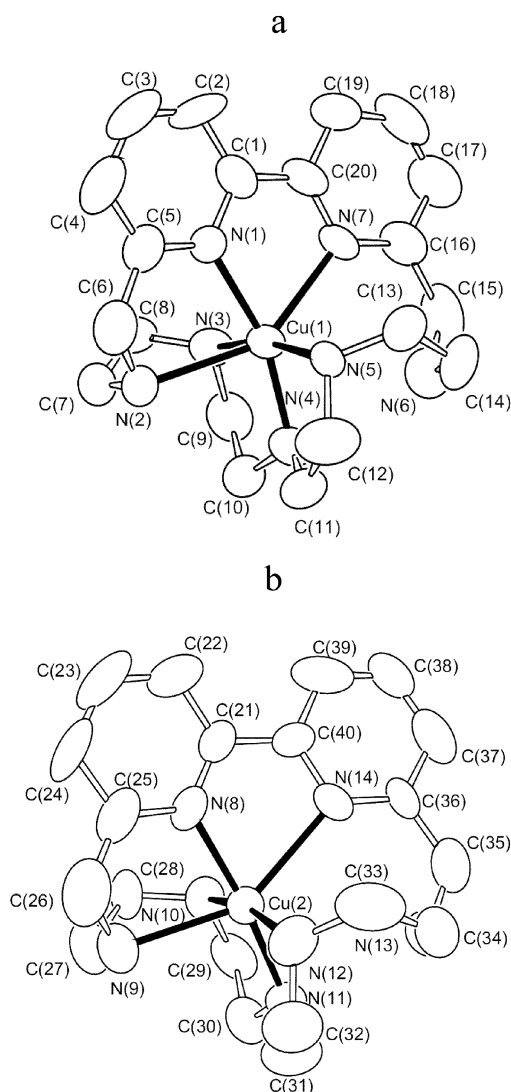


Fig. 1 ORTEP drawings of the [CuL1]²⁺ cations. (a): A unit, (b): B unit.

a much larger distance (Cu(1)–N(2): 2.46(1) Å; Cu(1)–N(7): 2.34(1) Å). The Cu(1)–N(2) and Cu(1)–N(7) bonds form dihedral angles of 14.28(1) and 24.02(1)°, respectively, with the normal to the basal plane. The metal ion lies 0.1906(2) Å above the equatorial plane, shifted toward N(7). One of the benzylic nitrogens, N(6), is not coordinated to the metal. This is a common feature of first-row transition metal complexes with polyamine macrocycles containing 1,10-phenanthroline or 2,2'-dipyridine units; the rigidity of these heteroaromatic units, in fact, does not allow the simultaneous binding to the metal of both the heteroaromatic nitrogens and the adjacent benzylic amine groups.^{25–27} Similarly to the present case, not bound benzylic donors have been already observed in mononuclear complexes with macrocyclic compounds containing heteroaromatic units²⁹ as pendant arms or *p*-phenylene moieties as integral part of macrocyclic frameworks.³⁰

In complex B, the equatorial plane of the distorted octahedron is defined by the N(8), N(10), N(11) and N(12) donors (max deviation 0.0108(3) Å for N(11)), while N(9) and N(14) occupy the apical positions, coordinated at longer distances (Table S1). The Cu(2)–N(9) and Cu(2)–N(14) bonds form dihedral angles of 13.54(1) and 19.99(2)° with the normal to the equatorial plane. The metal lies 0.0910(3) Å out of this plane, shifted toward N(14). These data account for a slightly less distorted coordination sphere of Cu(2) in B with respect to Cu(1) in A, as also testified by the N–Cu(2)–N bond angles along the axes of the octahedron, which are closer to the theoretical 180° value than the corresponding N–Cu(1)–N angles in A (Table S1). As in A, however, a benzylic nitrogen donor (N(13)) is not involved in metal coordination.

In both molecules the two pyridine rings are almost coplanar, with dihedral angles of 7.48(1) and 13.16(1)° in A and B, respectively. The ligand assumes a screw conformation, “wrapping” around the metal ion, which in consequence is embedded inside the macrocyclic cavity. Both in A and B, the equatorial plane of the octahedral coordination sphere is almost normal to the plane of the aromatic unit, forming dihedral angles of 88.64(1)° in A and 85.50(1)° in B.

The macrocyclic framework in A and B displays a marked molecular strain as shown by the C–C–N and C–N–C bond angle values of the polyamine chains, which span in the range 107(2)–119(2)° (A molecule) and 110(1)–121(2)° (B molecule).

In A and B, the corresponding torsion angles of the aliphatic polyamine chain display similar values. There are, however, slight differences (see the ESI †), which can be related to the somewhat more distorted coordination sphere of Cu(1) in the A unit with respect to Cu(2) in the B unit (see above).

Cu(II) coordination in aqueous solution. Cu(II) coordination by ligands **L1** and **L2** was studied by means of potentiometric measurements and the stability constants of the complexes formed in aqueous solutions are listed in Table 1. Both ligands can form mono- and dinuclear Cu(II) complexes in aqueous solutions.

Considering the mononuclear complexes, the data in Table 1 outline some interesting findings. Firstly, the stability constant of the [CuL1]²⁺ complex is by far higher than that of the corresponding **L2** complex. Secondly, Cu(II) forms stable complexes with protonated species of the ligands. This tendency is particularly marked in the case of **L2**, which can form up to a tetraprotonated [CuL2H₄]⁶⁺ complex. Consequently, protonated species of the complexes are present in solution from acidic to slightly alkaline pH values as shown in Fig. 2.

It can be of interest to compare the stability of the **L1** mononuclear complex with that of the corresponding Cu(II) complexes with the macrocyclic ligand **L3**,^{28b} where the dipyridine moiety of **L1** is replaced by an ethylenediamine chain. The stability constant of the **L1** complex is just slightly lower than that of the **L3** one (log *K* = 18.72 for [CuL1]²⁺, Table 1, vs. log *K* = 19.44 for [CuL3]²⁺). This difference may be ascribed to

Table 1 Log K for the Cu(II) complexes with **L1** and **L2** (NMe₄Cl 0.1 M, 298 K)^a

Equilibria	L1	L2
$L + Cu^{2+} \rightleftharpoons CuL^{2+}$	18.72(5)	13.91(6)
$CuL^{2+} + H^+ \rightleftharpoons CuLH^{3+}$	5.97(6)	6.89(7)
$CuLH^{3+} + H^+ \rightleftharpoons CuLH_2^{4+}$		5.89(7)
$CuLH^{3+} + 2H^+ \rightleftharpoons CuLH_3^{5+}$	7.28(7)	
$CuLH_2^{4+} + 2H^+ \rightleftharpoons CuLH_4^{6+}$		7.87(5)
$CuL^{2+} + OH^- \rightleftharpoons CuL(OH)^+$	4.41(1)	2.78(9)
$CuL^{2+} + Cu^{2+} \rightleftharpoons Cu_2L^{4+}$	9.43(8)	7.83(8)
$Cu_2L^{4+} + H^+ \rightleftharpoons Cu_2LH^{5+}$		6.27(5)
$Cu_2LH^{5+} + H^+ \rightleftharpoons Cu_2LH_2^{6+}$		4.92(6)
$Cu_2L^{4+} + OH^- \rightleftharpoons Cu_2L(OH)^{3+}$	7.27(8)	6.00(9)
$Cu_2L(OH)^{3+} + OH^- \rightleftharpoons Cu_2L(OH)_2^{2+}$		3.95(5)

^a The values in parentheses are the standard deviations of the last significant figure.

