Metal Ion Interaction of Two New Tritopic N_2O_{13} Macrobicycles with B15C5 Moieties in Acetonitrile Solution

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Abstract

The synthesis of two new tritopic crown ligands (L1 and L2) bearing two benzo-15-crown-5 lateral moieties linked through a dibenzo-trioxa chain together with their interaction with metal ions, in acetonitrile and acetonitrile–water (50%, v/v) solutions is reported. The influence of K^+, Na^+, Li^+, Ca^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and Al^{3+}, on the spectroscopic properties of these diaza-polyoxa ligands was investigated by absorption spectrophotometry and in some cases by fluorescence emission spectroscopy. Coordination with alkaline (Na^+, K^+ and Li^+) and alkaline earth ($Ca^{2+}$and Ba^{2+}) metal ions is assumed to be weak with both macrobicyclic ligands, while the interaction with both imine and amine derivatives causes a minor effect in the absorption spectra. Coordination with Cu^{2+}, Zn^{2+} and Pb^{2+} in acetonitrile solution causes a major change in the absorption spectra of the chromophores. In the case of Cu^{2+}, addition of the metal to L1 or L2 leads to a blue–violet complex in solution with an absorbance maximum centred at 590 nm. Interaction of the Schiff-base L1 with Pb^{2+} leads to a short wavelength shift in the absorption bands, comparable with the ZnL1 complex. Presence of transition metal ions such as Co^{2+}, $Ni^{2+}$and Cd^{2+} do not remarkably affect the absorption spectra of L1 and L2 in solution. Trivalent aluminium has a modest effect in the absorption bands of both N_2O_{13} donor set bismacrocyclic ligands. The fluorescence study of L2 in the presence of Na^+, K^+, Ca^{2+}, Ba^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Al^{3+}shows that Cu^{2+}, Pb^{2+} and Al^{3+} complexes form non-fluorescent complexes.

Introduction

Since Pedersen published (in 1967) his first results in crown ethers [1], the design of ligands involving benzo-15-crown-5 units has received considerable attention by many research groups. The synthesis of new macrocycle receptors with two crown moieties, is capable of coordinating two or more metal ions or to form sandwich complexes (*clam* type complexes [2]). It is a fascinating area of research, owing to their importance in basic and applied chemistry. This can be demonstrated by the development of analytical methods for application in medical or environmental sciences [3, 4].

Numerous examples can be found in the literature of sensors involving bis-crown ligands. Particularly elegant is the study made by Li and co-workers, in which a rigid dicyano-distyrylbenzene bridge (**I**) is included in the skeleton of several ligands used to determine Na^+, K^+

and Cs^+ or Pb^{2+} in solution [5, 6]. In addition, Ushakov and co-workers have reported an interesting case of sandwich-type complexes formed by an intramolecular coordination with large size cations such as Sr^{2+} and Ba^{2+}, using a rigid bis(benzo-15-crown-5 ether) bis-styryl derivative (**II**) [7].

Several attempts have been made to increase the analytical performance of ligands, i.e., to confer a better coordination capability which leads either to a better extraction efficiency or to a better selectivity of cations in solution. Thus, the rigid linker between both crown moieties can be replaced by a flexible aliphatic chain (**III**) [8]. On the other hand, the replacement can be made by an aliphatic bridge containing oxygen or nitrogen atoms (**IV**). An additional example can be found in the work of Weber and co-workers: the presence of an aliphatic polyoxa chain between the crown ethers, in the presence of large cations such as K^+, Cs^+ and Tl^+, induces the formation of sandwich-

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type complexes by the cooperative effect present by both terminal crown ether rings [9].

In the present work, we describe the synthesis and spectroscopic properties of two new diaza-polyoxa macrobicyclic ligands that contain benzo-15-crown-5 as lateral units with a semirigid linker between both macrocycles (see Scheme 1). The bridge in the macrocycles L1 and L2 includes the rigidity imposed by the presence of two lateral benzene rings and, at the same time, presents a flexible polyoxa chain with three oxygens donor atoms. This flexible chain is able to participate also in the co-ordination, forming polynuclear supra-complexes in solution or to help in the formation of *clam* structures, supporting the metal inside the ligand. The two ligands have considerable flexibility, so each one can adapt its shape to coordinate cations from a large range of sizes. We also report the spectroscopic properties of these ligands, which have been studied by UV-absorption and fluorescence emission spectrophotometries. Results regarding the interaction of the following metals: Na^+, K^+, Li^+, Ca^{2+}, Ba^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+} and Pb^{2+} with both macrobicyclic devices are also presented. In addition, we have studied the response of the amine-derived ligand L2 in water–acetonitrile solution on the pH variation in the presence of NaCl as supporting electrolyte. To clear the complex-ation properties of the new ligands, their capability to form solid complexes with inorganic salts has been studied. In order to understand the change in the absorption spectra induced by the presence of transition metal ions, such as Cu^{2+}, the Cu(II) complexes with bis-macrocycles L1 and L2 were synthesized. For comparative reasons, the interaction of the parent compound L3, i.e. 4′-aminobenzo-15-crown-5, in the presence of Cu(II) has also been studied.

