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ORIGINAL PAPER

Biological and electrochemical studies of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} metal complexes of Schiff base ligand derived from 4-amino benzoic acid and isonicotinic hydrazide

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Abstract

Ten metal complexes of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} were synthesized by two novel Schiff bases derived from condensation of *m*-pthalaldehyde with 4-amino benzoic acid and isonicotinic hydrazide. The as-synthesized metal complexes were characterized and explored by different spectroscopic techniques. FT-IR spectra have confirmed the presence of C=N bands as well as UV–Vis spectroscopy in both Schiff bases KM-1 and KM-2. All as-prepared compounds were evaluated for the antimicrobial activities against the *Escherichia coli* and *Propionibacterium acnes*. KM-1 and its metal complexes have shown efficient results compared to KM-2. The electrochemical study of M^{2+} complexes by cyclic voltammograms in electrolyte solution (Pt electrode) demonstrated electrochemically irreversible oxidative and reductive responses.

Keywords Schiff-base · Transition metal complex · 4-Amino benzoic acid · Isoniazid · Spectral and antibacterial study · Cyclic voltammograms

Introduction

Heterocyclic compounds are widely used as a pharmaceutically indispensible compounds. Schiff bases are one of those heterocyclic compounds which are used as versatile ligands. The ability of Schiff bases for intermolecular hydrogen bonding between oxygen and nitrogen atoms leads to ligand metal complexes in coordination chemistry [1]. A large number of Schiff bases and their metal complexes was investigated in last decade because of their extreme biological properties [2]. These organometallic complexes are key active pharmaceutical gradient in medicinal and pharmaceutical industries. They show various biological applications including anti-bacterial, anti-fungal and anti-tumor activity [3–6]. Schiff base metal complexes show significant role in different fields of synthetic chemistry like industrial chemistry, agricultural, etc. Schiff bases could be a catalyst for different synthetic organic reactions, biologically active compound, dyes, plant growth regulators, etc. [7]. They display a phenomenal role in anti-fungal and anti-tubercular activities [5, 6, 8–11]. Many metal complexes of Schiff bases show excellent catalytic activity in various aqueous reactions at high temperature (> 100 °C) which is ecofriendly [12].

Hugo Schiff firstly synthesized Schiff base compounds by the nucleophile condensation of an aldehyde and an amine in 1864 [13]. Schiff base acts as a ligand and it is able to coordinate metals through its imine nitrogen and another donating group, usually bonded with aldehyde group [14]. Research in invention of these Schiff base metal complexes is very fast-growing research field due to their wide range of possible structures as ligands which depends on the structures of aldehydes and amines [15]. The structural changes via substitutions in the reactants sometimes completely divert the desired reaction and enforce to a completely different course of reactivity. The changes in structure of aldehyde and amine can completely change the reaction and it can show the entirely different reactivity [16]. Schiff base ligands and their complexes

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are used as an intermediate in various enzymatic reactions because of their interactions between amino groups and enzymes [17]. Schiff base ligand formed from the condensation of KM-1 and KM-2 and its metal complexes were reported in this paper. Moreover, an electrochemical and antimicrobial evaluations of these complexes are also discussed in this paper.

Isoniazid used as an amine, shows various biological activities such as antibacterial, antiviral, antifungal and anti-tuberculosis. Literature clearly demonstrates that the metal complexes of this amine have also good activity. Isoniazid based metal complexes can be effectively used as anti-tuberculosis agents. They showed a vast variety of antimicrobial activities such as antibacterial, antiviral and antifungal [18].

The aim of the current study was to prepare new ligands, derived from 4-amino benzoic acid and isoniazid. We have also explored complexes of certain 3d and 4d series metals with the ligands KM-1 and KM-2. The novel Schiff bases were synthesized by the reaction of 4-amino benzoic acid and isoniazidand with *m*-pthalaldehyde (2:1) in ethanol. These ligands have excellent lone pair donor ability with transition metals ion. The ligands along with complexes of divalent metal ions such as Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} were characterized by spectroscopy and physical methods for evaluation of their photo-physical, biological and electrochemical studies.

Electron donating and accepting ability of a ligands are confirmed through electrochemical studies [19]. Our study are based on the redox behavior of the Schiff base and metal complex chelates, where the electron accepting and donating properties of the ligands were confirmed through electrochemical studies. By varying several experimental parameters such as the concentration, the speed of sweep of the electric field of study etc. different studies can be made out of electrochemical studies [20]. Not only concentration of solution even the pH of solution also affects the cyclic voltammograms or in other words its electrochemical behavior [21]. Scan rate may also change the voltammograms behaviors [22]. Electrocatalytic activity of various Schiff bases have been also studied in recent researches in different electrolytic solutions [23].

