



Spectroscopic and biological activity studies on tridentate Schiff base ligands and their transition metal complexes

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ABSTRACT

Schiff base ligands are prepared via condensation of pyridine-2,6-dicarboxaldehyde with 2-aminothiophenol (H_2L^1) and 2-aminobenzoic acid (H_2L^2), respectively. The ligands are characterized based on elemental analysis, mass, IR and 1H NMR spectra. Metal complexes are reported and characterized based on elemental analyses, IR, 1H NMR, solid reflectance, magnetic moment, molar conductance, and thermal analyses (TG, DTG and DTA). The molar conductance reveals that all the metal chelates are non-electrolytes except Th(IV) H_2L^2 complex which is 1:1 electrolyte. IR spectra show that H_2L^1 and H_2L^2 ligands behave as neutral tridentate ligands and bind to the metal ions via the two azomethine N and pyridine N. From the magnetic and solid reflectance spectra, it is found that the geometrical structures of these complexes are octahedral (Cr(III)- and Fe(III)- H_2L^1 and H_2L^2 , Th(IV)- H_2L^2 and Mn(II)- H_2L^1 complexes) and trigonal bipyramidal (Co(II), Ni(II), Cu(II), Cd(II) and $UO_2(II)$ - H_2L^1 and H_2L^2 and Mn(II)- H_2L^2 complexes). The thermal behaviour of these chelates is studied using TG and DTA techniques and the activation thermodynamic parameters are calculated using Coats-Redfern method. The synthesized ligands and their metal complexes were screened for their biological activity against bacterial species (*Escherichia coli*, *P. vulgavis*, *B. subtilis* and *S. pyogenes*) and fungi (*F. solani*, *A. niger* and *A. liavus*). The activity data show that the metal complexes have antibacterial and antifungal activity more than the parent Schiff base ligands against one or more bacterial or fungi species.

1. Introduction

The preparation of a new ligand was perhaps the most important step in the development of metal complexes which exhibit unique properties and novel reactivity. Since the electron donor and electron acceptor properties of the ligand, structural functional groups and the position of the ligand in the coordination sphere together with the reactivity of coordination compounds may be the factor for different studies [1]. Schiff bases are an important class of ligands, such ligands and their metal complexes had a variety of applications including biological, clinical, analytical and industrial in addition to their important roles in catalysis and organic synthesis [2-5]. In early work closely related to the system of interest here, Lions and Martin [6] synthesized Schiff base ligands from 2,6-pyridinedicarboxaldehyde (PDC) with aniline and benzylamine and noted that the free ligands were crystalline materials. Therefore, studies ensued in which this same pair of Schiff base linkages was incorporated in many different kinds of polydentate ligands, including various macrocyclic ligands [7,8]. Pursuing the analogy to the Sauvage template, *p*-aminophenol was used as the amine in the straightforward Schiff base condensation reaction with PDC to give the diphenolic ligand. Previous studies on ligands and metal complexes derived from the Schiff bases of *o*- and *p*-

aminophenol are few. In one case, the reaction between PDC and *o*-, *m*- and *p*-aminophenols in the presence of cadmium ions was used to differentiate aminophenol isomers [9] and *p*-aminophenol had appeared in some recent publications as a Schiff base precursor. Two of these studies examined hydrogen-bonding interactions of the phenolic hydrogen [10] while another involved esterification of the phenolic oxygen of the free Schiff base ligand to construct potential metallomesogen components [11]. The X-ray crystal structure of L^1 and its Ni(II) and Zn(II) complexes had been reported by Vance *et al.* [12]. Metal and mixed ligand complexes of L^1 and L^2 ligands have been reported [13,14]. The structures of these ligands are shown in Figure 1. Therefore, in continuation to our interest in Schiff base ligands and their metal chelates [13-15], this work deals with the synthesis and characterization of Schiff base ligands; H_2L^1 and H_2L^2 , and their complexes.

The coordination behaviour of H_2L^1 and H_2L^2 ligands (Figure 2) towards transition metal ions (Fe(II), Co(II), Ni(II), Cu(II) and Zn(II), $UO_2(II)$ and Th(IV)) is investigated via IR, molar conductance, magnetic moment, solid reflectance and thermal analysis. The thermal decomposition of the complexes is also used to infer the structure and different thermodynamic activation parameters are calculated. The biological activity of these Schiff bases and their metal chelates are reported.

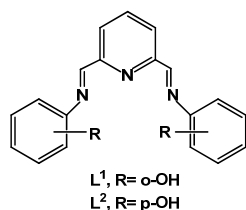


Figure 1. Structure of L¹ and L² ligands.

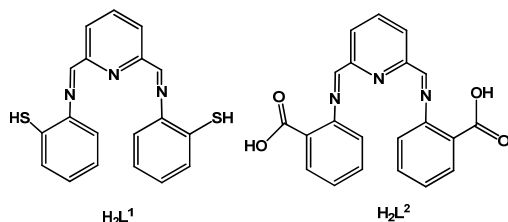


Figure 2. Structure of Schiff bases.

2. Experimental

2.1. Materials and reagents

All chemicals used were of the analytical reagent grade (AR), and of the highest purity available. They included anthranilic acid (Aldrich); 2-aminothiophenol, 2,6-pyridinedicarboxaldehyde (Sigma); ThCl₄.4H₂O (Sigma) and CdCl₂ and CuCl₂.2H₂O (Sigma); UO₂(CH₃COO)₂.2H₂O and FeCl₃.6H₂O (Prolabo); CrCl₃.6H₂O, CoCl₂.6H₂O and NiCl₂.6H₂O (BDH). Zinc oxide, disodium salt of ethylenediaminetetraacetic acid; EDTA; (Analar), ammonia solution (33%, v/v) and ammonium chloride (El-Nasr Pharm. Chem. Co., Egypt). Organic solvents used included absolute ethyl alcohol, diethylether, and dimethylformamide (DMF). These solvents were spectroscopic pure from BDH. Hydrogen peroxide, sodium chloride, sodium carbonate and sodium hydroxide (AR) were used. Hydrochloric and nitric acids (Merck) were used. De-ionized water collected from all glass equipments was usually used in all preparations.

2.2. Solutions

Fresh stock solutions of 1x10⁻³ M ligands; H₂L¹ and H₂L² were prepared by dissolving the accurately weighed amounts of H₂L¹ (0.215 g/L) and H₂L² (0.219 g/L) in the appropriate volume of absolute ethanol. 1x10⁻³ M Stock solutions of the metal salts were prepared by dissolving the accurately weighed amounts of the metal salts in the appropriate volume of de-ionized water. The metal salt solutions were standardized. Dilute solutions of the metal ions and Schiff bases of 2.5x10⁻⁶, 1x10⁻⁶, 2.5x10⁻⁵, 1x10⁻⁵ and 1x10⁻⁴ M were prepared by accurate dilution.

For potentiometric studies, all solutions of metal ions were prepared by dissolving the calculated amount of their salts in the least amount of water, then ethanol was added to the appropriate volume. 0.1 N hydrochloric acid was prepared and standardized using sodium carbonate. 1.0 M sodium chloride solution was also prepared. A 1:1 sodium hydroxide solution was prepared from A.R. product and stored in a well steamed waxed tall glass cylinder and shacked well for some days to obtain a carbonate free sodium hydroxide solution.

2.3. Instrumentations

pH measurements were carried out using 716 DMS Titrimo Metrohm connected with 728 Metrohm Stirrer. Elemental

microanalyses of the separated solid chelates for C, H, N and S were performed in the Microanalytical Center, Cairo University. The analyses were repeated twice to check the accuracy of the results obtained. The molar conductance of solid chelates in DMF was measured using Sybron-Barnstead conductometer (Meter-PM.6, E = 3406). Infrared spectra were recorded on a Perkin-Elmer FT-IR type 1650 spectrophotometer in wave number region 4000-400 cm⁻¹. The spectra were recorded as KBr pellets. The solid reflectance spectra were measured on a Shimadzu 3101pc spectrophotometer. The molar magnetic susceptibility was measured on powdered samples using the Faraday method. The diamagnetic corrections were made by Pascal's constant and Hg[Co(SCN)₄] was used as a calibrant. The mass spectra were recorded by the EI technique at 70 eV using MS-5988 GS-MS Hewlett-Packard instrument in the Microanalytical Center, Cairo University. The ¹H NMR spectra were recorded using 300 MHz Varian-Oxford Mercury. The deuterated solvent used was dimethylsulphoxide (DMSO) and the spectra extended from 0 to 15 ppm. The thermal analyses (TG, DTG and DTA) were carried out in dynamic nitrogen atmosphere (20 mL/min) with a heating rate of 10 °C/min using Shimadzu TG-60H and DTA-60H thermal analyzers. The biological activity was carried out at the Microanalytical center, Cairo University.

2.4. Procedures

2.4.1. Potentiometric measurements

The potentiometric measurements were carried out at 25 °C and at ionic strength $\mu = 0.1$ M by addition the appropriate amounts of 1.0 M sodium chloride solution. The pH-meter was calibrated before each titration using standard buffers. The ionization constants of the investigated Schiff bases and the stability constants of their metal chelates with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Th(IV), and UO₂(II) ions were determined potentiometrically using the technique of Sarin and Munshi [16]. The ionization constants of the ligands are calculated using the equation used by Irving and Rossotti [17]. While metal-ligand stability constants were calculated using methods applied for computing successive stability constants [18].

