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Cu(II) complexes of an ionic liquid-based Schiff base [1-{2-((2-hydroxybenzylidene)amino)ethyl}-3-methylimidazolium]PF_6: Synthesis, characterization and biological activities

SANJOY SAHA[1], DHIRAJ BRAHMAN[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: Two Cu(II) complexes of an ionic liquid based Schiff base 1-{2-[(2--hydroxybenzylidene)amino]ethyl}-3-methylimidazolium hexafluorophosphate, were prepared and characterized by different analytical and spectroscopic methods such as elemental analysis, magnetic susceptibility, UV–Vis, IR and NMR spectroscopy, and mass spectrometry. The Schiff base ligand was found to act as a potential bidentate chelating ligand with N, O donor sites and formed 1:2 metal chelates with Cu(II) salts. The synthesized Cu(II) complexes were tested for their biological activity.

Keywords: ionic liquid based Schiff base; salicylaldehyde; Cu(II) complexes; 1-(2-aminoethyl)-3-methylimidazolium hexafluorophosphate.

INTRODUCTION

Ionic liquids (ILs) are defined as organic salts formed by the combination of bulky organic cations with a wide variety of anions, that are generally liquid at room temperature.[1] ILs are made up of large ions that are held together by electrostatic interactions. Due to these interactions, the properties of ILs are considerably different from those of molecular liquids.[2] ILs have been widely studied as alternatives to volatile organic solvents for organic synthesis in homogeneous as well as biphasic processes.[3–5] Such compounds have received attraction in synthetic chemistry in recent years due to their excellent characteristics, such as low vapor pressure, inflammability, high thermal and chemical stability, outstanding solubility and the possibility of easy recycling, *etc*.[6,7] Based on these properties, ILs have emerged as a novel class of compounds that have been employed in many fields, such as electrochemistry, organic synthesis, catalysis,

* Corresponding author. E-mail: biswachem@gmail.com
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gas separation, *etc*. The use of ionic liquids has also received much attention as eco-friendly reaction media in organic synthesis.[5,8] The hydrophobicity/hydrophilicity of ionic liquids can be altered by manipulating the structures of the cations and anions.[9] In recent years, a number of ionic liquids have been identified as solvents for the dissolution of biopolymers such as cellulose, starch, wood, lignin, feather, wool, *etc*.[10–17] Recently, many workers have focused on the preparation and application of functionalized ionic liquids (FILs) for special tasks, such as those carrying hydroxyl, amino, sulfonic acid or carboxyl groups and so on.[18–24] The FILs have shown great promise not only as alternative green solvents, but also as reagents or catalysts in many organic transformations.[25]

Among many potential organic compounds, Schiff bases are widely employed as ligands in coordination chemistry.[26] These ligands are readily available, versatile and, depending on the nature of the starting materials (primary amines and carbonyl precursors), they exhibit various denticities and functionalities.[27] Schiff bases and their complexes are widely applied in biochemistry, material science, catalysis, encapsulation, activation, transport and separation phenomena, hydrometallurgy, *etc*.[28,29] Schiff bases have been reported to show a variety of biological actions, such as antibacterial, antifungal, herbicidal, clinical and analytical activities by virtue of the azomethine linkage.[30,31] Schiff base metal complexes have been the subject intensive study due to their industrial and biological applications.[32–37] Salicylaldehyde and its derivatives are useful carbonyl precursors for the synthesis of a large variety of Schiff bases with wide variety of interesting properties. Hence in this study, an attempt was made to synthesize an ionic liquid grafted Schiff base 1-{2-[(2-hydroxybenzylidene)amino]ethyl}-3--methylimidazolium hexafluorophosphate, and its Cu(II) complexes. The synthesized compounds were characterized by various analytical methods and tested for their biological activities.