Experimental

Materials

All reagents and solvents used in this work were purchased from Sigma Aldrich. Solvents were analytical grad as per receive, used purified and dried as per standard procedure. The Melting points of ligands and complexes were determined on electrochemical melting apparatus. Infrared spectroscopic analysis was done by FT-IR spectroscopy, Bruker and UV absorption study by rigol-360-UV spectroscopy instrument, NMR spectra obtained by Bruker 500 MHz spectrometer in instrument. Mass spectra obtained by waters xevo G2S QT of. The cyclic voltammograms obtained by software NOVA version 1.10.1.9.

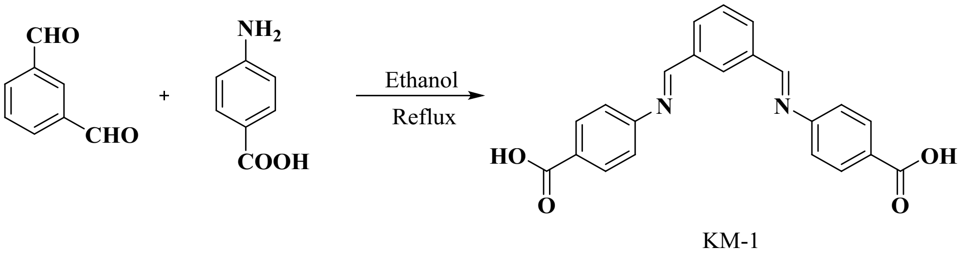
Synthesis of Schiff bases (KM)

KM-1 ligand was synthesized in ethanolic solution (20 mL) of *m*-pthalaldehyde (0.134 g, 1 mmol) and 4-aminobenzoic acid (0.274 g, 2 mmol) while as KM-2 was synthesized in ethenolic solution (20 mL) of *m*-pthalaldehyde (0.134 g, 1 mmol) by adding of isonicotinic hydrazide (isoniazid) (0.272 g, 2 mmol). To ethanolic solution of *m*-pthaladehyde in a round bottom flask and fix on a heating magnetic stirrer was added amine solution as dropwise at 75–80 °C and refluxed for 6–7 h. White/pale yellow colored precipitate obtained and allowed to cool down at room temperature, filtered and dried, then recrystallized from ethanol and water (2:1 ratio). The progress of reaction was monitored by TLC plate under UV–Vis chamber (Schemes 1, 2).

Synthesis of Complexes

To the methanolic solution of $ZnNO_2$, $CoNO_2$, $CuNO_2$, $CdNO_2$ and $NiNO_2$ (1 mmol, in 10 mL MeOH) was added Schiff base (KM-1 and KM-2) (1 mmol) in the presence of 4–5 mL KOH and was stirred for 6–7 h. After completion of the reaction, the solution was concentrated to 10 mL and was stirred for 3–4 h under reflux. Then the reaction mixture was cooled and the precipitated complexes was filtered, washed with ethanol followed by hot water (2:1

Scheme 1 Synthesis of 4,4′-(((1*E*,1′*E*)-1,3-phenylenebis(methanylylidene))bis(azanylylidene))dibenzoic acid



ratio) and dried. The reaction scheme for the synthesis of metal complex is given below (Schemes 3, 4).

Characterization of ligands

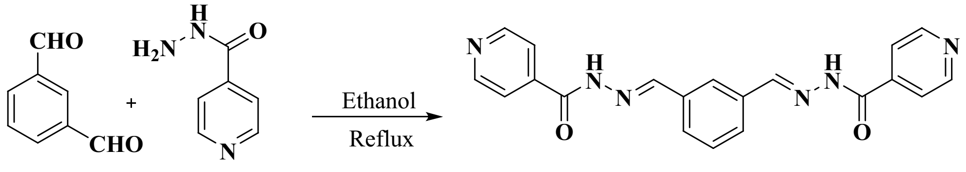
***4,4′-(((1E,1′E)-1,3-phenylenebis(methanylylidene))bis(azanylylidene))dibenzoic acid* (KM-1)** Pale brownish color powder; M. p.: 218–221 °C; Yield: 0.365 g (87%), FT-IR (KBr): $\bar{\nu}$ = 3852.58 (O–H medium, broad), 3739.95 (O–H medium, broad), 3615.69 (O–H medium, broad), 3349.96 (O–H medium, broad), 2970.35(C–H aromatic proton strong), 2875.07 (C–H aromatic proton strong), 2551.63 (C–H aromatic proton strong), 2358.68 (C–H aromatic proton strong), 1680.21 (–C=N–), 1633.76 (–C=N–), 1569.42 (C=C), 1444.90 (C=C), 1383.29 (C=C), 1288.26 (C=C), 1083.91 (C–H bending), 1040.73 (C–H bending), 918.41 (C–H bending), 880.28 (C–H bending), 785.49 (C–H bending), 746.23 (C–H bending), 674.18 (C–H bending) cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): $\delta = 7.4$ (m), 7.57δ (s), 7.85δ (s), 8.15 (s), 10.0δ (s), 8.2 (s) 8.37 (d) ppm; UV–Vis: $\lambda_{max} = 205–275$ nm; Chemical Formula: $C_{22}H_{16}N_2O_4$ Molecular Weight: 372.37 Elemental Analysis: C, 70.96; H, 4.33; N, 7.52; O, 17.19 s.

