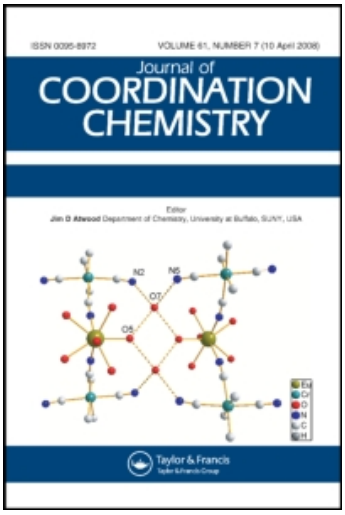

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pH-Controlled metal translocation outside/inside the cavity of a polyamine macrocycle

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pH-Controlled metal translocation outside/inside the cavity of a polyamine macrocycle

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The synthesis of the macrocyclic ligand 4,4′-(2,6,10,13,18-pentaaza[26])-2,2′-bipyridylcylophane (**L**), which contains a penta-amine chain linking the 4,4′ positions of a 2,2′-bipyridyl moiety, is reported. The heteroaromatic nitrogens of **L** are located outside the macrocyclic cavity. Ligand protonation, as well as Cu(II) and Ni(II) complexation by **L**, were studied by potentiometric and UV-Vis techniques in aqueous solution. Only mononuclear complexes are formed. In $[Cu\mathbf{L}]^{2+}$, the metal is encapsulated inside the cavity, not coordinated by the bipyridyl unit. Protonation of the complex occurs on the aliphatic polyamine chain and gives rise to translocation of the metal outside the cavity, bound to the heteroaromatic nitrogens. Conversely, Ni(II) is always bound to the bipyridyl nitrogens in both protonated and unprotonated complexes.

Keywords: Macrocycles; Bipyridyl moiety; Cu(II) complexes; Ni(II) complexes

1. Introduction

Macrocyclic polyamine ligands containing various binding functionalities are of current interest due to their ability in selective binding, transformation, and transfer of a large variety of substrates, from charged species [1–22] to neutral molecules [23]. Structural factors, such as ligand rigidity, electron-donor properties of nitrogens and their disposition within the cyclic framework, play significant roles in determining the binding features of polyamine macrocycles toward metal cations [1–13]. Heteroaromatic groups, such as 2,2′-bipyridine or 1,10-phenanthroline, are often used as building blocks for assembly of host molecules [24, 25]. These units are rigid and provide two aromatic nitrogens whose unshared electron pairs act cooperatively to bind cations. Incorporation of these moieties into macrocyclic structures allows combination within the same ligand, of the special complexation features of macrocycles with the photophysical and photochemical properties displayed by metal complexes of heterocycles.

We have synthesized the new macrocyclic ligand **L** (scheme 1) containing a 2,2′-bipyridine unit linked through its 4,4′ positions in such a way that the heteroaromatic

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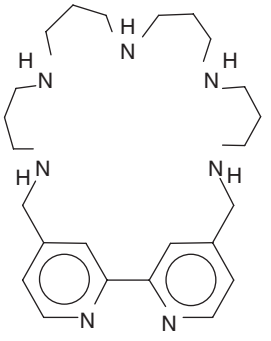
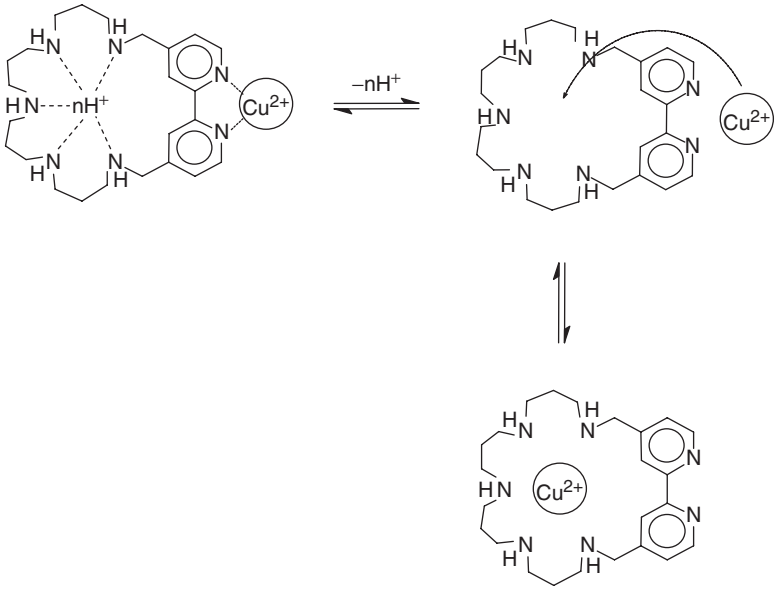
nitrogens point outside the cavity. The particular molecular architecture of **L** defines two well-separated binding zones, the macrocyclic cavity and the external bipyridine chelating unit. Since metal coordination is competitive with ligand protonation and aliphatic nitrogens are usually more basic than heteroaromatic ones [26], we hoped that a metal ion coordinated to **L** could change its coordination site upon protonation of the aliphatic amine, moving from inside to outside the macrocyclic cavity, as previously observed for an analogous ligand [27], as shown in scheme 2.