Experimental

Chemicals and starting materials

1,7-Bis(2′-formylphenyl)-1,4,7-trioxaheptane was pre-pared according to the literature method [10]. 4′-Aminobenzo-15-crown-5, NaCl, KCl, LiClO$_4$, Ba(-ClO$_4$)$_2$, Ca(ClO$_4$)$_2$ Cu(NO$_3$)$_2$, Ni(ClO$_4$)$_2$, Co(ClO$_4$)$_2$, Zn(NO$_3$)$_2$, Pb(NO$_3$)$_2$, CdCl$_2$ and AlCl$_3$ were commercial products from Aldrich Chemical Co., used without further purification. All solvents used were of reagent grade chromasolv. Deionised Milli-Q water twice dis-tilled was used for the preparation of all the solutions. Appropriate volumes of acetonitrile and water were mixed to give the 50% (v/v) solvent mixture.
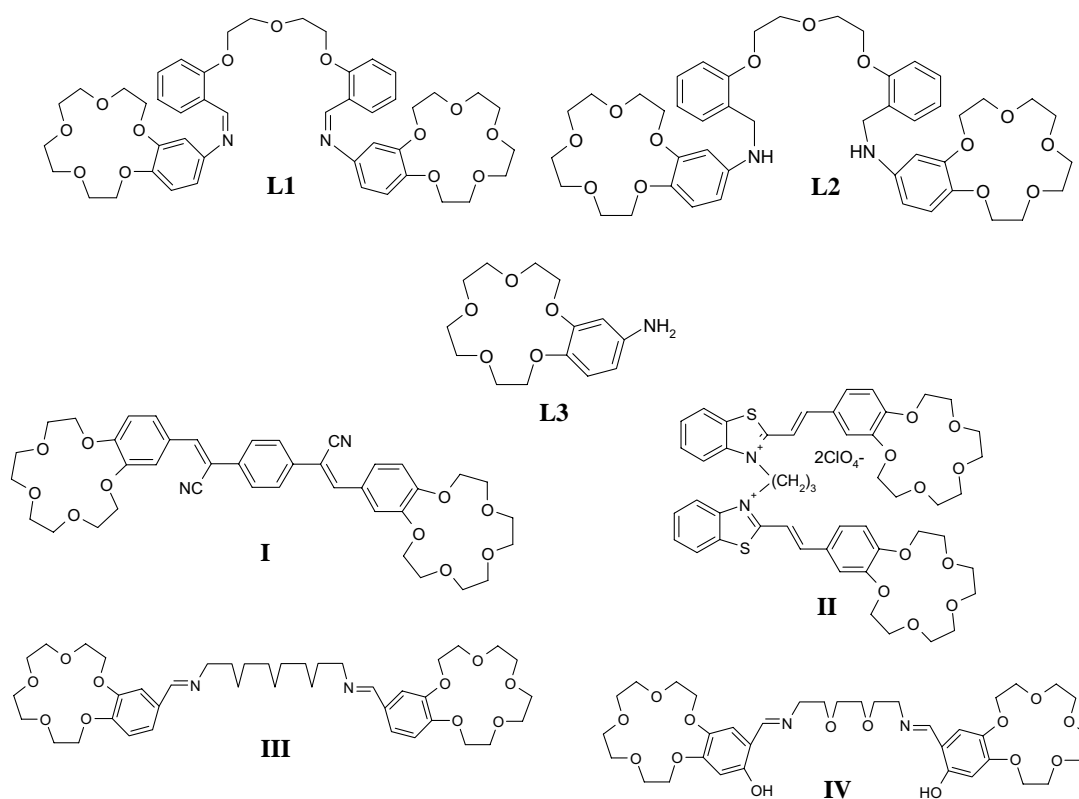
Scheme 1. Bismacrocycle ligands L1 and L2 reported and some related ligands with benzo 15-crown-5 moieteies. L1 = N-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)-{2-[2-(2-{2-[(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopenatoxacyclopentade cin-15-ylimino)methyl]phenoxy}-ethoxy)ethoxy]phenyl}methanimine.   L2 = N15-{2-[2-(2-{2-[(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzope-natoxacyclo pentaoxacyclopentadecin-15-ylamino)methyl]phenoxy}-ethoxy)ethoxy]phenyl}-2,3,5,6,8,9,11,12-octahydro-1,4,7,10, 13-benzopenta-oxacyclopentadecin-15-amine.

Synthesis

Synthesis of the Schiff-base bismacrocycle L1

A solution of 4'-aminobenzo-15-crown-5 (1 mmol) in hot methanol (50 cm^3) was added dropwise to a refluxing solution of 1,7-bis(2'-formylphenyl)-1,4,7-trioxaheptane (0.5 mmol) in the same hot solvent (50 cm^3) (Scheme 2). The resulting solution was gently refluxed with magnetic stirring for ca. 24 h under argon atmosphere. The colour of the solution changed to yellow. The progress of the reaction was controlled by TLC on silica gel, using dichloromethane/methanol. After completion of the reaction, the cold solution was filtrated and concentrated in a rotary evaporator. An orange–yellow oil was obtained, washed with diethyl ether and dried *in vacuum*.

L1; Solvent: methanol. Yield 64%. (Found: C, 63.74; H, 7.05; N, 3.40. $C_{46}H_{56}N_2O_{13} \cdot 1.5H_2O$ requires C, 63.36; H, 6.82; N, 3.20%); m.p. 250–260 °C (unextable); IR (KBr disc): $v(C{=}N)_{imi}$ 1640 cm^{-1}, $v(C{=}C)$ 1596–1449 cm^{-1}, $v(C{-}O{-}C)_{aromatic}$ 1235, $v(C{-}O{-}C)_{aliphatic}$ 1130–1055 . Mass spectrum (positive-ion FAB): m/z 845 $[L1 + H]^+$(100%). UV–vis spectrum (in CH_3CN), (λ (mn), ε ($M^{-1} \cdot cm^{-1}$)): (253, 32,610), (341, 22,390). ^1H NMR (CD_3CN, δ (ppm): 8.9(s), 2H, (C=NH); 8.1–6.9(m), 14H, (C_6H_6); 4.15–3.24(m), 40H.

The ligand is air stable, soluble in acetonitrile, absolute ethanol, methanol, chloroform, and dichloromethane, but insoluble in diethyl ether and water.

Synthesis of the reduced bismacrocycle L2

This ligand was prepared by a modification of the method reported in Refs. [10, 11]. A solution of 4'-aminobenzo-15-crown-5 (1 mmol) in hot methanol (50 cm^3) was added dropwise, during 1 h, to a refluxing solution of 1,7-bis(2'-formylphenyl)-1,4,7-trioxaheptane (0.5 mmol) in the same hot solvent (50 cm^3). The resulting solution was gently refluxed with magnetic stirring for ca. 24 h under Ar(g) atmosphere. Colour of the solution changed to yellow. The reaction mixture was cooled over ice-bath and then solid NaBH$_4$ (20 mmol) was added carefully in small amounts while stirring (Scheme 2). After effervescence had stopped, the solution was filtered and reduced to dryness by rotary evaporation. The oil obtained was dissolved in water, and extracted with three times with chloroform (150 cm^3 in total). The organic phase was dried over anhydrous sodium sulphate. The solvent was removed by rotatory evaporation to ca. 10–15 cm^3 and diethyl ether was added producing an oil product, which was decanted and dried *in vacuum*.

