

Synthesis, Characterization and Antibacterial Activities of Cd(II) and Co(II) Complexes of an Ionic Liquid based Schiff Base



CHEMISTRY

KEYWORDS : Ionic liquid based Schiff base; Cd(II) and Co(II) complexes; Antibacterial activities.

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ABSTRACT

Cd(II) and Co(II) complexes of ionic liquid grafted Schiff base, 1-[2-(2-hydroxybenzylideneamino)ethyl]-3-methylimidazolium hexafluorophosphate, were synthesized and characterized by various analytical and spectroscopic methods such as elemental analysis, UV-Visible, FT-IR, ¹H NMR, ESI-MS, TGA/DTG and magnetic susceptibility measurement. These studies indicated tetra coordinated 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 spp. The results showed that the Cd(II) complex have higher antibacterial activity than both the ligand and Co(II) complex.

Introduction

Ionic liquids (ILs) are defined as "ionic materials", because their structures are generally based on large non-centrosymmetric organic cations and anions. In recent years, ILs have received considerable attention due to their important properties such as high thermal stability, high density, extremely low volatility, non-flammability, high ionic conductivity and a large number of possible variation in cation and anion conformation. A major reason for the interest in ILs is their negligible vapour pressure that decreases the risk of technological exposure and loss of solvent to the atmosphere. Due to these properties they are considered as a new generation of solvents for catalysis, ecofriendly reaction media for organic synthesis and a successful replacement for conventional media in chemical processes. Functionalized ionic liquids (FILs) are generally recognized as ILs with functional groups in the cation. Functionalization of the cation requires in most cases only a single reaction process making them relatively easy to prepare. ILs containing functionalized cations has usually higher viscosity compared to conventional ionic liquids with same anions. Recently, many workers have focused on the preparation and application of FILs with different functional groups like hydroxyl, amino, sulfonic acid etc. Compared with conventional ILs such FILs possess three advantages: (i) they can be bio-regenerated and biodegradable, (ii) chirality in bio-precursor can be maintained in IL and (iii) further functionalization is also possible.

Among many potential organic compounds, Schiff bases are widely employed as ligands in coordination chemistry. These ligands are readily available, versatile and depending on the nature of the starting materials they exhibit various denticities and functionalities. Schiff bases and their metal complexes are also applied in biochemistry, material science, catalysis, encapsulation, activation, transport and separation phenomena and hydrometallurgy, etc [1, 2]. Transition metal complexes with oxygen and nitrogen donor Schiff base are of particular interest because of their ability to possess unusual configuration [3]. 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 we synthesized an ionic liquid grafted Schiff base 1-[2-(2-hydroxybenzylideneamino)ethyl]-3-methylimidazolium hexafluorophosphate and its Cd(II) and Co(II) complexes. The synthesized compounds were characterized by various analytical and spectroscopic methods. The Schiff base ligand and its complexes were tested for their in vitro antibacterial activity against escherichia coli and lactobacillus spp.

Experimental

(I) Synthesis of the ionic liquid [2-aemim]PF₆ (1)

The amino functionalized ionic liquid was prepared by following a literature procedure [4]. A mixture of 1-methylimidazole (4.10 g, 0.05 mol) and 2-bromoethylamine hydrobromide (10.25 g, 0.05

mol) in acetonitrile (40 mL) was heated with constant stirring at 80 °C for 4 h. On completion, the solvent was removed by distillation and the residue was recrystallized from ethanol to afford the hydrobromide of [2-aemim]Br as a white solid. Next KPF₆ (9.20 g, 0.05 mol) was added to hydrobromide of [2-aemim]Br in CH₃CN/H₂O (1:1, v/v). The solution was left for 24 h at room temperature and neutralized with NaOH (2.00 g, 0.05 mol). The precipitated KBr were filtered off and the solvents were evaporated under vacuum. The obtained yellow oil was washed successively with chloroform and ether. After drying for 6 h under vacuum at 80 °C, the expected ionic liquid was obtained as yellow oil. Yield 67%, IR (KBr, in cm⁻¹): 3412(N-H); 3086(C-H); 2896(Aliph-CH); 1581(C=N/imidazole); 1452(C=C); 847(PF₆). ¹H NMR (500 MHz, D₂O) δ, ppm: 3.25 (m, 2H, NH₂-CH₂); 4.12 (s, 3H, -CH₃); 4.49 (t, 1H, N-CH₂); 4.52 (t, 1H, N-CH₂); 7.68 (s, 1H, -NCH); 7.75 (s, 1H, -NCH); 8.63 (s, 2H, -NH₂); 8.99 (s, 1H, -N(H)CN). ESI-MS (positive ion mode, CH₃CN) m/z: 126.20 ([M]⁺).

