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ABSTRACT

Three new branched hexadentate amines, have been synthesized. Condensation with picolinaldehyde in methanol leads to produce three new Schiff base, with two 2-pyridylmethyl pendant arms. ⁷Li NMR spectroscopy was used to investigation the stability and stoichiometry information of a Li⁺ complex with three symmetrical branched Schiff base (Sc.B.¹), (Sc.B.²) and (Sc.B.³) in 0–100, 25–75, 50-50 and 75–25 w/w% acetonitrile – [(BMIM)(PF₆)] ionic liquid mixture solution. A competitive ⁷Li NMR manner was also used to probe the complexation of Schiff bases with Mn²⁺, Zn²⁺ and Cd²⁺ ions in the same solvent systems. The stability constants of the resulting complexes were estimated from computer fitting of the mole ratio information to an equation that relates the observed chemical shifts to the stable constant. There is a reverse relevance of the complex stability and the amount of ionic liquid in the solvent mixture. In of the all experimented solvent mixture, the stability of the resulted 1:1 complexes were found to change in the order M-Sc.B.¹>M-Sc.B.³ and Cd²⁺>Mn²⁺>Zn²⁺.

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1. Introduction

Schiff base ligands have played an important role in the development of coordination chemistry. Metal complexes of these ligands are ubiquitous due to their facile synthesis, wide applications and the possibility of diverse structural modifications [1-5].

Schiff base ligands have played an important role in the development of coordination chemistry. Metal complexes of these ligands are ubiquitous due to their facile synthesis, wide applications and the possibility of diverse structural modifications [6]. Schiff base complexes are considered to be among the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety [7]. The chemistry of Schiff base ligands and their metalcomplexes has expanded enormously and encompasses a vast area of organometallic compounds and various aspects of bioinorganic chemistry [8], and have various applications in catalysis [9–11], and as antibacterial agents [12–14] or chemosensors [15–18]. Many Schiff base have been designed and synthesized not only to mimic the functions of natural carriers in transporting metal ions but also for the development of new methodologies in separation science. Most of the work has been concerned with alkaline and alkaline earth cations, and transport studies have been made in parallel with the development of multidentate carriers containing oxygen donor atoms, in particular crown ethers and cryptands [19–23]. In contrast, much less attention has been devoted to transport processes involving d or f metal ions.

The complexation properties of macrocyclic amines, such as crown ethers and cryptands, in pure and mixed solvents, have been investigated extensively during the last three decades [24]. To date, our understanding of the macrocyclic and macroacyclic amines solution chemistry has been based on their behavior in molecular solvents, such as water, methanol and acetonitrile. The part of the solvent is very important, as the cation complexation competes with its solvation by solvent molecules. Stability constants of Li⁺ ion complexes with macroacyclic Schiff base were prescribe in a

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number of solvents. During recent decade, there has been an increasing interest in room temperature ionic liquids, which can be regarded as a new class of liquid media [25,26].

In this work, we report the Synthesis of three new branched octadentate (N₈) Schiff Base ligands with two 2-pyridylmethyl pendant arms. These Schiff Bases werecharacterized by several physicochemical techniques and ⁷Li NMR was used to determine the stability and stoichiometry action of complexation reaction of (Sc.B.¹), (Sc.B.²) [27,28] and (Sc.B.³) with Cd²⁺, Mn²⁺ and Zn²⁺ ions in binary 100–0, 75–25, 50-50 and 25–75 wt% acetonitrile - 1-Butyl-3-methylimidazolium hexafluorophosphate ion liquid ([BMIM][PF₆]) mixture solutions.

2. Materials and methods

2.1. Materials

The butane-1,4-diamine, sodium borohydride, ethane-1,2diamine, propane-1,3-diamine, N-(3-bromopropyl) phthalimide, picolinaldehyde were used of the maximum purity available from Fluka or Merck. Lithium perchlorate, Cadmium(II), Zinc(II), and Manganese(II) nitrate salts of all other cations were used of the maximum purity available from Merck and used without any extra purification except for vacuum drying over silicagel blue crystals. Spectroscopic grade 1-Butyl-3-methylimidazolium hexafluorophosphate [(BMIM)(PF₆)] ionic liquid] and acetonitrile (all from Merck), were used to do up prepare the solvent mixture by weight.



1-Butyl-3-methyl imidazolium hexa fluro phosphate [(BMIM)(PF₆)]

2.2. Instrumentation

CHN analyses were carried out using a Carlo-Erba Ea, CHN elemental analyzer. Infrared spectra were measured using KBr pellets on a Shimadzu FT-IR 8000 series spectrophotometer $(4000-400 \text{ cm}^{-1})$. FAB mass spectra were recorded using a Kratos-MS-50 T spectrometer connected to a DS90 data system using 3-nitrobenzyl alcohol as the matrix. 1H and 13C NMR spectra were recorded on a Bruker 500 and JEOL FX-90 Q using DMSO- d_6 and CDCl₃ as solvent. All NMR evaluations were made on a Jeol FX-FT NMR 90Q spectrometer with a temperature controller. The temperature of the probe was fixed to an accuracy of ± 0.1 °C using the temperature controller in the spectrometer. At this spectrometer, lithium-7 resonates at 33.742 MHz.

