Inorganica Chimica Acta 362 (2009) 3709–3714

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

A family of polyamino phenolic macrocyclic ligands. Acid–base and coordination properties towards Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) ions

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A R T I C L E I N F O

Article history:
Received 24 February 2009
Received in revised form 8 April 2009
Accepted 17 April 2009
Available online 3 May 2009

Keywords:
Polyamine
Phenol
Macrocyclic ligands
Metal complexes
Coordination chemistry

A B S T R A C T

The acid–base and coordination properties towards Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) of four polyamino-phenol macrocycles 15-hydroxy-3,6,9-triazabicyclo[9.3.1]pentadeca-11,13,1^{15}-triene **L1**, 18-hydroxy-3,6,9,12-tetraazabicyclo[12.3.1]octadeca-14,16,1^{18}-triene **L2**, 21-hydroxy-3,6,9,12,15-penta-azabicyclo[15.3.1]enaicosa-17,19,1^{21}-triene **L3** and 24-hydroxy-3,6,9,12,15,18-hexaazabicyclo[18.3.1]tetraicosa-20,22,1^{24}-triene **L4** are reported. The protonation and stability constants were determined by means of potentiometric measurements in 0.15 mol dm^{-3} NMe$_4$Cl aqueous solution at 298.1 K. **L1** forms highly unsaturated Co(II), Cu(II), Zn(II) and Cd(II) mononuclear complexes that are prone to give dimeric dinuclear species with $[(\mathrm{MH}_{-1}\mathbf{L1})_2]^{2+}$ stoichiometry, in solution. **L2** forms stable Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) mononuclear complexes that can coordinate external species as OH$^-$ anion, giving hydroxylated complexes at alkaline pH. **L3** forms stable Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) mononuclear complexes and Co(II), Ni(II), Cu(II) and Zn(II) dinuclear $[\mathrm{M_2H_{-1}}\mathbf{L3}]^{3+}$ species. **L4** forms stable mono- and dinuclear Co(II), Cu(II), Zn(II) and Cd(II) complexes, but only mononuclear species with Pb(II). The effect of macrocyclic size is considered in the discussion of results.

1. Introduction

Ligands able to selectively bind a specific metal ion undergoing a concomitant spectroscopic response (such color change or variation in fluorescence properties including emission wavelength or intensity) are important in host–guest chemistry. Macrocyclic ligands are more selective than open-chain ones and usually form complexed species with greater stability; for this reason many efforts have been devoted to the design and synthesis of macrocycles able to coordinate metal ions in their cavities [1]. What's more, the presence of a photosensitive group makes such compounds suitable for use as simple optical sensors [2–4]. Phenol, naphtol and biphenol groups are endowed with both photoactive and coordinative properties, and therefore these groups could be employed as building blocks in constructing highly sensitive and interesting polyaza-ligands [5].

Ligands able to form dinuclear metal complexes in which the two metal centers are forced by the molecular topology to stay close to each other are of great interest [6], because when the metal ions show an unsaturated coordination requirement they can be used as metallo-receptors which often show selectivity for the substrate. Selectivity can be achieved by the type of metal ions bound as well as by the distance between the two metal centers which can cooperate (or not) in the coordination of the guest [7–9].

Macrocycles bearing a phenolic group based upon crown ether or aza-crown ether derivatives have been studied together with their coordination properties towards hard alkali metal ions [5]. In this context, it is of interest to synthesize new ligands derived from the polyazamacrocycles containing the phenolic ionophores, for use in extending the coordination ability of metal ions and increasing the water solubility of the metal complex. Moreover, polyamine macrocycles may constitute an excellent base for the studies of molecular recognition of different kinds of substrates, such as inorganic or organic cations, anionic and neutral molecular species [10]. The presence of an aromatic optical sensor group in the ligand is particularly important, as this extends its ability to control the host–guest interaction.