EXPERIMENTAL

Materials and measurements

All the employed reagents were of analytical grade and used as received without further purification. 1-Methylimidazole, 2-bromoethylamine hydrobromide and potassium hexafluorophosphate were procured from Sigma–Aldrich, Germany. Salicylaldehyde, $CuCl_2 \cdot 2H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and all other chemicals were purchased from SD Fine Chemicals, India. The IR spectra were recorded in KBr pellets using a Perkin-Elmer Spectrum RX I FT-IR spectrometer, operating in the region 4000 to 400 cm^{-1}. The proton NMR spectra were recorded at room temperature on an FT-NMR Bruker Avance II 400 MHz spectrometer using DMSO-d_6 and D_2O as solvents. The chemical shifts are given in ppm downfield of internal standard tetramethylsilane (TMS). The melting points were recorded using the open capillary method. Elemental microanalyses (C, H and N) were realized using a Perkin–Elmer (Model 240C) analyzer. The Cu-content was determined by atomic absorption spectroscopy (AAS) employing a Varian SpectrAA 50B instrument using a standard Cu-solution from Sigma–Aldrich, Germany. The mass spectra were recorded on an Agilent 1100 LC equipped with an MSD

trap. The purity of the Schiff base and its complexes were confirmed by thin layer chromatography (TLC) on silica gel plates and TLC visualization was realized by UV-light and iodine. The antibacterial activities (*in vitro*) of the synthesized ligand and the complexes were studied by the disc diffusion method against commonly known bacteria, *viz.*, *Bacillus subtilis* and *Escherichia coli* with respect to the standard drug ampicilin.

Physical, analytical and spectral data of the prepared compounds are given in Supplementary material to this paper.

Synthesis of ionic liquid 1-(2-aminoethyl)-3-methylimidazoliumhexafluorophosphate ([2-aemim]PF_6)

The amino functionalized ionic liquid was prepared by following literature procedure.[38] In a typical experiment, a mixture of 1-methylimidazole (4.10 g, 0.05 mol) and 2-bromoethylamine hydrobromide (10.25 g, 0.05 mol) in 25 mL of acetonitrile was heated with constant stirring at 80 °C for 4 h. On completion of the reaction, the solvent was removed by distillation and the residue was recrystallized from ethanol to afford the hydrobromide [2-aemim]Br as a white solid. Then KPF_6 (9.20 g, 0.05 mol) was added to the hydrobromide [2-aemim]Br in 20 mL of CH_3CN/H_2O (1:1, *V*/*V*). The solution was left for 24 h at room temperature and then NaOH (2.00 g, 0.05 mol) was added for neutralization. The solvents were evaporated under vacuum. This was followed by the addition of CH_3OH (2 mL) and $CHCl_3$ (10 mL). The precipitated KBr was filtered off and the solvents were evaporated. The obtained yellow oil was washed successively with chloroform (3×10 mL) and diethyl ether (3×10 mL). After drying for 6 h under vacuum at 80 °C, the expected ionic liquid was obtained.

Synthesis of the ionic liquid-grafted Schiff base

The ionic liquid based Schiff base ligand (L) was synthesized by slight modification of a literature procedure.[39] A mixture of salicylaldehyde (1.22 g, 10 mmol) and [2-aemim]PF_6 (2.71 g, 10 mmol) in 10 mL methanol was stirred at room temperature for 1 h. After completion of the reaction, as indicated by TLC, the reaction mixture was diluted with MeOH (10 mL). The precipitate was then filtered and dried to afford the expected ligand as a pale yellow solid in good yield.

Synthesis of Cu(II) complexes of the ionic liquid-based Schiff base

To a solution of ligand, LH (0.50 g, 1.30 mmol), in EtOH (20 mL), copper salts, *viz.*, $CuCl_2 \cdot 2H_2O$ (0.11 g, 0.65 mmol) or $Cu(NO_3)_2 \cdot 3H_2O$ (0.17 g, 0.65 mmol) were added and the reaction mixture was refluxed for 8 h at 25 °C until the starting material was 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 collected by filtration, washed with C_2H_5OH (10 mL) and dry ether (10 mL) triply, and further dried in a desiccator to obtain the complex **2** as a deep green powder and complex **3** as a dark green powder.

Antibacterial activity

The newly synthesized Cu(II) complexes along with the ligand were tested against the gram-negative bacterium *Escherichia coli* ATCC 69905 and the gram-positive bacterium *Bacillus subtilis* ATCC 6633. Stock solutions of compounds were prepared by dissolving the compounds in distilled water and serial dilutions of the compounds were prepared in sterile distilled water for different concentrations to determine the minimum inhibition concentration (*MIC*). The concentrations of the tested compounds were 31.25, 62.5, 125 and 250 μg mL^{-1} in

comparison to the standard drug ampicillin. The nutrient agar medium was poured into 0.5 mL culture containing Petri plates. Then the well diffusion technique[40,41] was performed. Petri plates were incubated at 37 °C for 24 h.