***(N′,N″E,N′,N″E)-N′,N″-(1,3-phenylenebis(methan-1-yl-1-ylidene))diisonicotinohydrazide* (KM-2)** White color powder, m. p.: 228–231 °C, Yield; 0.333 g (81%), FT-IR (KBr): $\bar{\nu}$ = 3740.52 (O–H medium, broad), 1687.47 (–C=N–), 1508.15 (=C–H), 1338.43 (=C–H), 825.69 (C–H), 747.06, (C–H), ^1H NMR (500 MHz, DMSO-d_6): $\delta = 7.45$ (d), 7.85 (s), 7.93 (d), 8.1 (d), 8.4 δ (m), 8.7 (s), 9.17 (m) ppm; UV–Vis: $\lambda_{max} = 210–307$ nm; Chemical Formula: $C_{20}H_{16}N_6O_2$, Molecular Weight: 372.38, Elemental Analysis: C, 64.51; H, 4.33; N, 22.57; O, 8.5910.02.

Characterization of complexes

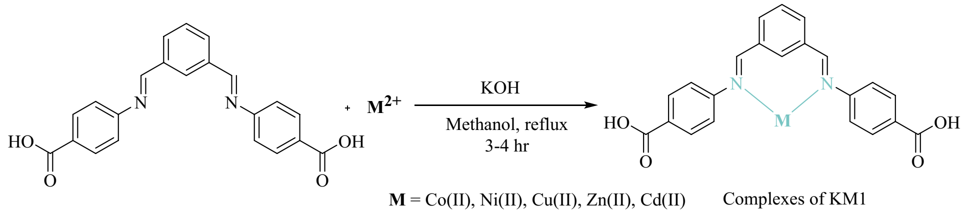
***4,4′((1E,1′E)(1,3phenylenebis(methanylylidene))bis(azanylylidene))dibenzoic acid, cadmium(II) salt* (KM-1[Cd])** Pale yellow color powder; M. p.: 269–272 °C; Yield: 0.666 g (68%); FT-IR (KBr): $\bar{\nu}$ = 3852 (O–H medium, broad), 3740.98 (O–H medium, broad, 3616.55 (O–H medium), 2361.64 (H–C aromatic proton strong), 1744.40 (–C=N–), 1687.64 (–C=N–), 1642.70 (C=O strong), 1525.81 (=C–H), 1462.13 (=C–H), 1389.39 (=C–H), 993.06 (–C–H), 766.78 (–C–H), 679.94 (–C–H), 610.43 (C–H), 574.20 (N–Cd), 551.14 (N–Cd), 540.25 (O–Cd), 527.87 (O–Cd) cm^{-1}; UV–Vis: $\lambda_{max} = 207–264$ nm, Chemical Formula: $C_{44}H_{30}CdN_4O_8{}^{2+}$; Molecular Weight: 855.14, Elemental Analysis C, 61.80; H, 3.54; Cd, 13.15; N, 6.55; O, 14.97.

Scheme 2 Synthesis of *N′*,*N‴*-((1*E*,1′*E*)-1,3-phenylenebis(methanylylidene)) di(isonicotinohydrazide)

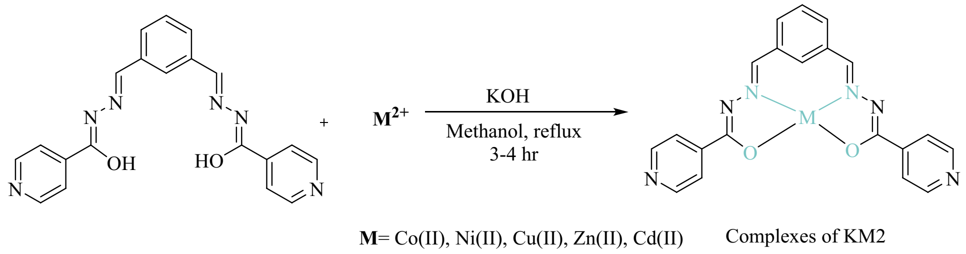


KM-2

Scheme 3 Synthesis of metal complexes from ligand-1(KM-1)



Scheme 4 Synthesis of metal complexes from ligand-2 (KM-2)