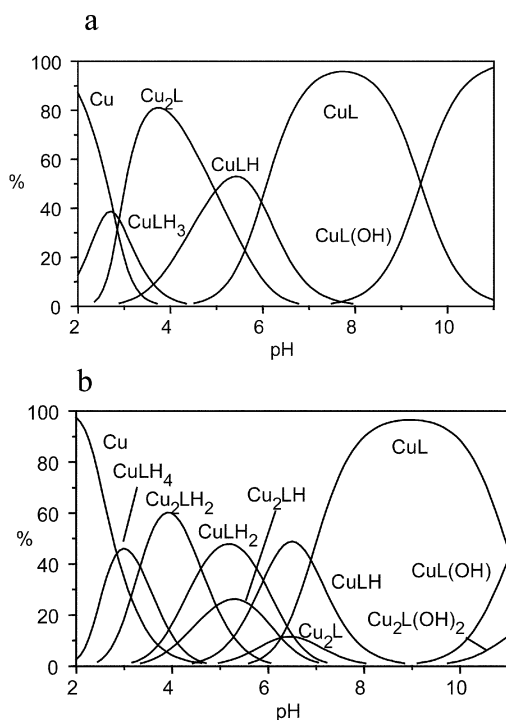


Fig. 2 Species distribution diagrams for the systems Cu(II)/**L1** (a) and Cu(II)/**L2** (b) in 1 : 1 molar ratio ($[L] = [Cu(II)] = 2.5 \times 10^{-5}$ M, NMe₄Cl 0.1 M, 298 K); charges have been omitted for clarity.

the somewhat lower binding ability of dipyrindine with respect to ethylenediamine (log $K = 9.00$ and 10.09 for the equilibrium $Cu^{2+} + L = [CuL]^{2+}$ with **L** = 2,2' dipyrindine³¹ and *N,N'*-dimethylethylenediamine,³² respectively), as well as to the higher flexibility of **L3**, which could allow a better arrangement of the donors around the metal ion.

The absorption spectrum of $[CuL1]^{2+}$ in the visible region displays a band at 629 nm ($\epsilon = 95 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) with a shoulder at *ca.* 750 nm. These spectral features are in accord either with a 6-coordinated Cu(II) ion with distorted octahedral geometry, as actually found in the solid state, or with a 5-coordinated metal ion. On the other hand, in the case of $[CuL3]^{2+}$ it was proposed that only five of seven amine groups are involved in metal coordination. The similar binding ability of **L1** and **L3** toward Cu(II) would suggest a similar coordination environment for the metal, or, at least, an equal number of nitrogen donors involved in metal coordination in the two complexes. This hypothesis is confirmed by the absorption spectrum displayed by $[CuL3]^{2+}$ (a band at 628 nm ($\epsilon = 193 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) with a shoulder at *ca.* 760 nm), very similar to that found

for $[CuL1]^{2+}$. Although the hypothesis of a Cu(II) ion hexacoordinated by the ligand donors cannot completely be dismissed, the similar features observed for $[CuL1]^{2+}$ and $[CuL3]^{2+}$ lead us to propose that in $[CuL1]^{2+}$ the metal would be coordinated by five nitrogen donors; therefore, two nitrogen donors are probably not involved in metal coordination and can easily bind protons, as testified by the tendency of this complex to form protonated species in aqueous solution. On the other hand, the crystal structure of the $[CuL1]^{2+}$ cation shows the metal coordinated by six donors of the ligand in a distorted octahedral geometry (Fig. 1), only one nitrogen being not involved in metal binding (N(6)). The contrast with the conclusions derived from the solution data can be tentatively solved considering that the two nitrogens in axial position in the coordination octahedron (N(2) and N(7)) are just weakly bound, interacting at a long distance with the metal center.

Ligand **L2** contains two well-separated binding units for the metal ion, *i.e.*, the external dipyrindine nitrogens and the macrocyclic cavity, where five nitrogen donors are potentially available for metal coordination. As previously anticipated, ligand **L2** gives a much less stable Cu(II) complex and, at the same time, the $[CuL2]^{2+}$ complex displays a higher tendency to form protonated species than **L1**, forming up to a tetraprotonated $[CuL2H_4]^{6+}$ species in aqueous solution. Aliphatic amine groups are by far more basic than the heteroaromatic nitrogens and the first two protonation constants of the $[CuL2]^{2+}$ complex are remarkably higher than that reported for 2,2'-dipyridine alone (log $K = 4.39$).³¹ This suggests that at least the first protonation steps of $[CuL2]^{2+}$ occur on the polyamine chain. These data may indicate that in the protonated Cu(II) complexes the metal ion is located outside the cavity, coordinated by the heteroaromatic nitrogen donors of dipyrindine, as already found in the case of the protonated Zn(II) and Cd(II) complexes with this ligand.²⁷ On the other hand, the stability constant of $[CuL2]^{2+}$ is by far higher than that reported for the Cu(II) complex with 2,2'-dipyridine (log $K = 13.91$ for $[CuL2]^{2+}$ vs. log $K = 9.00$ ³¹ for $[Cu(2,2'\text{-dipyridine})]^{2+}$) suggesting that in the $[CuL2]^{2+}$ complex the metal is lodged inside the macrocyclic cavity.