RESULTS AND DISCUSSION

All the isolated compounds were found to be air stable and were characterized based on elemental and different spectroscopic analyses. The data are given in the Supplementary material to this paper.

Infrared spectra of the Schiff base ligand and its complexes

The IR spectra of the free Schiff base and its Cu(II) complexes are presented in Figs. S-1–S-3 of the Supplementary material. In order to obtain conclusive insight concerning the coordination mode of the ligand (LH) to the metal ion and the structure of the metal complexes, the main IR bands were compared with those of the free ligand. The IR spectrum of the ligand showed a strong broad band at 3430–3151 cm^{-1}; this band was attributed to the hydrogen bonded –OH of the phenolic group with –N=C group of the ligand (OH···N=C).[42,43] This band was absent in the spectra of the complexes due to the involvement of the phenolic –OH group in coordination to the metal ion. A new band in the range of 3449.07 cm^{-1} appeared in case of Cu(II) complex **2** and this was assigned to coordinated water molecules in the complex,[44] although in case of the complex **3** no such band was observed in this region. This indicated the absence of coordinated water molecules in its structure A weak band at 3101–2923 cm^{-1} in the spectrum of the ligand was assigned to H–C(=N) stretching vibrations. The involvement of deprotonated phenolic moiety in metal complexes was confirmed by the shift of (–CO) of LH stretching band at 1465.5 cm^{-1} to lower frequency region of 1448–1445 cm^{-1} for the complexes **2** and **3**, respectively. In the spectrum of the ligand, a band corresponding to the azomethine group (–C=N) was found at 1640 cm^{-1}. On complexation, this band shifted to a lower wave number range of 1628–1622 cm^{-1}. This indicated the involvement of N-atom of the azomethine (–C=N) group in complex formation[45,46] and the band at 844.5–842.49 cm^{-1} in the spectra of the complexes **2** and **3** were assigned to P–F stretching frequency.

Therefore, the IR spectral data indicated that the coordination of ligand to metal ion occurred through the N-atom of the azomethine (–C=N) group and the O-atom of phenolic (O–Ar) group. Assignment of the proposed coordination sites was further supported by the appearance of medium bands at 634–620 cm^{-1} and 548–558 cm^{-1} due to M–O and M–N stretching frequencies, respectively.[47,48]

Mass spectra

The mass spectra of the compound [2-aemim]PF_6 and the ligand, LH, showed molecular ion peaks (*m*/*z*) at 126.20 and 231, which correspond to M^+, $[C_6H_{12}N_3]^+$ and M+1, $[C_{13}H_{16}N_3O+1]^+$ peaks, respectively. The observed mass

spectra confirmed the formation of the proposed ligand. Again the mass spectra of the Cu(II) complexes **2** and **3** showed molecular ion peaks (*m*/*z*) at 557 and 523, respectively. These molecular ion peaks were assigned to $Cu(C_{26}H_{34}N_6O_4)^{2+}$ and M″+2 (where M″ = $Cu(C_{26}H_{30}N_6O_2)^{2+}$) peaks, respectively. These peaks support the proposed structure of the complexes and confirmed the ML_2 stoichiometry for the complexes. It is assumed that the Cu(II) complex **2** had an octahedral coordination site with two water molecules occupying two axial positions; however, the Cu(II) complex **3** has square planar geometry. The different molecular ion peaks, appeared in the mass spectra of the complexes, were attributed to different fragmentations of the metal complexes by successive rupture of different bonds in order to form stable ions. The fragmentation patterns of the complexes **2** and **3** are shown in Figs. 1 and 2, respectively. The mass spectra of the ligand and complexes were in good agreement with the structure as revealed by elemental analyses and spectral analyses.