2.4.2. Synthesis of Schiff bases (H₂L¹ [20], H₂L²)

A hot solution (60 °C) of 2-aminothiophenol (1.85 g, 14.82 mmol) or 2-aminobenzoic acid (2.44 g, 17.78 mmol) in 25 mL ethanol was mixed with a hot solution (60 °C) of 2,6-pyridinedicarboxaldehyde (1.00 and 1.20 g, 7.41 and 8.89 mmol) for H₂L¹ and H₂L², respectively, and the reaction mixture was left under reflux for 4 h. The formed solid product was separated by filtration, purified by crystallization from ethanol, washed with diethyl ether and dried under vacuum over anhydrous calcium chloride. The yellow Schiff base products; H₂L¹ and H₂L², were produced in 85 and 87% yield, respectively.

2.4.3. Synthesis of metal complexes

The metal complexes of the Schiff bases were prepared by the addition of a hot solution (60 °C) of the appropriate metal chloride or acetate (1 mmol) in an ethanol-water mixture (1:1, 25 mL) to a hot ethanolic solution (60 °C) of the Schiff bases (0.30 g H₂L¹ or H₂L²; 25 mL). The resulting mixture was stirred under reflux for 1 h whereupon the complexes were precipitated. They were collected by filtration, washed several times with an ethanol-water mixture (1:1) and diethyl ether. The analytical data for C, H and N were repeated twice.

2.4.4. Determination of the metal content of the chelates

The metal contents were determined complexometrically by titration against standard EDTA solution at a suitable pH value using the suitable indicator.

2.5. Biological activity

Antimicrobial activity of the tested samples was determined using a modified Kirby-Bauer disc diffusion method [20]. 100 μ L of the tested bacteria or fungi were grown in 10 mL of fresh media until they reached a count of approximately 108 cells/mL for bacteria and 105 cells/mL for fungi [21]. 100 μ L of microbial suspension was spread onto agar plates corresponding to the broth in which they were maintained. Isolated colonies of each organism that might be playing a pathogenic role should be selected from primary agar plates and tested for susceptibility by disc diffusion method [22]. Of the many media available, NCCLS recommends Mueller-Hinton agar due to its results in good batch-to-batch reproducibility. Disc diffusion method for filamentous fungi tested by using approved standard method (M38-A) developed [23]. For evaluating the susceptibilities of filamentous fungi to antifungal agent, plates inoculated with filamentous fungi as *Aspergillus flavus* at 25 °C for 48 h were prepared. Gram (+) bacteria as *Staphylococcus aureus* and Gram(-) bacteria as *Escherichia coli* were incubated at 35-37 °C for 24-28 h. Yeast as *Candida albicans* was also incubated at 30 °C for 24-28 h. The diameters of the inhibition zones were measured in millimeters [24]. Standard discs of tetracycline (antibacterial agent), and amphotericin B (antifungal agent) served as positive controls for antimicrobial activity but filter discs impregnated with 10 μ L of solvent (distilled water, chloroform, DMSO) were used as a negative control. The agar used is Mueller-Hinton agar that is rigorously tested for composition and pH. Further the depth of the agar in the plate is a factor to be considered in the disc diffusion method. This method is well documented and standard zones of inhibition have been determined for susceptible and resistant values. Blank paper disks (Schleicher and Schuell, Spain) with a diameter of 8.0 mm were impregnated with 10 μ L of tested concentration of the stock solutions. When a filter paper disc impregnated with a tested chemical is placed on agar, the chemical will diffuse from the disc into the agar. This diffusion will place the chemical in the agar only around the disc. The solubility of the chemical and its molecular size will determine the size of the area of chemical infiltration around the disc. If an organism is placed on the agar, it will not grow in the area around the disc if it is susceptible to the chemical. This area of no growth around the disc is known as zone of inhibition or clear zone. For the disc diffusion, the zone diameters were measured with slipping calipers of the national committee for clinical laboratory standards [25]. Agar based methods such E test and disc diffusion can be good alternatives because they are simpler and faster than broth-based methods [26,27].

3. Results and discussion

3.1. Characterization of Schiff bases

The synthesized Schiff bases are subjected to elemental analyses, mass, IR and ^1H NMR spectroscopy. The results of elemental analyses (C, H and N) with molecular formulae and the melting points are presented in Tables 1 and 2. The results obtained are in good agreement with those calculated for the suggested formulae (Figure 2) and the melting point is sharp indicating the purity of the prepared Schiff bases.

3.2. Mass spectra of the Schiff bases

The electron impact mass spectra of H_2L^1 and H_2L^2 ligands are recorded and investigated at 70 eV of electron energy. The mass spectra of the studied Schiff bases are characterized by moderate to high relative intensity molecular ion peaks. The mass spectrum of H_2L^1 , and the possible molecular ion peaks with their respective relative intensities are shown in Scheme 1. Fragments at $m/z = 187$ (R.I. = 100 %, base peak) may be due to $\text{C}_{11}\text{H}_8\text{NS}$ ion. The other molecular ion peaks appeared in the mass spectrum (abundance range from 2-100 %) is attributed to the fragmentation of H_2L^1 molecule obtained from the rupture of different bonds inside the molecule. The mass spectra of H_2L^2 and the molecular ion peaks of the different suggested fragments are shown in Scheme 2. H_2L^2 shows a parent peak at $m/z = 373$ with a relative intensity = 11 %. Fragment at $m/z = 69$ (R.I. = 94 %, base peak) is attributed to $\text{C}_3\text{H}_2\text{O}_2$ ion.

3.3. Potentiometric determination of the ionization constants

The ionization constants of the ionizable groups in Schiff bases under investigation are determined by a method similar to that described by Sarin and Munshi [16]. The average of protons associated with the ligand (\bar{n}_A) at different pH values is calculated utilizing acid and ligand titration curves. The pK_a values can be calculated from the curves obtained by plotting \bar{n}_A versus pH. The formation curves are found between 0 and 1. This indicates that the ligands have one dissociable proton which is from the SH (ligand H_2L^1) and COOH groups (ligand H_2L^2). The pK_a values of 9.56 ($\Delta G^\circ = -54.11$ KJ/mol) and 6.81 ($\Delta G^\circ = -38.44$ KJ/mol) are attributed to the ionization of SH and COOH protons in the ligands, H_2L^1 and H_2L^2 , respectively. The free energy change is also calculated and the negative values indicate the spontaneous character of association reaction.

3.4. Potentiometric determination of the stability constants

The stability constants of the Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Th(IV) and $\text{UO}_2(\text{II})$ complexes with H_2L^1 and H_2L^2 are determined potentiometrically using the method described by Sari [28] and Bjerrum [29].

The formation curves of the investigated complexes are obtained by plotting a graph between the average number of ligands attached per metal ion (\bar{n}) and the free ligand exponent (pL). Values of \bar{n} and pL are calculated. The maximum \bar{n} values calculated for metal-ligand system are found not to exceed two indicating the formation of 1:1 and 1:2 (metal: ligand) complexes. The mean $\log \beta_1$ and $\log \beta_2$ values of the Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Th(IV) and $\text{UO}_2(\text{II})$ complexes with H_2L^1 and H_2L^2 are listed in Table 3.

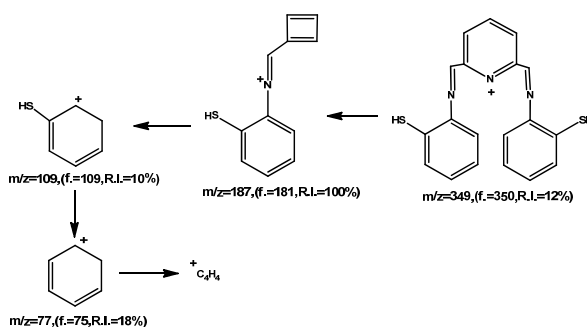
The order of stability constants is found to be $\text{Zn(II)} < \text{Cu(II)} > \text{Ni(II)} > \text{Co(II)} > \text{Mn(II)}$ and $\text{Cr(III)} > \text{UO}_2 = \text{Fe(III)} = \text{Th(IV)} = \text{Cd(II)}$ in accordance with the Irving and Williams order [30] for divalent metal ions of the 3d series. It is clear from Table 3 that the stability of Cu(II) complexes is considerably larger as compared to other metals of the 3rd series. Under the influence of the ligand field, Cu(II) ($3d^9$) will receive some extra stabilization [31] due to tetragonal distortion of octahedral symmetry in their complexes. The Cu(II) complexes will be further stabilized due to the Jahn-Teller effect [32]. One would expect a bigger difference between $\log K_1$ and $\log K_2$ values in such ligands because possible steric hindrance to the linking of the second ligand to the metal ion. The small difference may be due to trans-structure. The free energy of formation, ΔG° accompanying the complexation reaction has been determined at 25 °C.

