



SYNTHESIZE, STRUCTURAL, MAGNETIC AND THERMAL STUDIES OF TRIDENTATE SCHIFF BASES AND THEIR Co (II) COMPLEXES

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ABSTRACT

Schiff base tridentate ligands and their corresponding Co(II) complexes were synthesized and characterized by XRD, IR, NMR, UV-Visible spectra and thermal studies. The XRD revealed that the prepared complex have high degree of crystallinity with sharp crystalline peaks. The IR spectra confirm that the prepared ligands performed as monobasic tridentate towards central Co(II) ion. Elemental analysis revealed 1:2 metal to ligand stoichiometry and octahedral geometry for Co(II) complexes. IR spectra of the Schiff base ligands and its complexes are compared in order to determine the coordination sites on complexation.

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INTRODUCTION

Compounds consisting an azomethine group (-CH=N-), can be called as Schiff bases, which are formed by the condensation of a primary amine with a carbonyl compound. Schiff bases of aliphatic aldehydes are reasonably unstable and are readily polymerizable. On the other hand, Schiff bases of aromatic aldehydes having an effective conjugation system are more stable. Therefore, schiff bases have number of applications such as preparative use, identification, detection and determination of aldehydes and purification of carbonyl compounds [1]. Besides, Schiff bases form basic units in certain dyes. Commonly, schiff bases are bi- or tri- dentate ligands capable of forming very stable complexes with transition metals. A large number of Schiff bases and their complexes have been studied because of their ability to reversibly bind oxygen [2], act as catalysts [3] and exhibit photochromic properties [4,5]. The high affinity for the chelation of the Schiff bases towards the transition metal ions, especially copper ions, is utilized in preparing their complexes. The Schiff base ligands with sulphur, oxygen and nitrogen donor atoms act as good chelating agents forming stable chelates with transition metal ions. Such metal complex on coordination shown to exhibit increased potential biological activity [4] has prompted us to prepare a Schiff base by condensing aromatic o-hydroxyl aldehyde with 2-amino thiophene derivative.

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The chemistry of copper complexes is of interest owing to their importance in biological and industrial processes [6, 7]. The copper complexes derived from Schiff bases were found to be extremely efficient catalysts in both homogeneous [8] and heterogeneous [3] conditions. Among all the transition metal complexes, Cu (II) complexes with Schiff bases are a fascinating class owing to their luminescent abilities and potential applications in organic light emitting diodes [9 - 11]. In addition, it has gained considerable attention in recent years due to their diversity in magnetic exchange properties and coordination geometries [12, 13]. Therefore, we report the synthesis and spectroscopic characterization of a series of Co(II) complexes.

Experimental

MATERIALS AND METHODS

AR grade chemicals were used. Solvents were purified and distilled for synthesis and physical measurements. Various characterization techniques have been adopted to study the enhanced properties of grown crystals. The functional groups were observed using Perkin Elmer Spectrum in the range of 500-4000 cm⁻¹. The crystal structure of the metal complexes were confirmed by powder X-ray diffraction using ENRAF NONIUS CAD-4 powder crystal X-ray diffractometer with CuK α radiation. The optical properties of the crystals were examined between 100 and 1000 nm using LAMBDA-35 UV-Vis spectrophotometer. Thermo gravimetric analysis has been carried out to study the thermal stability for the complexes using a simultaneous thermal analyzer TGA7 (Perkin Elmer). The ¹H and ¹³C NMR spectra were recorded in CDCl₃.

and DMSO- d_6 solvent respectively on Mercury plus 300 MHz NMR spectrometer. The elemental analysis was carried out by Thermo finnigan CHNS(O) Analyzer, while metal content was determined by ARCOS, ICP-Atomic Emission Spectrometer and by standard methods [14]. Mass spectra were recorded on Varian Inc, USA made Liquid Chromatograph Mass Spectrometer.

Synthesis of ligand

The starting material, ethyl 2-amino-5,6-dihydro-4H-cyclopenta[b]thiophene-3-carboxylate (1) was synthesized as per the given in the Gewald synthesis [15]. To a solution of this 2-amino thiophene derivative (0.01 mol) in ethanol (20 ml) was added to o-hydroxyl aldehyde derivative (0.01 mol) (2a–2b) mixed in ethanol (20 ml) with constant stirring. The resulting mixture was refluxed on water bath for 1–2 h. On cooling the solution, the Schiff base (HL1–HL2) formed. It was filtered followed by washing and drying. Besides, purification and recrystallization process was made from ethanol [16]. The reaction scheme is given Fig. 1.