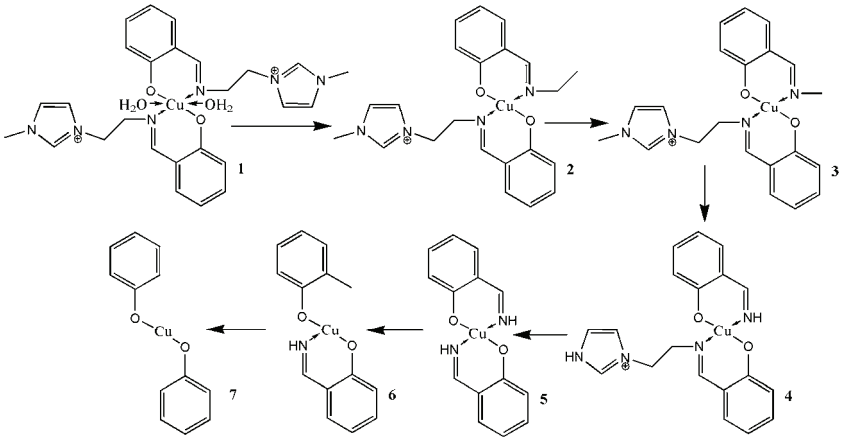

Fig. 1. The mass fragmentation pattern of the Cu(II) complex **2**. *m*/*z*: 1, 557; 2, 439; 3, 427; 4, 397; 5, 304; 6, 290 and 7, 250.

^{1}H-/^{13}C-NMR spectroscopy

The ^{1}H-NMR spectra of ligand and complexes were recorded in DMSO-d_6 and the spectra showed well-resolved signals as expected. The ^{1}H-NMR spectrum of the ligand showed a singlet at δ 3.82 ppm (3H, *s*, CH_3), a triplet at δ 3.99 ppm (2H, *t*, CH_2), a triplet at δ 4.52 ppm (2H, *t*, CH_2), a multiplet at δ 6.85–7.42 ppm (4H, *m*, Ar-H), a singlet at δ 7.67 ppm (1H, *s*, NCH) and a singlet at δ 7.33 ppm (1H, *s*, NCH). The spectrum of the ligand showed a sharp singlet at δ 8.56 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 sharp singlet in the downfield region at 12.56 ppm is attributed to the hydroxyl proton. The ^{13}C-

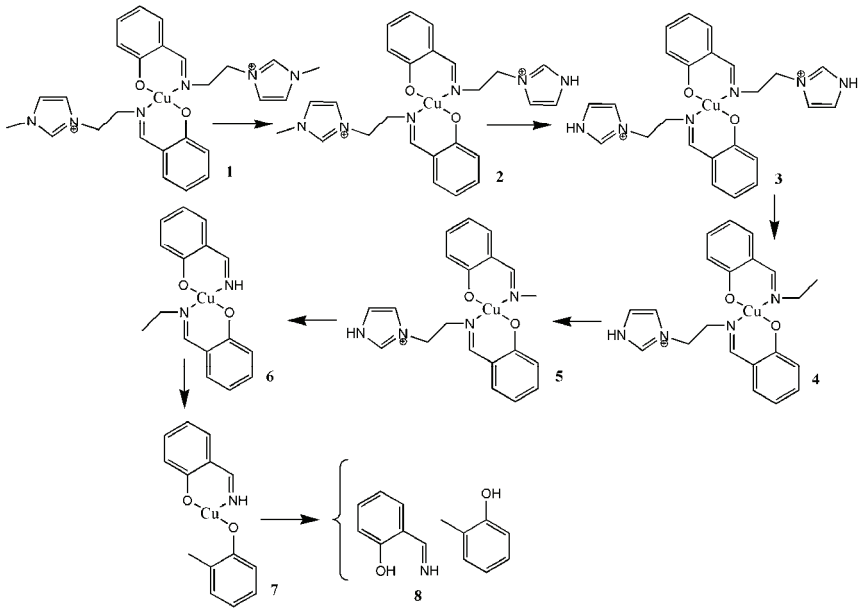

Fig. 2. The mass fragmentation pattern of the Cu(II) complex **3**. *m*/*z*: 1, 523; 2, 507; 3, 491; 4, 427; 5, 413; 6, 333; 7, 333; 8, 231 and 9, 231.