Table 1. Analytical and physical data of H₂L¹ ligand and its complexes.

| Compound | Colour (Yield, %) | M.p. (°C) | % Found (Calcd.) | | | | | $\mu_{\text{eff.}}$ (B.M.) | Λ_m $\Omega^{-1}\text{mol}^{-1}\text{cm}^2$ |
|--------------------------------------------------------------------------------------------------------|-------------------|-----------|------------------|--------|---------|---------|---------|----------------------------|-----------------------------------------------------|
| | | | C | H | N | S | M | | |
| H ₂ L ¹ | Brown | 190 | 65.68 | 4.53 | 12.32 | 18.90 | - | - | |
| C ₁₉ H ₁₅ N ₃ S ₂ | (85) | | (65.32) | (4.29) | (12.03) | (18.33) | | | |
| [Cr(H ₂ L ¹)(H ₂ O) ₃]Cl ₃ | Grey | 150 | 41.02 | 3.61 | 7.31 | 11.12 | 9.01 | 4.12 | |
| C ₁₉ H ₂₁ Cl ₃ CrN ₃ S ₂ O ₃ | (88) | | (40.60) | (3.73) | (7.47) | (11.39) | (9.26) | | |
| [Mn(H ₂ L ¹)Cl ₂]-2H ₂ O | Green | 145 | 44.49 | 4.12 | 8.15 | 12.31 | 10.56 | 3.30 | |
| C ₁₉ H ₁₉ MnCl ₂ N ₃ S ₂ O ₂ | (75) | | (44.62) | (3.71) | (8.22) | (12.52) | (10.74) | | |
| [Fe(H ₂ L ¹)(H ₂ O) ₃]Cl ₃ ·H ₂ O | black | 110 | 39.45 | 4.19 | 7.59 | 11.52 | 9.24 | 5.83 | |
| C ₁₉ H ₂₃ Cl ₃ FeN ₃ S ₂ O ₄ | (96) | | (39.08) | (3.94) | (7.20) | (10.97) | (9.56) | | |
| [Co(H ₂ L ¹)Cl ₂]-H ₂ O | Black | 110 | 45.69 | 3.25 | 8.76 | 13.07 | 11.63 | 4.49 | |
| C ₁₉ H ₁₇ Cl ₂ CoN ₃ OS ₂ | (76) | | (45.88) | (3.42) | (8.45) | (12.87) | (11.85) | | |
| [Ni(H ₂ L ¹)Cl ₂]-H ₂ O | Green | >300 | 45.85 | 3.69 | 8.36 | 12.65 | 11.53 | 3.73 | |
| C ₁₉ H ₁₇ Cl ₂ NiN ₃ S ₂ O | (83) | | (45.90) | (3.42) | (8.45) | (12.88) | (11.81) | | |
| Cu(H ₂ L ¹)Cl ₂ ·4H ₂ O | Black | 115 | 40.93 | 3.79 | 7.44 | 11.76 | 11.55 | 2.01 | |
| C ₁₉ H ₂₃ Cl ₂ CuN ₃ S ₂ O ₄ | (86) | | (41.04) | (4.14) | (7.56) | (11.52) | (11.43) | | |
| [Cd(H ₂ L ¹)Cl ₂]-4H ₂ O | Green | 240 | 37.89 | 3.66 | 6.65 | 10.22 | 18.33 | Diam. | |
| C ₁₉ H ₂₃ Cl ₂ CdN ₃ S ₂ O ₄ | (84) | | (37.72) | (3.80) | (6.94) | (10.58) | (18.59) | | |
| [UO ₂ (H ₂ L ¹)(CH ₃ COO) ₂]-H ₂ O | Green | 120 | 36.35 | 3.15 | 5.43 | 8.32 | 31.39 | Diam. | |
| C ₂₃ H ₂₃ N ₃ S ₂ O ₇ U | (80) | | (36.55) | (3.04) | (5.56) | (8.47) | (31.52) | | |

Table 2. Analytical and physical data of H₂L² ligand and its complexes.

| Compound | Colour (Yield, %) | M.p. (°C) | % Found (Calcd.) | | | | $\mu_{\text{eff.}}$ (B.M.) | Λ_m $\Omega^{-1}\text{mol}^{-1}\text{cm}^2$ |
|--------------------------------------------------------------------------------------------------------|-------------------|-----------|------------------|--------|---------|---------|----------------------------|-----------------------------------------------------|
| | | | C | H | N | M | | |
| H ₂ L ² | Brownish | 80 | 7.34 | 4.23 | 11.50 | - | - | |
| C ₂₁ H ₁₅ N ₃ O ₄ | (80) | | (67.56) | (4.02) | (11.26) | | | |
| [Cr(H ₂ L ²)Cl ₃]-3H ₂ O | Grey | 50 | 43.52 | 3.24 | 7.34 | 8.67 | 4.42 | |
| C ₂₁ H ₂₁ Cl ₃ CrN ₃ O ₇ | (91) | | (43.04) | (3.58) | (7.17) | (8.88) | | |
| [Mn(H ₂ L ²)(H ₂ O)Cl ₂]-3H ₂ O | yellowish | 150 | 4.39 | 4.13 | 7.67 | 9.42 | 3.01 | |
| C ₂₁ H ₂₃ Cl ₂ MnN ₃ O ₈ | (86) | | (44.14) | (4.02) | (7.35) | (9.61) | | |
| [Fe(H ₂ L ²)Cl ₃] | Black | >300 | 7.26 | 3.10 | 8.12 | 10.23 | 5.51 | |
| C ₂₁ H ₁₅ Cl ₃ FeN ₃ O ₄ | (86) | | (47.07) | (2.80) | (7.84) | (10.42) | | |
| [Co(H ₂ L ²)Cl ₂]-2H ₂ O | Blue | 100 | 6.54 | 3.28 | 7.46 | 10.21 | 4.91 | |
| C ₂₁ H ₁₉ Cl ₂ CoN ₃ O ₆ | (80) | | (46.76) | (3.52) | (7.79) | (10.92) | | |
| [Ni(H ₂ L ²)Cl ₂]-4H ₂ O | Green | 190 | 3.70 | 3.96 | 7.55 | 10.15 | 3.17 | |
| C ₂₁ H ₂₃ Cl ₂ NiN ₃ O ₈ | (71) | | (43.84) | (4.00) | (7.30) | (10.21) | | |
| [Cu(H ₂ L ²)Cl ₂]-3H ₂ O | Green | 170 | 5.16 | 4.01 | 7.30 | 11.14 | 1.96 | |
| C ₂₁ H ₂₁ Cl ₂ CuN ₃ O ₇ | (84) | | (44.87) | (3.73) | (7.47) | (11.30) | | |
| [Cd(H ₂ L ²)Cl ₂]-3H ₂ O | Yellowish | 105 | 1.56 | 3.52 | 6.70 | 18.35 | Diam. | |
| C ₂₁ H ₂₁ Cl ₂ CdN ₃ O ₇ | (79) | | (41.28) | (3.44) | (6.88) | (18.41) | | |
| [Th(H ₂ L ²)Cl ₃]Cl | Brownish | 170 | 3.49 | 2.31 | 5.41 | 31.16 | Diam. | |
| C ₂₁ H ₁₅ Cl ₄ ThN ₃ O ₄ | (83) | | (33.73) | (2.00) | (5.62) | (31.05) | | |
| [UO ₂ (H ₂ L ²)(CH ₃ COO) ₂]-H ₂ O | Yellow | >300 | 8.63 | 3.13 | 5.26 | 30.75 | Diam. | |
| C ₂₅ H ₂₃ N ₃ O ₁₁ U | (83) | | (38.51) | (2.95) | (5.39) | (30.55) | | |

**Scheme 1**

The results are given in Table 3. From the table, it is apparent that the negative values of ΔG° show that the driving tendency of the complexation reaction is from left to right and the reaction proceeds spontaneously.

3.5. Composition and structures of Schiff base complexes

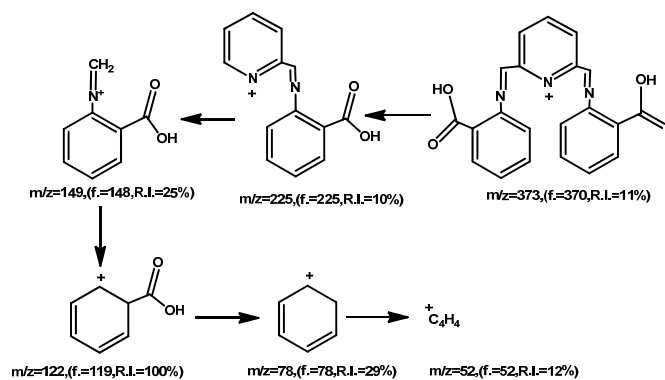
Although H₂L¹ [20] ligand is previously prepared but no studies concerning its Cr(III), Fe(III), Cu(II), Cd(II), Th(IV) and UO₂(II) complexes are given. In addition, the stability constants of the metal complexes of and H₂L¹ ligands and thermal stability of metal complexes of H₂L¹ ligand are not previously

reported. On screening the literature survey, the biological activities are not studied. So the main target of our work is to prepare the solid complexes of these ligands and carrying out their complete characterization using different physico-chemical techniques together with studying their biological activities. The isolated complexes were subjected to elemental analyses (C, H, N, S and metal content), infrared spectral studies (IR), nuclear magnetic resonance (¹H NMR), magnetic studies, molar conductance and thermal analyses (TG, DTG and DTA), to identify their tentative formulae in a trial to elucidate their molecular structures.

