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Competitive ^{7}Li NMR Study on the Mn^{2+}, Zn^{2+} and Cd^{2+} Complexes of Two New Branched Hexadentate (N_6) Amines Containing the Pyridine Moiety in Nitromethane and Acetonitrile Solutions

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Abstract Lithium-7 NMR spectroscopy was used to investigate the stoichiometry and stability of a Li^+ complex with two new branched amines, 4,7-bis(2-pyridylmethyl)-4,7-diazadecane-1,10-diamine (L^1) and 4,8-bis(2-pyridylmethyl)-4,8-diazaundecane-1,11-diamine (L^2), in acetonitrile and nitromethane. A competitive ^{7}Li NMR method was also employed to probe the complexation of Mn^{2+}, Zn^{2+} and Cd^{2+} ions with L^1 and L^2 in the same solvent systems. The formation constants of the resulting complexes were evaluated from computer fitting of the mole ratio data with an equation that relates the observed chemical shifts to the formation constant. In both solvents, the stability of the resulting 1:1 complexes was found to vary in the order $Cd^{2+} > Zn^{2+} > Mn^{2+} > Li^+$.

Keywords Competitive ^{7}Li NMR · Complexation · Nonaqueous solvent · Nitromethane · Acetonitrile · Pyridine moiety · Hexadentate (N_6) amines

1 Introduction

Polyamines constitute one of the categories of receptors most widely employed in coordination and supramolecular chemistry [1]. This broad interest stems from their versatility. Polyamine receptors can coordinate metal ions if the number of available amino groups is

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sufficient. On the other hand, they can coordinate anions or dipolar species at pH values low enough to allow extensive protonation of the amino groups. Different books and reviews cover this topic [2, 3]. It was anticipated that these ligands, which generate slightly rigid chelate rings with increased torsional strain, would support a wide range of coordination geometries. Studies using nickel have thus far revealed the expected structural diversity [4–9].

Polyamines, both cyclic and noncyclic, are the ligands studied most with respect to their basicity and coordination capability toward metal ions [10–13]. The structural variety of polyamines and the stability of their complexes are reflected in their remarkable coordination chemistry. In aqueous solution, most amines are basic and there will always be competition between the lone pairs on oxygen (OH^- or H_2O) and the lone pair on the nitrogen for the metal center. This competition can be overcome to a certain extent by using non-aqueous systems or the free amine as a solvent [14, 15]. Monodentate, and especially polydentate, amines have played an outstanding role in the development of coordination chemistry [16]. The study of polyamine complexes has contributed in large measure to the rationalization of coordination compound formation. Among the variety of spectroscopic and electrochemical methods used for the study of metal ion–amine complexes [17, 18], it has been found that nuclear magnetic resonance spectrometry offers a very sensitive technique for studying changes in the immediate chemical environment of metal ions in solution [19–23].

In previous works we have used proton and alkali metal NMR techniques to study the thermodynamics [24–26] and kinetics [27, 28] of metal ion complexation with some macrocyclic ligands in nonaqueous and mixed solvents. In this study, we are interested in investigating the complexation of Mn^{2+}, Zn^{2+} and Cd^{2+} ions with 4,7-bis(2-pyridylmethyl)-4,7-diazadecane-1,10-diamine (1) (L^1) and 4,8-bis(2-pyridylmethyl)-4,8-diazaundecane-1,11-diamine (L^2) in nonaqueous solvents. However, these cations have unsuitable NMR properties, such as low receptivity, high quadropole moment, insensitive chemical shifts, etc. [22, 23, 29]. Thus, we employed ^7Li NMR as a very sensitive probe [20, 21, 25–28] to study the metal ion–amine complexes of interest in nitromethane (NM) and acetonitrile (AN) solutions by a competitive technique. Our interest in the physicochemical properties of the branched hexadentate amines encouraged us to determine the formation constants of transition metal ion complexes with them and to gain some useful information about the properties of complex formation in the solvents.

2 Experimental Section

2.1 Chemicals Used

The ethane-1,2-diamine (Fluka, 99.5 %), propane-1,3-diamine (Fluka, 99 %), pyridine-2-carbaldehyde (Fluka, 98 %) and *N*-(3-bromopropyl)phthalimide (Merk, 98 %) used were of the highest purity available. Lithium perchlorate (Merck, 99 %) was purified and dried according to a literature method [30]. The nitrate salts of all other cations used were of the highest purity available from Fluka and used without any further purification except for vacuum drying over P_2O_5. Spectroscopic grade AN (Merk, 99.5 %) and NM (Merk, 99 %) were purchased from Merck and used as received. All NMR measurements were made on a Jeol FX90Q FT-NMR spectrometer with a field strength of 21.13 kG. At this field, lithium-7 resonates at 33.74 MHz. An aqueous 4.0 mol·L^{-1} LiCl solution was used as the external reference and the reported lithium-7 chemical shifts are referenced to this solution. The paramagnetic (downfield) shift from the reference is designated as being positive. The concentration of all cations used was 0.01 mol·L^{-1}. All chemical shift measurements were carried out at a temperature of 25.0 ± 0.1 °C.