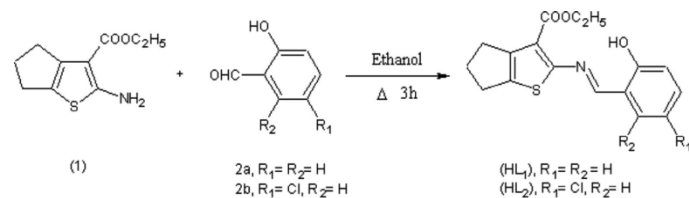


Figure 1 The reaction scheme of prepared ligands

Ethyl 2-amino-5,6-dihydro-4H-cyclopenta[b]thiophene-3-carboxylate – (1)

[$\text{C}_{10}\text{H}_{13}\text{NO}_2\text{S}$] Yield: 72%; M.P.: 90 °C; Colour: Brown; ^1H NMR (CDCl_3 , 300 MHz) δ : 1.29–1.34 (t, 3H, $-\text{CH}_3$), 2.25–2.84 (m, 6H, cyclopentane ring), 4.20–4.27 (q, 2H, $-\text{CH}_2-$), 5.84 (s, 2H, $-\text{NH}_2$); FTIR (KBr, ν , cm^{-1}): 3415 ($-\text{NH}$), 3297, 3174 ($-\text{NH}_2$), 1644 (C=O), 1263 (C–N), 1575, 1421, 1371 (thiophene ring).

Ethyl 2-[(E)-(2-hydroxyphenyl)methylidene]amino}-5,6-dihydro-4H-cyclopenta[b] thiophene-3-carboxylate –(HL₁)

[$\text{C}_{17}\text{H}_{17}\text{NO}_3\text{S}$] Yield: 80%; M.P.: 128°C; Colour: Golden Yellow; ^1H NMR (CDCl_3 , 300 MHz) δ : 1.36–1.41 (t, 3H, $-\text{CH}_3$), 2.34–2.43 (m, 2H, cyclopentane ring), 2.88–3.00 (m, 4H, cyclopentane ring), 4.35–4.42 (q, 2H, $-\text{CH}_2-$), 6.88–7.39 (m, 4H, salicylaldehyde ring), 8.54 (s, 1H, $-\text{CH}=\text{N}-$), 12.94 (s, 1H, $-\text{OH}$); ^{13}C NMR (DMSO- d_6 , 75 MHz) δ : 159.49 ($-\text{CH}=\text{N}-$), 160.11 ($-\text{C}-\text{OH}$), 162.11 ($-\text{C}=\text{O}-$), 157.95, 145.41, 136.22, 133.82, 132.88, 120.36, 119.34, 119.03, 116.84, 60.27, 30.18, 29.36, 26.74, 14.10; FTIR (KBr, ν , cm^{-1}): 3140 ($-\text{OH}$), 1682 (C=O), 1597 (C=N), 1310 (C–O), 616 (C=S); LCMS m/z: [M] $^+$ 315.9; Elemental analysis, found (calc.): C 64.45% (64.68%), H 5.45% (5.39%), N 4.20% (4.44%), S 9.96% (10.15%).

Ethyl 2-[(E)-(5-chloro-2-hydroxyphenyl)methylidene]amino}-5,6-dihydro-4H-cyclopenta[b]thiophene-3-carboxylate –(HL₂)

[$\text{C}_{17}\text{H}_{16}\text{NO}_3\text{SCl}$] Yield: 87%; M.P.: 166°C; Colour: Yelloworange; ^1H NMR (CDCl_3 , 300 MHz) δ : 1.36–1.40 (t, 3H, $-\text{CH}_3$), 2.34–2.44 (m, 2H, cyclopentane ring), 2.89–3.00 (m, 4H, cyclopentane ring), 4.35–4.42 (q, 2H, $-\text{CH}_2-$), 6.93–7.33 (m, 3H, salicylaldehyde ring), 8.45 (s, 1H, $-\text{CH}=\text{N}-$), 12.93 (s, 1H, $-\text{OH}$); ^{13}C NMR (DMSO- d_6 , 75 MHz) δ : 159.49

($-\text{CH}=\text{N}-$), 160.11 ($-\text{C}-\text{OH}$), 162.11 ($-\text{C}=\text{O}-$), 157.95, 145.41, 136.22, 133.82, 132.88, 120.36, 119.34, 119.03, 116.84, 60.27, 30.18, 29.36, 26.74, 14.10; FTIR (KBr, ν , cm^{-1}): 3140 ($-\text{OH}$), 1682 (C=O), 1597 (C=N), 1310 (C–O), 616 (C=S); LCMS m/z: [M] $^+$ 315.9; Elemental analysis, found (calc.): C 64.45% (64.68%), H 5.45% (5.39%), N 4.20% (4.44%), S 9.96% (10.15%).