Table 3. Cumulative data of $\log \beta_1$ and $\log \beta_2$ values for H_2L^1 and H_2L^2 complexes*.

| Complexes | $\log \beta_1$ | | | | $\log \beta_2$ | | | | |
|------------|----------------|-------|-------|----------------------------|----------------|-------|-------|-------|----------------------------|
| | A | B | M | $-\Delta G^\circ$ (KJ/mol) | A | B | C | M | $-\Delta G^\circ$ (KJ/mol) |
| H_2L^1 | | | | | | | | | |
| Cr(III) | 9.93 | 10.62 | 10.27 | 57.30 | 19.31 | 20.03 | 19.63 | 19.65 | 109.6 |
| Mn(II) | 9.95 | 10.65 | 10.30 | 57.46 | 19.36 | 20.07 | 19.69 | 19.70 | 109.9 |
| Fe(III) | 9.91 | 10.60 | 10.25 | 57.19 | 19.27 | 19.96 | 19.58 | 19.60 | 109.4 |
| Co(II) | 9.96 | 10.67 | 10.31 | 57.52 | 19.38 | 20.09 | 19.71 | 19.72 | 110.0 |
| Ni(II) | 9.99 | 10.73 | 10.36 | 57.80 | 19.43 | 20.13 | 19.75 | 19.77 | 110.3 |
| Cu(II) | 10.10 | 10.76 | 10.43 | 58.19 | 19.52 | 20.14 | 19.81 | 19.82 | 110.6 |
| Zn(II) | 9.98 | 10.68 | 10.33 | 57.63 | 19.40 | 20.11 | 19.72 | 19.74 | 110.1 |
| Cd(II) | 9.88 | 10.19 | 10.03 | 55.96 | 19.22 | 19.53 | 19.50 | 19.41 | 108.3 |
| Th(IV) | 9.89 | 10.20 | 10.04 | 56.01 | 19.24 | 19.55 | 19.56 | 19.45 | 108.5 |
| $UO_2(II)$ | 9.92 | 10.61 | 10.26 | 57.24 | 19.29 | 19.98 | 19.62 | 19.63 | 110.0 |
| H_2L^2 | | | | | | | | | |
| Cr(III) | 6.38 | 7.16 | 6.77 | 37.77 | 12.54 | 13.17 | 13.41 | 13.04 | 72.8 |
| Mn(II) | 6.44 | 7.18 | 6.81 | 37.99 | 12.63 | 13.23 | 13.42 | 13.09 | 73.0 |
| Fe(III) | 6.33 | 7.11 | 6.72 | 37.49 | 12.40 | 13.06 | 13.39 | 12.95 | 72.3 |
| Co(II) | 6.45 | 7.21 | 6.83 | 38.10 | 12.66 | 13.27 | 13.43 | 13.12 | 73.2 |
| Ni(II) | 6.58 | 7.26 | 6.92 | 38.61 | 12.79 | 13.37 | 13.44 | 13.20 | 73.7 |
| Cu(II) | 6.68 | 7.36 | 7.02 | 39.16 | 12.89 | 13.42 | 13.48 | 13.26 | 74.0 |
| Zn(II) | 6.54 | 7.24 | 6.89 | 38.44 | 12.72 | 13.33 | 13.45 | 13.16 | 73.4 |
| Cd(II) | 6.20 | 6.85 | 6.52 | 36.37 | 11.76 | 12.47 | 12.66 | 12.29 | 68.6 |
| Th(IV) | 6.30 | 7.08 | 6.69 | 37.32 | 12.33 | 13.02 | 13.32 | 12.89 | 72.0 |
| $UO_2(II)$ | 6.35 | 7.13 | 6.74 | 37.6 | 12.49 | 13.12 | 13.40 | 13.00 | 72.6 |

* (A) Interpolation at half values method, (B) Correction-term method, (C) Mid-point method.



3.6. Elemental analyses of the complexes

The results of elemental analyses, Tables 1 and 2 are in good agreement with those required by the proposed formulae.

3.7. Molar conductivity measurements

Tables 1 and 2 show the molar conductance values of the complexes. It is found that Fe(III) and Cr(III) chelates have molar conductance values of 365 and 370 $\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ of H_2L^1 , respectively. While Fe(III) and Cr(III) chelates of H_2L^2 ligand have molar conductance values of 16.35 and 18.50 $\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$, respectively. This indicates bonding of the chloride anions to the Fe(III) and Cr(III) ions. So, the Fe(III) and Cr(III) chelates are considered as non-electrolytes with H_2L^2 ligand.

On the other hand, the molar conductivity values of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) chelates of H_2L^1 and H_2L^2 ligands ($\Lambda_m = 13.52 - 30.04 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$) indicate that these complexes are non-electrolytes. While $UO_2(II)$ complexes of H_2L^1 and H_2L^2 ligands have molar conductivity values of 22.20 and 20.31 $\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$, respectively, which indicates the non-ionic nature of these complexes and hence they are considered as non-electrolytes. Th(IV) complex of H_2L^2 ligand has molar conductivity value 95 $\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$, indicating its ionic nature and of the type 1:1 electrolyte.

3.8. IR spectral studies

H_2L^1 and H_2L^2 Schiff base ligands are of significant interest from the point of view that they act as a pincer ligands, often found as a meridional ligand (i.e. the three nitrogen atoms possess will be approximately coplanar in metal coordination sphere) and exhibited a great variety of coordination modes with different coordinating power and these may give rise to varied bonding and different stereochemical patterns in their coordination complexes as a result for competition between the thiophenolic, carboxylic and azomethine nitrogen groups as a coordination sites [33,34]. The compounds containing a pyridinium moiety attached to a heterocyclic system are important in natural product chemistry and in organic synthesis [35]. This would lead us to obtain some new heterocyclic compounds with expected wide spectrum of potential applications that were extensively required for medicinal chemistry program.

The data of the IR spectra of Schiff base ligands (H_2L^1 , and H_2L^2) and their complexes are listed in Tables 4 and 5. The IR spectra of the complexes are compared with those of the free ligands in order to determine the coordination sites that may involved in chelation. The strong bands located at 1578 and 1586 cm^{-1} are assigned to the $\nu(\text{C}=\text{N})$ stretching vibrations of pyridyl nitrogen of the H_2L^1 and H_2L^2 ligands.

Table 4. IR data (4000-400 cm⁻¹) of H₂L¹ ligand and its metal complexes*.

| Compound | $\nu(\text{OH})$ (hydrated water) | $\nu(\text{S-H})$ | $\nu(\text{C=N})$ (azomethine) | $\nu(\text{C=N})$ (pyridine) | $\nu(\text{C-S})$ (symm.) | $\nu(\text{C-S})$ (asymm.) | $\delta(\text{C=N})$ (pyridine) | $\nu(\text{M-O})$ (coord. water) | $\nu(\text{M-N})$ |
|--------------------------------------------------------------------------------------------------------|--------------------------------------|-------------------|-----------------------------------|---------------------------------|------------------------------|-------------------------------|------------------------------------|-------------------------------------|-------------------|
| H ₂ L ¹ | - | 2370m | 1612sh | 1578sh | 751sh | 699sh | 647m | - | - |
| [Cr(H ₂ L ¹)(H ₂ O) ₃]Cl ₃ | 3379s | 2390sh | 1607sh | 1555sh | 762sh | 680sh | 680m | 516m | 450m |
| [Mn(H ₂ L ¹)Cl ₂]-2H ₂ O | Disapp | 2400sh | 1595sh | 1562br | 764sh | 720sh | 654m | Disapp. | 419m |
| [Fe(H ₂ L ¹)(H ₂ O) ₃]Cl ₃ ·H ₂ O | 3378br | 2375sh | 1651br | 1617sh | 763sh | 681sh | 625m | 597m | 430m |
| [Co(H ₂ L ¹)Cl ₂]-H ₂ O | Disapp | 2371sh | 1612sh | 1584sh | 765sh | 731sh | 674m | Disapp. | 425m |
| [Ni(H ₂ L ¹)Cl ₂]-H ₂ O | Disapp | Disapp | 1605sh | 1550sh | 762sh | 675sh | 675m | Disapp. | 423m |
| Cu(H ₂ L ¹)Cl ₂ ·4H ₂ O | Disapp | 2369sh | 1619sh | 1578sh | 765sh | 735sh | 685m | Disapp. | 424m |
| [Cd(H ₂ L ¹)Cl ₂]-4H ₂ O | Disapp | 2342sh | 1609sh | 1609sh | 762sh | 710sh | 660m | Disapp. | 450m |
| [UO ₂ (H ₂ L ¹)(CH ₃ COO) ₂]-H ₂ O | Disapp | 2373s | 1608br | 1566sh | 755sh | 730sh | 667m | 548m | 413m |

*sh = sharp, m = medium, br = broad, s = small, w = weak.

Table 5. IR data (4000-400 cm⁻¹) of H₂L² ligand and its metal complexes*.

| Compound | $\nu(\text{OH})$ (carboxylic) | $\nu(\text{C=O})$ (carboxylic) | $\nu(\text{C=N})$ (azomethine) | $\nu(\text{C=N})$ (pyridine) | $\nu(\text{COO})$ (asym.) | $\nu(\text{COO})$ (sym.) | $\delta(\text{C=N})$ (pyridine) | $\nu(\text{M-O})$ (carboxylic) | $\nu(\text{M-N})$ |
|--------------------------------------------------------------------------------------------------------|----------------------------------|-----------------------------------|-----------------------------------|---------------------------------|------------------------------|-----------------------------|------------------------------------|-----------------------------------|-------------------|
| H ₂ L ² | 3374sh | 1740w | 1618sh | 1586sh | 1586sh | 1485 | 656m | - | - |
| [Cr(H ₂ L ²)Cl ₃]-3H ₂ O | 3403br | 1750w | 1691br | 1627br | 1521s | 1397sh | 686sh | 562w | 446s |
| [Mn(H ₂ L ²)(H ₂ O)Cl ₂]-3H ₂ O | 3403sh | 1745sh | 1591sh | 1593sh | 1591sh | 1390s | 689br | 530s | 425s |
| [Fe(H ₂ L ²)Cl ₃] | 3400br | Disapp | 1627br | 1585sh | 1564s | 1418s | 656sh | 554s | 418s |
| [Co(H ₂ L ²)Cl ₂]-2H ₂ O | 3421br | 1705sh | 1622sh | 1570sh | 1570s | 1390sh | 685br | 535w | 433s |
| [Ni(H ₂ L ²)Cl ₂]-4H ₂ O | 3422br | 1718sh | 1628sh | 1569sh | 1569s | 1392sh | 685m | 561br | 424s |
| [Cu(H ₂ L ²)Cl ₂]-3H ₂ O | 3404sh | 1740w | 1626sh | 1554sh | 1554sh | 1471sh | 686sh | 526s | 422s |
| [Cd(H ₂ L ²)Cl ₂]-3H ₂ O | 3336br | 1715sh | 1618sh | 1583br | 1587s | 1384sh | 650m | 530s | 432s |
| [Th(H ₂ L ²)Cl ₃]Cl | 3404br | Disapp | 1625 | 1557br | 1557s | 1387sh | 688m | 525s | 421s |
| [UO ₂ (H ₂ L ²)(CH ₃ COO) ₂]-H ₂ O | 3436br | Disapp | 1607br | 1567sh | 1567sh | 1360sh | 689br | 542w | 445s |

*sh = sharp, m = medium, br = broad, s = small, w = weak.