2.3. Synthesis

2.3.1. General synthesis of the branched octadentate Schiff bases (Sc.B.¹), (Sc.B.²) and (Sc.B.³)

The general method for the synthesis of the pentadentate Schiff bases are as follows. A solution of butane-1,4-diamine, propane-1,3-diamine and ethane-1,2-diamine (10 mmol) in dry Methanol (MeOH) (40 mL) was added slowly to a warm solution of picolinaldehyde (2.14 g, 20.0 mmol) in dry MeOH (40 mL) over a period of 2 h. The mixture was refluxed under stirring for 10 h and then allowed to cool to room temperature. The sodium borohydride (3.78 g, 100 mmol) was then added slowly and the reaction mixture heated at reflux for a further 2 h. The solution was filtered and then

the filtrate volume reduced to 20 mL by rotary evaporator. Excess water was added and the product was extracted with chloroform $(3 \times 25 \text{ mL})$; the combined chloroform solutions were separated and dried by magnesium sulfate. The chloroform was separated by rotary evaporator to give up vellow oil (90%). The resulting product (10 mmol) was disolved in acetonitrile (20 mL) and K₂CO₃ (2.76 g. 20 mmol) was added. The mixture was refluxed and then a solution of N-(3-bromopropyl) phthalimide (3.217 g, 12.0 mmol) in acetonitrile (40 mL) was added. The mixture was refluxed for 24 h and then filtered while it was warm. The filtrate was reduced to dryness. The resulting product was boiled under reflux for about 20 h in aqueous HCl (25%, ~100 mL). Then the solution was evaporated to low volume (ca. 20 mL) under vacuum and cooled in a refrigerator for several hours. The solid result was filtered off, and the rest solvent on the solid product was evaporated to dryness under vacuum. Water (~40 mL) was added to the mixture and the pH was controlled to 12 with sodium hydroxide. The result product was extracted with chloroform $(3 \times 25 \text{ mL})$, and then the combined chloroform solutions were separated, and dried over magnesium sulfate. The chloroform was removed by vacuum desiccator to leave the product as brown oil [28,29].

A separation solution of all the brown oil amines, N¹, N¹-(ethane-1,2-diyl) bis [N¹-(pyridin-2-ylmethyl) propane-1,3-diamine] (A¹), N¹, N¹ - (propane-1,3-diyl) bis [N¹-(pyridin-2-ylmethyl) propane-1,3-diamine] (A²) and N¹, N¹-(butane-1,4-diyl) bis [N¹-(pyridin-2-ylmethyl) propane-1,3-diamine] (A³), (1 mmol) was added to a warm solution of picolinaldehyde (0.214 g, 2.00 mmol) in dry MeOH (~30 mL) over a period of 2 h. The mixture was refluxed under stirring for 10 h and then let to cool to room temperature. A low volume of diethyl ether was slowly added into the solution. The product Schiff bases were filtered off, washed with cold diethyl ether and dried under vacuum (Scheme 1).

2.3.2. Synthesis of Schiff base $(N^{3}Z, N^{3'}Z)-N^{1}, N^{1'}-(ethane-1,2-diyl)$ bis $[N^{1}-(pyridin-2-ylmethyl)-N^{3}-(pyridin-2-ylmethylene)$ propane-1,3-diamine] (Sc.B.¹)

Yield: (71%). *Anal.* Calc. for $C_{32}H_{38}N_8$ (MW: 534.32): C, 71.88; H, 7.16; N, 20.96 Found: 71.64; H, 7.32; N, 20.71. IR (Nujol mull, cm⁻¹): 1647 (ν_{C} —N Schiff base), 1585 (ν_{C} —N pyridine). ¹H NMR (DMSO- d_6 , ppm, 90 MHZ): δ 2.683 (s, 4H, H_{a,a'}), 3.753 (s, 4H, H_{b,b'}), 7.138 (d, 2H, H_{d,d'}), 7.683 (m, 2H, H_{e,e'}), 7.276 (m, 2H, H_{f,f}), 8.476 (d, 2H, H_{g,g'}), 3.641 (t, 4H, H_{h,h'}), 1.876 (p, 4H, H_{i,i'}), 2.601 (t, 4H, H_{j,j'}), 8.339 (s, 2H, H_{k,k'}), 7.980 (d, 2H, H_{m,m'}), 7.767 (m, 2H, H_{n,n'}), 7.581 (m, 2H, H_{0,0'}), 8.631 (d, 2H, H_{p,p'}). ¹³C NMR (DMSO- d_6 , ppm, 300 MHz): δ 54.66 (C_{a'a'}), 58.44 (C_{b,b'}), 155.66 (C_{c,c'}), 128.68 (C_{d,d'}), 145.47 (C_{e,e'}), 124.51 (C_{f,f}), 148.10 (C_{g,g'}), 52.51 (C_{h,h'}), 25.07 (C_{i,i'}), 58.28 (C_{j,j'}), 162.26 (C_{k,k'}), 155.77 (C_{I,I'}), 125.39 (C_{m,m'}), 141.14 (C_{n,n'}), 136.93 (C_{0,0'}), 149.33 (C_{p,p'}).