2.2 General Synthesis of the Branched Hexadentate Amines (L^1, L^2)

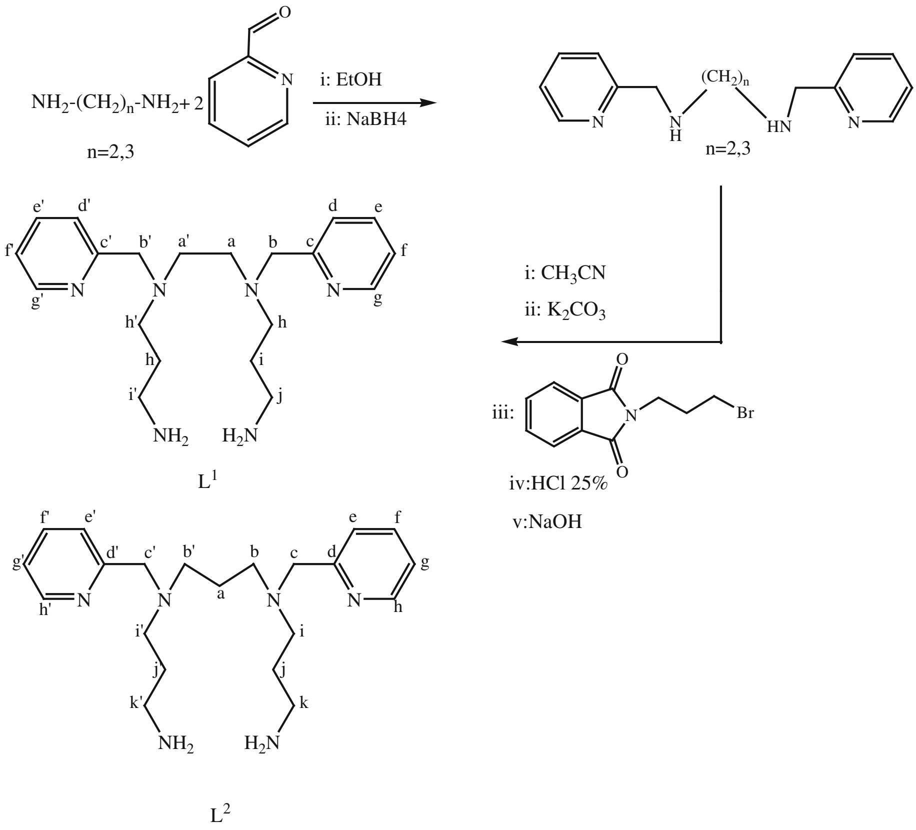
The general method for the synthesis of the hexadentate amines is as follows. A solution of diamines (10 mmol) in dry EtOH (30 mL) was added dropwise to a warm solution of pyridine-2-carbaldehyde (2.14 g, 20 mmol) in dry EtOH (30 mL) over a period of 2 h. The mixture was refluxed under stirring for 12 h and then allowed to cool to the room temperature. Solid sodium borohydride (3.78 g, 100 mmol) was then added slowly and the reaction mixture was heated at reflux for a further 2 h. The solution was filtered and the filtrate volume reduced to 20 mL by rotary evaporation. Excess water was added and the product was extracted with chloroform (3 × 25 mL); the combined chloroform solutions were separated and dried over magnesium sulfate. The chloroform was removed by rotary evaporation to leave a yellow oil (90–95 %). The resulting product (10 mmol) was dissolved in AN (20 mL), and K_2CO_3 (2.76 g, 20 mmol) was added. The mixture was refluxed and then a solution of *N*-(3-bromopropyl)phthalimide (3.28 g, 12 mmol) in AN (40 mL) was added. The mixture was refluxed for 24 h and then filtered while hot. The filtrate was reduced to dryness by rotary evaporation. The resulting product was boiled under reflux for 20 h in aqueous HCl (25 %, 100 mL). After this time the solution was evaporated to a small volume (ca. 25 mL) under vacuum and cooled in a refrigerator for several hours. The solid present was filtered off and the filtrate was evaporated to dryness under vacuum. Water (50 mL) was added to the mixture and the pH was adjusted to 12 with sodium hydroxide. The product was extracted with chloroform (3 × 25 mL), and then the combined chloroform solutions were separated and dried over magnesium sulfate. The chloroform was removed by rotary evaporation to leave a brown oil (Scheme 1).

