## ORIGINAL PAPER

Complexation studies of  $Mn^{2+}$ ,  $Zn^{2+}$  and  $Cd^{2+}$  ions with a series of tetradentate (N<sub>4</sub>) Schiff base ligands containing pyridine moiety in acetonitrile and nitromethane solutions by a competitive NMR technique using <sup>7</sup>Li nucleus as a probe

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Abstract Lithium-7 NMR spectroscopy was used to investigate the stoichiometry and stability of a Li<sup>+</sup> complex with  $N^1, N^2$ -bis(pyridin-2-ylmethylene)ethane-1,2diamine  $(L^1)$ ,  $N^1$ ,  $N^3$ -bis(pyridin-2-ylmethylene)propane-1,3-diamine ( $L^2$ ) and  $N^1, N^4$ -bis(pyridin-2-ylmethylene) butane-1,4-diamine (L<sup>3</sup>) in acetonitrile (AN) and nitromethane (NM) solutions. A competitive <sup>7</sup>Li NMR method was also employed to probe the complexation of  $Mn^{2+}$ ,  $Cd^{2+}$  and  $Zn^{2+}$  ions with  $L^1$ ,  $L^2$  and  $L^3$  in the same solvents. The formation constants of the resulting complexes were evaluated from computer fitting of the mole ratio data to an equation that relates the observed chemical shifts to the formation constant. In both solvents, the stability of the resulting 1:1 complexes were found to vary in the order Zn<sup>2+</sup>>Cd<sup>2+</sup>>Mn<sup>2+</sup>>Li<sup>+</sup>. In addition, the stability of M–L complexes of M<sup>2+</sup> with the Schiff base ligands found to vary in the order  $M^{2+}-L^1 > M^{2+}-L^2 > M^{2+}-L^3$ .

Keywords Competitive <sup>7</sup>Li NMR  $\cdot$  Schiff base ligand  $\cdot$  Complexation  $\cdot$  Nitromethane  $\cdot$  Acetonitrile  $\cdot$  Complexation study

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#### Introduction

Schiff base ligands have been extensively studied in coordination chemistry mainly due to their facile syntheses, easily tunable steric, electronic properties and good solubility in common solvents [1]. Transition metal complexes with oxygen and nitrogen donor Schiff-bases are of particular interest [2] because of their ability to possess unusual configurations and their sensitivity to molecular environments [3]. Schiff base ligands have proven to be very effective in constructing supramolecular architectures such as coordination polymers, double helixes, and triple helicates [4, 5]. The stability constants provide the information required to calculate the concentrations of the complexes in solution. There are many areas of application in many fields such as industrial chemistry [6], environmental studies [7], medicinal [8] and analytical chemistry [9]. Therefore, complexation reactions of metal ions with different ligands have been widely studied [10–12]. Several methods such as potentiometric titration [13], conductometry [14], and spectrophotometry [15] have been reported for the determination of stability constants [16]. Our interest in the physicochemical properties of the Schiff bases encouraged us to study the formation and stability of a number of transition metal Schiff base complexes. In recent years, we have introduced some spectrophotometric methods for the evaluation of the formation constants of some transition metal cations with new synthetic Schiff base ligands in various solvents [16, 17]. In this paper, we used <sup>7</sup>Li NMR as a very sensitive probe to study the complexation of Mn<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> ions with N<sup>1</sup>,N<sup>2-</sup> bis(pyridin-2-ylmethylene)ethane-1,2-diamine( $L^1$ ),  $N^1$ , $N^3$ bis(pyridin-2-ylmethylene)propane-1,3-diamine( $L^2$ ) and  $N^{1}$ ,  $N^{4}$ -bis(pyridin-2-ylmethylene)butane-1, 4-diamine( $L^{3}$ ) in acetonitrile (AN) and nitromethane (NM) by a competitive technique. It should be noted that transition metal ions used have unsuitable NMR properties such as low receptivity, high quadrupole moment, insensitive chemical shifts, etc.

