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Synthesis, characterization and antibacterial studies of Mn(II) and Co(II) complexes of an ionic liquid tagged Schiff base

SANJOY SAHA[1], ANANYA DAS[2], KAUSHIK ACHARJEE[2] and BISWAJIT SINHA[2]*

[1]*Department of Chemistry, Kalimpong College, Kalimpong-734301, India and*
[2]*Department of Chemistry, University of North Bengal, Darjeeling-734013, India*

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Abstract: Mn(II) and Co(II) complexes of an ionic liquid-based Schiff base, 1-{2-[(2-hydroxybenzylidene)amino]ethyl}-3-methyl-1*H*-imidazolium bromide, were synthesized and characterized by various analytical and spectroscopic methods, such as elemental analysis, UV–Vis, FT-IR, ^{1}H-NMR, ESI-MS and magnetic susceptibility measurement. These studies indicated tetrahedral geometry for the complexes. The Schiff base ligand and its complexes were tested for *in vitro* antibacterial activities to assess their inhibiting potentials against *Escherichia coli* and *Lactobacillus* sp.

Keywords: 1-methylimidazole; 2-bromoethylamine hydrobromide; salicylaldehyde; 1-{2-[(2-hydroxybenzylidene)amino]ethyl}-3-methyli-1*H*-midazolium bromide.

INTRODUCTION

Ionic liquids (ILs) are generally based on inorganic or organic anions paired with large, usually asymmetric organic cations, have low melting points below 373 K although many are in fact liquid at/below ambient temperature.[1,2] They are worthy of extensive investigation because of their unique physical and chemical properties, such as non-volatile, non-flammable, thermally stable and recyclable. In addition to these just mentioned properties, ILs exhibit a wide electrochemical window, high ionic conductivity, a broad temperature range of the liquid state and frequently possess excellent chemical inertness as well.[3–5] The hydrophobicity/hydrophilicity and other physical features of ionic liquids including density, melting point, conductivity, polarity, Lewis acidity, viscosity, enthalpy of vaporization can be altered by manipulating the structure of cations and anions[6] and issues such as their toxicity and biodegradability are now being explored to judge them as potentially green replacements for traditional molecular solvents.[7] To date, ILs have been used in organic synthesis, catalysis, industrial

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* Corresponding author. E-mail: biswachem@gmail.com

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processing, electrochemistry, pharmaceutics, biotechnology, nano-chemistry, analytical chemistry and separation technologies. Ionic liquids shaped for a particular function are referred to as functionalized ionic liquids (FILs). Recently, much attention has been paid to the preparation and application of FILs with special tasks carrying functional groups such as hydroxyl, amino, sulphonic acid, carbonyl, *etc*.[8–12] The increasing popularity of FILs lies in the fact that both the cationic and anionic parts can be altered and applied to a specific application. Again, the incorporation of functional groups can impart a particular capability to ILs by increasing their catalytic stability and reducing catalytic leaching.[12,13] Imidazolium-based systems play important roles in biochemical processes[14] having varied pharmacological properties. Schiff bases and their metal complexes play a significant role in the field of coordination chemistry and have been studied extensively; transition metal complexes of Schiff bases with oxygen and nitrogen donors are of particular interest because of their ability to possess unusual configurations and structure-related bioactivities.[15–17]

Hence herein, the synthesis of an imidazolium ionic liquid-tagged Schiff base 1-{2-[(2-hydroxybenzylidene)amino]ethyl}-3-methyl-1*H*-imidazolium bromide (LH) and its Mn(II) and Co(II) complexes are reported. The synthesized compounds were characterized by various analytical and spectroscopic methods. The Schiff base and its complexes were tested for their *in vitro* antibacterial activity against *Escherichia coli* and *Lactobacillus* sp.