L2; Yellow oil. Solvent: methanol. Yield 25%. (Found: C, 65.50; H, 3.30; N, 7.50. $C_{46}H_{60}N_2O_{13}$ requires C, 65.05; H, 3.30; N, 7.12%); IR (KBr disc): $v(NH)$ 3150 cm^{-1}, $v(C{=}C)$ 1597, 1453 cm^{-1}, $v(C{-}O{-}C)_{aromatic}$ 1233, $v(C{-}O{-}C)_{aliphatic}$ 1128–1053. Mass spectrum (positive-ion FAB): m/z 850 $[L2 + H]^+$ (100%). UV–vis spectrum (in CH_3CN), (λ (mn), ε ($M^{-1} \cdot cm^{-1}$)): (246, 22,160), (304, 7430), ^1H NMR (Cl_3CD-d), δ (ppm): 7.8–6.0(m), 14H, (C_6H_6); 4.20–3.5(m), 44H.

The ligand is air stable, soluble in acetonitrile, absolute ethanol, chloroform, and dichloromethane, moderately soluble in dichloromethane and water, but insoluble in diethyl ether and petroleum ether.

Cu^{2+} complexes with L1 and L2: General procedure

Three equivalents of Cu(NO$_3$)$_2 \cdot$3H$_2$O (0.0046 g) were added to an acetonitrile solution of L1 or L2 (3 cm^3) with a concentration of 8.0×10^{-3} M. The resulting solution was refluxed and stirred for ca. 4 h, allowed to cool to room temperature and left overnight. The
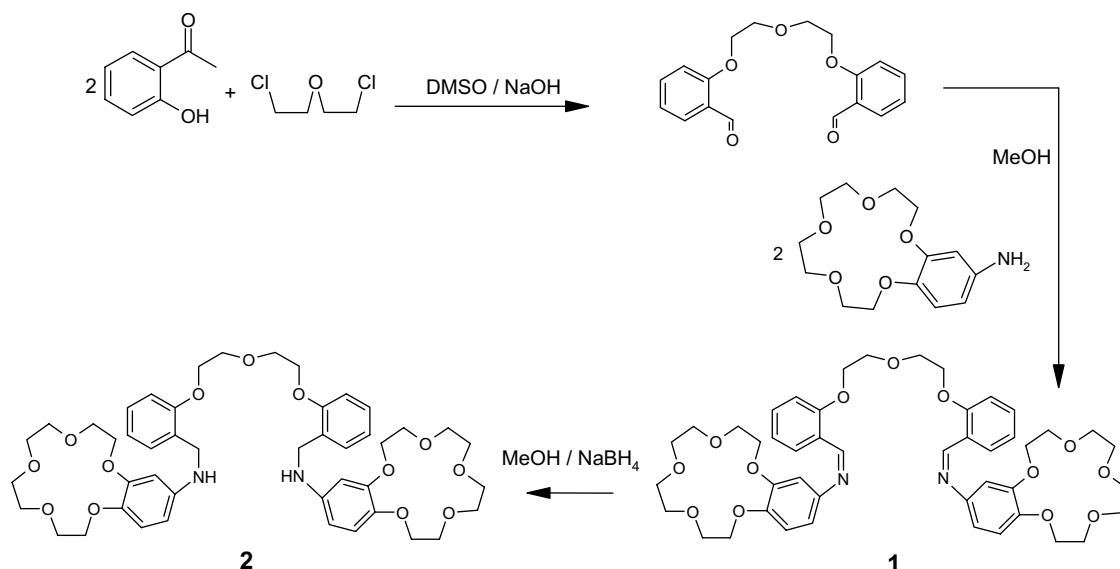
Scheme 2. Synthetic route for the synthesis of L1 and L2 macrobicycle ligands.

solution was then filtered and concentrated to a small volume; diethyl ether (ca. 1–2 cm^3) was slowly infused, leading to the formation of a precipitate. The solids were washed with cold absolute ethanol and diethyl ether.

L1Cu$_3$; dark violet solid. Yield 54%. (Found: C, 38.55; H, 4.30; N, 7.85; Cu, 13.10 C$_{46}$H$_{56}$N$_2$O$_{13}$Cu$_3$-(NO$_3$)$_6$·2H$_2$O requires C, 38.30%; H, 4.20%; N, 7.75%; Cu, 13.21%); (unextable); IR (KBr disc): v(C=N)$_{imi}$ 1648 cm^{-1}, v(C=C) 1598–1450 cm^{-1}, v(NO$_3$) 1384, 1303, 838, 814 cm^{-1}. Mass spectrum (positive-ion FAB): m/z 845 [L1H]$^+$(100%); m/z 909 [L1Cu]$^+$; m/z 972 [L1Cu$_2$]$^+$; m/z 1160 [L1Cu$_3$(NO$_3$)$_2$]$^+$. UV–vis spectrum (in CH$_3$CN), (λ (mn), ε (M^{-1}·cm^{-1})): 252 (51,015); 315 (sh)(20,324); 591 (7399).

The complex is air stable, soluble in acetonitrile, absolute ethanol, methanol, chloroform and dichloromethane.

L2Cu$_3$; brown solid. Yield 45%. (Found: C, 37.50; H, 4.90; N, 7.65. Cu, 12.90 C$_{46}$H$_{60}$N$_2$O$_{13}$Cu$_3$(NO$_3$)$_6$·4H$_2$O requires C, 37.30; H, 4.63; N, 7.55, Cu, 12.87%); IR (KBr disc): v(C=C) 1598, 1455 cm^{-1}, v(NO$_3$) 1384, 1287, 826, 752 cm^{-1}. Mass spectrum (positive-ion FAB): m/z 850 [L2 + H]$^+$ (100%); m/z 914 [L2Cu]$^+$; m/z 978 [L2Cu$_2$]$^+$; m/z 1103 [L2Cu$_3$(NO$_3$)]$^+$. UV–vis spectrum (in CH$_3$CN), (λ (mn), ε (M^{-1}·cm^{-1})): (269, 17004), (303sh, 11697), (366, 7836), (590, 5327).

The complex is air stable, soluble in acetonitrile, absolute ethanol, dichloromethane, and insoluble in diethyl ether and petroleum ether.

Physicochemical measurements

Absorption spectra of the molecular devices L1 and L2, in acetonitrile or water–acetonitrile (50/50, v/v) solutions, with concentrations between 1.0×10^{-4} and 4.0×10^{-5} M, were measured in the range 220–750 nm using a Shimadzu spectrophotometer. The complexation reaction was studied varying the ligand/metal molar ratio, between 0.5/1 and 50/1 molar equivalents of the appropriate metal perchlorate, nitrate or chloride salt. one centimeter long absorption cell was used in all the experiments. Fluorescence emission spectrum of **L2** was measured by a Jovin Ivon-Spex Fluorolog 3.22 spectrofluorometer using 306 nm excitation wavelength, in the range 315–500 nm, with a spectral bandwidth of 3.0 nm for excitation and emission. HCl and NaOH were used to adjust the pH values, which were measured on a Metrohm 713 pH meter. All pH measurements were made in 0.1 M NaCl solution.