These bands are shifted to 1550-1617 and 1554-1627 cm⁻¹ for H₂L¹ and H₂L² metal complexes, respectively [14]. The sharp IR ligand bands at 647 and 656 cm⁻¹ are assigned to the $\delta(\text{C=N})$ of pyridine for H₂L¹, and H₂L² ligands, respectively [14]. These bands are shifted to 650-680, and 650-689 for H₂L¹, and H₂L² metal complexes, respectively. The strong and sharp band of $\nu(\text{C=N})$ stretching vibration of the azomethine is found at 1612 and 1618 cm⁻¹ for H₂L¹ and H₂L², respectively. These bands are found at 1595-1651 and 1591-1691 cm⁻¹ in the H₂L¹ and H₂L² complexes, respectively, indicating the participation of the azomethine nitrogen in coordination (M-N) [13,14,35,36]. The $\nu(\text{OH})$, $\nu(\text{C=O})$, $\nu_{\text{asym}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$ stretching vibrations of the carboxylate O are observed at 3374, 1740, 1586 and 1485 cm⁻¹ for H₂L² ligand, respectively. These stretching vibrations are disappeared or shifted to higher or lower frequencies at 3336-3422, 1705-1750, 1521-1591 and 1360-1471 cm⁻¹ for H₂L²-metal complexes. These blue or red shifts may attribute to hydrogen bond formation [13,14]. The SH, $\nu_{\text{sym}}(\text{CS})$ and $\nu_{\text{asym}}(\text{CS})$ stretching vibrations are observed at 2370, 699 and 751 cm⁻¹ for H₂L¹ ligand, respectively. While in complexes, these bands are disappeared or shifted to lower or higher wavenumbers in the spectra at 2342-2400, 675-735 and 755-765 cm⁻¹ for H₂L¹ complexes may attributed to hydrogen bond formation [13,14]. New bands are found in the spectra of the complexes in the regions 516-597 (coordinated water O), and 530-542 (coordinate water and AcO) which are assigned to $\nu(\text{M-O})$ stretching vibrations for H₂L¹ and H₂L² metal complexes, respectively. The bands at 413-450 and 418-446 cm⁻¹ for H₂L¹ and H₂L² metal complexes, respectively, have been assigned to $\nu(\text{M-N})$ mode [14,37]. Therefore, from the IR spectra, it is concluded that H₂L¹ and H₂L² ligands behave as neutral tridentate ligands and bind to the metal ions via the two azomethine N and pyridine N.

The other series of weak bands between 3100 and 2800 cm⁻¹ are related to (C-H) modes of vibrations. Also, some weak bands located between 2000 and 1750 cm⁻¹ can be assigned to overtones of the aromatic rings. The shift to higher or lower wavenumbers can be attributed to important hydrogen bonding effects [12-14,37]. Most of the band shifts observed at the wave number region 1150-994 cm⁻¹ are in agreement with the structural changes observed in the molecular carbon

skeleton after complexation, which cause some important changes in (C-C) bond lengths.

3.9. ¹H NMR spectra

The NMR spectra of Schiff base and its Cd(II) complex are recorded in dimethylsulphoxide (DMSO-*d*₆) solution using tetramethylsilane (TMS) as an internal standard. The spectrum of the complex is examined in comparison with those of the parent Schiff base. Upon examinations it is found that the SH signal, appeared in the spectrum of H₂L¹ ligand at 4.03 ppm, is found in the spectrum of its Cd(II) complex at 4.10 ppm indicating that the SH proton is not participated in the chelation with metal ion. The COOH signal is found at 13.45 ppm in the spectrum of H₂L² ligand. This signal is deshielded at 13.40 ppm of Cd(II) complex. This indicates the non-involvement of the COOH group in chelation while its involvement in hydrogen bond formation.

3.10. Magnetic susceptibility and electronic spectral studies

The diffused reflectance spectra of Cr(III) chelates for H₂L¹ and H₂L² ligands exhibit bands at 21,047-23,741 which may be assigned to the ⁶A_{1g} → ⁴T_{2g} (G) transition in octahedral geometry of the complexes [38]. The ⁶A_{1g} → ⁵T_{1g} transition appears to be split into two bands at 15,348-16,452 cm⁻¹. The observed magnetic moments of Cr(III) complexes are 4.12 and 4.42 B.M. Thus, the complexes formed have the octahedral geometry involving sp³d² hybridization [15]. The spectra also show bands at 24,721-25,641 cm⁻¹ which may be attributed to ligand-metal charge transfer. While spectra of the Mn(II) complexes show three bands at 15,378-16,025, 21,839-22,056 and 26,577-27,330 cm⁻¹ assignable to ⁴T_{1g} → ⁶A_{1g}, ⁴T_{2g}(G) → ⁶A_{1g} and ⁴T_{1g}(D) → ⁶A_{1g} transitions, respectively [39]. The magnetic moment values are 4.80, and 3.01 B.M. for Mn-H₂L¹, and Mn-H₂L² complexes, respectively, which indicate the presence of Mn(II) ions in octahedral structure for H₂L¹ and in trigonal bipyramidal in H₂L². From the diffused reflectance spectra it is observed that, the Fe(III) chelates exhibit bands at 21,491-22,026 cm⁻¹ which may be assigned to the ⁶A_{1g} → ⁴T_{2g} (G) transition in octahedral geometry [38,15].

Table 6. Thermoanalytical results (TG, DTG and DTA) of H₂L¹ ligand and its metal complexes.

| Complex | TG range (°C) | DTG _{max} (°C) | Peak temp. In DTA (°C) | n* | Total mass loss Estim (Calcd)% | Assignment | Metallic residue |
|--------------------------------------------------------------------------------------------------------|---------------|-------------------------|------------------------|----|--------------------------------|----------------------------------------------------------------------------------|----------------------------------|
| H ₂ L ¹ | 180-390 | 225 | | 1 | 39.34 (39.00) | - Loss of C ₇ H ₆ NS. | - |
| | 390-580 | 400 | | 1 | 32.41 (33.23) | - Loss of C ₇ H ₄ N ₂ . | |
| | 580-1000 | 780 | | 1 | 28.25 (27.80) | - Loss of C ₅ H ₅ S. | |
| [Fe(H ₂ L ¹)(H ₂ O) ₃].Cl ₃ .H ₂ O | 30-160 | 70, 140 | 60(+), 130(-) | 2 | 8.94 (9.68) | - Loss of H ₂ O and HCl. | ½ Fe ₂ O ₃ |
| | 160-450 | 390 | 260(+), 610(+) | 1 | 32.13 (31.15) | - Loss of C ₆ H ₄ S. | |
| | 450-640 | 600 | | 1 | 46.68 (47.50) | - Loss of C ₁₃ H ₁₂ N ₃ SO _{1.5} . | |
| [UO ₂ (H ₂ L ¹)(CH ₃ COO) ₂].H ₂ O | 30-350 | 73, 180 | 50(+), 250(+), | 3 | 16.14 (16.48) | - Loss of H ₂ O, 2CO ₂ and C ₂ H ₆ . | UO ₂ |
| | 350-500 | 400 | 420(-), 580(+) | 1 | 17.06 (16.36) | - Loss of C ₇ H ₅ NS. | |
| | 500-675 | 550 | | 1 | 24.86 (25.45) | - Loss of C ₁₂ H ₆ N ₂ S. | |
| [Co(H ₂ L ¹)Cl ₂].H ₂ O | 30-160 | 78, 190 | 50(+), 180(+), | 2 | 29.95 (29.70) | - Loss of 2HCl and C ₆ H ₆ S. | CoO |
| | 160-370 | 240 | 250(+), 630(+) | 1 | 43.65 (44.45) | - Loss of 2HCl and C ₁₂ H ₃ N ₃ S. | |
| | 370-670 | 550 | | 1 | 3.44 (3.23) | - Loss of CH ₄ . | |
| [Cr(H ₂ L ¹)(H ₂ O) ₃].Cl ₃ | 30-230 | 75 | 60(+), 220(+), | 1 | 20.67 (20.22) | - Loss of 3HCl. | ½ Cr ₂ O ₃ |
| | 230-450 | 290 | 580(-) | 1 | 31.27 (31.94) | - Loss of C ₉ H ₅ N ₂ S. | |
| | 450-650 | 580 | | 1 | 33.39 (33.61) | - Loss of C ₁₀ H ₈ NSO _{0.5} . | |
| | | | | | 85.33 (85.77) | | |

n* = number of decomposition steps. (+) = Endothermic and (-) = Exothermic.