EXPERIMENTAL

Materials and methods

All the reagents were of analytical grade and used without further purification. 1-Methylimidazole and 2-bromoethylamine hydrobromide were procured from Sigma–Aldrich, Germany. Salicylaldehyde, $Mn(OCOCH_3)_2\cdot 4H_2O$, $Co(OCOCH_3)_2\cdot 4H_2O$ and all other chemicals were used as received from SD Fine Chemicals, India. The IR spectra were recorded in KBr pellets using a Perkin–Elmer Spectrum FT-IR spectrometer (RX-1) operating in the region 4000 to 400 cm^{-1}. The ^{1}H-NMR spectra were recorded at room temperature on a FT-NMR (Bruker Advance-II 400 MHz) spectrometer using DMSO-d_6 and D_2O as solvents. Chemical shifts are quoted in ppm downfield of the internal standard tetramethylsilane (TMS). Elemental microanalyses (C, H and N) were conducted on a Perkin–Elmer (model 240C) analyzer. The metal contents were determined by AAS (Varian, SpectrAA 50B) using standard metal solutions from Sigma–Aldrich, Germany. The mass spectra were recorded on a JMS-T100LC spectrometer. The purity of the synthesized compounds was checked by thin layer chromatography (TLC) on silica gel plates. The UV–Vis spectra were recorded in methanol using a Jasco V-530 spectrometer. The magnetic susceptibilities were measured at room temperature with a Sherwood Scientific Ltd. magnetic susceptibility balance (Magway MSB Mk1). The molar conductance was measured with a Systronics conductivity TDS meter (Model-308) with a cell (Type CD-30, cell constant 0.10±10%) at 298.15±0.01 K. Antibacterial activities (*in vitro*) of the synthesized ligand and the complexes were studied by the disc diffusion method against two bacteria, *viz*., *Lactobacillus* sp. (ATCC No. 33222) and *Escherichia coli* (ATCC No. 69905) with respect to the standard drug ampicilin.

*Synthesis of the imidazolium ionic liquid 3-(2-aminoethyl)-1-methyl-1*H*-imidazolium bromide ([2-aemim]Br,* ***1****)*

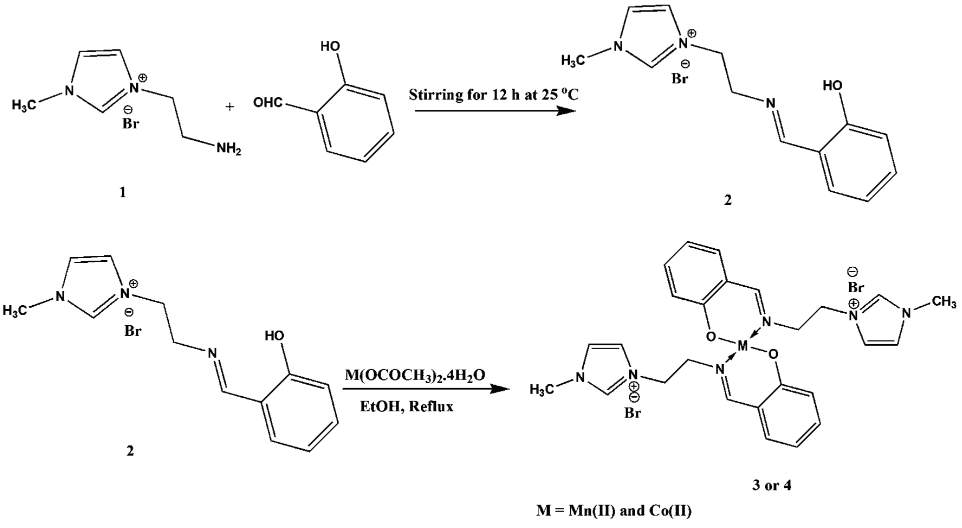
The amino functionalized ionic liquid was prepared following a literature procedure.[18] A mixture of 1-methylimidazole (4.10 g, 0.05 mol) and 2-bromoethylamine hydrobromide (10.25 g, 0.05 mol) in ethanol (50 mL) was refluxed under a nitrogen atmosphere at 80 °C for 24 h. On completion of the reaction, the solvent was distilled off and the residue recrystallized from ethanol and ethyl acetate. The resultant white powder was dissolved in methanol and then NaOH (2.00 g, 0.05 mol) was added to react for 8 h at room temperature. The excess NaOH was filtered off and the solvents were evaporated under vacuum. The obtained product was washed repeatedly with diethyl ether. After drying for 6 h under vacuum at 80 °C, the expected ionic liquid was obtained as a light-yellow oil. Yield: 69 %.