2.3.3. Synthesis of $(N^{3}Z, N^{3'}Z)-N^{1}, N^{1'}-(propane-1,3-diyl)$ bis $[N^{1}-(pyridin-2-ylmethyl)-N^{3}-(pyridin-2-ylmethylene)$ propane-1,3-diamine] (Sc.B.²)

Yield: (65%). Anal. Calc. for $C_{33}H_{40}N_8$ (MW: 548.34): C, 72.23; H, 7.35; N, 20.42%. Found: C, 71.83; H, 7.24; N, 20.29%. IR (Nujol mull, cm⁻¹) 1650 (ν_{C} —_N Schiff base), 1587 (ν_{C} —_N pyridine). ¹H NMR (DMSO- d_6 , ppm, 90 MHz): δ 1.658 (m, 2H, H_a), 2.693 (t, 4H, H_{b,b'}), 3.569 (s, 4H, H_{c,c'}), 7.127 (d, 2H, H_{e,e'}), 7.683 (m, 2H, H_{f,f}), 7.273 (m, 2H, H_{g,g'}), 8.470 (d, 2H, H_{h,h'}), 2.403 (t, 4H, H_{i,i'}), 1.590 (m, 4H, H_{j,j'}), 2.403 (t, 4H, H_{k,k'}), 8.333 (s, 2H, H_{1,1}), 7.969 (m, 2H, H_{n,n'}), 7.765 (m, 2H, H_{o,o'}), 7.575 (m, 2H, H_{p,p'}). ¹³C NMR (DMSO- d_6 , ppm, 300 MHz): δ 25.63 (C_a), 53.96 (C_{b,b'}), 60.38 (C_{c,c'}), 158.66 (C_{d,d'}), 125.26 (C_{e,e'}), 141.59 (Cf_f), 124.39 (Cg,g'), 147.68 (Ch,h'), 50.29 (C_{i,i'}), 20.77 (Cj,j'), 60.38 (C_{k,k'}), 163.41 (C_{1,1'}), 155.17 (C_{m,m'}), 126.76 (C_{n,n'}), 147.11 (C_{o,o'}), 140.54 (C_{p,p'}), 147.68 (C_{q,q'}).



Scheme 1. Synthesis of the branched octadentate Schiff bases showing the lettering scheme for NMR assignments.

2.3.4. Synthesis of $(N^{3}Z, N^{3'}Z)-N^{1}, N^{1'}$ -(butane-1,4-diyl) bis $[N^{1}-(pyridin-2-ylmethyl)-N^{3}-(pyridin-2-ylmethylene)$ propane-1,3-diamine] (Sc.B.³)

Yield: (62%). Anal. Calc. for C₃₄H₄₂N₈ (MW: 562.35): C, 72.57; H, 7.52; N, 19.91%. Found: C, 72.34; H, 7.38; N, 19.52%. IR (Nujol mull, cm⁻¹) 1650 (ν_{C} —_N Schiff base), 1587 (ν_{C} —_N pyridine). ¹H NMR (DMSO- d_{6} , ppm, 90 MHz): δ 1.426 (t, 4H, H_{a,a'}), 2.592 (t, 4H, H_{b,b'}), 3.605 (s, 4H, H_{c,c'}), 6.931 (d, 2H, H_{e,e'}), 7.567 (m, 2H, H_{f,f}), 7.076 (m, 2H, H_{g,g'}), 8.273 (d, 2H, H_{h,h'}), 2.590 (t, 4H, H_{i,i'}), 1.504 (m, 4H, H_{j,j'}), 2.420 (t, 4H, H_{k,k'}), 8.135 (s, 2H, H_{l,l}), 7.772 (m, 2H, H_{n,n'}), 7.688 (m, 2H, H_{o,o'}), 7.483 (m, 2H, H_{p,p'}). ¹³C NMR (DMSO- d_{6} , ppm, 300 MHz): δ 24.94 (C_{a,a'}), 54.18 (C_{b,b'}), 60.48 (C_{c,c'}), 160.50 (C_{d,d'}), 122.30 (C_{e,e'}), 136.48 (C_{f,f}), 121.68 (C_{g,g'}), 148.69 (C_{h,h'}), 51.90 (C_{i,i'}), 28.17 (C_{j,j'}), 30.89 (C_{k,k'}), 154.42 (C_{l,l'}), 161.86 (C_{m,m'}), 121.14 (C_{n,n'}), 124.60 (C_{o,o'}), 122.74 (C_{p,p'}), 149.30 (C_{q,q'}).