2.2.1 *4,7-Bis(2-pyridylmethyl)-4,7-diazadecane-1,10-diamine (L^1)*

Yield: 2.35 g (63 %). Analysis, found: C, 66.9; H, 8.73; N, 23.08 %. Calculated for $C_{20}H_{32}N_6$: C, 67.38; H, 9.05; N, 23.57. IR (Nujol, cm^{-1}): 3,350, 1,642 $\upsilon_{(C=N)}$, 1,591, 1,444 [$\upsilon_{(C=C)}$ and $\upsilon_{(C=N)py}$], 2,908, 2,851 [$\upsilon_{(CH2)}$], 3,350 [$\upsilon_{(NH2)}$]. EI-MS: *m*/*z* (%), $[L^1]^+$, 356 (100 %). ^{1}H NMR ($CDCl_3$ ppm): δH = 1.49 (m, 4H, Hi, i'), 2.33 (m, 4H, Hj,j'), 2.45 (t, 4H, Hh,h'), 2.76 (s, 4H, Ha,a'), 3.52 (s, 4H, Hb,b'), 3.84 (m, 4H, -NH_2), 7.20 (d, 2H, Hd,d'), 7.44 (d, 2H, He,e'), 7.19 (m, 2H, Hf,f'), and 8.36(d, 2H, Hg,g') (Scheme 1).

2.2.2 *4,8-Bis(2-pyridylmethyl)-4,8-diazaundecane-1,11-diamine (L^2)*

Yield: 2.01 g (54 %). Analysis, found: C, 68.0; H, 9.1; N, 22.5 %. Calculated for $C_{22}H_{36}N_6$: C, 68.1; H, 9.3; N, 22.7. IR (Nujol, cm^{-1}): 3,351, 3, 288 [υ(NH_2)], 1,590, 1,434 [υ(C=C) and υ(C=N)py]. EI-MS: *m*/*z* (%), $[L^1]^+$, 386 (100 %). ^{1}H NMR ($CDCl_3$ ppm): δH = 1.56 (m, 2H, Ha), 1.59 (m, 4H, Hj,j'), 2.40 (m, 4H, Hb,b'), 2.49 (m, 4H, Hi,i'), 2.69 (m, 4H,Hk,k'), 3.59 (s, 4H, Hc.c' Hd,d'), 4.50, 4.64 (m, 4H, Hl,l'),7.03 (m, 2H, He,e'), 7.23 (m, 2H, Hg,g'), and 7.53 (m, 2H, Hf,f') (Scheme 1).



Scheme 1 Synthesis of the branched hexadentate amines showing the lettering scheme for NMR assignments

2.3 Preparation of Solutions

Stock solutions of the amines were prepared by weighting appropriate amounts at concentrations of 0.12 mol·L^{-1} in AN and NM, respectively. Appropriate quantities of metal salts at concentrations of 0.01 mol·L^{-1} (dissolved in the same solvents, respectively) were added to the [ligand]/[metal] mole ratio of 4, using a microsyringe. Then, the mixture was under ultrasonic irradiation for 5 min and after that the ^{7}Li NMR spectra of the resulting solutions were recorded at 25.0 (±.1) °C.

3 Results and Discussion

The ^{7}Li chemical shifts were monitored as a function of the mole ratio of complexant, 4,7-bis(2-pyridylmethyl)-4,7-diazadecane-1,10-diamine (L^{1}) and 4,8-bis(2-pyridylmethyl)-4,8-diazaundecane-1,11-diamine (L^{2}), to lithium ion in AN and NM solutions, in the absence and presence of equimolar concentration of the different M^{2+} ions used. In all cases, only a single ^{7}Li resonance was observed, indicating that the exchange rate of Li^{+} ion between the bulk solution and the complexed sites is fast on the NMR time scale.

All the resulting chemical shift–mole ratio plots are illustrated in Figs. 1, 2 and 3. As can be seen, in the absence of other metal ions (Fig. 1), addition of L^1 and L^2 amines to the lithium ion solution causes an almost linear paramagnetic shift in the observed ^{7}Li chemical shift, where δ_{obs}, a population-averaged combination of the chemical shifts of Li^+ ion in the bulk solvent, δ_{Li}, and that of the Li^+ ion complexed with ligand, δ_{LiL}, which are quite different from each other due to differences in the electron densities surrounding the probe nucleus in the two sites, is given as $\delta_{\mathrm{obs}} = P_{\mathrm{Li}}\ \delta_{\mathrm{Li}} + P_{\mathrm{LiL}}\ \delta_{\mathrm{LiL}}$ (where, $P_{\mathrm{Li}} + P_{\mathrm{LiL}} = 1$ in the course of titration of metal ion with the ligand). However, as is obvious from Fig. 1, the δ_{obs} value begins to level off at mole ratios greater than unity, because after formation of a 1:1 complex almost all of the Li^+ ions are present as the LiL complex ($P_{\mathrm{Li}} = 0$ and $P_{\mathrm{LiL}} = 1$ so that $\delta_{\mathrm{obs}} = \delta_{\mathrm{LiL}}$). Figure 1 shows that the slope of the corresponding mole ratio plots changes significantly at the point where the ligand-to-cation mole ratio is equal to one, indicating the formation of a relatively stable 1:1 complex in solution. It is interesting to note that, in NM solutions (Figs. 2b, 3b), the inflection points of the mole ratio plots are clearly sharper than those obtained in AN solutions (Figs. 2a, 3a), indicating the higher stability of the resulting complexes in the NM solvent.