The ⁶A_{1g} → ⁵T_{1g} transition appears to be split into two bands at 11,742-12,782 cm⁻¹. The magnetic moment values of Fe(III) complexes are found to be 5.83 and 5.51 B.M. for H₂L¹ and H₂L² ligands, respectively, which indicates the presence of both complexes in octahedral geometry [38]. The spectra show also bands at 24,641-25,510 cm⁻¹ which may attribute to ligand - metal charge transfer. The diffused reflectance spectra of Co(II) complexes of H₂L¹ and H₂L² ligands resemble those of other five coordinate Co(II) complexes, where three bands are observed at 12,752-12,874, 15,542-15,671 and 17,491-17,514 cm⁻¹. The fourth band at 21,771-23,312 cm⁻¹ refers to the charge transfer band. The low magnetic moment values (μ_{eff} = 4.39-4.91 B.M.) compared with those observed for octahedral or tetrahedral complexes may support the five coordinate geometry [12-14]. The diffused reflectance spectra of the Ni(II) complexes show recognizable spectral bands at 13,470-23,984 cm⁻¹. The positions of these spectral bands are quite consistent with those predicted for five coordinate Ni(II) complexes [12-14]. The bands can be assigned, respectively, to ³B₁ → ³E, ³B₁ → ³A₂ and ³B₁ → ³E transitions assuming the effective symmetry to be C_{4v}. The bands at 27,560 and 27,457 cm⁻¹, for Ni (II) complexes with H₂L¹ and H₂L², respectively, may assigned to L → MCT band. The reflectance spectra of Cu (II) complexes of H₂L¹ and H₂L² ligands exhibit broad bands at 12,578-12,914, 15,612-16,001 and 19,214-19,874 cm⁻¹. These bands are generally consistent with a five coordinate geometry for Cu(II) complexes [12-14,38]. The spectra also show a band at 30,140-30,610 cm⁻¹ which may assign to L-MCT band. The magnetic moment values of 2.01 and 1.96 B.M. for Cu (II)-H₂L¹ and Cu (II)-H₂L², respectively, are indicative of trigonal bipyramidal structure [12-14]. The complexes of Cd(II) and UO₂(II) are diamagnetic. According to the empirical formulae of these complexes, trigonal bipyramidal geometry is proposed. According to the empirical formula, Th(IV) complex is proposed to have octahedral.

3.11. Thermal analyses (TG, DTG and DTA) of Schiff bases

The TG curve of Schiff base H₂L¹ exhibits a first estimated mass loss of 39.34% (calcd. 39.00%) at 180-390 °C, which may be attributed to the elimination of C₇H₆NS molecule as gases (Table 6). In the second estimated mass loss of 32.41% (calc. 33.23%), at 390-580 °C, which may be attributed to the liberation of C₇H₄N₂ molecule. In the 3rd stages within the temperature range from 580 to 1000 °C, H₂L¹ loss the remaining part with an estimated mass loss of 28.25% (calcd. 27.80%) with a complete decomposition as gases. The Schiff

base H₂L² decomposed in two stages (Table 7). From 30-250 °C, this step exhibits estimated mass loss of 64.38% (calcd. 64.88%), which may be attributed to the liberation of C₁₄H₁₀O₄ as gases. In the second step at temperature ranges from 250-970 °C it involve mass loss of 35.62% (calcd. 35.12%), which may be attributed to the liberation of C₇H₅N₃ molecule and corresponds to the complete decomposition of H₂L² as deduced from mass loss calculation (found mass loss = 100.0 %, calcd. mass loss = 100.0 %).

3.12. Thermal analyses (TG, DTG and DTA) of the metal chelates

Fe(III)-H₂L¹ and Fe(III)H₂L² chelates exhibit four steps of decomposition within the temperature range from 30-640 and 30-650 °C, respectively. For Fe(III)-H₂L¹ complex (Table 6), the first two steps of decomposition occur within the temperature range from 30-160 °C in which dehydration of water molecule and HCl gases occur with an estimated mass loss of 8.94% (calcd. 9.68%). The third step within the temperature range 160-450 °C, involves liberation of C₆H₄S molecule with an estimated mass loss of 32.13% (calcd. 31.15%). In the final step, liberation of C₁₃H₁₂N₃SO_{1.5} molecule occurs with estimated mass loss of 46.68% (calcd. 47.50%) within the temperature range 450-640 °C. While for Fe(III)-H₂L² chelate (Table 7), the first step of decomposition occurs within the temperature range 30-120 °C with an estimated mass loss of 6.51% (calcd. 6.82%) which can attributed to the loss of HCl gas. In the two successive decomposition steps within the temperature range 120-440 °C, liberation of HCl gas and C₇H₄O₂ molecule takes place with an estimated mass loss of 36.24% (calcd. 36.07%). In the final step, the estimated mass loss of 41.90% (calcd. 42.24%) may be attributed to the liberation of C₁₄H₈N₃O_{0.5} molecule within the temperature range from 440-650 °C.

For UO₂(II)-H₂L¹ chelate, the first three steps of decomposition involve the loss of hydrated water molecule, 2CO₂ and C₂H₆ with an estimated mass loss of 16.14% (calcd. 16.48%) within temperature range 30-350 °C (Table 6). The fourth step within the temperature range 350-500 °C in which liberation C₇H₅NS occurs with an estimated mass loss of 17.06 % (calcd. 16.36%) is observed. In the final step, an estimated mass loss of 24.76% (calcd. 25.45%) can be accounted for the loss of C₁₂H₆N₂S molecule.

Table 7. Thermoanalytical results (TG, DTG and DTA) of H₂L² ligand and its metal complexes.

| Complex | TG range (°C) | DTG _{max} (°C) | Peak temp. In DTA (°C) | n* | Total mass loss Estim (Calcd)% | Assignment | Metallic residue |
|--------------------------------------------------------------------------------------------------------|---------------|-------------------------|------------------------|----|--------------------------------|--------------------------------------------------------------------------------|----------------------------------|
| H ₂ L ² | 30-250 | 75 | | 1 | 64.38 (64.88) | - Loss of C ₁₄ H ₁₀ O ₄ . | - |
| | 250-970 | 610 | | 1 | 35.62 (35.12) | - Loss of C ₇ H ₅ N ₃ . | |
| [Fe(H ₂ L ²)Cl ₃] | 30-120 | 85 | 80(+), 180(+), | 1 | 6.51 (6.82) | - Loss of HCl. | ½ Fe ₂ O ₃ |
| | 120-440 | 180, 410 | 420(-), 600(+) | 2 | 36.24 (36.07) | - Loss of HCl and C ₇ H ₄ O ₂ . | |
| | 440-650 | 520 | | 1 | 41.90 (42.24) | - Loss of C ₁₄ H ₈ N ₃ O _{0.5} . | |
| [UO ₂ (H ₂ L ²)(CH ₃ COO) ₂].H ₂ O | 30-220 | 60, 180 | 70(+), 180(+), | 2 | 9.09 (9.05) | - Loss of H ₂ O, O ₂ and C ₂ H ₃ . | UO ₂ |
| | 220-460 | 275, 410 | 250(-), 440(+), | 2 | 19.82 (21.03) | - Loss of 2CO ₂ and C ₇ H ₇ . | |
| | 460-950 | 650 | 600(-) | 1 | 30.44 (29.73) | - Loss of C ₁₄ H ₁₁ O ₂ N ₃ . | |
| [Co(H ₂ L ²)Cl ₂].2H ₂ O | 60-220 | 99-199 | 80(+), 210(-), | 2 | 16.63 (16.88) | - Loss of HCl and H ₂ O. | CoO |
| | 220 | 410 | 430(+), 590(-) | 1 | 39.50 (39.29) | - Loss of C ₁₂ H ₇ O ₂ N. | |
| | 450 | 630 | | 1 | 32.24 (32.65) | - Loss of C ₉ H ₉ O ₂ N ₂ . | |
| | 450-820 | | | 1 | 88.37 (88.82) | | |
| [Cr(H ₂ L ²)Cl ₃].3H ₂ O | 30-140 | 94 | 80(+), 180(+), | 1 | 9.53 (9.22) | - Loss of 3H ₂ O. | ½ Cr ₂ O ₃ |
| | 140-450 | 190, 350 | 410(-), 590 (+) | 2 | 41.68 (41.59) | - Loss of 3HCl and C ₇ H ₄ NO ₂ . | |
| | 450-850 | 650 | | 1 | 36.07 (36.21) | - Loss of C ₁₄ H ₈ N ₂ O _{0.5} . | |
| | | | | | 87.28 (87.02) | | |

n* = number of decomposition steps. (+) = Endothermic and (-) = Exothermic.

From data listed in Table 7, it is clear that UO₂(II)-H₂L² chelat, the first two steps within the temperature range 30-220 °C may be attributed to loss of water and O₂ as gases and C₂H₃ molecule with an estimated mass loss 9.09% (calcd. 9.05%). The subsequent steps (220-950 °C) correspond to removal of organic part of ligand leaving metal oxide as a residue.