Elemental analyses were performed at the New University of Lisbon (Portugal) on a ThermoFinnigan Flash EA 1112 CHNS Elemental Analyzer. Infrared spectra were recorded as KBr pellets discs a Mattson Cygnus 100 spectrophotometer. Proton NMR spectra were recorded using a Bruker WM-300 spectrometer. Positive ion FAB mass spectra of L1, L2 and Cu^{2+} complexes were recorded at the University of Santiago de Compostela (Spain) on a Kratos MS50TC

spectrometer, using a 3-nitrobenzyl alcohol (MNBA) matrix.

Cu^{2+} determinations were performed on a Varian model Zeeman spectrAA300 plus atomic absorption spectrometer in combination with an autosampler; pyrolitic graphite-coated graphite tubes with platform were used [12]. For the determination of copper concentration, 20 μL of solution was injected into the graphite furnace, where it was dried, ashed and atomized. The signal was measured in the peak area mode. Each completed determination was followed by a 2 seg. clean-up cycle of the graphite furnace at 2800 °C. During the drying, ashing, and clean-up cycles, the internal argon gas was passed through the graphite furnace at 300 mL/min. The internal argon gas flow was interrupted during the atomisation cycle, but was restored for the clean-up cycle. The relative standard deviation among replicate was typically < 5%.

Results and discussion

Synthesis of the free ligands

Direct reaction of 1,7-bis(2′-formylphenyl)-1,4,7-trioxaheptane with two equivalents of 4′-aminobenzo-15-crown-5 in hot methanol under Ar atmosphere gives the corresponding [1 + 2] Schiff-base bismacrocycle L1, which can be reduced *in situ* with NaBH$_4$ to obtain the bismacrocycle L2. L1 and L2 were isolated as yellow–orange oils in ca. 64 and 25% yields, respectively, and they were characterized by elemental analysis, FAB mass spectrometry, IR and ^{1}H NMR spectroscopy. The FAB mass spectra show peaks, 100% intensity, attributable to the [L + H] bismacrocycles. The IR spectrum of L1 presents a band at ca. 1640 cm^{-1} assignable to the imine groups, as well as bands at ca. 1596 and 1449 cm^{-1}, due to the v(C=C). Similar results were found in monomacrocycle ligands synthesized employing the same dicarbonyl precursor [13]. The ^{1}H NMR spectrum of L1 in CD$_3$CN shows a peak at 8.9 ppm, corresponding to the imine protons, and no signals corresponding to the formyl or amine protons are present. The IR spectrum of L2 shows a broad band at 3150 cm^{-1}, assignable to the amine groups. Bands at ca. 1595 and 1445 cm^{-1} corresponding to the aromatic skeleton are also present. The ^{1}H NMR spectrum in CDCl$_3$, gave the expected signals, indicating the integrity of the ligand in solution.

Synthesis of the Cu^{2+} complexes

The direct reactions between the free bismacrocycles L1 or L2 and Cu(NO$_3$)$_2$ gave analytically pure trinuclear complexes with formula [L^{m}Cu$_3$](NO$_3$)$_6$·xH$_2$O. (L^m = L1 and L2), x = 2 or 4). This was confirmed by elemental analyses as well as FAB spectra. The FAB mass spectra feature in both cases peaks at m/z 845

[L1H]$^+$(100%) and m/z 850 [L2 + H]$^+$ (100%) as the most intense ones, confirming the stability of the bismacrocycles in the metal complexes. Peaks attributable to the fragments [Cu$_n$L^m]$^+$ can be observed for both complexes at m/z 909 [L1Cu]$^+$; m/z 972 [L1Cu$_2$]; m/z 914 [L2Cu]$^+$ and m/z 978 [L2Cu$_2$]$^+$. The spectra also feature peaks attributable to the species m/z 1160 [L1Cu$_3$(NO$_3$)$_2$]$^+$ and m/z 1103 [L2Cu$_3$(NO$_3$)]$^+$.

The IR spectra confirm the existence of the cyclic ligands in the complexes, with the presence of absorption bands due to imine groups in L1 at ca. 1648 cm^{-1} and the absence of bands due to vC=O or vNH$_2$ [14].

All spectra exhibit medium to strong bands at ca. 1600 and 1455 cm^{-1}, as expected for the two highest-energy benzene ring vibrations [15]. A broad absorption band in the region 3450–3385 cm^{-1} present in both complexes is probably due to the existence of lattice and/or co-ordinated water in the molecules [16]. In the case of the diamine complexes with L2 bands attributable to vNH cannot be observed due the existence of the aforementioned broad band at ca. 3450.

Absorption spectra

The absorption spectra for L1 and L2 are given in Figure 1. Both spectra exhibit two absorption bands each, one with a maximum at ca. 253 (L1) and 246 nm (L2), and the second one with a maximum at 341 (L1) and 304 nm (L2). In both cases, these bands are associated with the π–π* and n–π* electronic transitions of the chromophores present in the bismacrocyclic skeletons [17].

Table 1 shows the value for the electronic bands observed for the free ligands and in the presence of metal ions, in acetonitrile solution at room temperature, along with the molar absorption coefficients for all the complexes. As it can be seen, the changes in the band position caused by the introduction of metal cations are
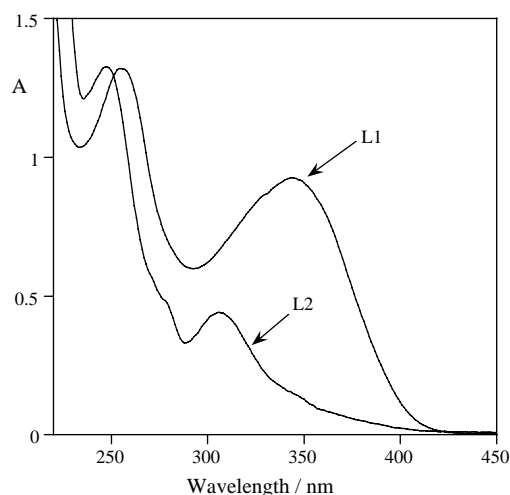
Table 1. UV–vis Spectral data for the ligands and metal complexes in acetonitrile solution at room temperature