The usefulness of polyazamacrocycle receptors characterized by different cavity size and bearing a chromogenic group led us to develop new synthetic strategy for use in producing simple azamacrocycles incorporating phenolic, biphenolic and various N- and O-based hetero-aromatic functions. The number of amine nitrogen atoms, as well as the dimensions of the macrocyclic cavity, can be varied to modulate the coordination properties. In our previous paper [12] we demonstrated that ligands **L1**, **L2** and **L4** (Chart 1) and their Cu(II) and Zn(II) mono- and dinuclear complexes bind differently to nitroxide radicals, derived from TEMPO

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doi:10.1016/j.ica.2009.04.027

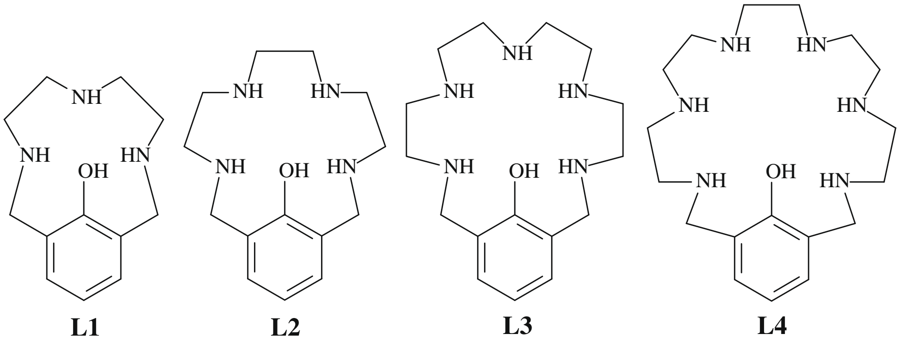

Chart 1.

(2,2,6,6-Tetramethylpiperidine-1-oxyl) that mimics well the properties of pollutant molecules such as organic species having different polarities and charges, surfactants and polyaromatic free radicals.

In this paper we report extensive studies on the acid–base and coordination behavior of a family of four macrocycles: 15-hydroxy-3,6,9-triazabicyclo[9.3.1]pentadeca-11,13,1^{15}-triene **L1** [11,12], 18-hydroxy-3,6,9,12-tetraazabicyclo[12.3.1]octadeca-14,16,1^{18}-triene **L2** [12,13], 21-hydroxy-3,6,9,12,15-pentaazabicyclo[15.3.1]enaicosa-17,19,1^{21}-triene **L3** [13] and 24-hydroxy-3,6,9,12,15,18-hexaazabicyclo[18.3.1]tetraicosa-20,22,1^{24}-triene **L4** [12,14] (Chart 1) that were previously synthesized by our group. All these molecules are phenol-based polyaza-macrocyclic ligands containing a polyaza-macrocyclic ring of increasing size; in particular from **L1** to **L4** the number of nitrogen atoms separated by ethylene chains increases from three to six, respectively.

2. Results and discussion

2.1. Synthesis

Ligands **L1**, **L2**, **L3** and **L4** were synthesized as previous reported [11,13,14].

2.2. Solution studies

2.2.1. Basicity

Table 1 summarizes the basicity constants of **L1**–**L4** as potentiometrically determined in 0.15 mol dm^{-3} NMe_4Cl aqueous solution at 298.1 K. Due to the presence of the phenolic functions, when ligands lose the hydroxyl proton, they are present in solution as anionic $H_{-1}L^-$ species. Analogously, when the secondary amine function in the macrocyclic unit are protonated, they can be present in solution as cationic H_kL^{k+} species, where k is the number of nitrogen atoms present in the polyamine macrocycle. Examining the stepwise protonation constants, it is clear that **L1**, **L2** and **L3**, but not **L4**, can be fully deprotonated in the pH range (2–11) investigated, and that **L1**, **L2** and **L4**, but not **L3**, can be fully protonated in the same pH-range. All four ligands show high basicity constants (Log $K > 11$) in the first protonation steps; it is to underline that the H_{-1}**L4**$^-$ species was not detectable because the neutral **L4** precipitates in the titration medium; however, a Log K_1 similar to those found for the other ligands can also be expected for H_{-1}**L1**$^-$ species. These remarkably high values can be explained by taking into account the fact that the addition of the proton occurs on an anionic species; in fact, the azamacrocycles of the polyazacyclophane ligands of analogous dimension show a lesser basicity in the first (and in all other) protonation steps [15].