4,4′-((1E,1′E)-(1,3-phenylenebis(methanylylidene))bis(azanylylidene))dibenzoic acid, cobalt(II) salt **(KM-1[Co])** Pale brown color powder; M. p.: 275–277 °C; Yield: 0.677 g (73%); FT-IR (KBr): $\bar{\nu} = 3852.93$ (O–H medium, broad), 3741.12 (O–H medium, broad), 2360.71 (H–C aromatic proton strong), 1687.53 (–C=N–), 1548.33 (–C–H), 1387.51 (=C–H), 762.20 (–C–H), 679.20 (C–H), 609.23 (C–H), 552.65 (Co–N), 528.30 (Co–O) cm^{-1}; UV–Vis: $\lambda_{max} = 208–258$ nm; Chemical Formula: $C_{44}H_{30}CoN_4O_8{}^{2+}$; Molecular Weight: 801.66, Elemental Analysis: C, 65.92; H, 3.77; Co, 7.35; N, 6.99; O, 15.97.

4,4′-((1E,1′E)-(1,3-phenylenebis(methanylylidene))bis(azanylylidene))dibenzoic acid, zinc(II) salt **(KM-1[Zn])** Brown color powder; M. p.: 265–268 °C; Yield: 0.707 g (76%); FT-IR (KBr): $\bar{\nu} = 3435$ (O–H medium, broad), 2357.39 (H–C aromatic proton strong),1620.47 (–C=N–), 1558.68 (–C–H), 1387.65 (=C–H), 1153.86 (–C–H), 914.13 (C–H), 768.89 (C–H), 687.04 (C–H), 555.85 (N–Zn) cm^{-1}; UV–Vis: $\lambda_{max} = 206–264$ nm; Chemical Formula: $C_{44}H_{30}N_4O_8Zn^{2+}$; Molecular Weight: 806.134,Elemental Analysis: C, 65.40; H, 3.74; N, 6.93; O, 15.84; Zn, 8.09.

4,4′-((1E,1′E)-(1,3-phenylenebis(methanylylidene))bis(azanylylidene))dibenzoic acid, nickel(II) salt **(KM-1[Ni])** Greenish color powder; M. p.: 276–279 °C; Yield: 0.640 g (69%); FT-IR (KBr): $\bar{\nu} = 3835.04$ (O–H medium, broad), 3741.20 (O–H medium, broad), 3616.79 (O–H medium, broad), 2361.55 (H–C aromatic proton strong),1687.77 (–C=N–), 1620.51 (–C=N–), 1553.39 (–C–H), 1392.02 (=C–H), 1152.39 (–C–H), 921.11 (C–H), 770.95 (C–H), 687.76 (C–H), 609.78 (C–H), 562.33 (N–Ni), 528.51 (Ni–O) cm^{-1}; UV–Vis: $\lambda_{max} = 208–266$ nm; Chemical Formula: $C_{44}H_{30}N_4NiO_8{}^{2+}$; Molecular Weight: 800.141, Elemental Analysis: C, 65.94; H, 3.77; N, 6.99; Ni, 7.32; O, 15.97.

4,4′-((1E,1′E)-(1,3-phenylenebis(methanylylidene))bis(azanylylidene))dibenzoic acid, copper(II) salt **(KM-1[Cu])** Green color powder; M. p.: 275–278 °C; Yield: 0.653 g (70%); FT-IR (KBr): $\bar{\nu} = 3852.46$ (O–H medium, broad), 3740.74 (O–H medium, broad), 3616.69 (O–H medium, broad), 2361.34 (H–C aromatic proton strong), 1687.55 (–C=N–), 1525.05 (–C=N–), 1389.79 (=C–H), 755.86 (–C–H), 563.77 (N–Cu), 550.07 (N–Cu), 540.30 (Cu–O), 528.32 (Cu–O) cm^{-1}; UV–Vis: $\lambda_{max} = 210–270$ nm; Chemical Formula: $C_{44}H_{30}CuN_4O_8{}^{2+}$; Molecular Weight: 805.135, Elemental Analysis: C, 65.54; H, 3.75; Cu, 7.88; N, 6.95; O, 15.87.

(4Z,4′Z,N′,N″E,N′,N″E)N′,N″(1,3phenylenebis(methanylylidene))diisonicotinohydrazonic acid, cadmium salt **(KM-2[Cd])** Yellow color powder; M. p.: 293–296 °C; Yield: 0.473 g (73%); FT-IR (KBr): $\bar{\nu} = 3852.13$ (O–H medium, broad), 3740.36 (O–H medium, broad), 3680.67 (O–H medium, broad), 2358.73 (C–N=N strong), 1687.32 (–C=N–), 1457.30 (=C–H), 1170.88 (C–H), 1048.87 (C–H), 973.93 (C–H), 855.56 (C–H), 800.33 (C–H), 680.40 (C–H)568.18 (Cd–N), 527.03 (Cd–O) cm^{-1}; UV–Vis: $\lambda_{max} = 209–288$ nm; Chemical Formula: $C_{20}H_{16}CdN_6O_2{}^{2+}$, Molecular Weight: 486.04, Elemental Analysis: C, 49.55; H, 3.33; Cd, 23.19; N, 17.34; O, 6.60.