To shed further light on the role played by the dipyrindine unit in metal binding, we carried out a UV-vis spectrophotometric study on solutions containing Cu(II) and ligands **L1** and **L2** in equimolar ratio. Ligands **L1** and **L2** each present a sharp band at 288 and 283 nm, respectively, in their UV spectra. As previously observed in the case of proton and Zn(II) binding,²⁷ Cu(II) coordination by the heteroaromatic unit gives marked changes in the absorption spectra of ligands **L1** and **L2**, with the appearance of new structured red-shifted absorption with absorption maximum above 300 nm. These new bands can be used as a diagnostic tool to prove the effective involvement of dipyrindine nitrogens in metal binding. Fig. 3 reports the UV spectra of **L1** in the absence of Cu(II) at pH 12 and in the presence of Cu(II) (1 : 1 molar ratio) at different pH values. A clear red-shift of the absorption band of dipyrindine is observed upon complexation, for both the $[CuL1]^{2+}$ complex and its protonated forms. The spectrum at pH 8, where the $[CuL1]^{2+}$ predominates in solution (spectrum d in Fig. 3), displays a single absorption maximum at 305 nm, while the spectra recorded at acidic pHs also present a shoulder at *ca.* 318 nm, probably due to the presence in solution of the $[Cu_2L1]^{4+}$ complex (see below). Therefore, in the Cu(II) complexes with **L1** the dipyrindine unit is involved in metal coordination, which occurs inside the macrocyclic cavity.

A different behavior is found for the mononuclear Cu(II) complex with **L2**. The analysis of the UV spectra recorded on aqueous solutions containing **L2** and Cu(II) in 1 : 1 molar ratio at different pH values (Fig. 4a) clearly points out a marked red-shift of the dipyrindine absorption band passing from the alkaline pH region, where the $[CuL2]^{2+}$ complex predominates in solution, to acidic pHs, where protonated forms of the complex are prevalent in solution. The comparison of the spectro-

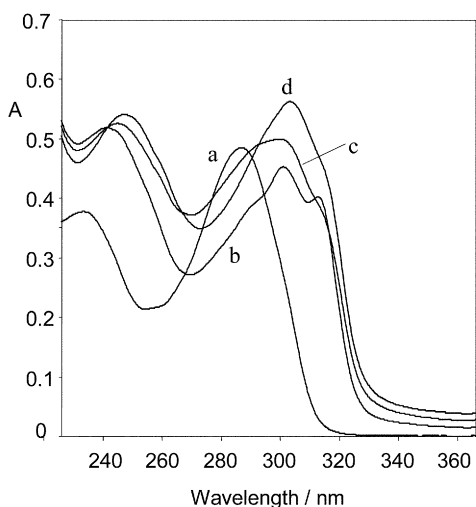


Fig. 3 Absorption spectra of **L1** at pH 12 (a), **L1** in the presence of **Cu(II)** (1 : 1 molar ratio) in aqueous solution at pH 3.7 (b), 5.0 (c) and 8.0 (d) ($[L1] = [Cu(II)] = 4.1 \times 10^{-5} M$).

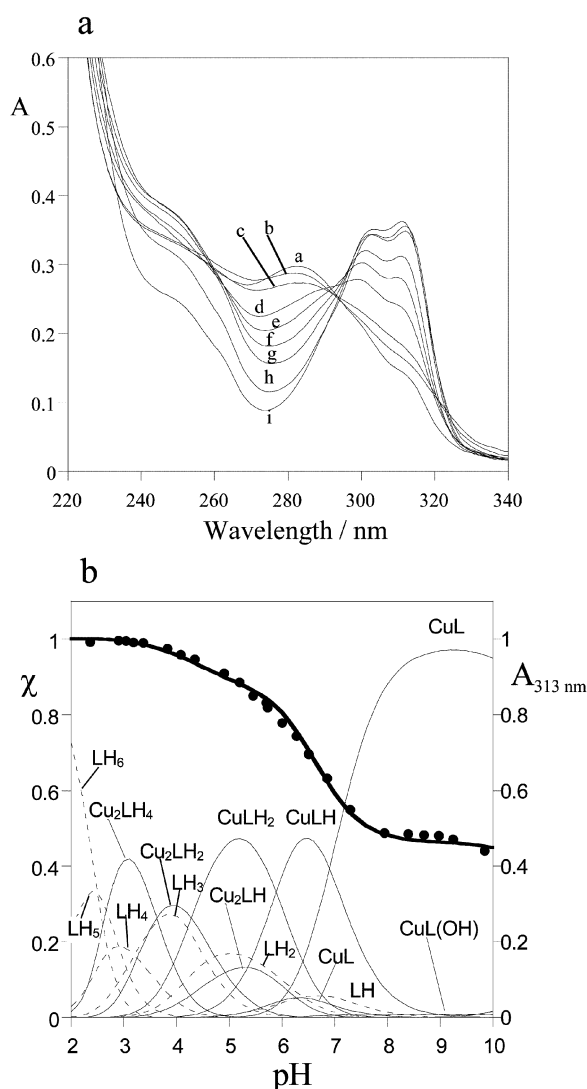
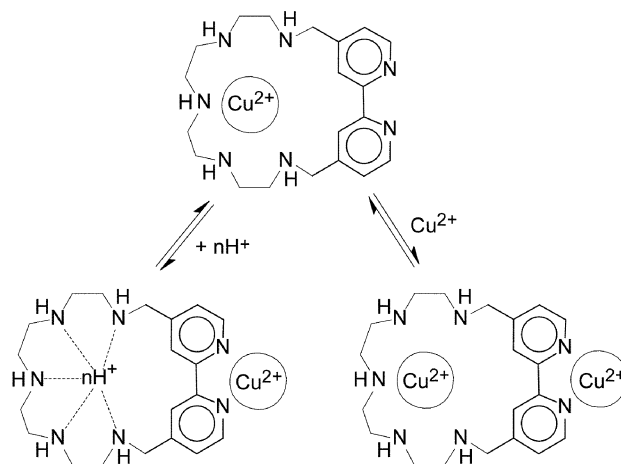


Fig. 4 (a) Absorption spectra of the **L2** in the presence of **Cu(II)** (1 : 1 molar ratio) in aqueous solution at pH 10.86 (a), 9.84 (b), 7.94 (c), 6.85 (d), 6.27 (e), 5.45 (f), 3.83 (g), 2.90 (h), 1.52 (i), ($[L2] = [Cu(II)] = 4.49 \times 10^{-5} M$). (b) Absorbance at 313 nm (●) and molar fraction (χ) of the protonated (dashed lines) and complexed (solid lines) species for the system **L2**/**Cu(II)** (1 : 1 molar ratio) as functions of pH ($[L2] = [Cu(II)] = 2.49 \times 10^{-5} M$, $I = 0.1 M$ NMe_4Cl). Charges have been omitted for clarity.

photometric titration curve with the distribution diagram of the protonated and complexed species of **L2** (Fig. 4b) shows a marked increase of the absorbance at 313 nm with the formation in solution of the protonated species of the **L2** complex (pH < 8). These data account for the involvement of the dipyridine unit in metal coordination in the protonated forms of the **Cu(II)** complex. In other words, in the protonated complexes, the metal is lodged outside the cavity, coordinated by the heteroaromatic nitrogens, while the acidic protons are bound by the polyamine chain (Scheme 2). In the not-protonated forms of the complex, instead, the dipyridine unit is not involved in metal coordination and **Cu(II)** is lodged inside the macrocyclic cavity. A red-shift upon complex protonation is also observed for the d-d band of the complex. The absorption band at 628 nm observed at pH 10, where the $[CuL2]^{2+}$ species prevails in solution, shifts up to 679 nm at pH 6, where protonated forms of the complex predominate in solution (Fig. S1, ESI).[†] This is in accord with a weaker ligand field operating at the metal center in the $[CuL2H_n]^{(x+2)+}$ species, where the metal is coordinated only by the two nitrogens of dipyridine.