2.4. Methods

An aqueous 4.0 M Lithium chloride solution was used as the external reference and the related lithium-7 chemical shifts are referenced to this solution. The downfield shift from the reference is designated as being positive. The concentration of all cations used was 0.02 M. Stock solutions of the Schiff bases were prepared by weighting adaption amounts at concentrations of 0.2 M in Ion liquid - Acetonitrile mixtures. Appropriate quantities of metal ions at concentrations of 0.02 M (dissolved in the same solvents,

respectively) were added to the [Sc.B.]/[Metal salt] mole ratio of 4, using a micro syringe, then the mixture was under ultrasonic for 10 min. Throughout the whole temperature range used, it was found that 10 min thermosetting prior to information accumulation was enough for each sample to give temperature equilibrium (Scheme 2). The ⁷Li-NMR spectra of the solutions were recorded at 25.0 (\pm 0.1) °C.

3. Results and discussion

The Lithium-7 chemical shifts were studied as a function of the mole ratio of complexant, Schiff Base (Sc.B.¹), (Sc.B.²) and (Sc.B.³) in binary 100–0, 75–25, 50-50 and 25–75 %wt acetonitrile – Ion liquid ([BMIM][PF₆]) mixture solution, in the absence and presence of equimolar concentration of different M^{2+} ions used. In all cases, show of only a single ⁷Li resonance locates that the exchange rate of Li⁺ ion between the bulk solution and the complexed sites is fast on the NMR time scale (Fig. 1).

All the resulting chemical shift - mole ratio plots are illustrated in Figs. 1 and 2. As can be seen, in the absence of other cations (Fig. 1-A), addition of Schiff base to the lithium ion solution causes an almost linear paramagnetic shift in the observed ⁷Li chemical shift, δ_{obs} , as 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 Schiff base, δ_{Li-Sc} , B, which are quite different from each other due to differences in the electron densities surrounding



Scheme 2. Synthesis of M²⁺-Schiff base octadentate complexes.



Fig. 1. ⁷Li NMR spectra of 0.02 M LiClO₄ in binary 50–50% acetonitrile – (BMIM)(PF₆) ionic liquid mixtures at various [Li⁺]/[Sc.B.¹] mole ratios in (A): the absence and (B) presence of equilimolar concentration of Cd²⁺ ion at 25.0 ± 0.1 °C.

the probe nucleus in the different two sites, as $\delta_{obs} = P_{Li} \delta_{Li} + P_{Li} \delta_{Li}$ s_{c.B.} (where, $P_{Li} + P_{Li-Sc.B.} = 1$ in the form of titration of metal ion with the Schiff base). However, as is obvious from Fig. (1-A), the δ_{obs} value begins to level off at mole ratios bigger than unity, because after formation of a 1:1 complex almost all Li⁺ ions present in (Li–Sc.B.)⁺ complex ($P_{Li} = 0$ and $P_{Li-Sc.B.} = 1$ so that $\delta_{obs} = \delta_{Li-Sc.B.}$) [29]. Lithium complexes in Fig. (1-B) show that the slope of the corresponding mole ratio plots change significantly at the point where the Schiff base to cation mole ratio is equal to one, emphasizing the formation of a relatively stable 1:1 complex in solution. The stability constants of 1:1 (Li–Sc.B.)⁺ complexes were studied from the difference of the ⁷Li chemical shift with Sc.B·/Li⁺ mole ratio. It has been shown formerly in Refs. [28–33].

It is well known that, most transition metals nuclei cannot be accurately used in an NMR study of their macroacyclic complexes. This is mainly because of their high quadruple moments and low receptivities [34]. Therefore, in this work, we decided to employ ⁷Li NMR as a much sensitive probe [35–39] to investigate the complex stability of Cd^{2+} , Zn^{2+} and Mn^{2+} ions with (Sc.B.¹), (Sc.B.²) and (Sc.B.²) in the mixture solutions used. In this case, known concentrations of each of the Li⁺ and M²⁺ ions (i.e., 0.02 M) present in solution are simultaneously titrated with each of Schiff bases (Sc.B.¹), (Sc.B.²) and (Sc.B.³), while controlling the changes in the chemical shift of ⁷Li nucleus in solution. The resulting plots of variation of ⁷Li chemical shift in the presence of equimolar concentrations of M²⁺ ions and Li⁺ (0.02 M) as a function of Sc.B.⁴/Li⁺