*Synthesis of imidazolium ionic liquid-tagged Schiff base, LH (****2****)*

A mixture of salicylaldehyde (1.22 g, 10 mmol) and [2-aemim]Br (2.06 g, 10 mmol) was stirred at room temperature for 12 h without a solvent, followed by washing with diethyl ether (3×30 mL) and vacuum evaporation which gave the product as a brown oil. Yield: 65–70 %.

Synthesis of metal complexes ***3*** *and* ***4***

To 20 mL of an ethanolic solution of ligand, LH (0.50 g, 1.30 mmol), metal acetate, *viz.*, $Mn(CH_3COO)_2\cdot 4H_2O$ (0.173 g, 0.65 mmol) or $Co(CH_3COO)_2\cdot 4H_2O$ (0.16 g, 0.65 mmol) dissolved in ethanol was added and the mixture was refluxed for 8 h until the starting materials had been completely consumed as monitored by TLC. On completion of the reaction, the solvent was evaporated and the reaction mixture was cooled to room temperature. The precipitate was filtered, washed successively with ethanol (3×10 mL) and dry ether (3×10 mL) and finally dried in a desiccator to obtain the solid product. A schematic representation of the synthesis is shown in Scheme 1.



Scheme 1. Synthesis of the ionic liquid-based Schiff base [1-{2-[(2-hydroxybenzylidene)-amino]ethyl}-3-methyl-1*H*-imidazolium bromide (LH, **2**), from ionic liquid **1**, and M(II) complexes **3** and **4** from LH (**2**).

The characterisation data for the ionic liquid, the ionic liquid-tagged Schiff base and the metal complexes are given in the Supplementary material to this paper.

RESULTS AND DISCUSSION

The complexes are moisture sensitive but stable in vacuum desiccator and soluble in *N*,*N*-dimethylformamide, dimethyl sulphoxide, acetonitrile and methanol. All the isolated compounds were found to be hygroscopic in nature and were characterized by different analytical and spectroscopic methods.

IR spectral studies

The IR spectra of the Schiff base LH (**2**) and its Mn(II) and Co(II) complexes (**3** and **4**, respectively) are given in Fig. 1.