Compound	λ (nm); ε (mol^{-1}·dm^3)
L1	253 (32,610); 341 (22,390)
L1/Na^{+*}	256 (33,465); 342 (27,195)
L1/Li^{+*}	256 (34,734); 343 (28,022)
L1/K^{+*}	253 (33,068); 341 (26,620)
L1/Ca^{2+*}	253 (29,701); 329 (26,929)
L1/Ba^{2+*}	254 (29,868); 329 (26,930)
L1/Co^{2+*}	253 (35,477); 342 (23,830)
L1/Ni^{2+*}	256 (34,628); 342 (27,475)
L1/Cu^{2+*}	250 (51,015); 315(*sh*)(20,324); 590 (7399)
L1/Zn^{2+*}	251 (26,282); 279 (9375); 316 (11,465)
L1/Cd^{2+*}	256 (35,022); 343 (28,039)
L1/Pb^{2+*}	248 (33,832); 313 (19,419)
L1/Al^{3+*}	255 (40,049); 344 (30,947)
L2	246, (22,160); 304, (7430)
L2/Na^{+*}	246 (23,197); 303 (7389)
L2/K^{+*}	245 (20,934); 303 (7746)
L2/Ca^{2+*}	245 (20,934); 303 (7745)
L2/Ba^{2+*}	245 (20,934); 303 (7745)
L2/Co^{2+*}	247 (26,848); 304 (9086)
L2/Ni^{2+*}	244 (27,081); 303 (9368)
L2/Cu^{2+*}	269 (17,004); 303(sh) (11,697); 366 (7836); 590 (5327)
L2/Zn^{2+*}	273 (11,148); 312 (4754); 372 (2881)
L2/Cd^{2+*}	243(sh) (20,221); 303 (7291); 363(sh) (2746)
L2/Pb^{2+*}	270 (10,897); 312 (4172); 366 (2992)
L2/Al^{3+*}	243(sh) (20,278); 303 (7278); 363(sh) (2746)

* 50 equivalents of the metal ion; sh = shoulder.

similar for both ligands. Alkaline metal ions studied, Na$^+$, K$^+$ and Li$^+$, as well as transition metal ions (Co^{2+}, Ni^{2+} and Cd^{2+}) leave it unchanged the long-wave absorption band (λ_{max} = 341 (L1) and 304 (L2) nm) (ca. 1–2 nm). Alkaline earth ions (Ca^{2+} and Ba^{2+}) shift this band by 12 nm to shorter wavelengths in the case of L1 and leave it unchanged at 303 nm for L2. The trivalent Al^{3+} ion induced a short shift to long-wave absorption by 3 nm in the Schiff-base complex with L1.

The second absorption band (L1, 253 nm and L2, 246 nm) is poorly affected by coordination to metal ions. In general, this band is shifted by ca. 1–6 nm.

Pb^{2+}, Zn^{2+} and Cu^{2+} ions caused major changes in absorption spectra with both macrobicycles. This could suggest a strong interaction between these ions and the N$_2$O$_{13}$ macrobicycles. Similar results for Pb^{2+} and Cu^{2+} were found previously by Ossowski and co-workers with a dansyl fluorophore (A15C5 derivate) [18].

In the case of L1, Zn^{2+} and Pb^{2+} ions lead to a change in the shape and position of the first UV-band. A strong blue-shift by ca. 25 (Zn^{2+}) and 28 (Pb^{2+}) nm is observed in the band at 341 nm, but a small change is observed in the band at 253 nm. For the case of the Zn^{2+} complex, a new band is observed at 279 nm. Both ultraviolet bands of L2 are shape and shifted from 304 nm to 312 (Zn^{2+}) and 303 (Pb^{2+}) nm, and from 246 nm to 273 (Zn^{2+}) and 270 (Pb^{2+}) nm. In both cases

Figure 1. Absorption spectra of L1 and L2 in acetonitrile solution. [L1] = [L2] = 2.5 × 10^{-4} M.

are observed a new red-shifted band centred at 372 (Zn^{2+}) and 366 nm (Pb^{2+}), respectively.

In Figure 2 are represented the absorption spectra of the free ligands L1 and L2, and in the presence of metal ions in acetonitrile solution at room temperature.

A special case is the interaction of Cu^{2+} ion with both the ligands, since a strong change in the UV-spectra of free bismacrocycles is observed. The band at 341 nm for L1 is blue-shifted to 315 nm, appearing as a shoulder. The second band at 253 nm is now blue shifted only 3 nm. In the case of L2, the band at 304 nm appears now as a shoulder centred at 303 nm but a new one is observed at 366 nm. The second band at 246 nm in the presence of copper(II) is red-shifted by 23 nm. The blue–violet complexes formed upon metal addition reflected in the formation of a new visible band centred in both cases at 590 nm (see Figure. 2).

The band at 590 nm observed for both Cu(II) complexes does not change with the polarity of the solvent used in the experiences (acetonitrile, ethanol, dichloromethane). By this reason a d–d electronic

transition band nature instead a charge transfer band (MLCT or LMCT) was assigned [19].

In order to study the number of the metal ions coordinated by each macrobicycle ligand in solution, a Cu^{2+} titration in acetonitrile solution was performed. In Figure 3, it can be observed in the insets that after the third equivalent added to each macrobicycle ligand, the absorption is stabilized. These data are in agreement with the results obtained during the synthetic approach of these trinuclear complexes (see Experimental).

An intensity decrease in the absorption band at 590 nm, was observed upon addition of the third equivalent, and after 2 h the blue colour of both complexes had disappeared. Probably this colour variation is induced by conformational changes in the coordination of the metal to the ligand. This colour change from blue to yellow in solution suggests a slow kinetic reorganizing mechanism. The first blue colour observed is probably due to the coordination of the metal ion by the nitrogen donor atoms present in the structure. After a reorganization of the ligand around
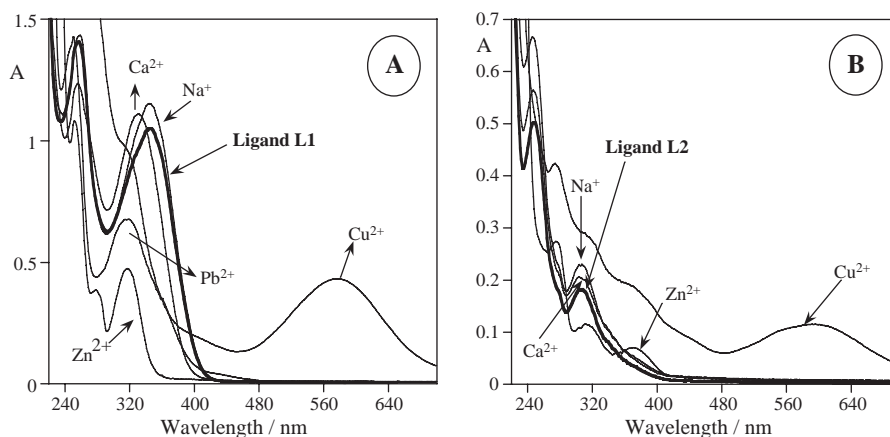