The formation constants of 1:1 $(\mathrm{LiL})^+$ complexes were calculated from the variation of the ^{7}Li chemical shift with the $\mathrm{L/Li}^+$ mole ratio. It has been shown previously [31] that the observed chemical shift of Li^+ at a fixed concentration, C_{Li}, upon titration with varying ligand concentrations, C_{L}, is given by:

$$\begin{aligned}\delta_{\mathrm{obs}} = \Big\{ \big[&(K_{\mathrm{Li}}C_{\mathrm{Li}} - K_{\mathrm{Li}} - K_{\mathrm{Li}}C_{\mathrm{L}} - 1) + (K_{\mathrm{Li}}^2 C_{\mathrm{L}}^2 + K_{\mathrm{Li}}^2 C_{\mathrm{Li}}^2 - 2K_{\mathrm{Li}}^2 C_{\mathrm{L}} C_{\mathrm{Li}} \\ &+ 2K_{\mathrm{Li}}C_{\mathrm{L}} + 2K_{\mathrm{Li}}C_{\mathrm{Li}} + 1)^{1/2} \big] \times (\delta_{\mathrm{Li}} - \delta_{\mathrm{Li-L}})/2K_{\mathrm{Li}}C_{\mathrm{Li}} \Big\} + \delta_{\mathrm{Li-L}}\end{aligned} \tag{1}$$

where δ_{Li} and $\delta_{\mathrm{Li\text{–}L}}$ are the respective chemical shifts of the free and complexed Li^+ ion. The nonlinear least-squares curve fitting program KINFIT [32] was used to evaluate the K_{Li} and $\delta_{\mathrm{Li\text{–}L}}$ values. A sample computer fit of the ^{7}Li chemical shift–mole ratio data is shown in Fig. 4 and the calculated $\log_{10} K_{\mathrm{f}}$ values are given in Table 1. The fair agreement between the observed and calculated chemical shifts shown in Fig. 4a further supports the formation of a complex between Li^+ and amines with 1:1 stoichiometry.

It is well known that, most transition metals nuclei cannot be accurately used for an NMR study of their macrocyclic complexes. This is mainly because of their high quadruple moments and low receptivities [33]. Thus, in this work, we decided to employ ^{7}Li NMR as a very sensitive probe [34–38] to investigate the complex formation of Mg^{2+}, Zn^{2+} and Cd^{2+} ions with L^1 and L^2 in the solvents used. In this case, known concentrations of each of the M^{2+} ions and Li^+ (i.e., 0.01 $\mathrm{mol{\cdot}L^{-1}}$), present in solution, are simultaneously titrated with each of ligands L^1 and L^2, while monitoring the changes in the chemical shift of the ^{7}Li nucleus in solution. The resulting plots of variation of the ^{7}Li chemical shift in the presence of equimolar concentrations of M^{2+} ions and Li^+ (0.01 $\mathrm{mol{\cdot}L^{-1}}$) as a function of the $\mathrm{L/Li}^+$ mole ratio in AN and NM solutions are shown in Figs. 2 and 3. As is obvious from Figs. 2 and 3, unlike the cases involving in the formation of a 1:1 Li^+–L complex in which the change in chemical shift with the $\mathrm{L/Li}^+$ mole ratio is quite linear at mole ratio <1, here the mole ratio plots in the presence of other M^{2+} ions used show a small change in chemical shift of Li^+ ion at $\mathrm{L/Li}^+$ mole ratios between 0 and 1, followed by a sharp linear increase in δ_{obs}, which begins to level off at mole ratios >2. More or less similar δ_{obs}–$\mathrm{L/Li}^+$ mole ratio behavior observed for all three Mg^{2+}, Zn^{2+} and Cd^{2+} ions in the presence of Li^+ ion clearly indicate that all 1:1 M^{2+}– L complexes formed in both AN and NM are more stable than their corresponding Li^+–L complex. Here the resulting mole ratio plots show that, due to higher stability of M^{2+}–L complexes over Li^+–L, the majority