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### Experimental

### Materials

Ethane-1,2-diamine, propane-1,3-diamine, butane-1,4-diamine and pyridine-2-carbaldehyde were used from Fluka. Lithium perchlorate (Merck) was purified and dried as reported elsewhere [18]. Except for vacuum drying, Reagent grade salts (all from Fluka) were applied with no further purification. Acetonitrile and nitromethane were commercially available from the Merk and used as received. A Jeol FX90Q FT-NMR spectrometer implementing <sup>7</sup>Li resonance at 33.74 MHz was used to measure all nuclear magnetic resonance with a field strength 2.12 T equipped with a temperature controller. Typical acquisition parameters were 4,000 Hz sweep width, 1 s relaxation delay, 1 s acquisition time, 15  $\mu$ s pulse width (45° pulse) in 90.0 MHz and 32 k = 32,768 words. In all <sup>7</sup>Li NMR experiments, a 4.0 M aqueous LiCl solution was used as external standard. The <sup>7</sup>Li NMR spectra of the resulting solutions were recorded at 25.0 ( $\pm 0.1$ ) °C.

## Synthesis of Schiff base ligands

The tetradentate Schiff base ligands were prepared according to literature method [19]. A solution of ethane-1,2-diamine, propane-1,3-diamine and butane-1,4-diamine (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 room temperature (Scheme 1).

### Sample preparation

Stock solutions of the Schiff base ligands were prepared by weighting an appropriate amount of the ligands at concentrations of 0.10 M in AN and NM. Appropriate quantities of metal salts at concentrations of 0.01 M dissolved in the mentioned solvents were added up to the [Schiff base]/ [Metal] mole ratio of 4, using a microsyringe. After mixing of the solutions under ultrasonic for 5 min, their <sup>7</sup>Li NMR spectra were recorded at 25.0( $\pm$ 0.1) °C.

# **Results and discussion**

The <sup>7</sup>Li chemical shifts were monitored as a function of the three Schiff base ligands  $(L^1-L^3)$  to lithium ion mole ratios in acetonitrile and nitromethane solutions, in the absence and presence of equimolar concentration of different  $M^{2+}$  ions used. In all cases, only one resonance line for the Li<sup>+</sup> ion was observed irrespective of the [Schiff base]/[Li<sup>+</sup>] mole ratio, indicating a fast exchange between the solvated and complexed cation sites. Typical <sup>7</sup>Li NMR spectra at varying [L<sup>1</sup>]/[Li<sup>+</sup>] mole ratios in acetonitrile in the absence and presence of Zn<sup>2+</sup> ion are shown in Figs. 1 and 2, respectively.



Scheme 1 Synthesis of the tetradentate Schiff base ligands

Fig. 1 Lithium-7 NMR spectra of 0.01 M LiClO<sub>4</sub> in acetonitrile at various  $[Li^+]/[L^1]$  mole ratios at 25.0± °C





Fig. 2 Lithium-7 chemical shifts as a function of the  $L^1$ ,  $L^2$  and  $L^3$  to lithium ion in acetonitrile and nitromethane solutions

All resulting chemical shift-mole ratio plots are illustrated in Figs. 3, 4, 5 and 6. As is seen from Fig. 3, in the absence of  $M^{2+}$  ions, addition of Schiff bases  $L^1$ ,  $L^2$  and  $L^3$ to lithium ion solutions causes an almost linear paramagnetic shift, which begins to level off at mole ratios greater than unity. The slope of the corresponding mole ratio plots changes sharply at a point where the ligand-to-cation mole ratio is equal to one, emphasizing the formation of a 1:1 complex. It is interesting to note that, in nitromethane solution, the inflection points of the mole ratio plots are clearly sharper than those obtained in acetonitrile solution, indicating the higher stability of all three Schiff base-Li<sup>+</sup> complexes in nitromethane.