Scheme 2

Therefore, the particular molecular topology of this ligand gives rise to a pH-controlled translocation of the metal, since protonation of the $[CuL2]^{2+}$ complex leads to a “jump” of the metal cation from inside to outside the cavity, as sketched in Scheme 2.

As previously observed, both ligands can add a second metal to give dinuclear metal complexes in aqueous solution. In the case of **L1**, the constant for the addition of the second metal to the $[Cu_2L1]^{4+}$ complex is by far lower than the formation constant of the $[CuL1]^{2+}$ (18.72 vs. 9.43 log units, Table 1), as expected considering that two metal cations are lodged at short distance inside the macrocyclic cavity. The seven nitrogen donors of the macrocycle, however, cannot fulfill the coordination sphere of both the two metals, leading to low coordination numbers for the **Cu(II)** ions in this complex. The remarkable red-shift of the d-d band observed in the visible spectrum of $[Cu_2L1]^{4+}$ ($\lambda_{max} = 718 \text{ nm}$, $\epsilon = 307 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) with respect to the mononuclear $[CuL1]^{2+}$ one ($\lambda_{max} = 629 \text{ nm}$), supports this hypothesis. The $[Cu_2L1]^{4+}$ complex also shows a marked tendency to form a monohydroxo species in aqueous solution (Table 1 and Fig. 5a). The constant for the addition of the OH^- anion to the $[Cu_2L1]^{4+}$ complex is high (log $K = 7.27$ logarithmic units) in comparison with the analogous constants for the addition of a hydroxide group to the corresponding mononuclear $[CuL1]^{2+}$ complex (log $K = 4.41$, see Table 1). This indication of a strong binding of the hydroxide ion leads to suppose that this group bridges the two metal centers. The UV region of the absorption spectrum of the dinuclear **Cu(II)** complexes displays a structured absorption band

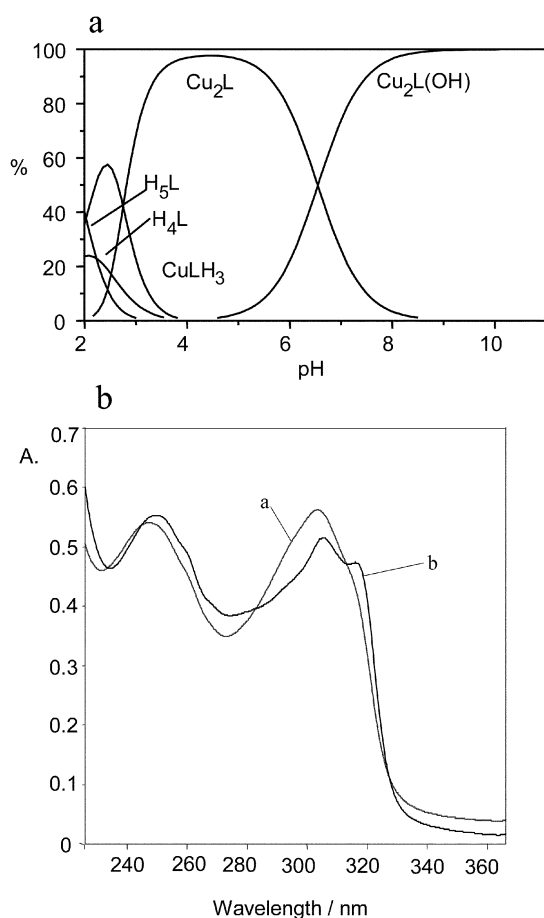


Fig. 5 (a) Species distribution diagram for the system Cu(II)/L1 in 2 : 1 molar ratio ($[L1] = 4.1 \times 10^{-5}$ M, $[Cu(II)] = 8.2 \times 10^{-5}$ M, NMe_4Cl 0.1 M, 298 K); charges have been omitted for clarity. (b) Absorption spectra of L1 in the presence of Cu(II) in 1 : 1 molar ratio at pH 8 (a) and in 1 : 2 molar ratio at pH 4.02 ($[L1] = 4.1 \times 10^{-5}$ M).

with $\lambda_{max} = 306$ and 319 nm, further red-shifted with respect to that of the $[CuL1]^{2+}$ complex (Fig. 5b). This would suggest a stronger interaction between the heteroaromatic nitrogens and Cu(II) in the dinuclear complexes with respect to the mononuclear one. Although conclusions on coordination properties of ligands in solution derived from solid state observations may sometimes be misleading, the crystal structure of the mononuclear $[CuL1](ClO_4)_2$ complex shows that one dipyrindine nitrogen is weakly involved in metal coordination (see above). It is reasonable that in the dinuclear $[Cu_2L1]^{4+}$ complex, which contains two metal ions enclosed within the macrocyclic framework, both the dipyrindine nitrogens are strongly involved in metal binding, leading to further red-shift of the dipyrindine band.

The dinuclear Cu(II) complex with L2 displays, once again, a different behavior. The difference between the addition constant of the first Cu(II) ion to L2 and that for the addition of a second metal ion to $[CuL2]^{2+}$ (13.91 vs. 7.83 log unit, Table 1) is remarkably lower with respect to that found for the Cu(II) complexes with L1. At the same time, the constant for the addition of the second metal to the $[CuL2]^{2+}$ complex is only slightly lower to that reported for Cu(II) complexation with 2,2'-dipyridine (7.83 vs. 9 log units). These data indicate that the second Cu(II) ion coordinates to the dipyrindine unit, giving rise to a dinuclear complex in which the two metals occupy the two separated binding zones of this ligand (Scheme 2). Actually, the UV absorption spectrum of the dinuclear $[Cu_2L2]^{2+}$ complex displays a structured band with two maxima at 302 and 313 nm, almost equal to that found for the protonated mononuclear $[CuL2H_x]^{(x+2)+}$ complexes, indicating that in

the dinuclear complex one metal cation is indeed coordinated by the dipyrindine unit.