(4Z,4′Z,N′,N″E,N′,N″E)N′,N″(1,3phenylenebis(methanylylidene))diisonicotinohydrazonic acid, cobalt salt **(KM-2[Co])** Brownish color powder; M. p.: 257–260 °C; Yield: 0.421 g (71%); FT-IR (KBr): $\bar{\nu} = 3835.33$ (O–H medium, broad), 3740.04 (O–H medium, broad), 2358.09 (C–N=N strong), 1686.64 (–C=N–), 1503.75 (=C–H), 1386.90 (=C–H), 1169.28 (C–H), 973.82 (C–H), 848.87 (C–H), 794.33 (C–H), 682.24 (C–H), 585.04 (Co–N), 528.50 (Co–O) cm^{-1}; UV–Vis: $\lambda_{max} = 212–301$ nm; Chemical Formula: $C_{20}H_{16}CoN_6O_2{}^{2+}$ Molecular Weight: 431.07, Elemental Analysis: C, 55.69; H, 3.74; Co, 13.66; N, 19.48; O, 7.42.

(4Z,4′Z,N′,N″E,N′,N″E)N′,N″(1,3phenylenebis(methanylylidene))diisonicotinohydrazonic acid, zinc salt **(KM-2[Zn])** White color powder; M. p.: 286–288 °C, Yield: 0.408 g (68%); FT-IR (KBr): $\bar{\nu} = 3852.36$ (O–H medium, broad), 3740.05 (O–H medium, broad), 3680.21 (O–H medium, broad), 3615.95 (O–H medium, broad), 2358.56 (C–N=N strong), 1744.46 (–C=N–), 1687.40 (–C=N–), 1652.66 (–C=N–), 1507.89 (–C–H), 1383.93 (=C–H), 1169.50 (–C–H), 1048.11 (–C–H), 973.26 (–C–H), 848.96 (–C–H), 677.73 (–C–H)554.89 (Zn–N), 527.72 (Zn–O) cm^{-1}; UV–Vis: $\lambda_{max} = 216–260$ nm; Chemical Formula: $C_{20}H_{16}ZnN_6O_2{}^{2+}$, Molecular Weight: 437.77, Elemental Analysis: C, 54.87; H, 3.68; N, 19.20; O, 7.31; Zn, 14.94.

(4Z,4′Z,N′,N″E,N′,N″E)N′,N″(1,3phenylenebis(methanylylidene))diisonicotinohydrazonic acid, nickel salt **(KM-2[Ni])** Pale green color powder, M. p.: 281–283 °C, Yield: 0.362 g (61%); FT-IR (KBr): $\bar{\nu} = 3852.24$ (O–H medium, broad), 3740.33 (O–H medium, broad), 3680.97 (O–H medium, broad), 3616.74 (O–H medium, broad), 2358.95 (C–N=N strong), 1744.20 (–C=N–), 1687.23 (–C=N–), 1653.00 (–C=N–), 1507.19 (–C–H), 1389.23 (=C–H), 1170.56 (=C–H), 1048.91 (C–H), 973.58 (–C–H), 847.53 (–C–H), 797.61 (–C–H), 677.44 (–C–H),577.97 (Ni–N), 526.65 (Ni–O) cm^{-1}; UV–Vis: $\lambda_{max} = 217–265$ nm; Chemical Formula: $C_{20}H_{16}NiN_6O_2{}^{2+}$, Molecular Weight: 430.07, Elemental Analysis: C, 55.72; H, 3.74; N, 19.50; Ni, 13.62; O, 7.42.

(4Z,4′Z,N′,N″E,N′,N″E)N′,N″(1,3phenylenebis(methanylylidene))diisonicotinohydrazonic acid, copper salt

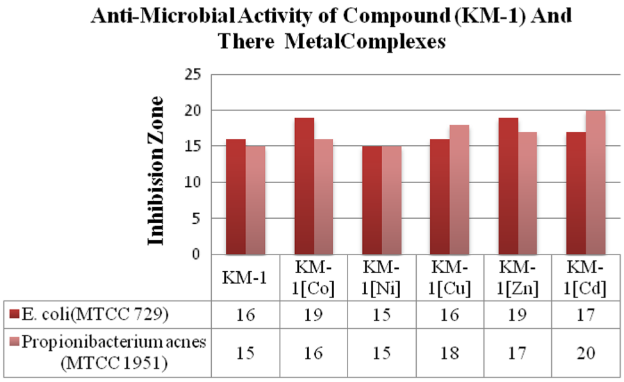


Fig. 1 Anti-Microbial Activity of Compounds (KM-1)