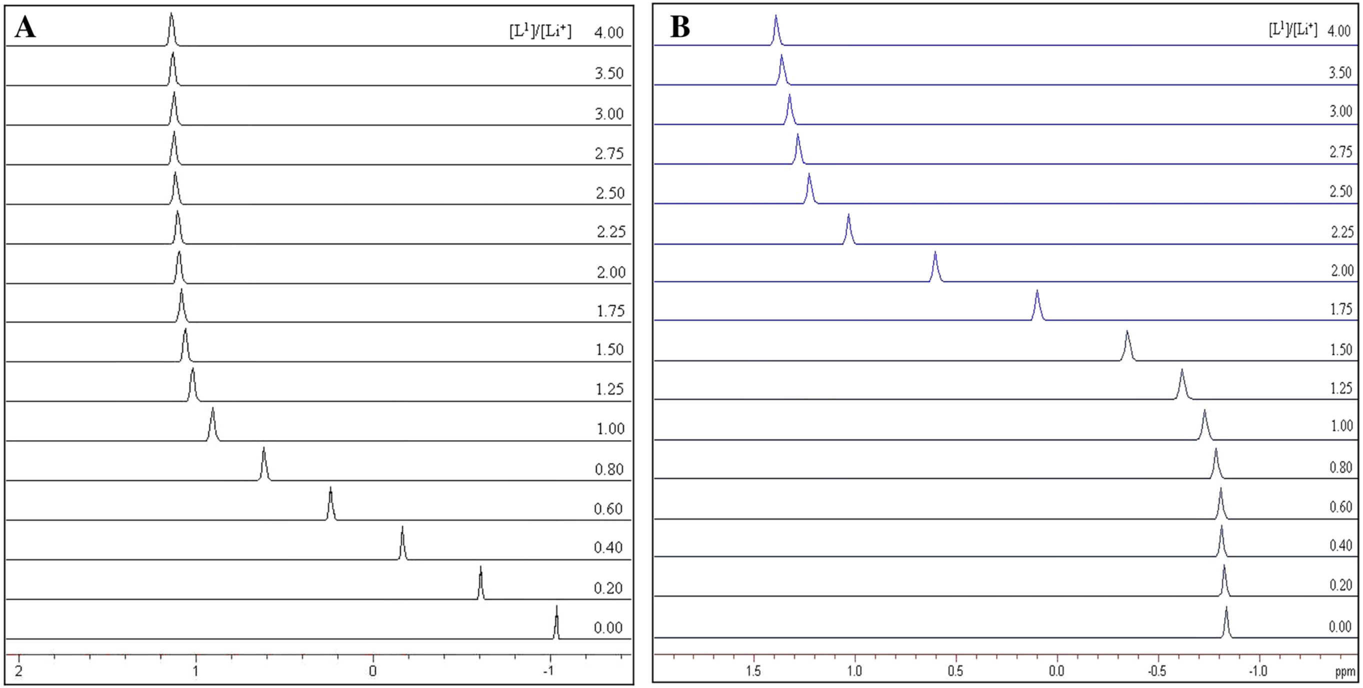


Fig. 1 Lithium-7 NMR spectra of 0.01 mol·L^{-1} $LiClO_4$ in nitromethane at various L^1/Li^+ mole ratios in the absence (**a**) and presence of equimolar concentration of Zn^{2+} ion (**b**) at 25.0 ± 0.1 °C

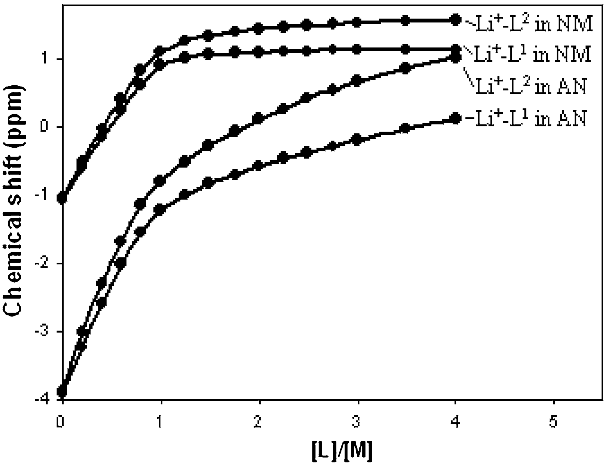


Fig. 2 Lithium-7 chemical shifts as a function of the L/Li^+ mole ratio in acetonitrile and nitromethane solutions

of ligand molecules interact with M^{2+} ions at L/Li^+ mole ratios <1 so that most of the Li^+ ions present remain free in solution and, consequently, the ^{7}Li chemical shift changes only slightly. However, at mole ratios >1, where the number of free M^{2+} ions in solution has largely diminished, the Li^+ ions present begin to form their 1:1 complexes with added ligand molecules and, thus, the δ_{obs}–mole ratio behavior at mole ratios >1 shows a trend more or less similar to that observed in the case of titration of Li^+ ion alone with the ligand (see Fig. 1), and levels off at mole ratios >2. This indicates quantitative formation of 1:1 complexes of the ligands with both Li^+ and all three M^{2+} ions studied.

Another point which worth noting in Figs. 2 and 3 is that, in all cases, the addition of nitrate salts of Mg^{2+}, Zn^{2+} and Cd^{2+} ions to a solution containing equimolar amounts of $LiClO_4$ causes some changes of about 0.1 to about 0.9 ppm in the ^{7}Li NMR chemical shift of free Li^+ ions at the L/Li^+ mole ratio = 0, as compared with the case of the lithium salt alone. This is most probably due to increasing the ionic strength of the solution by 100 % and, consequently, in increasing the extent of ion pairing of the Li^+ ion with the counter anions present.