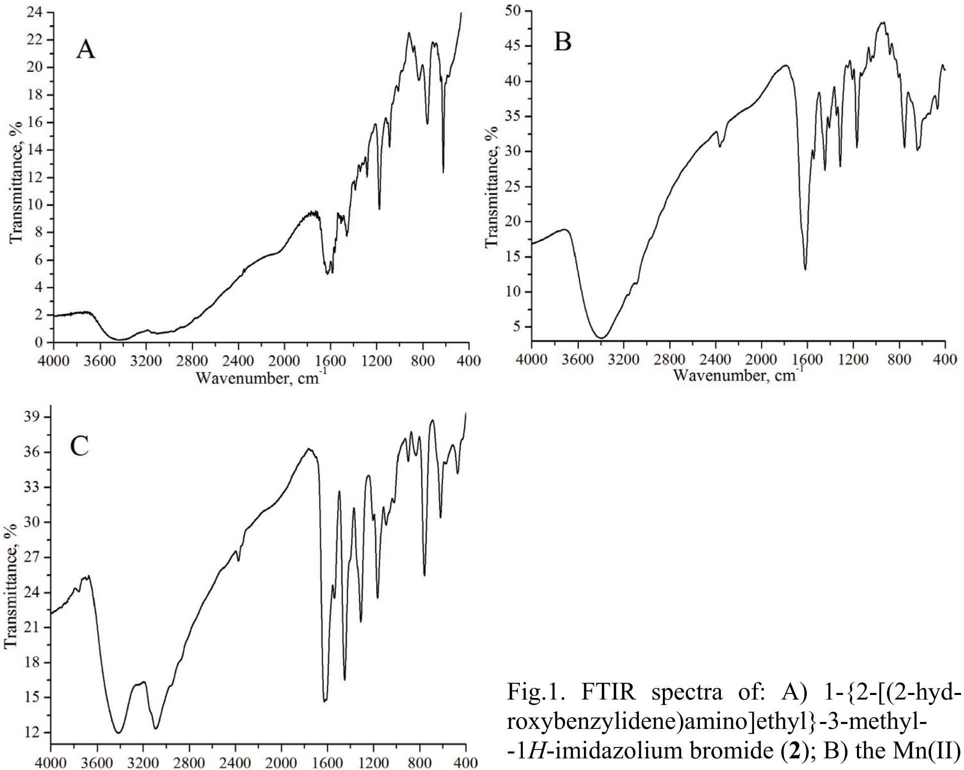


Fig.1. FTIR spectra of: A) 1-{2-[(2-hydroxybenzylidene)amino]ethyl}-3-methyl-1*H*-imidazolium bromide (**2**); B) the Mn(II) complex (**3**) and C) the Co(II) complex (**4**).

The IR spectra of the complexes were compared to that of the free ligand in order to determine the coordination sites involved in the complexation. IR spectrum of the ligand showed a strong broad band at 3429–3143 cm^{-1}; this band was attributed to the –OH of the phenolic group hydrogen bonded with the H–C(=N) group of the ligand (OH···N=C).[19] The broad band that appeared in the range 3398–3423 cm^{-1} in the spectra of the Mn(II) and Co(II) complexes was due to absorption of water molecules, as reported earlier by Gruzdev *et al.*[20] The band at 1454 cm^{-1} observed for the phenolic –CO of the free ligand was shifted to a lower frequency region, 1444–1449 cm^{-1}, for the complexes[21] on chelation. In the ligand, a band corresponding to the azomethine group (–C=N) was found at 1626 cm^{-1}. On complexation, this band was shifted to the range of 1616–1601 cm^{-1}. This indicated the involvement of N-atom of azomethine (–C=N) group in complex formation.[22]

Therefore, the IR spectra suggest that the ligand (LH) coordinates to the metal ions ($Mn^{2+}$and Co^{2+}) through the N-atom of the azomethine (–C=N) group and the O-atom of the phenolic group (Ar-O). The peak in the range 756–761 cm^{-1} in the spectra of complexes was assigned to bromide. The new bands appearing in the regions 565–590 cm^{-1} and 460–475 cm^{-1} in the spectra of Mn(II) and Co(II) complexes could tentatively be assigned to the M–O and M–N stretching frequencies, respectively.[23]

Mass spectral studies

The mass spectra of the ligand (LH) showed molecular ion peak at *m/z* 227 corresponding to $[M–3H–Br]^+$, where M stands for $C_{13}H_{16}N_3OBr$. The mass spectra of the Mn(II) complex (**3**) showed peaks at *m/z* 675, 503, 401, 321, 251, 169 and 121, whereas the Co(II) complex (**4**) displayed peaks at *m/z* 679, 409, 330, 245, 148 and 124. The molecular ion peaks at *m/z* 675 and 679 could be assigned to (M + 4H), where M stands for $C_{26}H_{30}MnN_6O_2Br_2$ and $C_{26}H_{30}CoN_6O_2Br_2$ for Mn(II) and Co(II) complexes, respectively. The different molecular ion peaks of the complexes could be attributed to different fragmentations of the metal complexes by successive rupture of different bonds in their structures. The mass fragmentations of complexes are given in Figs. S-1 and S-2 of the Supplementary material. The mass spectra of the ligand and complexes show good correlation with the respective structures as revealed by the elemental and other spectral analysis.