(II) Synthesis of ionic liquid grafted Schiff base (2)

The ionic liquid grafted Schiff base (LH) was synthesized by a slight modification of a literature procedure [5]. A mixture of salicylaldehyde (1.22 g, 10 mmol) and [2-aemim]PF₆ (2.71 g, 10 mmol) in 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. The precipitate was filtered and dried to afford the expected ligand as a pale yellow solid. Yield: 65-70%; mp 132-133 °C, IR (KBr, in cm⁻¹): 3430(O-H); 3101(N-H); 2923.9(Ar-CH); 2866(Aliph-CH); 1640(C=N); 1616.2, 1569.9(C=N/imidazole); 1465.5(C-O); 1278.31(Ar-O); 837(PF₆). ¹H NMR: (400 MHz, DMSO-*d*₆) δ, ppm: 3.89 (s, 3H, -CH₃); 4.01 (t, 2H, -CH₂); 4.48 (t, 2H, -CH₂); 6.79-6.85 (m, 4H, Ar-H); 7.66 (s, 1H, -NCH); 7.76 (s, 1H, -NCH); 8.56 (s, 1H, N=CH); 9.12 (s, 1H, -CH); 12.56 (s, 1H, -OH). ESI-MS (positive ion mode, CH₃CN) m/z: 231 ([M]⁺).

(III) Synthesis of metal complexes (3,4)

To a solution of ligand, LH (0.25 g, 0.65 mmol), in EtOH (20 mL), metal acetate, viz., Cd(CH₃COO)₂·2H₂O (0.173 g, 0.65 mmol) or Co(CH₃COO)₂·4H₂O (0.16 g, 0.65 mmol) also in the same solvent was added and the reaction mixture was refluxed for 8 h at 25 °C until the starting materials were completely consumed as monitored by TLC. On completion of the reaction, solvents were evaporated and the reaction mixture was cooled to room temperature. The precipitate was collected by filtration, washed with cold C₂H₅OH (10 mL × 3), dry ether (10 mL × 3) respectively and finally dried in desiccator to obtain the solid product. The complexes are soluble in N,N-dimethylformamide, dimethylsulphoxide, acetonitrile and methanol. A schematic representation of the synthesis is shown in Scheme 1.

(i) Cd(II) complex (3)

Yellow solid, Yield: 0.45 g (67%). mp 45-47 °C. Anal. calcd. for C₁₃H₁₈CdF₆N₃O₃P (%): C, 29.93; H, 3.48; N, 8.05; Cd, 21.55.

Found: C, 29.12; H, 3.13; N, 7.79; Cd, 20.96 %. IR (KBr, in cm^{-1}): 3449(O-H/ H_2O), 2933.9(Ar-CH); 2863(Aliph-CH); 1634(C=N); 1545(C=N/imidazole); 1459(C-O); 842(PF_6); 618(M-O); 548(M-N). ^1H NMR(400 MHz, $\text{DMSO}-d_6$) δ , ppm: 3.99 (s, 3H, $-\text{CH}_3$); 4.11 (t, 2H, $-\text{CH}_2$); 4.38 (t, 2H, $-\text{CH}_2$); 6.98–6.85 (m, 4H, Ar-H); 7.43 (s, 1H, $-\text{NCH}$); 7.31 (s, 1H, $-\text{NCH}$); 7.68 (s, 1H, $-\text{N}=\text{CH}$); 3.21 (m, 2H, coordinated water); 8.41 (s, 1H, $-\text{OH}$). ESI-MS (positive ion mode, CH_3CN) m/z : 381 ($[\text{M}+3\text{H}]^+$).

(ii) Co(II) complex (4)

Brown solid, Yield: 0.47 g (71%). mp 142-145 °C. Anal. calcd. for $\text{C}_{13}\text{H}_{18}\text{CoF}_6\text{N}_3\text{O}_3\text{P}$ (%): C, 33.35; H, 3.88; N, 8.97; Co, 12.59. Found: C, 33.05; H, 3.36; N, 8.22; Co, 11.84 %. IR (KBr, in cm^{-1}): 3447 ν (O-H/ H_2O), 2926 ν (Ar-CH), 2867 ν (Aliph-CH), 1620 ν (C=N), 1526 ν (C=N/imidazole), 1448 ν (C-O), 844 ν (PF_6), 620 ν (M-O), 555 ν (M-N). ESI-MS (positive ion mode, CH_3CN) m/z : 325 ($[\text{M}+2\text{H}]^+$).

Results and discussion

All the isolated compounds were found to be air stable and were characterized by different analytical and spectroscopic methods.