Ni(II) complexation

Crystal structure of $[NiL1](ClO_4)_2$. The crystal structure of $[NiL1](ClO_4)_2$ is composed by $[NiL1]^{2+}$ cations and perchlorate anions. Fig. 6 shows an ORTEP drawing of $[NiL1]^{2+}$ selected bond angles and distances for the metal coordination environment are reported within the ESI (Table S2).[†] The Ni(II) ion is hexa-coordinated by the heteroaromatic nitrogens N(1) and N(7) and by the secondary amine groups N(2), N(3), N(4) and N(5). As in the $[CuL1]^{2+}$ complex, the benzylic N(6) nitrogen is not coordinated. The resulting coordination geometry is a tetragonally distorted octahedron, where N(2) and N(7) define the apical positions and N(1), N(3), N(4) and N(5) the equatorial plane (max deviation 0.100(7) Å for N(4)). The tetragonal distortion, however, is smaller than in the $[CuL1]^{2+}$ complex, the apical bond distances being by far shorter than those found in the Cu(II) complex. The metal lies 0.094(1) Å out of the equatorial plane, shifted toward N(7).

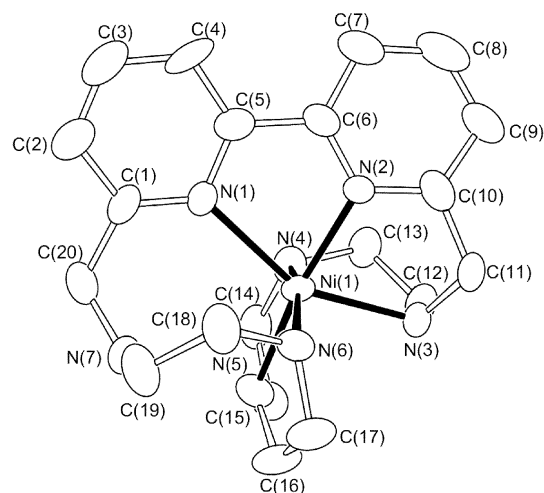


Fig. 6 ORTEP drawing of the $[NiL1]^{2+}$ cation.

A similar distorted octahedral coordination geometry has been also found in the crystal structure of the Ni(II) complex with ligand L3.^{28a}

The overall conformation of the complex cation is quite similar to that found in $[CuL1]^{2+}$. The ligand adopts a screw-shaped conformation and envelops the metal. The two heteroaromatic rings are almost coplanar, with a dihedral angle of 7.9(3)°. The equatorial plane is almost perpendicular to the dipyrindine unit (86.6(3)°). Finally, the aliphatic polyamine chain displays a marked conformational strain, the C–C–N and C–N–C bond angles ranging from 106.8(7)° for C(10) to 118.8(7)° for C(15).

Ni(II) coordination in aqueous solution. The L1 complexation features toward Ni(II) are similar to those observed for Cu(II). As shown in Table 2, both mono- and dinuclear complexes are formed in aqueous solution. Considering the mononuclear complexes, the most significant difference with respect to the Cu(II) complexes is the lower stability of the $[NiL1]^{2+}$ complex than $[CuL1]^{2+}$. This behavior, however, is usually observed in Cu(II) and Ni(II) complexation by polyamines.³³ The formation constant of the $[NiL1]^{2+}$ complex is only slightly lower than that of corresponding complex with L3 (log $K = 15.54$ and 16.56 for the equilibrium $Ni + L = NiL^{2+}$ with $L = L1$ and $L3$,^{28a} respectively). For $[NiL3]^{2+}$ it was found that the metal is hexa-coordinated by six nitrogen donors of the macrocycle. By far higher drops in stability (3–4 log units) are usually observed passing from hexa-coordinated to penta-coordinated Ni(II)

Table 2 Log *K* for the Ni(II) complexes with **L1** and **L2** (NMe₄Cl 0.1 M, 298 K)^a

Equilibria	L1	L2
$L + Ni^{2+} \rightleftharpoons NiL^{2+}$	15.54(3)	5.71(4)
$NiL^{2+} + H^+ \rightleftharpoons NiLH^{3+}$	7.44(4)	10.55(2)
$NiLH^{3+} + H^+ \rightleftharpoons NiLH_2^{4+}$	4.12(4)	7.80(3)
$NiLH_2^{4+} + H^+ \rightleftharpoons NiLH_3^{5+}$		6.21(4)
$NiLH_3^{5+} + H^+ \rightleftharpoons NiLH_4^{6+}$		5.02(4)
<hr/>		
$2Ni^{2+} + L + OH^- \rightleftharpoons Ni_2L(OH)^{3+}$	23.61	
$Ni_2L(OH)^{3+} + OH^- \rightleftharpoons Ni_2L(OH)_2^{2+}$	4.71	

^a The values in parentheses are the standard deviations of the last significant figure.

complexes with polyamine ligands.³³ This suggests that, similarly to $[NiL_3]^{2+}$, in $[NiL_1]^{2+}$ the metal is coordinated to six nitrogen donors, as actually shown by the crystal structure of the $[NiL_1](ClO_4)_2$ solid complex. Furthermore, the $[NiL_1]^{2+}$ complex in aqueous solution presents a typical spectrum for an octahedral high-spin Ni(II) chromophore (a band at 848 nm ($\epsilon = 19 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) with a shoulder at *ca.* 800 nm, and a band at 544 nm ($\epsilon = 8 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$), due to the ${}^3A_2 \rightarrow {}^3T_2$ and ${}^3A_2 \rightarrow {}^3T_1$ transitions). As sometimes observed in 6-coordinated Ni(II) complexes, the band at highest energy (${}^3A_2 \rightarrow {}^3T_1(P)$) is hidden by the charge transfer transitions. The band at the lowest energy yields the octahedral splitting parameter Δ_o of 11790 cm^{-1} , a value close to those reported for octahedral complexes with polyamine macrocycles;³⁴ the Racah parameter *B* is found to be 804 cm^{-1} .³⁵ The reflectance spectrum of the $[NiL_1](ClO_4)_2$ solid complex shows similar spectral features (two bands at 850 and 550 nm). These data suggest that the coordination environment for Ni(II) found in $[NiL_1](ClO_4)_2$ is also maintained in aqueous solution. Therefore, in $[NiL_1]^{2+}$ one nitrogen is not bound to the metal, accounting for the high value of the equilibrium constant for binding of the first proton to the complex (log *K* = 7.44).