-NMR spectra of the ligand and complexes were recorded in DMSO-d_6 as solvent. The number of signals of sharp peaks represents the number of carbons of the compound that are chemically non-equivalent. The spectra exhibited the azomethine, C=N carbon at δ 159.91 ppm and the phenolic, C–OH carbon at δ 161.29 ppm. The chemical shifts of the aromatic carbons appeared at 137.31, 135.59, 123.75 and 122.41 ppm. The magnetic moment measurement of both the Cu(II) complexes, in which the electronic configuration is d^9, showed that these complexes are paramagnetic (the observed magnetic moments of Cu(II) complex **2** and complex **3** were 1.89 and 1.72 μ_B, respectively) and their ^{1}H-NMR spectra displayed only the broad signals assignable to the alkyl group as all of these proton signals are in close proximity. However, a signal for the Cu(II) center was not detectable.[49]

Antibacterial activity

The newly synthesized Cu(II) complexes along with the ligand were tested against the gram negative bacterium *E. coli* and the gram positive bacterium *B. subtilis* using the well diffusion technique.[40,41] No clear inhibition zone surrounding the well were formed against the ligand and its Cu(II) complexes (inhibition zones against *E. coli* are shown in Fig. 3), whereas $CuCl_2 \cdot 2H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ showed antibacterial activities with clearly defined well diameters at a concentration of 250 μg mL^{-1} against the bacteria selected for this study.

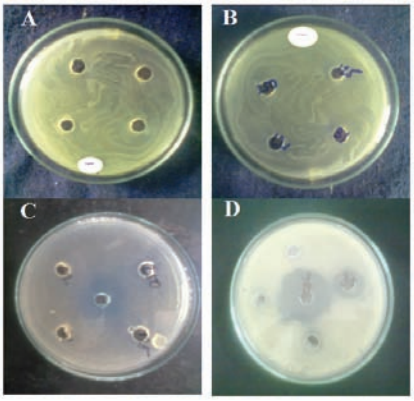

Fig. 3. Inhibition zones for anti-bacterial activities: A: for 1-{2-[(2-hydroxybenzylidene)amino]ethyl}--3-methyimidazolium hexaflurophosphate (**1**); B: for the Cu(II) complex **2**; C: for $CuCl_2 \cdot 2H_2O$; D: for $Cu(NO_3)_2 \cdot 3H_2O$ against *E. Coli*.

CONCLUSION

In this paper, the synthesis, characterization and biological activities of the synthesized ionic liquid based Schiff base and its two Cu(II) complexes were reported. The complexes were formed in 1:2 (metal:ligand) ratio, as confirmed by the spectral analysis. The results of different analytical and spectroscopic analyses revealed that the complexes have different coordination geometries. The Schiff base ligand acts as a bidentate ligand and binds to metal ions through the phenolic oxygen and the azomethine nitrogen Again the synthesized ligand and the complexes showed no antibacterial activities against two commonly known bacteria, *viz.*, *B. subtilis* and *E. coli*.

SUPPLEMENTARY MATERIAL

Physical, analytic and spectral data of the prepared compounds and their IR spectra are available electronically from http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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ИЗВОД

КОМПЛЕКСИ БАКРА(II) СА ШИФОВОМ БАЗОМ ДОБИЈЕНОМ ИЗ ЈОНСКЕ ТЕЧНОСТИ [1-{2-((2-ХИДРОКСИБЕНЗИЛИДЕН)АМИНО)ЕТИЛ}-3-МЕТИЛИМИДАЗОЛИЈУМ]PF_6: СИНТЕЗА, КАРАКТЕРИЗАЦИЈА И БИОЛОШКА АКТИВНОСТ

SANJOY SAHA[1], DHIRAJ BRAHMAN[2] AND BISWAJIT SINHA[2]

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

Синтетизована су два комплекса бакра(II) са Шифовом базом добијеном из јонске течности, 1-{2-[(2-хидроксибензилиден)амино]етил}-3-метилимидазолијум-хексафлуорофосфата. Добијени комплекси су окарактерисани применом различитих аналитичких и спектроскопских метода, као што су елементарна микроанализа, магнетна сусцептибилност, UV–Vis, IR и NMR спектроскопија и масена спектрометрија. Применом ових

метода утврђено је да се Шифова база бидентатно координује преко атома азота и атома кисеоника, при чему настају комплекси у којима су два молекула лиганда координована за Cu(II) јон. Поред тога, испитивана је биолошка активност комплекса бакра(II).

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