IR spectral studies

IR spectra 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 H-C(=N) group of the ligand (OH...N=C). This band disappeared in the complexes due to the involvement of phenolic -OH group in coordination to metal ion. The -OH stretching frequency that appeared as a broad band in the range 3449-3447 cm^{-1} in the spectra of Cd(II) complex and Co(II) complex respectively were due to the presence of water of hydration or coordinated water. The involvement of deprotonated phenolic moiety in metal complexes was confirmed by the shift of -CO stretching band at 1465.5 cm^{-1} to lower frequency region of 1448-1459 cm^{-1} for the complexes. In the ligand a band corresponding to the azomethine group (-C=N) was found at 1640 cm^{-1} . On complexation, this band gets shifted to lower wave number range of 1620-1634 cm^{-1} . This indicated the involvement of N-atom of azomethine (-C=N) group in the complex formation [6] and the band at the range of 842-844 cm^{-1} was assigned for P-F stretching frequency. Therefore the IR spectra suggest that the ligand (LH) coordinates to metal ions M^{2+} (M = Cd and Co) through the N-atom of azomethine (-C=N) group and the O-atom of phenolic (O-Ar) group. The new bands appearing in the regions 618-620 cm^{-1} and 555-548 cm^{-1} in the spectra of metal complexes (3, 4) were assigned to M-O and M-N stretching frequencies, respectively [7].

Mass spectral studies

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; these peaks corresponds to M^+ , $[\text{M}=\text{C}_6\text{H}_{12}\text{N}_3]^+$ and $[\text{M}=\text{C}_{13}\text{H}_{16}\text{N}_3\text{O}]^+$ peaks, respectively. Again the mass spectra of the Cd(II) complex (3) and Co(II) complex (4) showed molecular ion peaks (m/z) at 381 and 325, respectively. These molecular ion peaks were assigned for $(\text{M}+3\text{H})^+$ [where $\text{M} = \text{Cd}(\text{C}_{13}\text{H}_{18}\text{N}_3\text{O}_3)$] and $(\text{M}+2\text{H})^+$ [where $\text{M} = \text{Co}(\text{C}_{13}\text{H}_{18}\text{N}_3\text{O}_3)$] peaks, respectively. These peaks supported the proposed structure of the complexes and confirmed the ML (1:1) type of stoichiometry for the two complexes. Thus the ligand behaves as a bidentate ligand towards the metal ions to form tetra-coordinated chelates. The different molecular ion peaks, appearing for the complexes, were attributed to different fragmentations of the metal complexes by successive rupture of different bonds in order to form stable ions. The mass spectra of the ligand and complexes were in good agreement with the respective structures as revealed by the elemental and other spectral analyses.

^1H NMR spectral studies

The ^1H NMR spectra of ligand and complexes were recorded in

$\text{DMSO}-d_6$. Upon examination it was observed that: i) the -OH signal, appearing in the spectrum of LH at 12.56 ppm, completely disappeared in the spectrum of the Cd(II) complex (3) indicating that the -OH proton was removed by the chelation with the metal ion. ii) the signal observed at 8.52 ppm, presumably due to the effect of the ortho-hydroxyl group in the aromatic ring of LH, was assigned to azomethine protons. This signal was found at 7.68 for Cd(II) complex, indicating that the azomethine (-C=N) group was coordinated to the Cd(II) ion [8-10], iii) a new signal, observed at 8.41 ppm for Cd(II) complex, was assigned to -OH coordination and iv) the signal, appearing at 3.21 ppm was assigned to the proton of H_2O , attached to the Cd(II) ion

Electronic absorption spectral and magnetic moment studies

The UV-Visible of the ligand and the metal complexes were recorded in methanol at ambient temperature. The UV-Vis spectrum of ligand exhibited three absorption bands at 318, 254 and 214 nm due to $\pi \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and transitions involved with the imidazolium moiety, respectively [11,12]. The spectra of the Cd(II) complex(3) exhibited three bands at 318, 254 and 210 nm. Interestingly, the ligand band at 318 nm and 254 nm only showed hypochromic and hyperchromic shifts due to coordination with Cd^{2+} (d^{10}) ion, respectively. This spectral pattern normally prefers tetrahedral geometry. The electronic spectra of the Co(II) complex (4) also showed three bands at 334, 249 and 210 nm and a shoulder around 390 nm. The ligand band at 318 nm arising from $n \rightarrow \pi^*$ transition was red shifted to 334 nm for the Co(II) complex due to coordination. Also the peak at 254 and 214 nm for the ligand were blue shifted to 249 and 210 nm, respectively. These band shifts reflect structural changes due to coordination of the ligand in the Co(II) complex; The shoulder around 390 nm is most probably due to $^4\text{T}_{1(\text{F})} \rightarrow ^4\text{A}_{1(\text{F})}$ transition suggesting a distorted tetrahedral geometry for the Co(II) complex [13-15]. The observed magnetic moment (3.87 B.M) at ambient temperature for Co-complex also suggests tetrahedral geometry of this complex. The slightly lower magnetic moment is probably due to the distortion of the regular tetrahedral geometry. The 210 nm peak is a characteristic band [12] for the imidazolium moiety in the ligand.