The variations of <sup>7</sup>Li chemical shift with the [Schiff base]/[Li<sup>+</sup>] mole ratio were used to calculate the formation constants of Li<sup>+</sup> complexes with L<sup>1</sup>, L<sup>2</sup> and L<sup>3</sup>. The formation constant of 1:1 complexes are calculated from the variation of metal chemical shift with the [Schiff base]/[Li<sup>+</sup>] mole ratio [20]. The observed chemical shift of the <sup>7</sup>Li<sup>+</sup> ( $\delta_{obs}$ ) is a mass average of the characteristic chemical shifts of Lithium ion at each site (i.e., Li<sup>+</sup> in the bulk solution and Li<sup>+</sup> in the complex). Assuming that a fast exchange occurs between these two sites with respect to the NMR time scale [21].

$$\delta_{\rm obs} = P_{\rm Li} \delta_{\rm Li} + P_{\rm (Li-L)} \delta_{\rm (Li-L)} \tag{1}$$

where  $\delta_{\text{Li}}$  and  $\delta_{(\text{Li}-\text{L})}$  are the characteristic chemical shifts for  $\text{Li}^+$  in the bulk solution and in the complex, respectively, and  $P_{\text{Li}}$  and  $P_{(\text{Li}-\text{L})}$  are the respective mole fractions of these species.

Knowing that  $P_{Li} + P_{(Li-L)} = 1$  and  $P_{Li} = [Li^+]/C_{Li}$  then:

$$\delta_{\rm obs} = P_{\rm Li} \delta_{\rm Li} + (1 - P_{\rm Li}) \,\delta_{\rm (Li-L)} \tag{2}$$

$$\delta_{\rm obs} = P_{\rm Li}(\delta_{\rm Li} - \delta_{\rm (Li-L)}) + \delta_{\rm (Li-L)}$$
(3)

$$\delta_{\rm obs} = \frac{[\rm Li^+]}{C_{\rm Li}} (\delta_{\rm Li} - \delta_{\rm (Li-L)}) + \delta_{\rm (Li-L)}$$
(4)

$$C_{\rm Li} = [\rm Li] + [\rm Li - \rm L] \tag{5}$$



**Fig. 3** Computer fit of lithium-7 chemical shift vs.  $L^1:Li^+$  mole ratio for  $Li^+-L^2$  (a) and  $Li^+-L^2-Cd^{2+}$  (b) systems in nitromethane solution. (*x*) Experimental point; (*o*) calculated point; (=) experimental and calculated points are the same within the resolution of the plot

$$C_{\rm SB} = [L] + [Li - L] \tag{6}$$

$$Li^{+} + L = Li - L \quad K_{Li} = [Li - L]/[Li^{+}][L]$$
 (7)

By substitution of Eqs. (5), (6) and (7) in Eq. (4), one obtains the following equation:

Fig. 4 Lithium-7 NMR spectra of 0.01 M LiClO<sub>4</sub> in acetonitrile at various  $[Li^+]/[L^1]$  mole ratios at 25.0± °C in the presence of equilimolar concentration of Zn<sup>2+</sup> ion

$$\delta_{\text{obs}} = \left\{ [(K_{\text{f}}C_{\text{Li}} - K_{\text{f}}C_{\text{L}} - 1) + (K_{\text{f}}^{2}C_{\text{L.}}^{2} + K_{\text{f}}^{2}C_{\text{Li}}^{2} - 2K_{\text{f}}^{2}C_{\text{L.}}C_{\text{Li}} + 2K_{\text{f}}C_{\text{L}} + 2K_{\text{f}}C_{\text{Li}} + 1)^{1/2}](\delta_{\text{Li}} - \delta_{\text{Li}-\text{L}})/2K_{\text{f}}C_{\text{Li}} \right\} + \delta_{\text{Li}-\text{L}}$$
(8)

where  $K_{\rm f}$  is the formation constant for the 1:1 complex,  $C_{\rm L.}$ and  $C_{\rm Li}$  are the total concentrations of the Schiff base and lithium ion, respectively,  $\delta_{\rm Li}$  and  $\delta_{\rm Li-L}$  are the respective chemical shifts of the free and complexed lithium ion. The non-linear least-squares curve fitting program KINFIT [22] was used to evaluate  $K_{\rm f}$  and  $\delta_{\rm Li-L}$  values for the 1:1 the calculations.