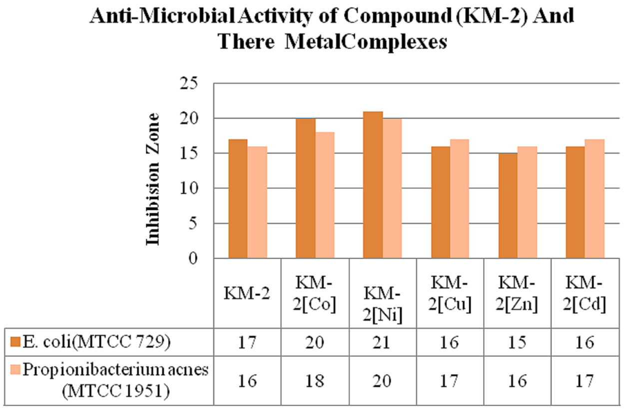


Fig. 2 Anti-Microbial Activity of Compounds (KM-2)

(KM-2[Cu]) Dark green color powder; M. p.: 297–299 °C; Yield: 0.419 g (70%); FT-IR (KBr): $\bar{\nu}=3835.94$ (O–H medium, broad), 3739.61 (O–H medium, broad), 3680.57 (O–H medium, broad), 2358.50 (C–N=N strong), 1686.77 (–C=N–), 1506.07 (–C=N–), 2170.56 (=C–H), 1170.56 (C–H), 1046.86 (–C–H), 972.49 (–C–H), 848.46 (–C–H), 794.04 (–C–H), 679.70 (–C–H), 614.21 (–C–H), 566.72 (Cu–N), 523.64 (Cu–O) cm^{-1}; UV–Vis: $\lambda_{max}=211$–302 nm; Chemical Formula: $C_{20}H_{16}NiN_6O_2^{2+}$, Molecular Weight: 435.07, Elemental Analysis: C, 55.10; H, 3.70; Cu, 14.58; N, 19.28; O, 7.34.

Biological study of compounds and their complexes

The antibacterial study of the explored compounds was carried out by well diffusion method by using Muller Hinton agar. The synthesized ligands and metal complexes were used as antimicrobial agents against bacterial cultures such as *Escherichia coli* (MTCC 729) and *Propionibacterium acnes* (MTCC 1951). First of all, we revived the deep freeze bacterial culture on agar media of Luria burtani agar then inoculated into broth media of Luria burtani and let them stand for 24 h for incubation and at the turbidity of bacterial culture by suspensions of microorganism (0.47 McFarland) solution at 582 nm followed by Preparation of sterilized Muller Hinton agar medium. We picked out the bacterial suspension of broth culture 24 h old turbidity 0.47 and was set at 582 nm and incubated for 10 min. 8 mm wells were prepared aseptically and then the prepared solutions of compounds and complexes (300 PPM/mL) 100/L were filled in each well and let it to incubate at 37 °C for 48 h. The inhibition of bacterial culture is illustrated in Figs. 1 and 2 (Tables 1, 2).

Table 1 Anti-microbial activity of KM-1 and their metal complexes

Entry	Compound and complexes	*Escherichia coli* (MTCC 729) (mm)	*Propionibacterium acnes* (MTCC 1951) (mm)
1	KM-1	16	15
2	KM-1[Co]	19	16
3	KM-1[Ni]	15	15
4	KM-1[Cu]	16	18
5	**KM-1[Zn]**	**19**	17
6	**KM-1[Cd]**	17	**20**

Table 2 Anti-microbial activity of KM-2 and their metal complexes

Entry	Compound and complexes	*Escherichia coli* (MTCC 729) (mm)	*Propionibacterium acnes* (MTCC 1951) (mm)
1	KM-2	17	16
2	KM-2[Co]	20	18
3	**KM-2[Ni]**	**21**	**20**
4	KM-2[Cu]	16	17
5	KM-2[Zn]	15	16
6	KM-2[Cd]	16	17

Electrochemical studies

Electrochemical properties of the complexes were performed on Metrohm Autolab B.V. PGSTAT 128 N controlled with software NOVA version 1.10.1.9., assembled with conventional three electrode system of Ag/AgCl/KCl (3 M) as reference electrode, a platinum wire as counter electrode and glossy carbon electrode as a working electrode Electrochemical analyzer in $K_4[Fe(CN)_6]$ containing 0.1 M KCl as the supporting electrolyte. A cyclic voltammogram of KM-1[Zn] and KM-2[Ni] displays a reduction peak at Epc −0.210 and −0.175 respectively and KM-1[Zn] and KM-2[Ni] displays an oxidation peak at Epa 0.615 and 0.606 respectively. All the reported complexes have same pattern of cyclic voltammograms but the position of KM-1[Zn] and