Synthesis of metal complexes

To a magnetically stirred hot ethanolic solution of ligand HL₁–HL₂ (20 ml, 0.01 mol), a hot ethanolic solution of cobalt(II) chloride (10 ml, 0.005 mol) was added in small parts. After complete addition of the metal salt solution, the pH was adjusted to 6.5 by adding ethanolic ammonia. It was then refluxed for 6–8 h in a water bath and the solution was reduced to half and kept overnight. The complex [Co(L)₂] formed was filtered, washed sequentially with aqueous ethanol and ether. Finally the complex was dried in vacuum over P_4O_{10} .

[Co(L₁)₂]

Brown solid of $\text{CoC}_{34}\text{H}_{32}\text{N}_2\text{O}_6\text{S}_2$ (687.69); FTIR (KBr, ν , cm^{-1}): 1653 (C=O), 1567 (C=N), 1337 (C–O), 617 (C=S), 518 (M \leftarrow O), 424 (M \leftarrow N); Elemental analysis, found (calc.): C 60.22% (59.33%), H 4.52% (4.65%), N 4.16% (4.07%), S 9.16% (9.30%), Co 8.12% (8.57%); Molar conductivity (DMF): 5.90 ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$).

[Co(L₂)₂]

Maroon solid of $\text{CoC}_{34}\text{H}_{30}\text{N}_2\text{O}_6\text{S}_2\text{Cl}_2$ (756.58); FTIR (KBr, ν , cm^{-1}): 1651 (C=O), 1575 (C=N), 1343 (C–O), 618 (C=S), 518 (M \leftarrow O), 422 (M \rightarrow N); Elemental analysis, found (calc.): C 54.22% (53.93%), H 4.02% (3.97%), N 3.63% (3.70%), S 8.25% (8.46%), Co 7.67% (7.79%); Molar conductivity (DMF): 1.20 ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$).

RESULTS AND DISCUSSION

Structure of Schiff base ligands

Analytical data suggested that o-hydroxyl aldehyde derivative (2a–2b) condensed with Ethyl 2-amino-4,5,6,7-tetrahydrobenzo(b)thiophene 3-carboxylate (1) in 1:1 molar ratio to form Schiff base ligand (HL₁, HL₂).

^1H NMR spectra

The ^1H NMR spectra of the Schiff base ligands were recorded in CDCl_3 solvent using TMS as internal reference over the range of 0–16 ppm. The disappearance of the singlet at 5.92 ppm of aminothiophene (1) and appearance of new singlet peak in the range of 8.40–9.50 ppm can be assigned to the azomethine protons which confirmed the condensation of aminothiophene and o-hydroxyl aldehyde derivative. The singlet observed in the range of 12.53–14.32 ppm is attributable to the phenolic $-\text{OH}$ of aldehyde derivative (2a–2b). Also a set of multiplets observed in the range 6.75–8.02 ppm can be ascribed to the aromatic protons. The important ^1H NMR signals are listed in Table 1.

^{13}C NMR spectra

The ^{13}C NMR spectra of the Schiff base ligands were recorded in DMSO- d_6 solvent. In the spectra, ester carbonyl carbon appeared most downfield in the range 161.08–161.89 ppm followed by phenolic carbon in the range of 159.07–159.12 ppm and azomethine carbon in the range 159.01–160.14 ppm.

The ^{13}C spectral data confirmed the formation of the Schiff bases. The important ^{13}C NMR signals are summarized in Table 1.

Table 1 ^{13}C & ^1H NMR signals for Schiff base ligands

Schiff base ligand	C=O Ester	C-OH Phenolic	-CH=N-Azomethine	
^{13}C NMR signals (ppm)	HL ₁	161.08	159.07	160.12
	HL ₂	161.89	159.12	159.01
^1H NMR signals (ppm)	-NH ₂ Amine	C-OH Phenolic	CH=N-Azomethine	
	HL ₁	-	13.01	13
	HL ₂	-	13.18	9.42

IR spectra

IR spectra of Schiff base ligands shows band in the region 3100–3300 cm^{-1} corresponding to phenolic hydroxyl group (-OH) and strong peak in the regions of 1600–1591 cm^{-1} corresponding to the azomethine group (C,N). A strong band appearing in the region 1690–1700 cm^{-1} was assigned to ester carbonyl band. Substituted thiophene ring vibrations were observed at 1550, 1474 and 1298 cm^{-1} .