In Eq. (8) Values of  $C_{\text{Li}}$ ,  $C_{\text{L}}$  and  $\delta_{\text{Li}}$  are known.  $\delta_{\text{Li}-\text{L}}$ . and  $K_{\text{f}}$  are the two unknowns. These parameters are initially estimated and used to calculate  $\delta_{\text{cal}}$  for different values of [Schiff base]/[Li<sup>+</sup>] mole ratio with the aid of Eq. (8). The calculated chemical shifts are iteratively fitted to the observed chemical shifts and the values of  $\delta_{\text{Li}-\text{L}}$  and  $K_{\text{f}}$ are varied to obtain the best fit. A sample computer fit of the <sup>7</sup>Li chemical shift-mole ratio data is shown in Fig. 7a and all the calculated log  $K_{\text{f}}$  values are summarized in Table 1. As seen from Fig. 7a, there is a satisfactory agreement between the calculated and observed chemical shifts, supporting the formation of a complex with 1:1 stoichiometry between Li<sup>+</sup> and L<sup>2</sup> in solution.

It is well known that most transition metal nuclei cannot be accurately used in NMR studies of their macroacyclic complexes, because of their low receptivities and high quadrupole moments [23]. Thus, in this work, <sup>7</sup>Li NMR





Fig. 5 Lithium-7 chemical shifts as function of  $L^{1}:Li^{+}$  mole ratio in pure acetonitrile and nitromethane solutions in the presence of different  $M^{2+}$  ions



Fig. 6 Lithium-7 chemical shifts as function of  $L^2:Li^+$  mole ratio in pure acetonitrile and nitromethane solutions in the presence of different  $M^{2+}$  ions

was used as a very sensitive probe [20, 24–26] to investigate the complex formation of  $Mn^{2+}$ ,  $Cd^{2+}$  and  $Zn^{2+}$  ions with  $L^1$ ,  $L^2$  and  $L^3$  in acetonitrile and nitromethane solutions. Variation of <sup>7</sup>Li chemical shift, in the presence of an equimolar concentrations of different  $M^{2+}$  ions, as a function of [Schiff base]/[Li<sup>+</sup>] for three Schiff bases in acetonitrile and nitromethane was obtained. Typical spectra are shown in Fig. 2, and the resulting chemical shiftmole ratio plots are included in Figs. 4, 5 and 6.

In spite of the cases involving the formation of 1:1 Li-Schiff base complexes (Fig. 3), as is obvious from Figs. 4, 5 and 6, in which the change in chemical shift with the [Schiff base]/[Li<sup>+</sup>] mole ratio is approximately linear at mole ratios less than 1, the mole ratio plots in the presence of  $M^{2+}$  ions illustrate a curved relationship between 0 and 2. However, in all cases, a plateau is reached for mole



Fig. 7 Lithium-7 chemical shifts as function of  $L^3:Li^+$  mole ratio in pure acetonitrile and nitromethane solutions in the presence of different  $M^{2+}$  ions

ratios more than 2, because of the quantitative formation of 1:1 complexes of Schiff bases with both  $Li^+$  and  $M^{2+}$  ions. It is interesting to note that, in cases of  $Mn^{2+}$ ,  $Zn^{2+}$  and  $Cd^{2+}$  ions in both solvent systems, the mole ratio plots also show a distinct inflection point at a [Schiff base]/[Li<sup>+</sup>] mole ratio of about 1 (Figs. 4, 5, 6), most probably due to significant differences in the formation constants of the Li<sup>+</sup>-Schiff base and M<sup>2+</sup>-Schiff base complexes in solution [27, 28].