Differently from Cu(II) complexation, the slightly lower stability of the $[NiL_1]^{2+}$ with respect to $[NiL_3]^{2+}$ cannot be ascribed to the replacement of the heteroaromatic nitrogens of dipyrindine in **L1** with the amine groups of ethylenediamine in **L3**, since dipyrindine and ethylenediamine shows a similar binding ability toward Ni(II) (log *K* = 7.04 and 7.11 for the equilibrium $Ni^{2+} + L = [NiL]^{2+}$ with **L** = 2,2' dipyrindine³⁶ and *N,N'*-dimethylethylenediamine,³⁷ respectively). The lower stability of $[NiL_1]^{2+}$ is probably related to the more stiffened **L1** framework, due to the presence of a dipyrindine unit, more rigid than an ethylenediamine chain, within the macrocyclic ring. Such an increased rigidity may reduce the ability of the ligand to adapt itself to the stereochemical requirements of Ni(II), which are much stricter than the Cu(II) ones, producing a decrease in thermodynamic stability of the $[NiL_1]^{2+}$ complex.

As already observed in the Cu(II) complexes, Ni(II) complexation by **L1** in aqueous solutions gives rise to a new red-shifted band at 305 nm. Fig. 7a clearly shows a marked increase of the absorbance at 305 nm in the pH range 3.7–6, where the process of complex formation occurs. The spectral data in Fig. 7a account for the involvement of the dipyrindine moiety in metal coordination in the mononuclear complexes $[NiL_1]^{2+}$ and $[NiL_1H]^{3+}$.

Similarly to Cu(II) complexation, **L1** can also form dinuclear Ni(II) complexes in aqueous solutions. In this case, however, the formation of the $[Ni_2L_1]^{4+}$ complex is not detected in our experimental conditions and dinuclear complexes are only present in their hydroxylated forms $[Ni_2L_1(OH)]^{3+}$ and $[Ni_2L_1(OH)_2]^{2+}$, the second one being largely prevalent at alkaline pHs (Fig. 7b). The UV spectra of the dipyrindine unit in these complexes are similar to that of the mononuclear complexes, displaying band with absorption maximum at 307 nm. As shown in Fig. 7b, the absorbance at 307 nm increases with the

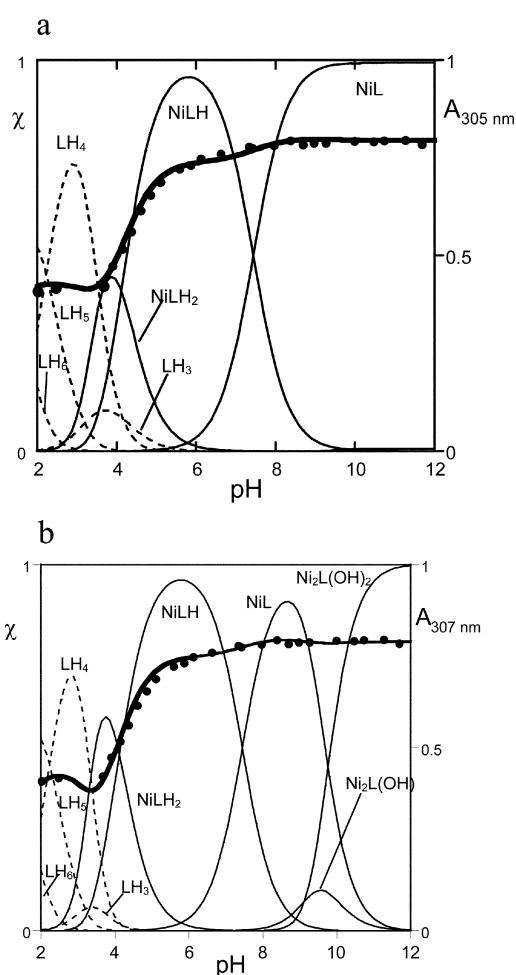


Fig. 7 (a) Absorbance at 305 nm (●) and molar fraction (χ) of the protonated (dashed lines) and complexed (solid lines) species for the system **L1**/Ni(II) (1 : 1 molar ratio) as function of pH ($[L_1] = [Ni(II)] = 4.97 \times 10^{-5} \text{ M}$, $I = 0.1 \text{ M NMe}_4\text{Cl}$). (b) Absorbance at 307 nm (●) and molar fraction (χ) of the protonated (dashed lines) and complexed (solid lines) species for the system **L1**/Ni(II) (1 : 2 molar ratio) as function of pH ($[L_1] = 4.97 \times 10^{-5} \text{ M}$, $[Ni(II)] = 9.95 \times 10^{-5} \text{ M}$, $I = 0.1 \text{ M NMe}_4\text{Cl}$). Charges have been omitted for clarity

formation of the mononuclear complexes at acidic pHs and does not change with the formation of the dinuclear species in the alkaline pH region, accounting for a similar coordination mode of dipyrindine to Ni(II) in both mono- and dinuclear complexes. The d–d absorption bands observed in the vis-NIR spectra (two bands respectively at 938 nm ($\epsilon = 25 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) and 560 nm ($\epsilon = 16 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$)) of the dinuclear Ni(II) complexes account, once again, for an octahedral coordination of Ni(II). These bands, however, are markedly red-shifted with respect to the corresponding bands of the mononuclear complex $[NiL_1]^{2+}$. As in the binuclear Cu(II) complexes, the weaker ligand field operating on the metal centers is probably due to the lower number of nitrogen donors bound to each metal ion with respect to the single Ni(II) ion in $[NiL_1]^{2+}$.

Since **L1** shows similar coordination features toward Cu(II) and Ni(II), we expected for **L2** a similar coordination behavior toward the two metals. On the contrary, potentiometric measurements showed that **L2** forms only mononuclear complexes with Ni(II). The absorption spectrum of the $[NiL_2]^{2+}$ complex displays in the vis-NIR region two bands at 930 nm ($\epsilon = 8.4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) and 577 nm ($\epsilon = 88 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$), due to the ${}^3A_2 \rightarrow {}^3T_2$ and ${}^3A_2 \rightarrow {}^3T_1$ transitions, respectively. Once again these spectral features can be attributed to a high spin octahedral complex, the band at the highest energy (${}^3A_2 \rightarrow {}^3T_1(P)$) being hidden by the charge transfer and/or dipyrindine bands. The observed absorption bands allows one to calculate Δ_o and *B* values of 10740 and 902 cm^{-1} . Their values are in the

range generally observed for Ni(II) octahedral complexes.³⁵ The process of Ni(II) complexation was followed by means of spectrophotometric measurements at 298 K, evidencing that complete formation of the complex occurs in *ca.* 1 h at pH 11.