NMR spectral studies

The ^{1}H-NMR spectrum of the ligand was recorded in DMSO-d_6 and the spectrum showed well resolved signals, as expected. The ^{1}H-NMR of the ligand showed a singlet at δ 3.95 ppm (3H, *s*, CH_3), a triplet at δ 4.58 ppm (2H, *t*, CH_2), a triplet at δ 4.68 ppm (2H, *t*, CH_2), a multiplet at δ 7.72–7.83 ppm (4H, *m*, Ar-H), a singlet at δ 7.90 (1H, *s*, NCH) and a singlet at δ 7.92 ppm (1H, *s*, NCH). ^{1}H-NMR spectrum of the ligand also showed a sharp singlet at δ 9.20 ppm assignable to the proton of the azomethine group (–CH=N–), presumably due to the effect of the *ortho*-hydroxyl group in the aromatic ring. A singlet in the downfield region at δ 8.31 ppm could be ascribed to the phenolic proton. The Schiff base displayed a downfield shift of the –OH proton due to intermolecular

(O–H···N) hydrogen bonding interactions.[24] The ^{1}H-NMR spectrum of the cationic moiety of the ligand was almost the same as that previously reported in the literature.[25,26]

Molar conductance measurements

The molar conductance values of the complexes (Λ_m) were obtained from the relation $\Lambda_m = 1000\kappa/c$, where c and κ stand for the molar concentration and specific conductance of the metal complexes, respectively. The complexes (1.8×10^{-3} M) were dissolved in *N*,*N*-dimethylformamide and their specific conductivities were measured at 25 °C. The molar conductance values were found to be in the range 212–238 Ω^{-1} cm^{-1} mol^{-1}, indicating their 1:2 electrolytic (M:L) behaviour.[27]

Electronic absorption spectral and magnetic moment studies

The UV–Vis spectra of the ligand and the metal complexes (as depicted in Fig. 2) were recorded in methanol at ambient temperature. The electronic absorption spectrum of the ligand (**2**) showed three absorption bands at 318, 255 and 214 nm, respectively due to n→π* and π→π* transitions and transitions involving the imidazolium moiety.[28,29] The Mn(II) complex (**3**) showed three absorption bands at 314, 255 and 211 nm; that is the ligand band at 318 nm showed a hypsochromic shift probably due to coordination with Mn^{2+} (d^5) ion. The Co(II) complex (**4**) also showed three absorption bands at 220, 248 and 403 nm due to $^4A_2\rightarrow{}^4T_1(P)$, $^4A_2\rightarrow{}^4T_1(F)$ and $^4A_2\rightarrow{}^4T_2$ transitions, respectively. Thus, UV–

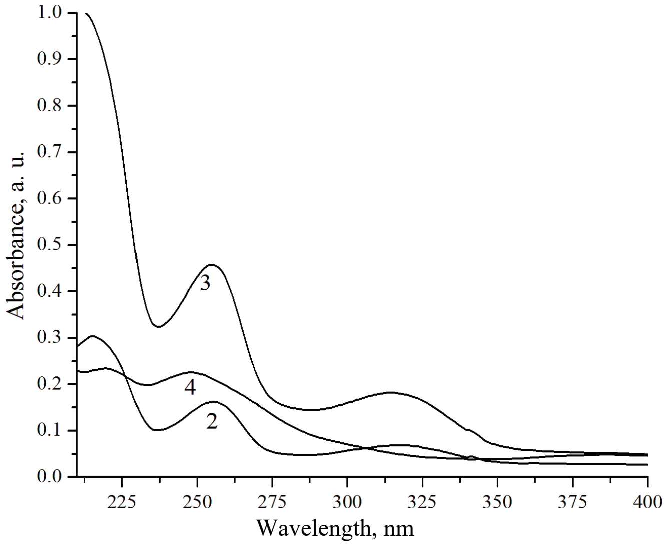


Fig. 2. The UV–Vis spectra of the ligand (**2**), the Mn(II) complex (**3**) and the Co(II) complex (**4**).

–Vis spectra of both the complexes suggest no Jahn–Teller distortion and tetrahedral geometry is thus suggested for both the complexes.[30] This fact was substantiated by the results obtained from IR, ESI-MS, UV–Vis spectra and the measured magnetic moments (5.86 and 4.67 μ_B for the Mn(II) and Co(II) complexes, respectively).