The competitive complexation equilibria for the case of 1:1 complexation between amines and Li^+ and proposed ions can be written as:

$$Li^+ + L \rightleftharpoons Li^+L \quad K_{Li} = [Li^+L]/[Li^+][L] \tag{2}$$

$$M^{2+} + L \rightleftharpoons M^{2+}L \quad K_M = [M^{2+}L]/[M^{2+}][L] \tag{3}$$

The free amine concentration is then obtained from Eq. 4 [39]:

$$\begin{aligned} &K_{Li}K_M[L]^3 - \{K_{Li}K_M(C_L - C_{Li} - C_M) - K_{Li} - K_M\}[L]^2 \\ &- \{K_{Li}(C_L - C_{Li}) + K_M(C_L - C_M) - 1\}[L - 1][L] - C_L = 0 \end{aligned} \tag{4}$$

where C_L, C_{Li}, and C_M are the analytical concentrations of the amine, Li^+ and M^{2+} ion, respectively. In this case, the observed [^{7}Li] NMR chemical shift is obtained from Eq. 5 [35]:

$$\delta_{obs} = P_{Li}\delta_{Li} + P_{LiL}\delta_{LiL} \tag{5}$$

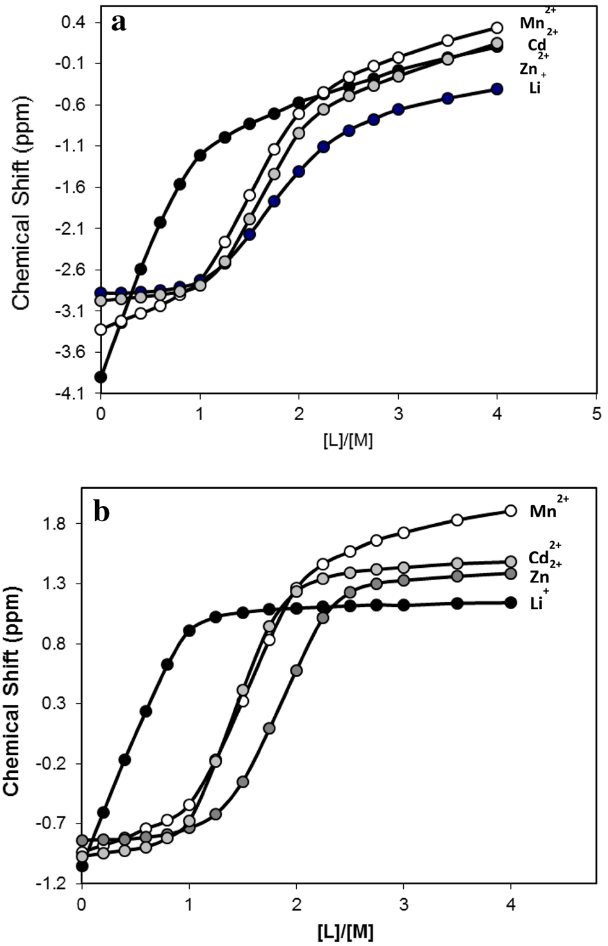


Fig. 3 Lithium-7 chemical shifts as a function of the L^1/Li^+ mole ratio in acetonitrile (**a**) and nitromethane (**b**) solutions in the absence and presence of different M^{2+} ions

where P_{Li} and P_{LiL} are the mole fractions of the free and complexed lithium ion, respectively. By substitution from Eq. 2 and the mass balance equation $C_{Li} = [Li^+] + [Li^+L]$, Eq. 5 can be written as:

$$\delta_{obs} = \{\delta_{Li} + \delta_{LiL}[L]K_{Li}\}/\{1 + K_{Li}[L]\}. \qquad (6)$$

The K_M values were evaluated by obtaining the free amine concentration from Eq. 4 and fitting the chemical shift–mole ratio data to Eq. 6 by using the KINFIT program.

A sample computer fit of the data is shown in Fig. 4b and the resulting $\log_{10} K_f$ values are included in Table 1. Our assumption of 1:1 stoichiometry for both Li^+–L and M^{2+}–L complexes seems reasonable in the light of a fair agreement between the observed and calculated chemical shifts.

The apparent stability constants of the complexes formed between the two ligands and all metal ions used in AN and NM, as solvents of much lower dielectric constants than water, are expected to be significantly affected by both the nature of the counter anions and