To elucidate the relationship between the structural features of **L** and its coordination properties toward metal ions, we have carried out a potentiometric and spectrophotometric (UV-Vis) study on the interaction of Cu(II) and Ni(II) in aqueous solutions.



Scheme 1. The macrocyclic ligand L.



Scheme 2. pH-Controlled translocation of Cu(II) inside/outside the ligand cavity.

2. Experimental

2.1. *Synthesis*

4,4′-*Bis*(bromomethyl)-2,2′-bipyridine [28] (**1**) and 1,5,9,13,17-pentakis(*p*-tolylsulfonyl)-1,5,9,13,17-pentaazatridecane [28] (**2**) were synthesized as previously described.

2.1.1. 4,4′-(2,6,10,13,18-Pentatosyl-2,6,10,13,18-pentaaza[19])-2,2′-bipyridylophane (3). A solution of **1** (6 g, 17.5 mmol) in dry CH_3CN (500 cm^3) was added over a period of 4 h to a refluxing and vigorously stirred suspension of **2** (17.8 g, 17.5 mmol) and K_2CO_3 (28 g, 0.20 mol) in CH_3CN (1 L). After the addition was completed, the solution was refluxed for an additional 3 h. Then the suspension was filtered through celite, and the solution was vacuum evaporated to yield a crude oil, which was purified by column chromatography on neutral alumina with a ligroin : ethyl acetate 1 : 2 mixture. The eluted fractions were collected and evaporated to dryness to afford **3** as a colorless solid. Yield: 13.9 g (11.6 mmol, 66.3%). El. Anal: found: C, 59.4; H, 5.7; N, 8.3. Calcd for $C_{59}H_{69}N_7S_5O_{10}$: C, 59.22; H, 5.81; N, 8.19. ^{1}H NMR ($CDCl_3$): δ(ppm): 1.20 (m, 4H), 1.68 (t, 4H), 2.41 (s, 3H), 2.48 (s, 6H), 2.43 (s, 6H), 2.69 (t, 4H), 2.81 (t, 4H), 2.99 (t, 4H), 3.16 (t, 4H), 4.31 (s, 4H), 7.63–7.58 (m, 6H), 7.45-7.28 (m, 12H), 7.75 (m, 4H), 8.36 (s, 2H), 8.63 (d, 2H).

2.1.2. 4,4′-(2,6,10,13,18-Pentaaza[26])-2,2′-bipyridylocyclophane hexahydrobromide (L.6HBr). Compound **3** (2.85 g, 2.38 mmol) and phenol (33 g, 0.350 mol) were dissolved in 33% HBr/CH_3COOH (250 cm^3). The reaction mixture was stirred at 90°C for 24 h until a precipitate formed. The solid was filtered out and washed several times with CH_2Cl_2. The hexahydrobromide salt was recrystallized from a EtOH : water 2 : 1 mixture. Yield 1.6 g (1.76 mmol; 73.7%). El. Anal.: found: C, 31.4; H, 5.1; N, 11.1. Calcd for $C_{24}H_{45}N_7Br_6$: C, 31.64; H, 4.98; N, 10.76. ^{1}H NMR (D_2O, pH = 4): δ(ppm): 8.74 (d, 2H), 8.46 (s, 2H), 7.72 (d, 2H), 4.46 (s, 4H), 3.22-3.07 (m, 16H), 2.11–1.98 (m, 8H).

2.2. *Potentiometric measurements*

Equilibrium constants for protonation and complexation reactions with **L** were determined by pH-metric measurements at 298.1 ± 0.1 K in 0.1 mol dm^{-3} NMe_4Cl using equipment that has been already described [29]. The combinated Ingold 405 S7/120 electrode was calibrated as a hydrogen concentration probe using known amounts of HCl with CO_2-free NaOH solutions and determining the equivalent point by Gran's method [30]. This allows one to determine the standard potential E° and the ionic product of water ($pK_w = 13.83 \pm 0.01$). 1×10^{-3}–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. Three titration experiments (about 100 data points each) were performed for each system. The computer program HYPERQUAD [31] was used to calculate equilibrium constants from Electromotive Force (e.m.f.) data.