The stability constant of the $[\text{NiL}_2]^{2+}$ complex is just somewhat lower than that found for 2,2'-dipyridine, suggesting that Ni(II) is coordinated by the heteroaromatic nitrogens of the dipyrindine unit, outside the macrocyclic cavity. Therefore, facile protonation may occur on the pentaamine chain of the macrocycle, accounting for the high values of the protonation constant of the $[\text{NiL}_2]^{2+}$ (Table 2). Actually, the protonation constants of the complex are only 1–1.5 log units lower than the corresponding protonation constant of the free ligand **L2**. As a consequence, protonated species of the complex are prevalent in aqueous solution from acidic to alkaline pH values (Fig. 8a). Interestingly, the possible formation of Ni(II) complexes with a metal to ligand 1 : 2 stoichiometry was not evidenced neither by potentiometry or spectrophotometric measurements at different pHs. The absorption spectra of solutions containing Ni(II) and **L2** in 1 : 2 molar ratio display the same bands of the 1 : 1 complex and no change was observed in ten days at 298 K. This result can be tentatively explained considering that the formation of 1 : 2 complexes is extremely slow at room temperature. Furthermore, the $[\text{NiL}_2]^{2+}$ complex forms protonated species from acidic to alkaline pH values (Fig. 8a); therefore, the assembly of $[\text{NiL}_2\text{H}_x]^{(2+x)+}$ species could be also inhibited by electrostatic repulsions between the two protonated macrocyclic moieties.

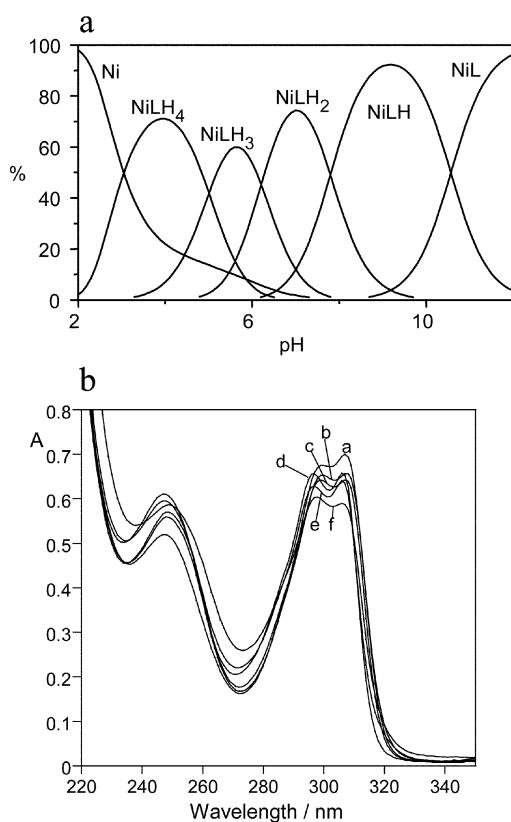


Fig. 8 (a) Species distribution diagrams for the systems Ni(II)/**L2** in 1 : 1 molar ratio ($[\text{L}] = [\text{Cu(II)}] = 1 \times 10^{-3}$ M, NMe_4Cl 0.1 M, 298 K); charges have been omitted for clarity. (b) Absorption spectra of the **L2** in the presence of Ni(II) (1 : 1 molar ratio) in aqueous solution at pH 1.75 (a), 3.61 (b), 5.65 (c), 7.48 (d), 8.55 (e), 12.21 (f).

The UV absorption spectrum of the $[\text{NiL}_2]^{2+}$ complex displays a structured band with two maxima at 298 and 307 nm. As discussed above, these spectral features account for metal coordination by the dipyrindine unit. As shown in Fig. 8b, these spectral features are almost independent of pH, indicating

that, differently from Cu(II), the Ni(II) binding site is not pH-controlled. These results are rather surprising since, in the case of Cu(II), Zn(II),^{27a} Cd(II)^{27b} and Pb(II)^{27b} complexation, the macrocyclic cavity is the preferred binding site for the metal, at least in the $[\text{ML}_2]^{2+}$ complexes.

It is known that, in comparison with Cu(II), Zn(II) or Cd(II), Ni(II) complexation is often affected by kinetic inertness, in particular with sterically hindered ligands. Therefore, the process of Ni(II) encapsulation may be extremely slow at room temperature and Ni(II) coordination may occur at the less hindered binding site (the external dipyrindine nitrogens), even if Ni(II) external binding is not thermodynamically favored. In this case the log *K* values for Ni(II) complexation by **L2** should be referred to an intermediate step of the process of complex formation. It is to be noted that prolonged (up to seven days) heating in water (100 °C, pH 10.5) or in methanol (65 °C) does not lead to significant changes in both the d–d and dipyrindine absorption bands of the complex, indicating that the metal does not translate inside the macrocyclic cavity even in drastic conditions.

Similarly, prolonged heating of the complex in the presence of a further equivalent of metal does not affect the d–d bands of mononuclear complex; this would indicate that dinuclear metal complexes, containing an inner-cavity coordinated metal ion, are not formed.

All these experiments strongly suggest that the outer-cavity Ni(II) coordination is kinetically controlled.

On the other hand, the hypothesis of a thermodynamic control of Ni(II) complexation cannot be completely dismissed. Coordination of Ni(II) by dipyrindine nitrogens, outside the cavity, could be also favored from a thermodynamic point of view. It is to be noted that Ni(II) has a greater tendency to impose its own geometry on ligands than Cu(II), Zn(II) or Cd(II). At the same time, the presence of a rigid dipyrindine moiety leads to an overall ligand stiffening and to a reduced ability of the “intra-cavity” **L2** amine donors to adapt themselves to the rather strict stereochemical requirements of Ni(II). This could thermodynamically favor Ni(II) complexation by dipyrindine nitrogens, outside the cavity.

Conclusions

Both Cu(II) and Ni(II) form 1 : 1 and 1 : 2 complexes in aqueous solutions with ligand **L1**, which contains a pentaamine chain linking the 6,6' position of a dipyrindine unit. In the mononuclear complexes the metal is coordinated by the dipyrindine moiety, as shown by the appearance of new red-shifted bands in the UV absorption spectra as well as by the crystal structure of the $[\text{CuL}_1]^{2+}$ and $[\text{NiL}_1]^{2+}$ complexes. On the other hand, the high values of the protonation constants of the complexes suggest that some aliphatic amine groups are weakly bound or not bound to these metals.