Co(II)-H₂L¹ chelate shows four decomposition steps within the temperature range 30-670 °C. The first two steps are found to correspond to loss of 2HCl and C₆H₆S with an estimated mass loss of 29.95% (calcd. 29.70%) in the temperature range from 30 to 160 °C (Table 6). The subsequent 3rd and 4th steps within the temperature range 160-670 °C are corresponding to removal of the organic part of the ligand and leaving metal oxide as residue. The data listed in Table 7 show that Co(II)-H₂L² chelat has four steps of decomposition within the temperature range from 60-820 °C. The first two steps involve the loss of one water molecule and HCl gas with estimated mass loss of 16.63% (calcd. 16.88%) within the temperature range from 60-220°C. The other two subsequent steps in the temperature range 220-820 °C involve the loss of the remaining part of the ligand leaving metal oxide residue. The TG curves of the Cr(III)-chelates, show three to five stages of decomposition within the temperature range of 30-1000 °C with total mass loss of 85.33% (calcd. 85.77%) and 87.28% (calcd. 87.02%) for Cr(III)-H₂L¹ and Cr(III)-H₂L² chelates, respectively, (Tables 6 and 7). In all steps, decomposition of the ligand occurred and residues of metal oxide are left.

The decomposition steps of these complexes are accompanied by the appearance of endothermic and exothermic peaks through all stages of decomposition as shown in Tables 6 and 7.

3.13. Calculation of activation thermodynamic parameters

The thermodynamic activation parameters of decomposition processes of dehydrated complexes namely activation energy (E*), enthalpy (ΔH*), entropy (ΔS*) and Gibbs free energy change of the decomposition (ΔG*) are evaluated graphically by employing the Coats-Redfern relation [40] and the data are summarized in Tables 8 and 9.

$$\log \left[\frac{\log \{W_f / (W_f - W)\}}{T^2} \right] = \log \left[\frac{AR}{\theta E^*} \left(1 - \frac{2RT}{E^*} \right) \right] - \frac{E^*}{2.303 RT} \quad (1)$$

where W_f is the mass loss at the completion of the reaction, W is the mass loss up to temperature T; R is the gas constant, E* is

the activation energy in kJ/mol, θ is the heating rate and (1 - (2RT/E*)) ≅ 1. A plot of the left-hand side of equation (1) against 1/T gives a slope from which E* is calculated and A (Arrhenius factor) is determined from the intercept. The entropy of activation (ΔS*), enthalpy of activation (ΔH*) and the free energy change of activation (ΔG*) are calculated using the following equations:

$$\Delta S^* = 2.303 [\log(Ah/kT)]R \quad (2)$$

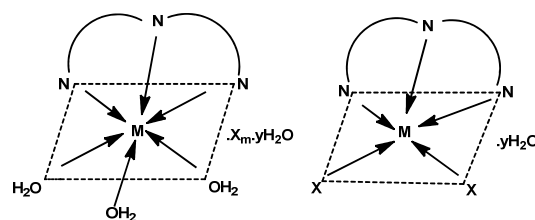
$$\Delta H^* = E^* - RT \quad (3)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (4)$$

The activation energies of decomposition are found to be in the range from 30.77 to 250.8 kJ/mol. The high values of the activation energies reflect the thermal stability of the complexes. The entropy of activation is found to have negative values in all the complexes which indicate that the decomposition reactions proceed with a lower rate than the normal ones or the decomposition process occurs spontaneously.

3.14. Structural interpretation

The suggested structures of the complexes of Schiff bases; H₂L¹ and H₂L², with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Cd(II), Th(IV) and UO₂(II) ions are given in Figures 3 and 4.



M= Cr(III), X= Cl, m=3, y=0
M= Mn(II), X= Cl, y=2
M= Fe(III), X= Cl, m=3, y=1
M= Co(II), X= Cl, y=1
M= Ni(II), X= Cl, y=1
M= Cu(II), X= Cl, y=4
M= Cd(II), X= Cl, y=4
M= UO₂(II), X= AcO, y=1

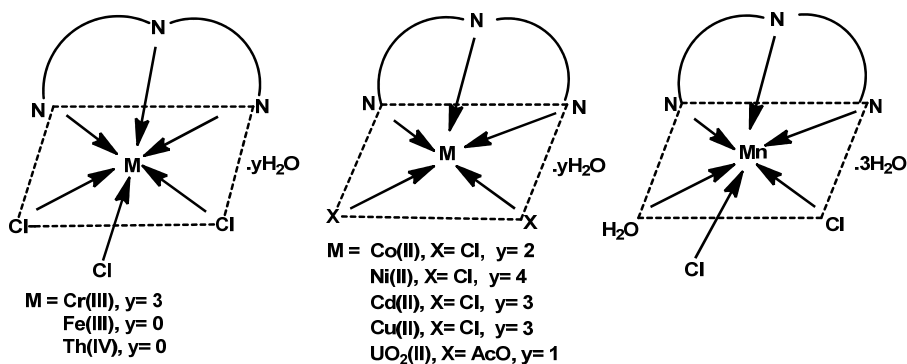
Figure 3. Structural formulae of H₂L¹ metal complexes.

Table 8. Thermodynamic data of the thermal decomposition of metal complexes of H₂L¹.

| Complex | Decomp. Temp. (°C) | E*(CR) kJ/mol | A 1/s | ΔS* kJ/mol | ΔH* kJ/mol | ΔG* kJ/mol |
|--------------------------------------------------------------------------------------------------------|--------------------|---------------|-----------------------|------------|------------|------------|
| [Fe(H ₂ L ¹)(H ₂ O) ₃]Cl ₃ ·H ₂ O | 25-190 | 57.6 | 1.25×10 ¹⁶ | -39.3 | 57.05 | 59.7 |
| | 190-395 | 40.2 | 1.07×10 ⁷ | -106.4 | 38.69 | 58.4 |
| | 395-520 | 27.9 | 2.57×10 ⁶ | -121.2 | 25.59 | 57.5 |
| | 520-650 | 41.9 | 1.52×10 ⁶ | -131.9 | 37.17 | 111.5 |
| [UO ₂ (H ₂ L ¹)(CH ₃ COO) ₂]·H ₂ O | 25-245 | 34.8 | 7.71×10 ⁵ | -126.2 | 33.60 | 51.9 |
| | 245-420 | 28.7 | 4.61×10 ⁶ | -115.8 | 26.69 | 55.2 |
| | 420-580 | 66.1 | 3.16×10 ⁶ | -123.6 | 62.54 | 116.1 |
| | 580-680 | 66.1 | 1.46×10 ⁶ | -132.2 | 61.46 | 135.5 |
| [Co(H ₂ L ¹)Cl ₂]·H ₂ O | 28-195 | 46.4 | 6.35×10 ⁴ | -145.4 | 45.42 | 62.8 |
| | 195-300 | 60.3 | 1.09×10 ⁷ | -109.4 | 58.01 | 87.6 |
| | 300-570 | 173.5 | 3.54×10 ¹¹ | -27.5 | 169.60 | 182.3 |
| | 570-690 | 234.1 | 2.90×10 ⁵ | -145.7 | 229.40 | 312.5 |
| [Cr(H ₂ L ¹)(H ₂ O) ₃]Cl ₃ | 25-185 | 41.3 | 8.21×10 ⁴ | -142.7 | 40.37 | 56.3 |
| | 185-260 | 60.3 | 1.92×10 ⁷ | -101.7 | 58.70 | 77.91 |
| | 260-450 | 82.6 | 8.54×10 ⁶ | -113.5 | 79.75 | 118.9 |
| | 450-610 | 86.5 | 1.46×10 ⁵ | -151.3 | 81.80 | 166.6 |

Table 9. Thermodynamic data of the thermal decomposition of metal complexes of H₂L².

| Complex | Decomp. Temp. (°C) | E*(CR) kJ/mol | A 1/s | ΔS* kJ/mol | ΔH* kJ/mol | ΔG* kJ/mol |
|--------------------------------------------------------------------------------------------------------|--------------------|---------------|-----------------------|------------|------------|------------|
| [Fe(H ₂ L ²)Cl ₃] | 30-120 | 56.5 | 2.60×10 ⁷ | -92.7 | 55.8 | 63.9 |
| | 120-180 | 86.3 | 9.14×10 ⁸ | -69.4 | 84.8 | 97.5 |
| | 180-410 | 144.8 | 1.39×10 ¹⁰ | -53.5 | 141.3 | 163.5 |
| | 410-620 | 136.5 | 3.55×10 ⁶ | -124.3 | 132.1 | 197.6 |
| [UO ₂ (H ₂ L ²)(CH ₃ COO) ₂]·H ₂ O | 30-160 | 28.2 | 7.72×10 ⁶ | -108.1 | 26.8 | 44.5 |
| | 160-320 | 181.3 | 6.24×10 ⁷ | -94.4 | 179.2 | 203.3 |
| | 320-440 | 212.8 | 3.66×10 ⁹ | -62.5 | 209.6 | 229.8 |
| | 440-600 | 105.0 | 4.47×10 ⁶ | -120.9 | 101.3 | 154.7 |
| [Co(H ₂ L ²)Cl ₂]·2H ₂ O | 30-100 | 72.0 | 1.63×10 ⁹ | -59.1 | 71.2 | 76.8 |
| | 100-199 | 79.7 | 2.34×10 ⁷ | -100.7 | 77.9 | 98.4 |
| | 199-380 | 66.3 | 6.86×10 ⁶ | -112.9 | 64.1 | 93.4 |
| | 380-520 | 210.0 | 7.76×10 ⁶ | -116.7 | 206.2 | 260.2 |
| [Cr(H ₂ L ²)Cl ₃]·3H ₂ O | 30-90 | 239.3 | 4.14×10 ⁹ | -151.2 | 238.5 | 243.3 |
| | 90-210 | 58.6 | 1.90×10 ⁵ | -140.4 | 57.0 | 84.5 |
| | 210-450 | 185.6 | 3.21×10 ⁹ | -64.9 | 182.4 | 206.9 |
| | 450-620 | 250.8 | 4.22×10 ¹² | -6.8 | 247.0 | 250.1 |