2.3. *Spectrophotometric measurements*

Absorption spectra were recorded on a Perkin–Elmer Lambda 6 spectrophotometer. HCl and NaOH were used to adjust the pH values that were measured on a Metrohm 713 pH meter.

2.4. *NMR and electronic spectroscopy*

The 300.07 MHz ^{1}H spectra in D_2O solutions at different pH values were recorded at 298 K in a Varian Unity 300 MHz spectrometer. In order to adjust the pD, small amounts of 0.01 mol dm^{-3} NaOD or DCl solutions were added to solutions containing **L**. The pH was calculated from the measured pD values using the relationship: pH = pD − 0.40 [32].

3. Results and discussion

3.1. *Ligand protonation*

3.1.1. Solution studies. The protonation equilibria of **L** were studied by potentiometric measurements in aqueous solution (0.1 mol dm^{-3} NMe_4Cl, 298.1 K) leading to determination of the protonation constants reported in table 1.

Although **L** contains seven amine groups, only six protonation constants were determined, the seventh protonation stage taking place at very low pH, outside the pH range (2.5–11.5) useful for potentiometric measurements. Since bipyridine nitrogens are characterized by far lower basicity than amine nitrogens, it is expected that at least the first protonation steps of **L** take place on the polyamine chain. This hypothesis is confirmed by analysis of the absorption spectra recorded on solutions containing **L** at various pH values [figure 1(a) and (b)].

Protonation of the heteroaromatic nitrogens can be easily monitored by UV-Vis spectrophotometric titrations, since protonation of bipyridine is accompanied by the appearance of a band at ca 306 nm, red-shifted with respect to the typical band of free bipyridine. According to figure 1, this occurs with formation of $[H_6\mathbf{L}]^{6+}$, i.e. protonation of the bipyridine nitrogen takes place only in the sixth protonation step of **L**.

As can be seen from the values reported in table 1, the basicity of **L** decreases with increasing positive charge on the molecules, the large difference between successive

Table 1. Protonation constants (log K) of **L** (0.1 M NMe_4Cl, 298.1 K).

Reaction	Log K
$\mathbf{L} + H^+ = [\mathbf{LH}]^+$	10.51(3)
$[\mathbf{LH}]^+ + H^+ = [\mathbf{LH}_2]^{2+}$	9.68(5)
$[\mathbf{LH}_2]^{2+} + H^+ = [\mathbf{LH}_3]^{3+}$	7.94(8)
$[\mathbf{LH}_3]^{3+} + H^+ = [\mathbf{LH}_4]^{4+}$	6.52(8)
$[\mathbf{LH}_4]^{4+} + H^+ = [\mathbf{LH}_5]^{5+}$	4.50(6)
$[\mathbf{LH}_5]^{5+} + H^+ = [\mathbf{LH}_6]^{6+}$	3.23(4)

protonation constants being observed between the fourth and fifth protonation stages due to the high-electrostatic repulsion experienced by the last proton binding the polyamine chain.

3.1.2. Cu(II) coordination in aqueous solution. Cu(II) coordination by **L** in aqueous solutions was studied by potentiometric measurements, leading to determination of the complex stability constants listed in table 2. Data in table 2 outline two main complexation features. First, the ligand forms only mononuclear Cu(II) complexes in