mole ratio in acetonitrile-ion liquid mixture solutions are shown in Fig. (2). As is obvious from Figs. (1-A, 1-B and 2), unlike the cases involving in the stability of 1:1 Li⁺-Sc.B. complex in whichever the change in chemical shift with the Sc.B·/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 Sc.B \cdot /Li⁺ mole ratios at Li⁺ ion between 0 and 1, followed by a sharp linear increase in δ_{obs} , whichever begins to level off at mole ratios >2. Such more or less similar δ_{obs} Sc.B·/Li⁺ mole ratio behavior observed for all three Cd²⁺, Zn²⁺ and Mn²⁺ ions in the presence of Li⁺ ion clearly indicate that all 1:1 M²⁺-Sc.B. complexes formed in both acetonitrile-ionic liquid mixtures are more stable than the Li⁺-Sc.B. complex. Here the resulting mole ratio plots show that, due to higher stability of M²⁺-Sc.B. complexes over Li⁺-Sc.B, the majority of Schiff base molecules interact with M^{2+} ion at $\text{Sc.B}\cdot/\text{Li}^+$ -mole ratios <1 so that most of the Li⁺ ions present remain free in solution and, therefore, the ⁷Li chemical shift changes only slightly. However, at mole ratios >1, where the number of free M^{2+} ions in solution has greatly diminished, the Li⁺ ions present begin to form their 1:1 complexes with the added Schiff base ligands 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 Schiff base (see Fig. 1), and levels off at mole ratios >2indicating the quantitative stability of 1:1 complexes of the Schiff bases with both Li^+ and all three M^{2+} ions studied.

Another point which worth to notice in Figs. 1 and 2 is that, in all



Fig. 2. ⁷Li NMR chemical shifts as a function of the Sc.B.¹, Sc.B.² and Sc.B.³ to metal ions mole ratios in (A) 100% AN, (B) 75% AN -25% [(BMIM)(PF₆)], (C) 50% AN -50% [(BMIM)(PF₆)], (D) 75% AN -25% [(BMIM)(PF₆)] mixture solutions at 25.0 ± 0.1 °C.

cases, the addition of nitrate salts of each of all ions to a solution containing equimolar of LiClO₄ causes some changes of about 0.2 to about 1 ppm in ⁷Li NMR chemical shift of free Li⁺ ions at Sc.B·/Li⁺ mole ratio = 0, as it as compared to the case of lithium salt alone. This is most possibly due to increased ionic power of solution, as a result, in the measure of ion coupling of Li⁺ ion with the counter anions extant. Chemical schift in Lithium ion in the presence of Mn^{2+} ion respect to Cd²⁺ and Zn²⁺ is due to paramagnetic behavior conduct of Mn^{2+} .

The competitive complexation equilibria about the case of 1:1 complexation between Schiff bases and Li⁺ proposed ions were calculated using equation in Refs. [40,41]. The resulting log K_f values are included in Table 1. The obvious apparent stability constants of the complexes formed between the two Schiff bases and all metal ions used in ion liquid - acetonitrile mixture solutions are expected to significantly affected by both the concentrations of the salts used and the nature of counter anions, due to variations in extent of ion pairing between the metal ions and their counter anions. Therefore,

Table 1

Stability constants of different $M^{2+}\mbox{-}Schiff$ base complexes in various acetonitrileionic liquid mixtures at 25 $^\circ\mbox{C}.$

Complexions	Log K_f in Solvent Composition (w/w% ionic liquid in acetonitrile)			
	0	25	50	75
$(Mn-Sc.B.^{1})^{2+}$	4.09 ± 0.04	3.72 ± 0.03	3.24 ± 0.04	2.81 ± 0.09
$(Zn-Sc.B.^{1})^{2+}$	4.40 ± 0.05	3.99 ± 0.04	3.62 ± 0.02	3.42 ± 0.05
(Cd-Sc.B. ¹) ²⁺	4.99 ± 0.08	4.62 ± 0.06	4.17 ± 0.07	3.82 ± 0.04
$(Mn-Sc.B.^{2})^{2+}$	3.94 ± 0.02	3.60 ± 0.04	3.22 ± 0.03	2.80 ± 0.04
$(Zn-Sc.B.^{2})^{2+}$	4.15 ± 0.04	3.72 ± 0.05	3.45 ± 0.06	3.24 ± 0.04
$(Cd-Sc.B.^{2})^{2+}$	4.47 ± 0.03	4.12 ± 0.04	3.76 ± 0.03	3.39 ± 0.05
$(Mn-Sc.B.^{3})^{2+}$	3.83 ± 0.08	3.33 ± 0.04	2.91 ± 0.05	2.54 ± 0.03
(Zn-Sc.B. ³) ²⁺	3.91 ± 0.04	3.55 ± 0.02	3.24 ± 0.03	3.08 ± 0.06
(Cd-Sc.B. ³) ²⁺	4.11 ± 0.05	3.70 ± 0.07	3.42 ± 0.08	3.21 ± 0.09

in this work, we used the same salt concentration of 0.02 M with the same counter anions, in order to have a constant influence of counter anion and salt concentration on all apparent stability constants of the complexes of interest.