X ray diffraction studies

Powder X-ray patterns of [Co(L1)2] and [Co(L2)2] complex is shown in Fig. 2. The powder X ray diffraction of the complex were scanned for two theta ranging from to scan the sample were recorded diffraction angle from 0 to 80 at the wavelength of 1.5406 Å using X-ray diffractometer. XRD profile confirm that the complex are in pure phase with well crystalline nature with sharp crystalline peaks. The maximum reflection was observed at 28.653° corresponding to interplanar distance of $d = 4.5133 \text{ Å}$. The single crystals of the complexes were difficult to isolate from the solvent, hence powder diffraction data were acquired [17]. The average crystalline sizes of the complex were calculated by using Scherrer's equation [18]

$$d = \frac{K\lambda}{\beta \cos\theta}$$

Where d is the mean crystallite size, K is the shape factor taken as 0.89, λ is the wavelength of the incident beam, β is the full width at half maximum and θ is the Bragg angle. The average crystallite size of the complex was calculated, the [Co(L1)2] and [Co(L2)2] complex has an average crystallite size of 47 and 58 nm respectively.

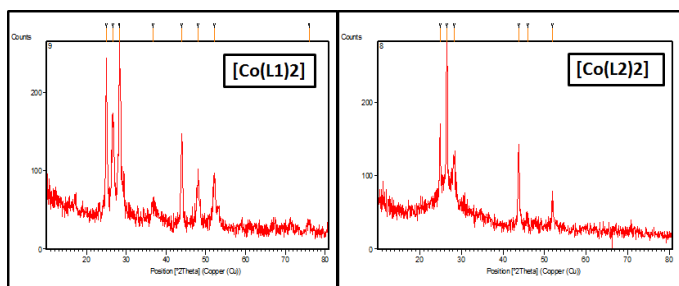


Figure 2 Powder X-ray diffraction profile of [Co(L1)2] and [Co(L2)2] complex

Electronic spectra and magnetic moments

Electronic spectra of [Co(L1)2] and [Co(L2)2] complexes were recorded in DMF at room temperature and displayed in Fig. 3. These two complexes [Co(L1)2] and [Co(L2)2] revealed three absorption bands in the range 10,000–10,200 cm^{-1} , 18,500–20,100 cm^{-1} and 23,600–25,000 cm^{-1} . These

bands can be assigned to the three spin allowed transitions, $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{F})$ (ν_1), $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{A}_{2g}(\text{F})$ (ν_2) and $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{P})$ (ν_3) respectively. Using Konig equations [19], the covalency factor (b) and transition ratio (ν_1/ν_2) were observed in the range 0.87–0.96 and 1.90–1.98 respectively, while LFSE values were obtained between -78.12 and -74.84 kJ/mol. Lower B values of the complexes than the free ion, indicates orbital overlap and delocalization of d -orbitals [20]. Magnetic moment values of Co(II) complexes were observed in the range 4–5 BM which confirmed the octahedral geometry of the complexes. The electronic spectral data and magnetic moments of the complexes are illustrated in Table 2.

Table 2 Electronic and magnetic field parameters of [Co(L1)2] and [Co(L2)2] complex

Complex	Absorption Band cm^{-1}	Tentative Assignment	Magnetic Moment (BM)	ν_2/ν_1	Dq cm^{-1}	B cm^{-1}	β	LFSE (kJ/mol)
[Co(L1)2]	10182 20100 23542	$^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{F})$ $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{A}_{2g}(\text{F})$ $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{P})$	4.75	1.97	990	906	0.92	-78.12
[Co(L2)2]	10104 18458 24800	$^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{F})$ $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{A}_{2g}(\text{F})$ $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{P})$	4.78	1.90	924	922	0.94	-74.84