Ligand **L2** contains two well-separated binding moieties. This particular molecular architecture gives rise to a different coordination behavior toward Cu(II) and Ni(II) in aqueous solutions. In the mononuclear $[\text{CuL}_2]^{2+}$ complex, the metal is coordinated inside the macrocyclic cavity, not bound by the heteroaromatic moiety. Protonation of the complex takes place on the more basic aliphatic amine groups and leads to translocation of the metal from inside to outside the cavity. Therefore, in the $[\text{CuL}_2\text{H}_n]^{(2+n)+}$ complexes, the metal is coordinated to the heteroaromatic nitrogens. In all the Ni(II) complexes with **L2** the metal is surprisingly coordinated to the dipyrindine nitrogens, outside the cavity. Thermodynamic and kinetic factors can account for this coordination mode.

Both the $[\text{CuL}_2]^{2+}$ and $[\text{NiL}_2]^{2+}$ complexes display a “metal-free” binding unit (the dipyrindine nitrogens in $[\text{CuL}_2]^{2+}$ and the polyamine chain in $[\text{NiL}_2]^{2+}$) as a potential coordination site for different metal cations. Therefore, it can be of interest, in future studies, to explore the ability of these mononuclear

Table 3 Crystal data and structure refinement for [CuL1](ClO₄)₂ and [NiL1](ClO₄)₂

	[CuL1](ClO ₄) ₂	[NiL1](ClO ₄) ₂
Empirical formula	C ₂₀ H ₃₁ Cl ₂ CuN ₇ O ₈	C ₂₀ H ₃₁ Cl ₂ N ₇ NiO ₈
Formula weight	631.96	627.13
Temperature/K	298	298
Wavelength/Å	0.71069	1.54180
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>
<i>a</i> /Å	14.245(5)	11.7484(6)
<i>b</i> /Å	18.438(7)	11.2278(6)
<i>c</i> /Å	20.233(7)	19.6420(10)
β /°	101.26(3)	95.359(2)
Volume/Å ³	5212(3)	2579.6(2)
<i>Z</i>	8	4
Calculated density/Mg m ⁻³	1.611	1.615
Absorption coefficient/mm ⁻¹	1.102	3.520
Reflections collected/unique [<i>R</i> (int)]	6583/6361 [0.0711]	7612/2762 [0.0415]
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>): <i>R</i> ₁ , <i>wR</i> ₂ ^a	0.0882, 0.2225	0.0809, 0.1776
<i>R</i> indices (all data): <i>R</i> ₁ , <i>wR</i> ₂ ^a	0.2377, 0.2892	0.0969, 0.1857

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$$

complexes to add a second metal, yielding heterodinuclear metal complexes.

Experimental

Synthesis

Ligands **L1** and **L2** were obtained as previously reported.^{26d,27} Crystals of [CuL1](ClO₄)₂ and [NiL1](ClO₄)₂ were obtained by slow evaporation at room temperature of aqueous solutions containing ligand **L1** and Cu(ClO₄)₄·6H₂O or Ni(ClO₄)₄·6H₂O in equimolecular ratio.

X-Ray structure analysis

Single crystals of [CuL1](ClO₄)₂ (a) and [NiL1](ClO₄)₂ (b) were analyzed by means of X-ray crystallography and a summary of the crystallographic data is reported in Table 3. The intensities of some reflections were monitored during data collection to check the stability of the crystals: no loss of intensity was observed during data collections. The integrated intensities were corrected for Lorentz and polarization effects. Both structures were solved by direct methods (SIR-97).³⁸ Refinements were performed by means of full-matrix least-squares using the SHELXL-97 program.³⁹ In both structures all non-hydrogen atoms were anisotropically refined while the hydrogen atoms were introduced in calculated position and their coordinates were refined according to the linked atoms. An overall fixed isotropic thermal parameter was used for the hydrogen atoms in structure (a) while in (b) the isotropic thermal factors were refined according to the linked atoms. No residual electron density was found at the end of refinements.

CCDC reference numbers 199214 and 199215.

See <http://www.rsc.org/suppdata/dt/b2/b211904h/> for crystallographic data in CIF or other electronic format.

(a) An empirical absorption correction was applied. Unfortunately, the crystal quality was very poor. The completeness for the Cu(II) data collection was only 77.5%, because of the too low intensity of reflections with high θ . This also leads to a low number of observed reflections (2775) vs. the number of collected reflections (6361). Disorder and/or thermal motion affects the structure of [CuL1](ClO₄)₂ and high thermal parameters were found for several atoms, in particular for the oxygen atoms belonging to the perchlorate anions, but no model able to solve this disorder was recognised. In the case of one perchlorate, the disorder affects also the chlorine atoms (Cl(4)).

(b) Data acquisition, integration, reduction and absorption correction were performed using SMART, SAINT and SAD-

ABS program.⁴⁰ Disorder or thermal motion affects one perchlorate. Among the different models used to try to interpretate the disorder of this perchlorate, the better one consists in fixing the O21 position and introducing four oxygens with partial occupation parameters (O22, O23, O24 and O25) each corresponding to the four peaks at bond distance from the Cl atom and residual electron density greater than 1.

Potentiometric measurements

Equilibrium constants for complexation reactions with **L1** and **L2** were determined by means of potentiometric measurements (pH = -log [H⁺]), carried out in 0.1 mol dm⁻³ NMe₄Cl at 298.1 ± 0.1 K, in the pH range 2.5–11, by using the equipment that has been already described.²⁸ The reference electrode was an Ag/AgCl electrode in saturated KCl solution. The glass electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO₂-free NaOH solutions and determining the equivalent point by Gran's method.⁴¹ This allow one to determine the standard potential *E*^o, and the ionic product of water (p*K*_w = 13.83 ± 0.01). 1 × 10⁻³ to 2 × 10⁻³ mol dm⁻³ ligand and metal ion concentrations were employed in the potentiometric measurements, varying the metal to ligand molar ratio from 0.5 : 1 to 2 : 1. The process of Ni(II) complexation is slow at room temperature; therefore, to achieve equilibrium conditions, 1 h was allowed to elapse after each titrant addition before acquiring the emf values. At least three measurements (about 100 experimental points each one) were performed for each system. The computer program HYPERQUAD⁴² was used to calculate the stability constants of metal complexes from emf data. The titration curves for each system were treated either as a single set or as separated entities without significant variations in the values of the protonation or metal complexation constants.

Spectrophotometric measurements

All aqueous solutions were prepared in 0.10 mol dm⁻³ NaCl. HCl and NaOH were used to adjust the pH values that were measured on a Metrohm 713 pH meter. Absorption spectra were recorded on a Perkin-Elmer Lambda 6 spectrophotometer.

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