Figure 2. (Left) Absorption spectra of L1 and its metal complexes in acetonitrile. [L1] = 4.11×10^{-5} M, [L1]/[M] = 1/50. (right) Absorption spectra of L2 and its metal complexes in acetonitrile. [L2] = 2.44×10^{-5} M, [L2]/[M] = 1/50 (free ligands in bold).
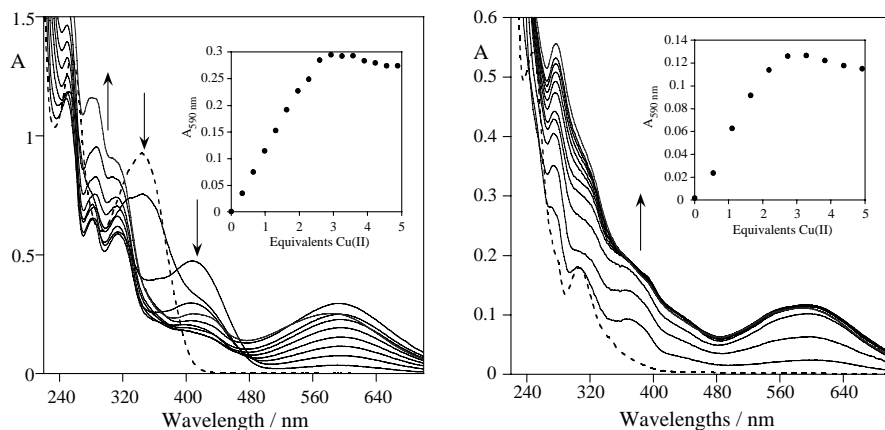

Figure 3. (Left) Cu^{2+} titration of the Schiff-base ligand L1 in acetonitrile solution. Free ligand dotted spectrum. (molar ratio Cu:L1 = 0:1, 0.3:1, 0.6:1, 1:1, 1.30:1, 1.5:1, 2:1, 2.3:1, 3:1, 5:1) [L1] = 4.11×10^{-5} M; (right) Cu^{2+} titration of the ligand L2 in acetonitrile solution. Free ligand dotted spectrum. (molar ratio Cu:L2 = 0:1, 0.5:1, 1:1, 1.6:1, 2.20:1, 2.7:1, 3.3:1, 3.8:1, 4.4:1, 5:1, 5.5:1, 6.5:1) [L2] = 2.44×10^{-5} M.

the metal ions it may become more important the coordination by the oxygen donor atoms presents in the crown ethers moieties and in the polyoxa chain.

This conclusion about colour variation induced by conformational changes is also pointed out by NMR spectroscopy data. Both complexes, blue and yellow, present a broad and not structured NMR spectrum in deuterated acetonitrile, typically for Cu(II) paramagnetic (d^9) complexes.

The parent compound L3 was studied in similar conditions as L1 and L2, in order to observe the coordination capability of this benzo crown amine derivative in presence of Cu^{2+} in acetonitrile solution. In Figure 4 is shown the formation of the mononuclear Cu^{2+} complex in solution (inset), stabilized after 1 h. Once again, the blue band centered at 585 nm for this L3Cu complex disappears, leading after 24 h to a yellow copper complex in acetonitrile solution.

Further studies in order to stabilize this blue colour were carried on the L2Cu₃ complex. The complex was studied in the presence of 50 equivalents of Na^+, K^+, Pb^{2+} and Zn^{2+}. Only in the case of L2Cu₃ with 50 equivalents of NaCl the blue colour was observed upon 48 and 72 h, suggesting that the sodium(I) ions are first coordinated by the two crown ethers, preventing the copper(II) detachment from the amine nitrogen atoms present in the ligand (see Figure 5).

The changes in the absorption spectra of this type of bismacrocycle ligands, or systems in which at least one moiety of B15C5 is incorporated, depend on several factors, such as the size of the crown cavity, the charge and the size of the metal ion, and sometimes the solvent used. In our case, appear to be very important the coexistence of nitrogen and oxygen donor atoms in both ligands. While alkaline, alkaline earth and Al^{3+} ions are known, by the Pearson's theory [20], to show a strong preference by oxygen donor atoms and consequently they preferred the coordination by the crown ethers, Cu^{2+} could be coordinated by oxygen or nitrogens,
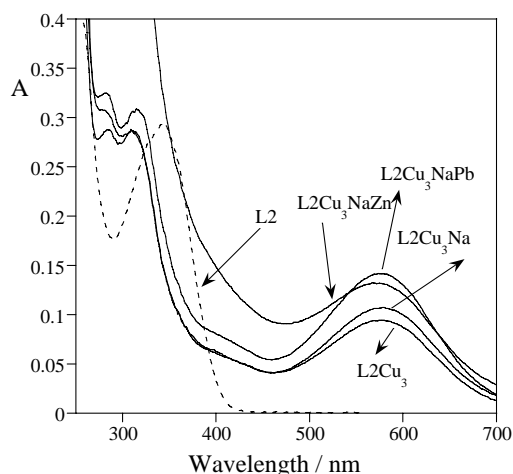

Figure 5. Intensity changes of the absorption band at 590 nm of L2Cu₃ complex in the presence of Na^+, Zn^{2+} and Pb^{2+}, [L2Cu₃] = 2.44×10^{-5} M.

suggesting in this case two different mechanisms of interaction.

Figure 6 presents bar chart graphics describing the $\varepsilon_C/\varepsilon_L$ ratio for each metal complex with L1 and L2. Only a small variation in the molar absortivity in the presence of the majority of metal ions studied is observed. For the ligand L1 (top), both ultraviolet bands at 253 and 341 nm are poorly affected after coordination with the metal ion, in comparison with the free ligand. Only the band at 253 in the case of Cu^{2+} and the band at 341 nm for Zn^{2+} are two exceptions. Both ultraviolet bands at 246 and 304 nm of ligand L2 (Figure 6, bottom) are equally affected by all metals studied.