The results given in Table 1 clearly demonstrated that, in 100–0%, 75-25%, 50-50% and 25–75% acetonitrile-ion liquid mixture solutions and in the cases of all three metal ions studied, the resulting complexes with the Schiff bases change in the order of M-Sc.B.¹> M-Sc.B.²> M-Sc.B.³. This is due to the fact that the Schiff bases (Sc.B.¹), (Sc.B.²) and (Sc.B.³) differ in the size of their in chelate rings in order that they can shape five, six and seven membered rings, separately (see Scheme 3). As it is well documented in the literature [42,43], the complexes forming a seven-membered chelate rings are expected to be less stable than those forming a five or six membered chelate rings.

In fact, (Sc.B.¹), (Sc.B.²) and (Sc.B.³) are a series of octadentate (N₈) Schiff bases including two pyridine moiety groups at end position. It has been shown that, the complexation ability of the Schiff bases to metal ions can be considerably increased by attaching a more rigid carbon chain in between the donor nitrogen groups [44,45]. In the cases of Schiff bases (Sc.B.¹), (Sc.B.²) and (Sc.B.³), the stability of the resulting metal ion complexes arises from the three types nucleation centers: (1) the amine nitrogen's of carbon chain, (2) the imine nitrogen's on Schiff bases and (3) the pyridine moiety affects remainders, which control the strength of complexation by π -electron interactions, steric influences and by supplying three terminal nitrogen atoms [45]. 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 two terminal pyridine groups [46-49]. Therefore, as is obvious from Table 1, in all cases the stability of M^{2+} -(Sc.B.¹) is more stable than M^{2+} - $(Sc.B.^{2})$ in the solvents.

According to the information given in Table 1, it is immediately obvious that for a given Schiff bases the stability of the resulting



Scheme 3. Purposed structures of M-Sc.B. octadentate complexes.

complex is dependent on the solvent mixture composition. In all cases the stability increases significantly with decreasing amount of ionic liquid in the solvent mixture. It has been well documented that the solvating ability of the solvent, plays a role in different complexation reactions [50-54]. Ionic liquid ([BMIM][PF₆]) is a solvent of comparatively high solvating ability which can compete with the metal ion for Schiff base. Thus, it is not unexpected that the addition of acetonitrile as a low density solvent to ionic liquid will increase the stability of the complex considerably.

The data given in Table 1 obviously indicate that, in a given acetonitrile-ion liquid mixture, the stability of the resulting complex changes in the order Mn²⁺<Zn²⁺<Cd²⁺. The complex stability results from the superposition of several factors including: the extent of interaction of donor groups of the nitrogen amine with the cation, the consonance between the size of metal ion and the satirical size of the Schiff base cavity formed, the extent of Schiff base conformational changes as a consequence of complex stability, soft-hard acid-base characters of the metal ion and the donating groups of the Schiff base nitrogen's, desolvation of the Schiff base and cation and solvation of the resulting complex, the two later factors being strongly dependent on the nature of solvents used.

The size and cationic charge (the consequent charge density) be able play a fundamental role in the complexation sequential process since the viewpoints of ionic solvation and binding energy with the nitrogen's giving atoms. By increasing charge density of a cation, both its binding energy and salvation energy to the Schiff base are expectedly increased, so that the increased binding energy of the cation to the amine acts against its increased desolvation energy, from the other point of view, since the change in configuration of the chain Schiff base 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.

Meanwhile, the sequence of stability of the Zn^{2+} and Mn^{2+} complexes with both Schiff base (i.e., $Zn^{2+} < Mn^{2+}$) most probably due to its stronger ionic solvation in the solvents used [49]. At last, the results show the highest stability for Cd^{2+} complexes with Schiff bases, among all three M^{2+} ions employed. This is most possibly due to proper size of large Cd²⁺ ion at soft nature which could favor a suitable spatial with flexible donating atoms of the Schiff bases. In order that, in this case, the central metal ion induced lest amount of steric deformation to the Schiff bases' structures [55-58].

4. Conclusion

We presented the successful synthesis of three new Schiff bases with two 2-pyridylmethyl pendant arms. The complexes have been characterized by some spectroscopic methods such as FT-IR, ¹H and ¹³C NMR spectroscopy and elemental analysis. The complexation reaction between two asymmetrical branched octadentate (N₈) Schiff base with the Cd²⁺, Zn²⁺ and Mn²⁺ metal ions having pyridine moiety, (Sc.B.¹), (Sc.B.²) and (Sc.B.³) in binary acetonitrile -Ionic liquid ([BMIM][PF₆]) mixtures were inspected by NMR spectroscopy. In all studied instances, the distinction of ⁷Li chemical shift with the [Sc.B.]/[M] mole ratio showed the stability of 1:1 complexes in total solvents. While the synthesized ligands are susceptible to moisture and unstable, the resulting complexes are stable in solution and in a pure state for a long time. It was found that, stability of the ending in complexes is powerfully dependent on the quantity of Ionic liquid in the solution. In all cases, the stability decrease significantly with increasing the amount of Ionic liquid in the solvent mixture. In the total solutions, the stability of all complexes increases in the order $Cd^{2+}-Sc.B. > Zn^{2+}-Sc.B. >$ Mn²⁺-Sc.B. The resulting complexes with the Schiff bases (Sc.B.¹), (Sc.B.²) and (Sc.B.³) vary in the order of M-Sc.B.¹ > M-Sc.B.² > M-Sc.B.³. This is because the Schiff bases are different in the size of the chelate rings so that they can form five, six and seven membered rings, respectively. As it is well substantiated in, the complexes shaping a five-membered chelate ring are anticipated to be stable more than those creating a six or seven membered chelate ring.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molstruc.2019.126965.