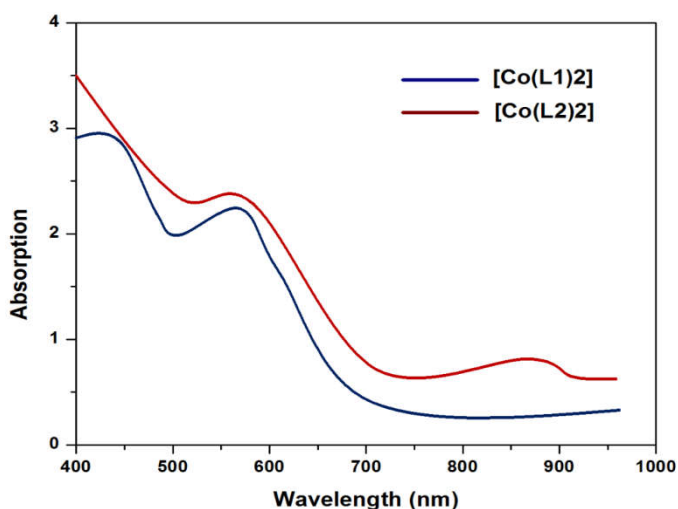


Figure 3 Electronic spectra of [Co(L1)2] and [Co(L2)2] complex

Thermo gravimetric studies

The thermal decomposition analysis of the [Co(L1)2] and [Co(L2)2] metal complexes were carried out under nitrogen atmosphere from room temperature to 1000 $^{\circ}\text{C}$. The metal complexes of the [Co(L1)2] and [Co(L2)2] were stable up to 205 and 200 $^{\circ}\text{C}$ respectively, indicating absence of coordination water. The thermogram of complex is given in Fig. 4, which shows two stage decomposition pattern. First TG loss corresponds to the aminothiophene moiety in the temperature range 200–390 $^{\circ}\text{C}$ (found 44.18%, calc. 45.89%). Second TG loss occurred in the temperature range 400–480 $^{\circ}\text{C}$ with a loss of salicylaldehyde moiety (found 46.02%, calc. 45.95%) leaving behind cobalt oxide as residue (found 8.90%, calc. 8.86%). Observed TG data are in good agreement with the proposed molecular formula of the cobalt complex.

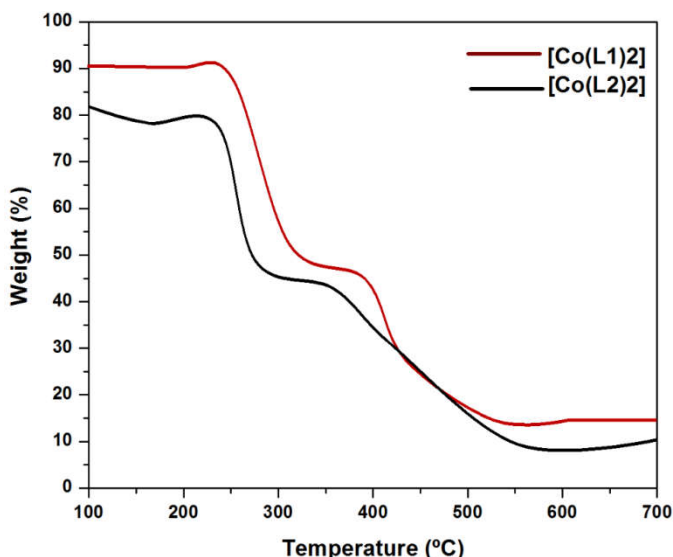


Figure 4 Thermogram of [Co(L1)2] and [Co(L2)2] complex

SEM Micrographs

The surface morphology of the metal complexes was studied using SEM. The SEM micrographs of [Co(L1)2] and [Co(L2)2] complexes are shown in Fig. 5a, and b respectively. These were recorded at an energy of 20 KV with magnification X5000 for both the metal complexes. Agglomeration of thin flakes was seen for [Co(L1)2] complex while [Co(L2)2] complex exhibit the cauliflower-like structure. The particle sizes of the [Co(L1)2] and [Co(L2)2] complexes were in the diameter range of few microns. However, particles with size less than 100 nm were also observed which groups to form agglomerates of larger size. The average crystallite size obtained from XRD also shows that the particles were agglomerated that these complexes have polycrystalline with nanosized grains.

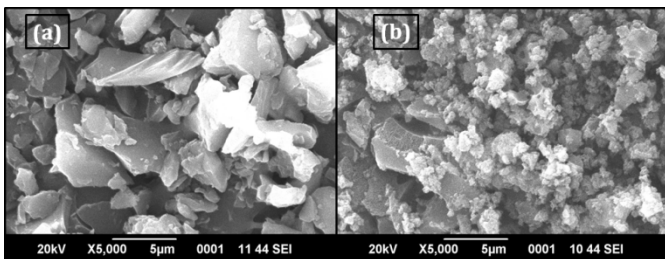


Figure 5 SEM images of metal complexes: a) [Co(L1)2] and b) [Co(L2)2] complex

CONCLUSION

We have synthesized, Schiff bases by condensation of ethyl-2-amino-5,6-dihydro-4H-cyclopenta[b]thiophene-3-carboxylate and o-hydroxyl aldehyde derivative and their Co(II) complexes. Physico-chemical and various spectral studies revealed, monobasic trident nature of ligands with ONO donor atoms towards central Co(II) ion and octahedral geometry of complexes with 1:2 (metal: ligand) stoichiometry.

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