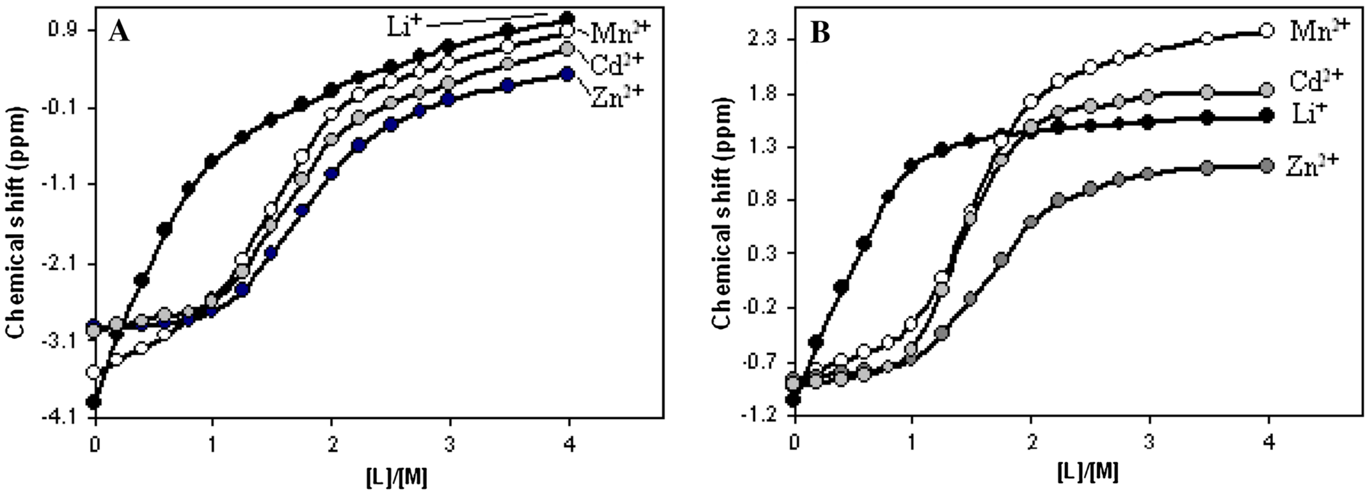


Fig. 4 Lithium-7 chemical shifts as a function of the L^2/Li^+ mole ratio in acetonitrile (**a**) and nitromethane (**b**) solutions in the absence (Li^+) and presence of different M^{2+} ions

Table 1 Formation constants for metal ion complexes with L^1 and L^2 in AN and NM solutions at 25 °C

Cation[a]	$\log_{10} K_f$			
	Acetonitrile		Nitromethane	
	A^1	A^2	A^1	A^2
Li^+ (0.76)	2.65 ± 0.05	2.49 ± 0.04	3.87 ± 0.04	3.36 ± 0.04
Mn^{2+} (0.83)	3.97 ± 0.05	3.85 ± 0.06	4.45 ± 0.07	4.35 ± 0.09
Zn^{2+} (0.74)	4.32 ± 0.09	3.99 ± 0.05	4.87 ± 0.06	4.48 ± 0.02
Cd^{2+} (0.95)	4.93 ± 0.32	4.28 ± 0.10	5.58 ± 0.20	5.29 ± 0.17

[a] Values in parentheses are the ionic sizes of cations in Å

the concentrations of the salts used, due to variations in extent of ion pairing between the metal ions and their counter anions. Thus, in this work, we used the same salt concentration of 0.01 $\text{mol}\cdot\text{L}^{-1}$ with the same counter anion, in order to have a constant effect of salt concentration and counter anion on all apparent stability constants of the complexes of interest.

The results given in Table 1 clearly demonstrated that, in both NM and AN solutions and for all four metal ions studied, the resulting complexes with the Schiff bases L^1 and L^2 vary in the order of $ML^1 > ML^2$. This is due to the fact that the ligands L^1 and L^2 differ in the size of their central chelate rings so that they can form five- and six- membered rings, respectively (see Fig. 5). As it is well documented in the literature [40, 41], the complexes forming a six-membered chelate ring are expected to be less stable than those forming a five-membered chelate ring.

In fact, *N*1,*N*1′-(ethane-1,2-diyl)bis(*N*1-(pyridin-2-ylmethyl)propane-1,3-diamine) (L^1) and *N*1,*N*1′-(propane-1,3-diyl)bis(*N*1-(pyridin-2-ylmethyl)propane-1,3-diamine) (L^2) are both hexadendate (N_6) amine ligands containing two pyridine moiety groups at terminal positions. It has been shown that the complexation ability of the amines to metal ions can be considerably increased by attaching a more rigid carbon chain between the donor nitrogen groups [43–45]. In the cases of ligands L^1 and L^2, the stability of the resulting metal ion complexes arises from the two types of nucleation centers: (1) the amine nitrogens of the carbon chain and (2) the pyridine moiety residues, which control the strength of complexation by π-electron interactions, steric influences and by supplying two terminal nitrogen atoms [45–47]. Subsequently, the metal ion is surrounded by the flexible carbonic chain, which can easily adapt to different cation sizes, and is better shielded from the solvent and the counter ions by the two terminal pyridine groups [46–49]. Therefore, as is obvious from Table 1, in all cases the M^{n+}–L^1 complexes are more stable than the M^{n+}–L^2 complexes in the solvents.

The data given in Table 1 also illustrate the influence of solvent properties on the stability of the resulting complexes between ligands L^1 and L^2 and Li^+ and all three M^{2+} metal ions used. It is obvious that the nature of solvent plays a fundamental role in complex formation; in all cases, the complexes are more stable in NM than in AN. It should be noted that, while NM and AN have about the same dielectric constants, their solvating abilities as expressed by the Gutmann donor number [42], are quite different (i.e., $\varepsilon = 35.9$ and $\text{DN} = 2.7$ for NM and $\varepsilon = 36.1$ and $\text{DN} = 14.1$ AN). AN as a solvent of higher solvating ability that can compete more strongly with amines for the metal ions than NM as a poor solvating solvent and, thus, the complexes formed in NM are expectedly to be more stable than those in AN.