References

- [1] W. Zhang, X. Jiang, Y. Zhao, A. Carné-Sánchez, V. Malgras, J. Kim, J.H. Kim,
- S. Wang, J. Liu, J. Jiang, Y. Yamauchi, M. Hu, Chem. Sci. 8 (2017) 3538. C. Young, J. Wang, J. Kim, Y. Sugahara, J. Henzie, Y. Yamauch, Chem. Mater. 30 [2] (2018) 3379.
- [3] C. Wang, Y. Kaneti, Y. Valentino, J. Lin, C. Liu, J. Li, Y. Yamauchi, Mater. Horizons 5 (2018) 394.
- [4] S.H. Hsu, C.T. Li, H.T. Chien, R.R. Salunkhe, N. Suzuki, Y. Yamauchi, K. Ho, K.C.-W. Wu, Sci. Rep. 4 (2014) 6983.
- [5] N.L. Torad, Y. Li, S. Ishihara, K. Ariga, Y. Kamachi, H.Y. Lian, H. Hamoudi, Y. Sakka, W. Chaikittisilp, K.C.-W. Wu, Y. Yamauchi, Chem. Lett. 43 (2014) 717.
- [6] S. Coles, M. Hursthouse, D. Kelly, A. Toner, N.M. Walker, J. Chem. Soc. Dalton Trans. (1998) 3489.
- V. Alexander, Chem. Rev. 95 (1995) 273.
- S. Yamada, Coord. Chem. Rev. 190 (1999) 537. [8]
- [9] M. Rezaeivala, H. Keypour, Coord. Chem. Rev. 280 (2014) 203.
- [10] W. Ye, D.M. Ho, S. Friedle, T.D. Palluccio, E.V. Rybak-Akimova, Inorg. Chem. 51 (2012) 5006
- [11] V.G. Organo, A.S. Filatov, J.S. Quartararo, Z.M. Friedman, E.V. Rybak-Akimova, Inorg. Chem. 48 (2009) 8456.

- [12] M. Rezaeivala, H. Keypour, S. Salehzadeh, R. Latifi, F. Chalabian, F. Katouzian, J. Iran. Chem. Soc. 11 (2014) 431.
- [13] H. Keypour, M. Liyaghati-Delshad, M. Rezaeivala, H.R. Khavasi, J. Iran. Chem. Soc. 11 (2014) 1473.
- [14] H. Keypour, M.H. Zebarjadian, M. Rezaeivala, A. Chehreghani, H. Amiri-Rudbari, G. Bruno, J. Iran. Chem. Soc. 11 (2014) 101.
- [15] M.P. Clares, J. Aguilar, R. Aucejo, C. Lodiero, M.T. Albeld, F. Pina, J.C. Lima, A.J. Parola, J. Pina, J.S. Melo, C. Soriano, A.J. Parola, J. Pina, J.S. Melo, C. Soriano, E. Garcia-Espana, Inorg. Chem. 43 (2004) 6122.
- [16] R. Azadbakht, T. Almasi, H. Keypour, M. Rezaeivala, Inorg. Chem. Commun. 33 (2013) 63.
- [17] A. Afkhami, H. Ghaedi, T. Madrakian, M. Rezaeivala, Electrochim. Acta 89 (2013) 377.
- [18] A. Afkhami, F. Soltani-Felehgari, T. Madrakian, H. Ghaedi, M. Rezaeivala, Anal. Chim. Acta 771 (2013) 21.
- [19] K. Henrick, P. A. Tasker, L. Lindoy, S. J. Lippard (Ed.), Wiley, New York, 33 (1985)
- [20] M.F. Loncin, J.F. Desereux, E. Merciny, Inorg, Chem. 25 (1986) 2646.
 [21] D.A. Gutowsky, L.A. Echegoyen, D.M. Goli, A. Kaifer, R.A. Schulz, G.W. Gokel, J. Am. Chem. Soc. 105 (1983) 6717.
- [22] S.I. Kang, A. Czech, B.P. Czech, L.E. Stewart, R.A. Bartsch, Anal. Chem. 57 (1985) 1713
- [23] Y. Katayama, R. Fukuda, M. Takagi, Anal. Chim. Acta 185 (1986) 295.
- [24] R.M. Izatt, K. Pawlak, J.S. Bradshaw, R.L. Bruening, Chem. Rev. 95 (1995) 2529.
- [25] H. Keypour, M.H. Zebarjadian, M. Rezaeivala, A. Afkhami, J. Mol. Struct. 1075 (2014) 525.
- [26] H. Keypour, M.H. Zebarjadian, M. Rezaeivala, M. Shamsipur, H.R. Bijanzadeh, J. Solut. Chem. 43 (2014) 1218.
- [27] H. Keypour, A.A. Dehghani-Firouzabadi, H.R. Khavasi, Trans. Met. Chem. 36 (2011) 307.
- [28] H. Keypour, A.A. Dehghani-Firouzabadi, H.R. Khavasi, Polyhedron 28 (2009) 1546
- [29] H. Keypour, M.H. Zebarjadian, M. Rezaeivala, A. Chehreghani, H. Amiri-Rudbari, G. Bruno, J. Iran. Chem. Soc. 13 (2013) 280.
- [30] H. Keypour, M.H. Zebarjadian, S.J. Sabounchei, J. Iran. Chem. Soc. 14 (2014) 464
- [31] H. Keypour, M.H. Zebarjadian, M. Rezaeivala, M. Shamsipur, H.R. Bijanzadeh, J. Solut. Chem. 14 (2014) 196.
- [32] H. Keypour, M.H. Zebarjadian, M. Rezaeivala, A. Afkhami, J. Mol. Struct. 20