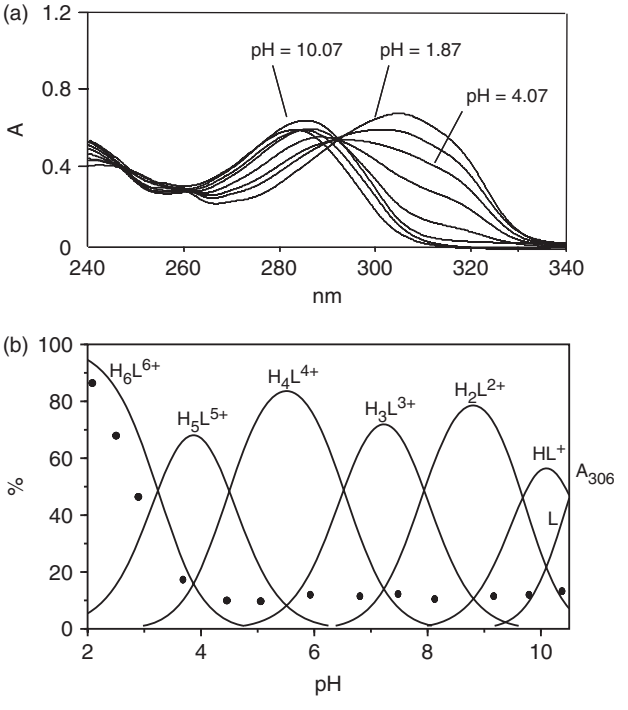


Figure 1. (a) pH dependence of the absorption spectra of **L** ($[\mathbf{L}] = 8.35 \times 10^{-5}$ M, I = 0.1 M; (b) absorbance at 306 nm (•) superimposed to the distribution diagram of the protonated species of **L** (dashed lines).

Table 2. Log *K* for the Cu(II) and Ni(II) complexes with **L** (0.1 M NMe_4Cl, 298.1 K).

	Log *K*	
Reaction	Cu^{2+}	Ni^{2+}
$\mathbf{L} + M^{2+} = [ML]^{2+}$	8.87(6)	8.68(6)
$[ML]^{2+} + H^+ = [MLH]^{3+}$	9.11(7)	
$[ML]^{2+} + 2H^+ = [MLH_2]^{4+}$		18.26(4)
$[MLH]^{3+} + H^+ = [MLH_2]^{4+}$	8.30(7)	
$[MLH_2]^{4+} + H^+ = [MLH_3]^{5+}$	7.01(4)	7.09(6)
$[MLH_3]^{5+} + H^+ = [MLH_4]^{6+}$	6.39(5)	6.42(5)
$[MLH_4]^{6+} + H^+ = [MLH_5]^{7+}$	5.62(5)	5.00(4)
$[ML]^{2+} + 2OH^- = [ML(OH)_2]$	7.46(9)	9.90(8)

aqueous solutions. Second, the Cu(II) complex is able to bear extensive protonation up to formation of the pentaprotonated $[Cu\mathbf{L}H_5]^{7+}$ species. Consequently, protonated species of the complexes are present in solution from acidic to alkaline pH values, as shown in figure 2.

L contains two well-separated binding units for the metal ion, i.e., the external bipyridine nitrogens and the macrocyclic cavity where five nitrogen donors are potentially available for metal coordination. As previously anticipated, the $[Cu\mathbf{L}]^{2+}$ complex displays a high tendency to form protonated species, forming up to a pentaprotonated species. Since aliphatic amine groups are by far more basic than heteroaromatic nitrogen atoms and protonation constants of the $[Cu\mathbf{L}]^{2+}$ complex (table 2) are remarkably higher than that reported for free 2,2′-bipyridine ($\log K = 4.39$) [33], it seems likely that all five protonation steps of $[Cu\mathbf{L}]^{2+}$ occur on the polyamine chain. Accordingly, in the protonated Cu(II) complexes the metal ion would be located outside the cavity, coordinated by the heteroaromatic nitrogen donor atoms of bipyridine, as already found for a previous ligand with similar molecular architecture [27]. In that case, the ligand containing ethylenic chains displayed higher stability constants for formation of $[CuL]^{2+}$ ($\log K = 13.91$) [27] according to the greater stability of five-membered chelate rings with respect to six-membered ones, while it showed a lower tendency to protonation due to its lower basicity.

To shed further light on the role played by the bipyridine unit in metal binding, we carried out an UV-Vis spectrophotometric study on solutions containing equimolar amounts of Cu(II) and **L** at different pH values. **L** has a band at 285 nm in the UV spectrum. Similarly to bipyridine protonation, Cu(II) coordination to the heteroaromatic unit gives rise to marked changes in the absorption spectra of the ligand with the appearance of new structured red-shifted absorption band at 300 nm on passing from the alkaline pH region, where $[Cu\mathbf{L}]^{2+}$ and $[Cu\mathbf{L}(OH)_2]$ are predominant, to acidic pH, where protonated forms of the complex are present in solution (figure 3). This new band can be used as a diagnostic tool to prove involvement of bipyridine nitrogens in metal binding. As shown by figure 3(b), where the variation of the 300 nm absorbance with pH has been superimposed to the distribution diagram of the species formed in the system Cu(II)/**L**, the 300 nm absorbance decreases with increasing pH in very acidic