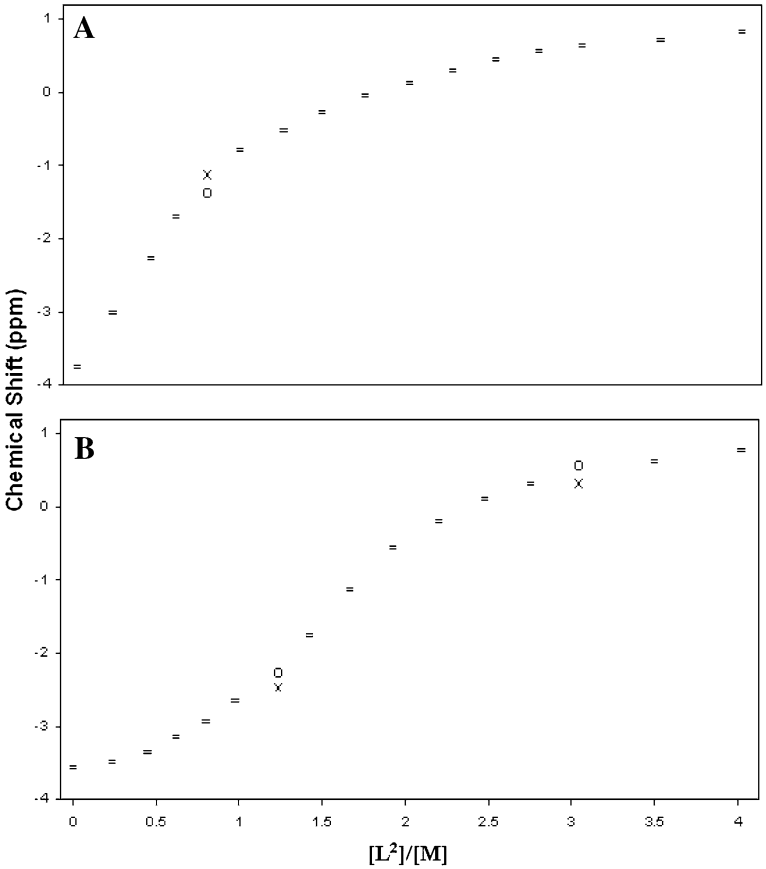


Fig. 5 Computer fit of lithium-7 chemical shift versus the L^1:Li^+ mole ratio for Li^+–L^2 (**a**) and Li^+–L^2–Mn^{2+} (**b**) systems in acetonitrile solution: (x) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot

The data given in Table 1 reveal that, in both solvents used, the stability of the resulting complexes varies in the order $Cd^{2+} > Zn^{2+} > Mn^{2+} > Li^+$. The complex stability order results from the superposition of several factors including the extent of interaction of donor groups of the ligand with the cation, the consonance between the size of metal ion and the steric size of the ligand cavity formed, the extent of ligand conformational changes as a consequence of complex formation, the hard-soft acid–base characters of the metal ion and the donating groups of the ligand, desolvation of the ligand and cation and solvation of the resulting complex, the two later factors being strongly dependent on the nature of solvents used.

The cationic charge and size (and the consequent charge density) can play a fundamental role in the complexation process from the viewpoints of ionic solvation and binding energy with the ligand's donating atoms. By increasing the charge density of a cation, both its solvation energy and binding energy to a ligand are expected to increase, so that the increased binding energy of the cation to the ligand acts against its increased desolvation energy. On the other hand, since the change in topology of the open chain ligand from a flexible free state in solution to a helical rigid conformation in the complexed form leads to a large loss of entropy, the decrease in cation size and increase in charge density may induce steric deformations of the ligand and reduce the entropy of complexation.

As is obvious from Table 1, among the different cations used, the Li^+ ion forms the least stable complexes with ligands L^1 and L^2 in both solvent systems. In fact, the lithium ion is a single charged hard acid that is expected to have weak interactions with the intermediate–soft amine and pyridine nitrogen's of the ligand molecules. On the other hand, the bivalent transition metal ions form stronger complexes with both ligands than does the Li^+ ion. This is due to the soft character of the transition metal ions, which result in stronger interactions with the donating nitrogen's of the ligands [50].

Meanwhile, the sequence of stability of the Zn^{2+} and Mn^{2+} complexes with both ligands (i.e., $Zn^{2+} > Mn^{2+}$) follows the Irving–Williams order [51], which generally governs the equilibrium constants of first row transition metal ions. Finally, the results show the highest stability for Cd^{2+} complexes with ligands L^1 and L^2, among all three M^{2+} cations used. This is most probably due to the proper size of the large Cd^{2+} ion with soft nature which could favor a suitable spatial fit with flexible donating atoms of the ligands (i.e., the four amine- and two pyridine-nitrogens of L^1 and L^2) so that, in this case, the central metal ion induces the lest amount of steric deformation to the ligands' structures [52, 53].

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