(2014) 796.

- [33] M. Shamsipur, E. Karkhaneei, A. Afkhami, J. Coord. Chem. 44 (1998) 23.
- [34] P.R. Bevington, Data Reduction and Error Analysis for the Physical Sciences, McGraw-Hill, New York, 1969.
- [35] R.K. Harris, B.E. Mann, NMR and the Periodic Table, Academic Press, New York, 1978
- [36] J. Kim, M. Shamsipur, S.Z. Huang, R.H. Huang, J.L. Dye, J. Phys. Chem. A 103 (1999) 5615.
- M. Shamsipur, A.I. Popov, J. Am. Chem. Soc. 101 (1979) 4051. B.O. Strasser, M. Shamsipur, A.I. Popov, J. Phys. Chem. 89 (1985) 4822. [37]
- 1381
- M. Shamsipur, A.I. Popov, I. Phys. Chem. 91 (1987) 447. Í391
- [40] R.D. Shannon, Acta Crystallogr. E E. 32 (1976) 751.
- [41] J. Ghasemi, M. Shamsipur, J. Coord. Chem. 31 (1994) 265.
- [42] M. Shamsipur, M. Irandoust, K. Alizadeh, V. Lippolis, J. Incl. Phenom.Macrocycl. Chem. 59 (2007) 203.
- [43] H. Keypour, M. Dehdari, S. Salehzadeh, K.P. Wainwright, Trans. Met. Chem. 28 (2003) 425
- [44] H. Keypour, M.H. Zebarjadian, M. Rezaeivala, M. Shamsipur, S.J. Sabounchei, . Iran. Chem. Soc. 10 (2013) 1137.
- [45] B. Tüemmler, G. Maass, E. Weber, W. Wehner, F. Vögtle, J. Am. Chem. Soc. 99 (1977) 4683
- [46] B. Tüenmler, G. Maass, F. Vögtle, H. Sieger, U. Heimann, E. Weber, J. Am. Chem. Soc. 101 (1979) 2588.
- J.H. Jung, I. Yoon, K.J. Park, S.S. Lee, K.S. Choi, S.B. Park, Microchem. J. 63 (1999) [47] 100
- [48] J.M. Larson, L.R. Sousa, J. Am. Chem. Soc. 100 (1978) 1943.
- I. Yoon, Y.H. Lee, J.H. Jung, K.M. Park, J. Kim, S.S. Lee, Inorg. Chem. Commun. 5 [49] (2002) 820.
- [50] E. Karkhaneei, A. Afkhami, M. Shamsipur, Polyhedron 15 (1996) 1989.
- [51] J. Kim, M. Shamsipur, S.Z. Huang, J.L. Dye, J. Phys. Chem. A 103 (1999) 5615.
- [52] M. Shamsipur, T. Madrakian, Polyhedron 19 (2000) 1681.
- [53] S. Kashanian, M. Shamsipur, Inorg. Chim. Acta 155 (1989) 203.
- [54] A. Semnani, M. Shamsipur, J. Electroanal. Chem. 315 (1991) 95.
- [55] J. Burger, Ionic Solvation and Complex Stability Reactions in Non-aqueous Solvents, Akdemiai Kiado, Budapest, 1993.
- [56] M. Shamsipur, N. Alizadeh, Talanta 39 (1992) 1209.
- [57] T. Madrakian, M. Shamsipur, Pol. J. Chem. 73 (1999) 1405.
- [58] M. Shamsipur, E. Karkhaneei, A. Afkhami, Polyhedron 17 (1998) 3809.