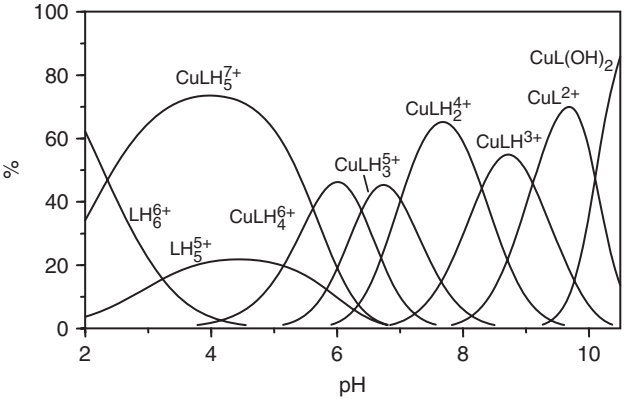


Figure 2. Species distribution diagrams for the systems Cu(II)/**L** in 1 : 1 molar ratio ($[\mathbf{L}] = [Cu(II)] = 1 \times 10^{-3}$ M NMe_4Cl 0.1 M, 298 K).

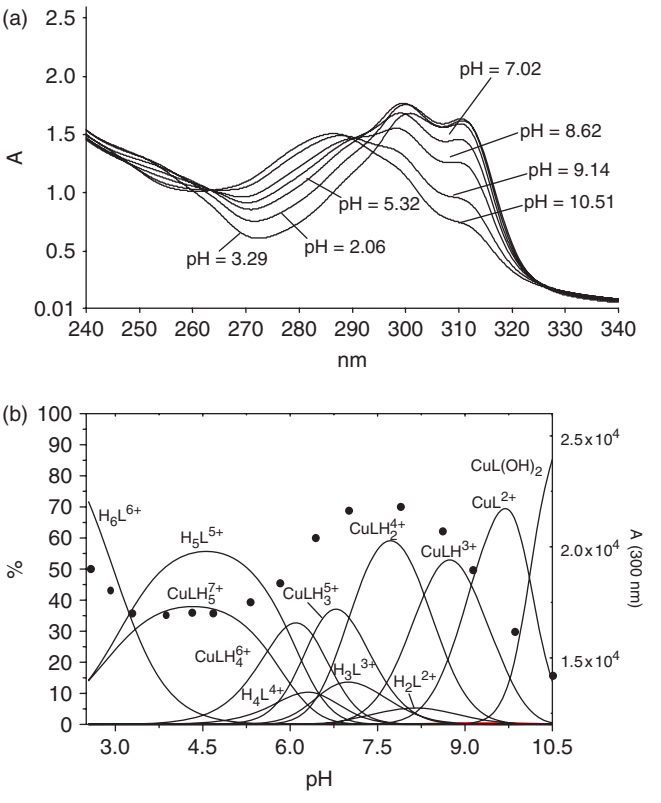


Figure 3. (a) Absorption spectra of **L** in the presence of Cu(II) (1 : 1 molar ratio) in aqueous solution at various pH values ([**L**] = [Cu(II)] 8.85×10^{-5} M); (b) Absorbance at 300 nm (•) superimposed to the distribution diagram of the protonated and complexed species of **L** (dashed lines).

solution (pH < 3.5). In this pH range the highly protonated species of the ligand are prevalent and the absorbance decrease is mainly due to bipyridine deprotonation occurring on passing from $[H_6\mathbf{L}]^{6+}$ to $[H_5\mathbf{L}]^{5+}$, as already observed in the spectrophotometric titration of the free ligand. Above pH 6, the 300 nm absorbance increases with formation of the $[Cu\mathbf{L}H_3]^{5+}$, $[Cu\mathbf{L}H_2]^{4+}$ and $[Cu\mathbf{L}H]^{3+}$ species to successively decrease in alkaline solutions when the protonated complexes disappear. These data account for the involvement of the bipyridine unit in metal coordination in the protonated forms of the Cu(II) complexes. In other words, in the protonated complexes, the metal is lodged outside the cavity, coordinated by the heteroaromatic nitrogen atoms, while the acidic protons are bound by the polyamine chain (scheme 2).

The most interesting finding, however, is the sharp decrease of the absorbance occurring in alkaline solution upon formation of the $[Cu\mathbf{L}]^{2+}$ complex and its dihydroxo derivatives. Such behavior implies that in the non-protonated forms of the complex the bipyridine unit is not involved in metal coordination and Cu(II) is inside the macrocyclic cavity. The particular molecular topology of this ligand gives rise to a pH-controlled change of binding site for the metal, which translocates from inside to outside the cavity upon complex protonation.