The competitive complex formation equilibria, where only the 1:1 complexes between the Schiff bases and both  $Li^+$  and  $M^{2+}$  ions are shown in Eqs. (7) and (9).

$$Li^{+} + L = Li - L$$
  $K_{Li} = [Li - L]/[Li^{+}][L]$  (7)

$$M^{2+} + L \Leftrightarrow M - L^{2+}$$
  $K_M = [M - L^{2+}]/[M^{2+}][L]$  (9)

The free Schiff base concentration, [L], is then obtained from Eq. (10):

$$K_{\text{Li}}K_{\text{M}}[\text{L}]^{3} - \{K_{\text{Li}}K_{\text{M}}(C_{\text{L}^{1}} - C_{\text{Li}} - C_{\text{M}}) - K_{\text{Li}} - K_{\text{M}}\}[\text{L}]^{2} - \{K_{\text{Li}}(C_{\text{L}} - C_{\text{Li}}) + K_{\text{M}}(C_{\text{L}} - C_{\text{M}}) - 1\}[\text{L}] - C_{\text{L}} = 0$$
(10)

where  $C_{\rm L.}$ ,  $C_{\rm Li}$  and  $C_{\rm M}$  are the analytical concentrations of L, Li<sup>+</sup> ion and M<sup>2+</sup> ion, respectively. In this case, the observed <sup>7</sup>Li NMR chemical shift is obtained from Eq. (1) and then by substitution from Eq. (7) and the mass balance equation  $C_{\rm Li} = [\rm Li^+] + [\rm Li-L]$ , Eq. (1) can be written as:

$$\delta_{\text{obs}} = \left\{ \delta_{\text{Li}} + \delta_{\text{Li}-\text{L}}[\text{L}]K_{\text{Li}} \right\} / \left\{ 1 + K_{\text{Li}}[\text{L}] \right\}$$
(11)

The  $K_{\rm M}$  values were evaluated by obtaining the free Schiff base ligand concentration [L] from Eq. (10) and fitting the chemical shift-mole ratio data to Eq. (11) using the KINFIT program. A sample computer fit of the mole ratio data is shown in Fig. 7b and the resulting log  $K_{\rm f}$ values are included in for all M<sup>2+</sup>–L complexes in Table 1. Our assumption that the 1:1 stoichiometry of both Li<sup>+</sup>–L

| Cation <sup>a</sup>    | $\log K_f$    |               |                |               |                |                |
|------------------------|---------------|---------------|----------------|---------------|----------------|----------------|
|                        | Acetonitrile  |               |                | Nitromethane  |                |                |
|                        | $L^1$         | $L^2$         | L <sup>3</sup> | $L^1$         | $L^2$          | L <sup>3</sup> |
| Li <sup>+</sup> (0.76) | $3.27\pm0.03$ | $3.02\pm0.03$ | $2.93\pm0.05$  | $3.41\pm0.05$ | $3.51\pm0.06$  | 3.39 ± 0.07    |
| $Mn^{2+}$ (0.83)       | $3.91\pm0.08$ | $3.82\pm0.04$ | $3.58\pm0.08$  | $4.36\pm0.06$ | $4.07\pm0.09$  | $4.02\pm0.06$  |
| $Cd^{2+}$ (0.95)       | $4.33\pm0.09$ | $3.95\pm0.08$ | $3.82\pm0.05$  | $4.61\pm0.07$ | $4.461\pm0.04$ | $4.06\pm0.03$  |
| $Zn^{2+}$ (0.74)       | $4.75\pm0.05$ | $4.26\pm0.11$ | $4.09\pm0.06$  | $5.24\pm0.18$ | $4.78\pm0.17$  | $4.49\pm0.10$  |

Table 1 Formation constants for metal ion complexes with  $L^1$ ,  $L^2$  and  $L^3$  in acetonitrile and Nitromethane solutions at 25 °C

<sup>a</sup> Values in parentheses are the ionic sizes of cations in Å

and  $M^{2+}-L$  complexes seems reasonable in the light of a fair agreement between the observed and calculated chemical Shifts (Fig. 7b).