Table 1
Protonation constants (Log *K*) of ligands **L1**, **L2**, **L3** and **L4**, potentiometrically determined in 0.15 mol dm^{-3} NMe_4Cl aqueous solution at 298.1 K.

Reaction	Log *K*			
	L1	**L2**	**L3**	**L4**
H_{-1}**L**$^-$ + H^+ = **L**	11.66(4)[a]	11.10(4)	11.40(5)	
L + H^+ = H**L**$^+$	11.17(3)	10.73(2)	10.48(3)	10.09(3)
H**L**$^+$ + H^+ = H_2**L**$^{2+}$	5.54(3)	8.05(2)	9.78(2)	9.75(3)
H_2**L**$^{2+}$ + H^+ = H_3**L**$^{3+}$	2.28(3)	4.03(2)	5.83(2)	8.39(2)
H_3**L**$^{3+}$ + H^+ = H_4**L**$^{4+}$		1.40(3)	3.22(3)	6.10(2)
H_4**L**$^{4+}$ + H^+ = H_5**L**$^{5+}$				4.29(2)
H_5**L**$^{5+}$ + H^+ = H_6**L**$^{6+}$				2.65(2)

[a] Values in parentheses are the standard deviations on the last significant figure.

L1 shows similar basicity constants in the first two protonation steps with Log K_1 = 11.66 and Log K_2 = 11.17, while the values decrease by about six logarithm units in the third proton addition (Log K_3 = 5.54); the last constant is rather low (Log K_4 = 2.28).

The acid–base behavior of ligands **L2** and **L3** was discussed in a previous paper [13]. Both ligands behave as a pentaprotic base in the pH range (2–11) examined.

L4 behaves as heptaprotic base. It was not possible to determine the protonation constant of the anionic H_{-1}**L4**$^-$ species, as mentioned above. The following three protonation steps are rather high (Log K_2 = 10.09, Log K_3 = 9.75 and Log K_4 = 8.39), while from the fifth to seventh protonation step the constants undergo a drastic decrease (Log K_5 = 6.10, Log K_6 = 4.29 and Log K_7 = 2.65). The trends for all ligands can be rationalized in terms of minimization of the electrostatic repulsion between the positive charges in the protonated species. For example, due to the high number of protonation amine group sites and the large size of the ON_6-type macrocyclic host of **L4**, the first three protons can occupy positions in the macrocycle alternated by unprotonated sites; the lower affinity of the ligand for the fourth proton is due to the fact that this protonation reaction occurs on positions having another close protonated site.

UV–Vis absorption electronic spectra of **L1** and **L4** were carried out to understand the role of the phenolic function in the acid–base behavior of these ligands. The involvement of the phenolic group in the protonation steps is well depicted by these spectra, as shown for **L4** in Fig. 1, which depicts the trend of the absorbance values at λ = 298 nm, typical for the anionic phenolate group, and the distribution diagram of the protonated species of **L4** as a function of pH. Monitoring the spectra from acidic to basic pH, the band with λ_{max} = 298 nm starts from pH 4 and reaches its maximum absorbance at pH 6.5, where the tetraprotonated H_4**L4**$^{4+}$ is prevalent in solution (see Fig. 1). This means that the deprotonation of the hydroxyl function occurs in this pH range in correspondence with the deprotonation from the H_5**L4**$^{5+}$ to the H_4**L4**$^{4+}$ species. For **L1**, this happens from H_2**L1**$^{2+}$ and H**L1**$^+$ (spectra not reported), while for ligands **L2** and **L3** the phenol deprotonation occurs from H_3**L2**$^{3+}$ and H_2**L2**$^{2+}$ species and from H_3**L3**$^{3+}$ and H_2**L3**$^{2+}$ species, respectively