3.1.3. Ni(II) coordination in aqueous solution. The complexation features of **L** toward Ni(II) are rather different from those observed for Cu(II), despite the fact that the stoichiometry of the species formed is practically the same (table 2). The main difference was revealed by the absorption spectra of the Ni(II) complex.

The UV absorption spectrum of the Ni(II) complex displays a structured band with maxima at 298 and 306 nm (figure 4). As discussed above, these spectral features account for metal coordination to the bipyridine unit. As shown in figure 4(b), the spectrum is independent of pH, indicating that different from Cu(II), Ni(II) is always bound to the bipyridine moiety, outside the macrocyclic cavity, in all complex species. It is known that Ni(II) complexation can be 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 occurs at the less hindered binding site, namely the external bipyridine nitrogen atoms. It is to be noted that prolonged (up to seven days) heating in water (100°C, pH 10.5) does not lead to significant changes in bipyridine absorption bands, indicating that the metal does not move inside the macrocyclic cavity even in drastic conditions.

However, coordination of Ni(II) by bipyridine nitrogens, outside the cavity, could be also favored from a thermodynamic point of view. It is to be noted that Ni(II) has

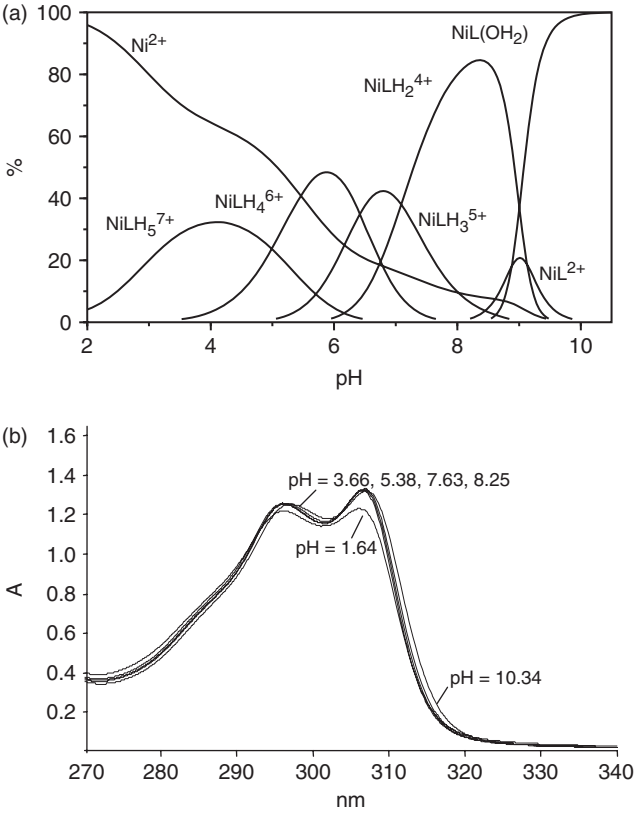


Figure 4. (a) Species distribution diagrams for the system Ni(II)/**L** in 1 : 1 molar ratio $[\mathbf{L}] = 1 \times 10^{-3}$ M, NMe_4Cl 0.1 M, 298 K; (b) Absorption spectra of **L** in the presence of Ni(II) $[Ni(II)] = [\mathbf{L}] = 8.85 \times 10^{-5}$ M in aqueous solution at various pH values.

a marked tendency to impose its own geometry to ligands. At the same time, the presence of a rigid bipyridine moiety leads to an overall ligand stiffening and to reduced ability of the "intra-cavity" **L** amine donors to adapt themselves to the rather strict stereochemical requirements of Ni(II). This could thermodynamically favor Ni(II) complexation by bipyridine nitrogens, outside the cavity. These data are consistent with those already found for Ni(II) complexes of a similar ligand containing ethylenic chains instead of propylenic ones [27]. It is to be noted that the stability constants of the $[NiL]^{2+}$ complex with the previous ligand ($\log K = 5.71$) [27] is significantly lower than that determined for $[Ni\mathbf{L}]^{2+}$ ($\log K = 8.68$, table 2), which is slightly higher than the stability constant of the Ni(II) complex with 2,2′-bipyridine ($\log K = 7.04$) [34]. It seems reasonable that in the case of the complex with the more flexible ligand **L**, some participation of aliphatic amine groups in the coordination to the metal ion bound by the bipyridine moiety outside the cavity might be possible.