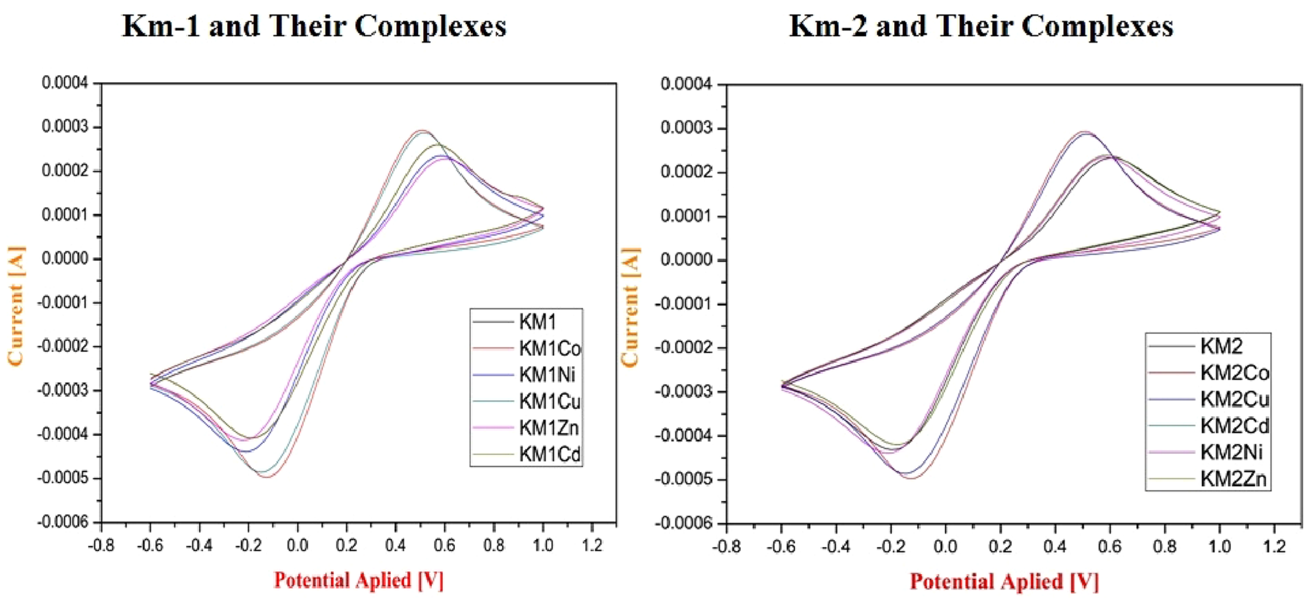


Fig. 3 Cyclic voltammograms of KM-1 and KM-2 and their metal complexes

KM-2[Ni] displays a reduction and oxidation peak different (Fig. 3, Table 3).

Results and discussion

The synthesized Schiff bases (ligands) and their metal complexes was purified as solid and amorphous state, they were stable at room temperature. The prepared ligands were soluble in methanol and DMSO whereas metal complexes were insoluble in methanol and ethanol but soluble in DMSO. Their melting points were determined by electrochemical melting point apparatus.

(1) Infrared (IR) spectral studies

The synthesized compounds show characteristic transitional band; stretching frequency of highly electronegative atom bond with electron withdrawing group show maximum transition band at 3852–3600 cm^{-1} (O–H medium, broad) due to presence of acidic group, the multiple bonded electron withdrawing group show transitional bending frequency at 2358.73 cm^{-1} due to presence of C–N=N strong group. Schiff base formation between aldehyde and amine group is due to imine bond which show stretching frequency at 1687–1655 cm^{-1} because of –C=N– bond and this is significantly shown by the formation of actual product, 1457.30 (=C–H), 1170.88 (=C–H), 1048.87 (=C–H), 973.93 (C–H), 855.56 (C–H), 800.33 (C–H), 680.40 (C–H), 568.18 (M–N), 527.03 (M–O) $cm^{-1.}$

(2) UV–Vis spectral studies

Table 3 Electrochemical study of KM-1 and KM-2 and their metal complexes

Entry	Compounds and complexes	E_{Pc}v	I_{Pc}(A)	E_{Pa}	I_{Pa}(A)
1	KM-1	−0.106	-494×10^{-6}	0.535	287×10^{-6}
2	KM-1[Co]	−0.128	-483×10^{-6}	0.537	284×10^{-6}
3	KM-1[Cu]	−0.145	-400×10^{-6}	0.576	250×10^{-6}
4	KM-1[Zn]	−0.210	-410×10^{-6}	0.615	220×10^{-6}
5	KM-1[Ni]	−0.165	-420×10^{-6}	0.542	227×10^{-6}
6	KM-1[Cd]	−0.172	-407×10^{-6}	0.576	259×10^{-6}
7	KM-2	−0.192	-431×10^{-6}	0.610	233×10^{-6}
8	KM-2[Co]	−0.160	-420×10^{-6}	0.603	237×10^{-6}
9	KM-2[Cu]	−0.160	-415×10^{-6}	0.593	235×10^{-6}
10	KM-2[Zn]	−0.158	-418×10^{-6}	0.579	238×10^{-6}
11	KM-2[Ni]	−0.175	-419×10^{-6}	0.606	239×10^{-6}
12	KM-2[Cd]	−0.153	-416×10^{-6}	0.579	238×10^{-6}