Antibacterial activities

The Schiff base ligand and their metal complexes were studied against the gram negative bacteria *Escherichia coli* and gram positive bacteria *Lactobacillus* sp. to assess their potentials as antibacterial agents. Stock solutions of the synthesised compounds were prepared by dissolving the compounds in dimethyl sulphoxide and serial dilutions of the solutions were made with sterile distilled water for different concentrations to determine the minimum inhibition concentration (*MIC*). The concentrations of the tested compounds were 31, 62, 125 and 250 µg mL^{-1} in comparison to the standard drug ampicillin (100 µg mL^{-1}). The nutrient agar medium was poured into 0.5 mL culture contained in Petri dishes and the well diffusion technique[31,32] was applied. The Petri dishes were placed in an incubator at 37 °C for 24 h. No significant inhibition zones surrounding the well were observed against the complexes (the inhibition zones against *Escherichia coli* are shown in Fig. 3), but the ligand showed very low antibacterial activities with well diameters in the range of 1.0–1.2 mm at a concentration of 250 µg mL^{-1} against the studied bacteria.

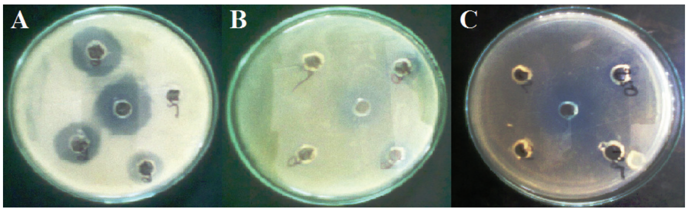


Fig. 3. Inhibition zones for anti-bacterial activities: A) 1-{2-[(2-hydroxybenzylidene)amino]-ethyl}-3-methyl-1*H*-imidazolium bromide (**2**); B) the Mn(II) complex (**3**) and C) the Co(II) complex (**4**) against *Escherichia coli*.

CONCLUSIONS

Herein, the synthesis and physicochemical characterization of an imidazolium ionic liquid-tagged Schiff base, *i.e.*, 1-{2-[(2-hydroxybenzylidene)amino]-ethyl}-3-methyl-1*H*-imidazolium bromide, and its Mn(II) and Co(II) complexes were described. Different analytical and spectral studies revealed that the Schiff base acts as a bidentate ligand that coordinates through the azomethine nitrogen and phenolic oxygen atoms to Mn(II) and Co(II) ions and thus formed tetrahedral 1:2 (M:L) complexes. The synthesized compounds were tested for their antibacterial activities against the bacteria *Escherichia coli* and *Lactobacillus* sp.

The observed minimum inhibition (*MIC*) zones suggested that the synthesized complexes have no significant antibacterial activities against the bacteria *Escherichia coli* and *Lactobacillus* sp.

SUPPLEMENTARY MATERIAL

Characterization data and mass fragmentation schemes are available electronically at the pages of journal website: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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ИЗВОД

СИНТЕЗА, КАРАКТЕРИЗАЦИЈА И АНТИБАКТЕРИЈСКА ИСПИТИВАЊА Mn(II) И Co(II) КОМПЛЕКСА СА ЈОНСКОМ ТЕЧНОСТИ ИЗ ГРУПЕ ШИФОВИХ БАЗА КАО ЛИГАНДОМ

SANJOY SAHA[1], ANANYA DAS[2], KAUSHIK ACHARJEE[2] и BISWAJIT SINHA[2]

[1]*Department of Chemistry, Kalimpong College, Kalimpong-734301, India и* [2]*Department of Chemistry, University of North Bengal, Darjeeling-734013, India*

Синтетисани су Mn(II) и Co(II) комплекси са јонском течности из групе Шифових база као лигандом, 1-{2-[(2-хидроксибензилиден)амино]етил}-3-метил-1*H*-имидазолијум-бромидом. Комплекси су окарактерисани применом различитих аналитичких и спектроскопских метода, као што су елементална анализа, UV–Vis, FT-IR, ^{1}H-NMR, ESI-MS и магнетна мерења. На основу ових испитивања закључено је да комплекси имају тетраедарску геометрију. Лиганд типа Шифове базе и одговарајући комплекси су *in vitro* испитивани на антибактеријску активност према *Escherichia coli* и *Lactobacillus* sp. сојевима.

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