4. Conclusions

Ligand **L** contains two well-separated binding moieties. This particular molecular architecture gives rise to different coordination behaviors toward Cu(II) and Ni(II) in aqueous solutions. In the $[Cu\mathbf{L}]^{2+}$ 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 $[Cu\mathbf{L}H_n]^{2+n}$ complexes, the metal is coordinated to the heteroaromatic nitrogens. On the contrary, in Ni(II) complexes the metal is always coordinated to the bipyridine nitrogens, outside the cavity. Thermodynamic and kinetic factors can account for the different coordination modes.

Both $[Cu\mathbf{L}]^{2+}$ and $[Ni\mathbf{L}]^{2+}$ complexes display a "metal-free" binding unit (the bipyridine nitrogen atoms in $[Cu\mathbf{L}]^{2+}$ and the polyamine chain in $[Ni\mathbf{L}]^{2+}$) 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 complexes to add a second metal, yielding heterodinuclear metal complexes.

References

[1] (a) J.S. Bradshaw. *Aza-Crown Macrocycles*, Wiley, New York (1993); (b) K.E. Krakowiak, J.S. Bradshaw, D.J. Zamecka-Krakowiak. *Chem. Rev.*, **89**, 929 (1989); (c) R.M. Izatt, K. Pawlak, J.S. Bradshaw. *Chem. Rev.*, **95**, 2529 (1995).
[2] G.W. Gokel. In *Crown Ethers and Cryptands*, J.F. Stoddart (Ed.), The Royal Society of Chemistry, Cambridge, UK (1991).
[3] J.M. Lehn. *Supramolecular Chemistry*, VCH, New York (1995).
[4] P. Guerriero, S. Tamburini, P.A. Vigato. *Coord. Chem. Rev.*, **110**, 17 (1995).
[5] D.A. Nation, A.E. Martell, R.I. Carroll, A. Clearfield. *Inorg. Chem.*, **35**, 7246 (1996).
[6] L.F. Lindoy. *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge, UK (1989).
[7] L.F. Lindoy. *Pure Appl. Chem.*, **69**, 2179 (1997).
[8] (a) V. Amendola, L. Fabbrizzi, C. Mangano, P. Pallavicini, A. Perotti, A. Taglietti. *J. Chem. Soc., Dalton Trans.*, 185 (2000); (b) L. Fabrizzi (Ed.), *Luminescent Sensors*, *Coord. Chem. Rev.*, **205**, (2000).