The synthesized ligand (KM-1) phenylenebis-(methanylylidene))bis-(azanylylidene))di-benzoicacid show absorption at $\lambda_{max} = 205–275$ nm found $\pi–\pi^*$ transition of electron in C=N bond and conjugated double in aromatic system similarly in ligand (KM-2)3,3′-((1*E*,1′*E*)-(1,3 and (*E*)-N-((1*H*-indol-3-yl) methylene)-4*H*-1,2,4-triazol-4-amine show absorption on $\lambda_{max} = 205–260$ nm. Complexes of these ligands coordinate with empty d orbital of metal ions form different coordination sphere, complex of Cd having d^9 configuration and show $\lambda_{max} = 260–300$ nm, complex of Co having d^7 configuration and show $\lambda_{max} = 258–$

Table 4 Mass spectroscopic data for Schiff base ligands and some metal complexes

Entry	Sample code	Molecular weight (Calculated) M^+	Molecular peak (Observed) M^+	Molecular peak (Observed) M+1	Molecular peak (Observed) M+2	Molecular peak (Observed) M−1	Molecular peak (Observed) M−3
1	KM-1	372.17	372.32	–	374.13	–	–
2	KM-2	373.13	373.19		375.23	–	–
3	KM-1[Co]	431.31	431.2	–	–	430.19	428.16
4	KM-1[Ni]	431.07	431.07	–	–	430.06	–
5	KM-1[Cu]	435.92	435.72	436.04	–	435.82	
6	KM-2[Cd]	484.79	484.72	485.01	486.7	–	–
7	KM-2[Zn]	437.77	437.77	–	–	463.06	

315 nm, complex of Zn having d^9 configuration and show $\lambda_{max} = 300–306$ nm, complex of Ni having d^8 configuration and show $\lambda_{max} = 265–305$ nm, complex of Cu having d^9 configuration and show $\lambda_{max} = 310–325$ nm.

(3) Nuclear magnetic resonance spectral studies

^{1}HNMR spectra of compound are found as per expected and predicted for structure of ligands. compound having aromatic proton which is shown by the chemical shift on 7.5–7.8 ppm (doublet and multiplet) to determine the ring structure of *m*-pthalaldehyde core of synthesized compound and in benzyl amine ring show chemical shift at 8.10 ppm due to the presence of electron withdrawing group, pyridine ring containing proton show chemical shift at 9.3 (s), 8.1 (s) ppm and this COOH (acidic proton) show chemical shift at 10.0 (s) ppm evidence for presence of acidic group. Schiff base (–CH=N–) proton show chemical shift at 8.1 to 8.5 ppm we determine the formation of bond between aldehyde and amine group.

(4) Mass spectral study

Mass study of synthesized compounds and complex is studies by mass spectroscopy instrument (microOTOF-Q II 10348 MS–ESI on 3000 m/z). These spectral data show fundamental mass peak of (M^+) and some other isotopic peaks (Table 4). In ligand compound KM-1 and KM-2 show M^+ at 372.3 and 373.1 and some other isotopic peaks also. By the complexation of these ligands with di-cationic transition metal ion they form coordination complexes in which KM-1 form bidented and KM-2 form tetra-dented complexes with 1:1 ratio of ligand and metal ion. Mass of these complexes is also analyzed and they give M^+, M ± 1, M ± 2, M ± 3 peaks.

Conclusion

In this study, we have explored some Schiff bases complexes successfully and characterized by IR spectroscopic studies which observed the C=N bond formation with transition frequency in the range 1682 to 1650 cm^{-1}. The FT-IR signals of bond formation between metal and donor atoms such as N or O exhibited in very low transition frequency at 580–540 cm^{-1} and the another important bands described by this technique, too. The UV–Vis spectra provided noteworthy information about the electronic transitions between different energy levels in the wavelengths of 205–330 nm. With help of ^{1}HNMR the presence of Schiff base (–CH=N–) proton was verily confirmed. All of ^{1}HNMR signals proved that similar molecules have been formed. All prepared compounds in this work showed antibacterial properties against pathogenic bacteria. From the results obtained, it is confirmed that these as explored compounds and complexes have a great phramaceutical importance.

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