More analytical information can be obtained from Figure 7, if we notice the relative intensity absorption at 590 nm for all metal complexes. At this wavelength, only the Cu^{2+} complex presents a strong change in absorption and thus could be used as a chemosensor to determine the presence of Cu^{2+} in acetonitrile solution.
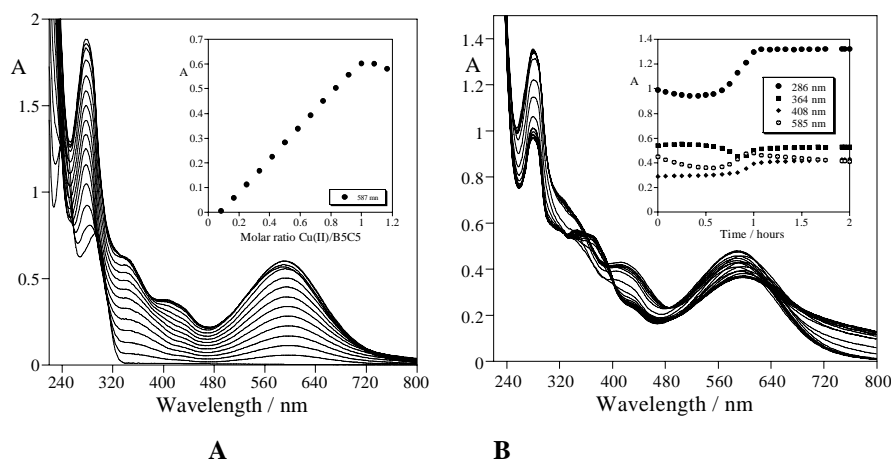

A

B

Figue 4. (A) Spectroscopic titration of CuL3 complex (L3 = parent ligand) in acetonitrile solution. (B) Kinetic study of 1:1 complex, Cu:parent ligand L3 in acetonitrile solution. [L3] = 1.55×10^{-4} M.
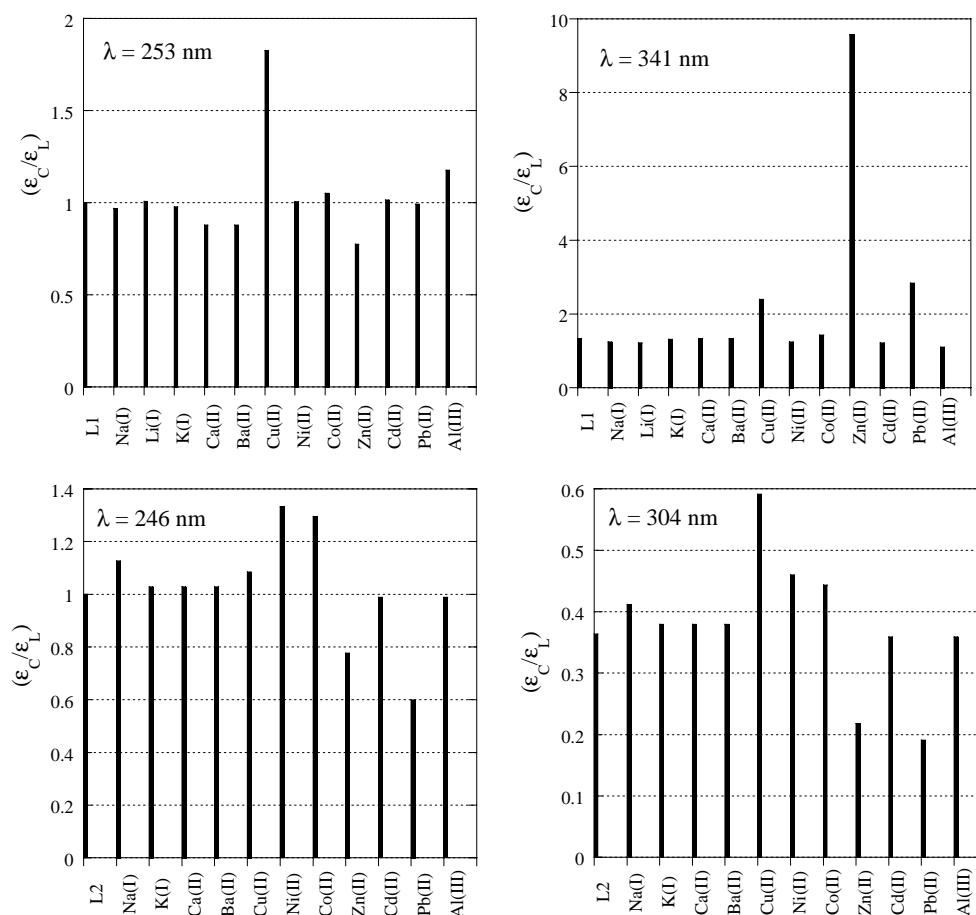
Figure 6. Bar chart graphic of absorption coefficient molar ratio of the complexes (ε_C) to that the free ligands (ε_L) for L1 (top) and for L2 (bottom) upon addition of metal ions, measured at wavelengths: 253 and 341 nm (top) and 246 and 304 nm (bottom).
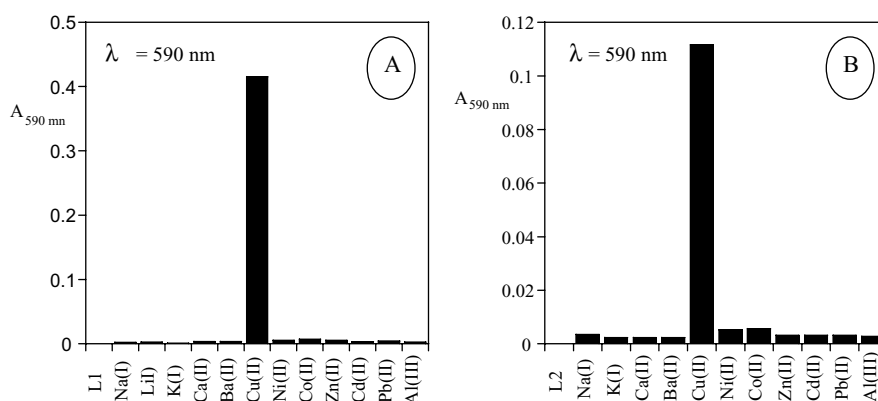

Figure 7. Bar chart graphic of the ratio between the absorption at 590 nm for the metal complexes (A_C) and the free ligands (A_L). L1 (A) and L2 (B).