[9] T.A. Kaden, D. Tschudin, M. Studer, U. Brunner. *Pure Appl. Chem.*, **61**, 879 (1989).
[10] T.A. Kaden. *Pure Appl. Chem.*, **60**, 117 (1988).
[11] A.J. Blake, N.R. Champness, P. Hubberstey, W.S. Li, M. Schröder, M.A. Withersby. *Coord. Chem. Rev.*, **183**, 117 (1999).
[12] J. Nelson, V. McKee, G. Morgan. *Progr. Inorg. Chem.*, **47**, 167 (1998).
[13] (a) C. Bazzicalupi, A. Bencini, V. Fusi, C. Giorgi, P. Paoletti, B. Valtancoli. *Inorg. Chem.*, **37**, 941 (1998); (b) C. Bazzicalupi, A. Bencini, E. Berni, V. Fedi, V. Fusi, C. Giorgi, P. Paoletti, B. Valtancoli. *Inorg. Chem.*, **38**, 4115 (1999).
[14] R.M. Izatt, K. Pawlak, J.S. Bradshaw, R.L. Bruenig. *Chem. Rev.*, **91**, 1721 (1991).
[15] A. Bianchi, E. Garcia-España, K. Bowman-James (Eds.). *Supramolecular Chemistry of Anions*, Wiley-VCH, New York (1997).
[16] M.W. Hosseini, A.J. Blaker, J.M. Lehn. *J. Am. Chem. Soc.*, **112**, 3896 (1990).
[17] J.A. Aguilar, E. Garcia-España, J.A. Guerrero, S.V. Luis, J.M. Llinares, M.F. Miravet, J.A. Ramirez, C. Soriano. *J. Chem. Soc. Chem. Commun.*, 2237 (1995).
[18] A.V. Eliseev, H.J. Schneider. *J. Am. Chem. Soc.*, **116**, 6081 (1994).
[19] (a) C. Bazzicalupi, A. Beconcini, A. Bencini, V. Fusi, C. Giorgi, A. Masotti, B. Valtancoli. *J. Chem. Soc., Perkin Trans.*, **2**, 1675 (1999); (b) C. Bazzicalupi, A. Bencini, A. Bianchi, M. Cecchi, B. Escuder, V. Fusi, E. Garcia-España, C. Giorgi, S.V. Luis, G. Maccagni, V. Marcelino, P. Paoletti, B. Valtancoli. *J. Am. Chem. Soc.*, **121**, 6807 (1999).
[20] (a) M.P. Mertes, K.B. Mertes. *Acc. Chem. Res.*, **23**, 413 (1990); (b) S. Mason, T. Clifford, L. Seib, K. Kuzcera, K. Bowman-James. *J. Am. Chem. Soc.*, **120**, 8899 (1998).
[21] V. Kràl, H. Furuta, K. Shreder, V. Lynch, J.L. Sessler. *J. Am. Chem. Soc.*, **118**, 1595 (1996).
[22] V. Balzani, A. Credi, F.M. Raymo, J.F. Stoddart. *Angew. Chem. Int. Ed.*, **39**, 3348 (2000) and references cited therein.
[23] R.M. Izatt, J.S. Bradshaw, K. Pawlak, R. Bruening, L. Tarbet. *Chem. Rev.*, **92**, 1261 (1992).
[24] (a) J.C. Rodriguez-Ubis, B. Alpha, D. Plancherel, J.M. Lehn. *Helv. Chim. Acta*, **67**, 2264 (1984); (b) B. Alpha, J.M. Lehn, G. Mathis. *Angew. Chem. Int. Ed. Engl.*, **26**, 266 (1987); (c) M. Cesario, J. Guilhem, E. Pascard, E. Anklam, J.M. Lehn, M. Pietraskiewicz. *Helv. Chim. Acta*, **74**, 1157 (1991); (d) I. Bkouche-Waksmann, J. Guilhem, C. Pascard, B. Alpha, R. Deschenaux, J.M. Lehn. *Helv. Chim. Acta*, **75**, 1163 (1991); (e) J.M. Lehn, J.B. Regnouf de Vains. *Helv. Chim. Acta*, **75**, 1221 (1992); (f) C. Roth, J.M. Lehn, J. Guilheim, C. Pascard. *Helv. Chim. Acta*, **78**, 1895 (1995); (g) J. Azéma, C. Galaup, C. Picard, P. Tisnès, O. Ramos, O. Juanes, J.C. Rodrigez-Ubis, E. Brunet. *Tetrahedron*, **56**, 2673 (2000); (h) G.R. Newkome, S. Pappalardo, V.K. Gupta, F. Fronczek. *J. Org. Chem.*, **48**, 4848 (1983).
[25] (a) P.L. Vidal, B. Divisia-Blohorn, G. Bidan, J.M. Kern, J.P. Sauvage, J.L. Hazemann. *Inorg. Chem.*, **38**, 4203 (1999); (b) M. Weck, B. Mohr, J.P. Sauvage, R.H. Grubbs. *J. Org. Chem.*, **64**, 5463 (1999); (c) G. Rapenne, C. Dietrich-Buchecker, J.P. Sauvage. *J. Am. Chem. Soc.*, **121**, 994 (1999); (d) M. Meyer, A.M. Albrecht-Gary, C.O. Dietrich-Buchecker, J.P. Sauvage. *Inorg. Chem.*, **38**, 2279 (1999).
[26] A. Bencini, A. Bianchi, E. Garcia-España, M. Micheloni, J.A. Ramirez. *Coord. Chem. Rev.*, **118**, 97 (1999).
[27] C. Anda, C. Bazzicalupi, A. Bencini, A. Bianchi, P. Fornasari, C. Giorgi, B. Valtancoli, C. Lodeiro, A.J. Parola, F. Pina. *J. Chem. Soc., Dalton Trans.*, 1299 (2003).
[28] C. Kaes, M.W. Hosseini, A. De Cian, J. Fischer. *Tetrahedron Lett.*, **38**, 4389 (1997).
[29] A. Bianchi, L. Bologni, P. Dapporto, M. Micheloni, P. Paoletti. *Inorg. Chem.*, **23**, 1201 (1984).
[30] G. Gran. *Analyst (London)*, **77**, 661 (1952).
[31] P. Gans, A. Sabatini, A. Vacca. *Talanta*, **43**, 807 (1996).
[32] A.K. Covington, M. Paabo, R.A. Robinson, R.G. Bates. *Anal. Chem.*, **40**, 700 (1968).
[33] A. Odani, M. Masuda, K. Inumai, O. Yamauchi. *J. Am. Chem. Soc.*, **114**, 6294 (1992).
[34] A. Das. *Trans. Met. Chem.*, **16**, 108 (1991).