Thermogravimetric study

The thermal behaviour of the complexes was studied by TGA and DTG. The samples were analysed over a temperature range of 30-600 °C in Al_2O_3 crucible under N_2 atmosphere. The temperature programmed to increase linearly at 10 °C/min. In case of Cd(II) complex(3) the coordinated water molecule was eliminated in the temperature range 260-420 °C. At the temperature range 420-539 °C mass losses occurred due to the decomposition of the organic fragments of the complex. For Co(II) complex (4) a mass loss occurred within the temperature range 360-480 °C corresponding to the loss of coordinated water molecule and around 570 °C the organic fragments were eliminated. These decompositions intermediates continued till stable metal oxides were formed. The oxides formed were 27.61 and 39.34 % for Cd(II) complex (3) and Co(II) complex(4), respectively. These quantities of respective oxides are as per the stoichiometry of the complexes obtained from elemental analysis.

Antibacterial activities

The antibacterial activities of the metal salts, ligand, its newly synthesized Cd(II) and Co(II) complexes were studied against the gram negative bacteria escherichia coli(JM109) ATCC No. 69905 and gram positive bacteria lactobacillus spp. ATCC No. 6633. Stock solutions of the compounds were prepared by dissolving the compounds in sterile distilled water and serial dilutions were done for different concentrations to determine the minimum inhibition concentration (MIC) of the respective compounds. The concentrations of the tested compounds were 125, 250, 500, 750 and 1000 $\mu\text{g}/\text{mL}$ in comparison to the stand-

ard drug ampicilin. The nutrient agar medium was poured into 0.5 mL culture contained in Petri plate. Then well diffusion technique [16-17] was performed. Petri plates were placed in an incubator at 37 °C for 24 h. No clear inhibition zone surrounding the well were formed against the ligand and its Co(II) complexes (inhibition zones against lactobacillus spp. is shown in Table. 1), whereas Cd(CH₃COO)₂·2H₂O, Co(CH₃COO)₂·4H₂O and Cd(II) complex showed antibacterial activities with well diameter in the range of 3.5-1.3 mm, respectively at the concentrations of 125, 250, 750 and 1000 µg/mL against the bacteria studied.

Table.1 Inhibition zones against lactobacillus spp.

Compound	1000 ug/ml	750 ug/ml	500 ug/ml	250 ug/ml	125 ug/ml
Cd(CH ₃ COO) ₂ ·2H ₂ O	3.5 mm	3.2 mm	3.0 mm	2.8 mm	2.0 mm
Co(CH ₃ COO) ₂ ·4H ₂ O	2.6 mm	2.3 mm	1.8 mm	-	-
LH	-	-	-	-	-
Cd(II)complex(2)	1.5mm	1.3 mm	1.1mm	-	-
Co(II)complex(3)	-	-	-	-	-

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SCHEME CAPTION

SCHEME 1. Syntheses of the M(II) complexes (3 and 4) from the ionic liquid based Schiff base, [1-{2-(2-hydroxybenzylideneamino) ethyl}-3-methylimidazoliumhexafluorophosphate (LH).

FIGURE CAPTION

FIGURE. 1. The UV-visible spectra of: (a) the ligand (2), (b) the Cd(II) complex (3) and (c) the Co(II) complex (4).

SCHEME. 1

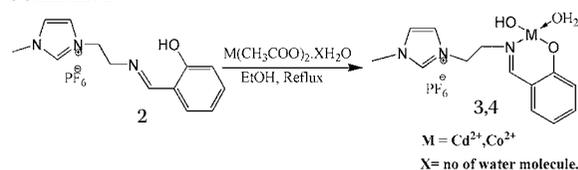
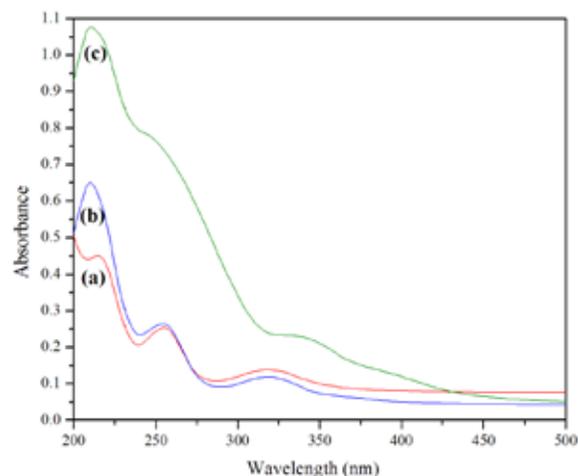


FIGURE 1



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