The complexation ability of the Schiff base ligands to metal ions can be considerably increased by attaching rigid aromatic donor end groups to the amines backbone [29–32]. In fact, the stability of its complexes arises from the two types nucleation centers, namely, the carbon chain nitrogen and the pyridine aromatic residues, which can control the strength of complexation by  $\pi$ -electron interactions, steric influences and by supplying two nitrogen atoms [30, 31, 33]. Subsequently, the metal ion is surrounded by the flexible carbon chain, which can easily adapt to different cation sizes, and is better shielded from the solvent and the counter ions by two terminal pyridine groups [31–33].

Thus, the complex stability results from the superposition of several factors including the extent of interaction of donor groups of the Schiff base ligands and the cations, the consonance between the size of metal ion and the sterical size of the ligand cavity formed, the extent of ligand conformational changes as a consequence of complex formation, desolvation of the Schiff base ligands 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 also play a fundamental role in the complexation process from the view points of ionic solvation and binding energy with the Schiff base's donating atoms. By increasing charge density of cations, both its salvation energy and binding energy to the ligand are expectedly increased, 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 the steric deformations of Schiff base and reduce the entropy of complexation [30]. Consequently, it is expected that by increasing the cation size, the stability of complex will be increased.

The data given in Table 1 revealed that the stability of  $M^{2+}-L$  complexes vary in the order  $Zn^{2+}>Cd^{2+}>Mn^{2+}>Li^+$ . As is obvious, transition metal complexes form stronger complexes with all Schiff bases than the Li<sup>+</sup> ion used. This is due to the soft character of the transition metal ions, which result in stronger interactions with the donating nitrogens of the Schiff base as soft bases [34]. Lithium ion with the lowest charge density and a hard character forms the least stable complex among the four cations studied.

Furthermore, Table 1 shows that in both acetonitrile and nitromethane solutions, the stability of all three  $M^{2+}$  ions studied, the resulting complexes with the Schiff base ligands  $L^1$ ,  $L^2$  and  $L^3$  vary in the order of  $M^{2+}-L^1 > M^{2+}-L^2 > M^{2+}-L^3$ . This is due to the fact that the ligands  $L^1$ ,  $L^2$ and  $L^3$  differ in the size of their central chelate rings so that they can form five-, six- and seven- membered rings, respectively (Fig. 8). It should be noted that the selectivity order thus obtained is in according to the well known rule which states that the seven-membered chelate rings are less stable than six-membered ones and both are less stable than five-membered chelate rings [35, 36].

As can be seen from the data given in Table 1, solvent plays a fundamental role in complex formation process. This is due to the fact that the solvent molecules are directly involved in three possible equilibria in the process complex formation, including desolvation of the metal ion, desolvation of the ligand and solvation of the resulting charged 1:1, so that the nature of solvent is expected to affect the overall energy balances involved in the metal ion complexation in solution [33, 34, 37–46]. In all cases studied, the resulting complexes are more stable in NM than in AN. It should be noted that, while NM and AN have about the same dielectric constants (i.e.,  $\varepsilon = 35.9$  for NM and  $\varepsilon = 36.1$  for AN), their solvating abilities, as expressed by the Gutmann donor number [47], are quite different (i.e., DN = 2.7 for NM and DN = 14.1 for AN). Thus, AN, as a solvent of higher solvating ability, can compete more strongly with the Schiff bases for the metal ions than does NM with poor solvating ability; this will, consequently, results in the formation of weaker complexes in the acetonitrile solvent.



M=Li<sup>+</sup>,Mn<sup>2+</sup>,Zn<sup>2+</sup>,Cd<sup>2+</sup>

Fig. 8 Purposed structures of M-L tetradentate Schiff base complexes

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