For L1Cu complex, the absorbance increase was linear up to 1.0×5.10^{-4} M, for L2Cu, the linearity in the absorption was up to 5.30×10^{-5} M.

pH titration and emission spectra of L2 and its complexes.

Several ligands with benzo-crown ether moieties are used as chemical sensors in non-aqueous solutions [21,22]. In order to study the use of L2 as potential chemosensor in acetonitrile and acetonitrile–water solutions, the pH titrations of this free ligand using HCl(aq), NaOH(aq), organic trifluoroacetic acid and tetramethyl ammonium hydroxide were performed.

The absorption and fluorescence emission spectra of compound L2 in acetonitrile–water solution are depicted in Figure 8. Both the spectra are similar to those obtained for the model compound benzo-15-crown-5, with similar aromatic chromophore unit. The absorp-
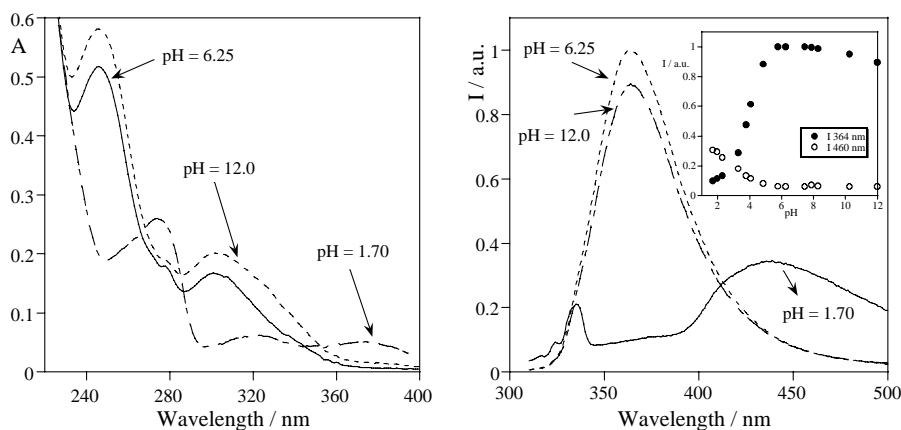
Figure 8. Absorption and fluorescence titration of L2 in acetonitrile–water solution at function of pH. (λ_{exc} = 300 nm, [L2] = 2.44 × 10^{-5} M).

tion and emission spectra are highly dependent on the protonation state of the diamine present on the bismacrocyclic skeleton. As can be seen in Figure 8, the absorption and the emission spectra in the pH range ~5–12 (see Figure 8, right inset) remain similar and only in the acidic pH range 3–5 the emission and the absorption spectra change.

The absorption bands at 246 and 304 nm in the presence of protons (acidic pH values) are red-shifted to 274 and 320 nm respectively, and a new band centred at 370 nm appears.

In the emission spectra, a band centred at 365 nm is observed for basic and neutral pH. This band is shifted to higher wavelength values in acidic media, appearing unstructured and centred at 440 nm for acidic species. In addition, for these acidic pH values, a strong quenching in the emission intensity is observed. These results suggest that between pH 3 and 5 both nitrogen atoms become deprotonated, leading an increase in fluorescence intensity.

At more alkaline pH values, pH > 10, a photoinduced electron transfer from the amine lone pairs to the excited aromatic fluorophore usually takes place in aromatic substituted polyamine receptors [23]. The fluorescence emission titration depicted in Figure 8 (inset) results from a competition between the possible formation of O···H—N$^+$ hydrogen bonds at acidic pH values, and photoinduced electron transfer processes at very alkaline pH values.

The fluorescence intensity of compound L2 remains unchanged upon addition of 50 equivalents of divalent metal ions as Co^{2+} and Ni^{2+} but alkaline and alkaline earth Na$^+$, K$^+$ and Ba^{2+} induce small red shifts in the band. At the same time, a small quenching effect can also be observed (see Figure 9). Only with Cu^{2+}, Pb^{2+} and Al^{3+} ions, L2 forms in practice non-fluorescent complexes. This decrease of the fluorescence intensity caused by the presence of Cu^{2+}, Pb^{2+} and Al^{3+} ions in acetonitrile solution is probably a result of the 'heavy atom effect' causing the increase of energy transfer
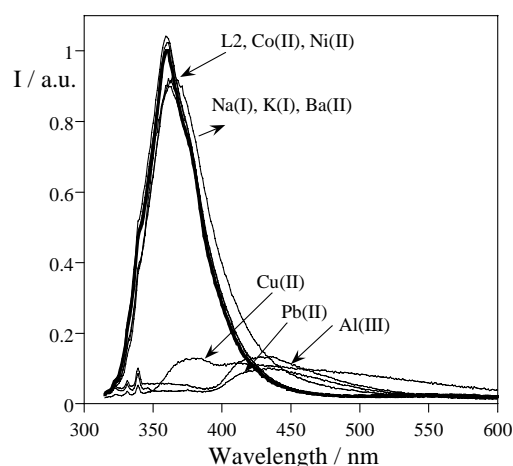

Figure 9. Fluorescence spectra of L2 and its complexes with metal ions (M) in acetonitrile solution. [L2] = 2.44 × 10^{-5} M, [L2]/[M] = 1/50.

phenomena [24] or the increase of intersystem crossing rate constant [25].

Conclusions

We have found some interesting behaviour in the ability presented by these new ligands, L1 and L2, to form polynuclear metal complexes, both having a remarkable selectivity for Cu^{2+} ions in solution at the concentration range tested, monitoring the system at 590 nm.

In our opinion, these results show that with these new receptors, copper(II) could be detected at 590 nm, by the formation of the corresponding polynuclear metal complexes in acetonitrile solution, also in the presence of another cations as Zn^{2+}, Pb^{2+} or Na$^+$, suggesting that the presence of the iminic or amine groups in the bismacrocycle skeletons play an important role in the nature of their coordinative behaviour. The presence of a polyoxa chain in both ligands precludes the possibility of testing the dependence on the ion size and cavity sizes observed in other similar systems.

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The determination of the equilibrium constants for some metal complexes and extraction–selectivity capability interaction between some studied ions and both bismacrocycles are currently under study.

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