**Figure 4.** Structural formulae of H₂L² metal complexes.

3.15. Biological activity

In testing the antibacterial and antifungal activity of these compounds we used more than one test organism to increase the chance of detecting antibiotic principles in tested materials. The sensitivity of a microorganism to antibiotics and other antimicrobial agents was determined by the assay plates which incubated at 28 °C for two days for yeasts and at 37 °C for one day for bacteria. All of the tested compounds showed a remarkable biological activity against different types of Gram-positive (*Bacillus Subtilis* ATTC 6051 and *S. pyogones* ATTC 12600) and Gram-negative bacteria (*Escherichia Coli* ATTC 11775 and *Proteus Vulgaris* ATTC 13315) and *Fusarium Solani Martius* and *Aspergillus Niger* Fungus. The data are listed in Tables 10 and 11. On comparing the biological activity of the

Schiff bases and their metal complexes, the following results are obtained:

Bacteria: H₂L¹ ligand is found to have no biological activity against all tested bacteria. But metal complexes are found to have sensitivity for inhibition of Gram-positive more than Gram-negative bacteria. According to the data listed in Table 10, biological activity of metal complexes are found to follow the order Co(II) > Cd(II) > Cr(III) > Fe(III) > Ni(II) > Mn(II) > UO₂(II) for Gram-positive and Ni(II) > Fe(III) > Cd(II) > Co(II) > Mn(II) > UO₂(II) > Cr(III) for Gram-negative bacteria. But Cu(II) complex do not show any antibacterial activity. Therefore, it is concluded that the present of metal ions as the result of complexation enhance the biological activity of the parent Schiff base.

Table 10. Biological activity and MIC₅₀ of H₂L¹ ligand and its metal complexes.

| Sample | Fungus | | Bacteria | | | |
|--------------------------------------------------------------------------------------------------------|------------------|-----------------|----------------|--------------------|--------------------|--------------------|
| | <i>F. Solani</i> | <i>A. Niger</i> | G. -ve | | G. +ve | |
| | | | <i>E. Coli</i> | <i>P. Vulgaris</i> | <i>B. Subtilis</i> | <i>S. Pyogones</i> |
| H ₂ L ¹ | 1.1 | 0.9 | -ve | -ve | -ve | -ve |
| MIC ₅₀ | >100 µg/mL | >100 µg/mL | -ve | -ve | -ve | -ve |
| [Cr(H ₂ L ¹)(H ₂ O) ₃]Cl ₃ | 2.1 | 2.6 | 2.2 | 2.3 | 3.4 | 3.2 |
| MIC ₅₀ | >100 µg/mL | >100 µg/mL | >100 µg/mL | >100 µg/mL | 50 µg/mL | 50 µg/mL |
| [Mn(H ₂ L ¹)Cl ₂].2H ₂ O | 1.3 | 1.8 | 2.7 | 2.6 | 2.9 | 2.7 |
| MIC ₅₀ | >100 µg/mL | >100 µg/mL | >100 µg/mL | >100 µg/mL | 50 µg/mL | >100 µg/mL |
| [Fe(H ₂ L ¹)(H ₂ O) ₃]Cl ₃ .H ₂ O | 1.5 | 1.7 | 2.9 | 3.1 | 3.3 | 3.1 |
| MIC ₅₀ | >100 µg/mL | >100 µg/mL | 50 µg/mL | 50 µg/mL | 50 µg/mL | 50 µg/mL |
| [Co(H ₂ L ¹)Cl ₂].H ₂ O | 2.0 | 2.3 | 2.8 | 2.9 | 3.8 | 3.7 |
| MIC ₅₀ | >100 µg/mL | >100 µg/mL | 50 µg/mL | 50 µg/mL | 25 µg/mL | 25 µg/mL |
| [Ni(H ₂ L ¹)Cl ₂].H ₂ O | 2 | 2.1 | 2.9 | 3.1 | 3.2 | 3.2 |
| MIC ₅₀ | >100 µg/mL | >100 µg/mL | 50 µg/mL | 50 µg/mL | 50 µg/mL | 50 µg/mL |
| Cu(H ₂ L ¹)Cl ₂ .4H ₂ O | 3.0 | 3.0 | -ve | -ve | -ve | -ve |
| MIC ₅₀ | 50 µg/mL | 50 µg/mL | -ve | -ve | -ve | -ve |
| [Cd(H ₂ L ¹)Cl ₂].4H ₂ O | 5.0 | 4.5 | 2.9 | 2.8 | 3.6 | 3.4 |
| MIC ₅₀ | 12.5 µg/mL | 25 µg/mL | 50 µg/mL | 50 µg/mL | 50 µg/mL | 50 µg/mL |
| [UO ₂ (H ₂ L ¹)(CH ₃ COO) ₂].H ₂ O | 0.5 | 0.9 | 2.3 | 2.5 | 2.6 | 2.4 |
| MIC ₅₀ | >100 µg/mL | >100 µg/mL | >100 µg/mL | >100 µg/mL | >100 µg/mL | >100 µg/mL |

Table 11. Biological activity of H₂L² ligand and its metal complexes.

| Sample | Fungus | | Bacteria | | | |
|--------------------------------------------------------------------------------------------------------|-----------------|------------------|----------------|--------------------|--------------------|--------------------|
| | <i>A. Nigar</i> | <i>A. Llavus</i> | G. -ve | | G. +ve | |
| | | | <i>E. Coli</i> | <i>P. Vulgaris</i> | <i>B. Subtilis</i> | <i>S. Pyogones</i> |
| H ₂ L ² | 2.0 | 1.8 | 2.2 | 2.1 | 2.2 | 2.0 |
| MIC ₅₀ | >100 µg/mL | >100 µg/mL | >100 µg/mL | >100 µg/mL | >100 µg/mL | >100 µg/mL |
| [Cr(H ₂ L ²)Cl ₃].3H ₂ O | -ve | -ve | 2.1 | 2.0 | 0.9 | 0.7 |
| MIC ₅₀ | -ve | -ve | >100 µg/mL | >100 µg/mL | >100 µg/mL | >100 µg/mL |
| [Mn(H ₂ L ²)(H ₂ O)Cl ₂].3H ₂ O | -ve | -ve | 1.9 | 1.8 | 2.3 | 2.3 |
| MIC ₅₀ | -ve | -ve | >100 µg/mL | >100 µg/mL | >100 µg/mL | >100 µg/mL |
| [Fe(H ₂ L ²)Cl ₃] | -ve | -ve | 1.3 | 1.0 | 1.4 | 1.1 |
| MIC ₅₀ | -ve | -ve | >100 µg/mL | >100 µg/mL | >100 µg/mL | >100 µg/mL |
| [Co(H ₂ L ²)Cl ₂].2H ₂ O | -ve | -ve | 3.0 | 2.9 | 2.0 | 2.2 |
| MIC ₅₀ | -ve | -ve | 50 µg/mL | 50 µg/mL | >100 µg/mL | >100 µg/mL |
| [Ni(H ₂ L ²)Cl ₂].4H ₂ O | -ve | -ve | 2.8 | 2.4 | 3.2 | 3.1 |
| MIC ₅₀ | -ve | -ve | >100 µg/mL | >100 µg/mL | >100 µg/mL | 50 µg/mL |
| [Cu(H ₂ L ²)Cl ₂].3H ₂ O | 0.7 | 0.5 | 1.2 | 1.0 | 2.0 | 1.8 |
| MIC ₅₀ | >100 µg/mL | >100 µg/mL | >100 µg/mL | >100 µg/mL | >100 µg/mL | >100 µg/mL |
| [Cd(H ₂ L ²)Cl ₂].3H ₂ O | 2.5 | 2.7 | 1.7 | 1.6 | 2.1 | 1.7 |
| MIC ₅₀ | >100 µg/mL | >100 µg/mL | >100 µg/mL | >100 µg/mL | >100 µg/mL | >100 µg/mL |
| [Th(H ₂ L ²)Cl ₃].Cl | -ve | -ve | 2.2 | 2.0 | 2.1 | 2.0 |
| MIC ₅₀ | -ve | -ve | >100 µg/mL | >100 µg/mL | >100 µg/mL | >100 µg/mL |
| [UO ₂ (H ₂ L ²)(CH ₃ COO) ₂].H ₂ O | -ve | -ve | -ve | -ve | -ve | -ve |
| MIC ₅₀ | -ve | -ve | -ve | -ve | -ve | -ve |

Fungus: Schiff base H₂L¹ ligand shows antifungal activity against *F. Solani* and *A. Niger*. From Table 10, H₂L¹ is found to have high sensitivity against *F. Solani* than *A. Niger*. Metal complexes have antifungal biological activity and follow the order Cd(II) > Cu(II) > Cr(III) > Co(II) > Ni(II) > Fe(III) > Mn(II) > UO₂(II). It is also clear from Table 10 that the Cr (III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Cd(II) complexes are found to have antifungal activity more than the parent H₂L¹ ligand.

Bacteria: Biological activity of H₂L² ligand and its metal complexes are given in Table 11. Schiff base H₂L² is found to inhibit all tested bacteria at different rates. Sensitivity of Schiff base H₂L² toward the organisms has follow the order *B. Subtilis* > *S. Pyogones* for Gram-positive and *E. Coli* > *P. Vulgaris* for Gram negative. Metal complexes are also found to inhibit all the tested bacteria at different rates. Sensitivity of metal complexes towards organisms are found to follow the order Ni(II) > Mn(II) > Co(II) > Th(IV) > Cu(II) > Cd(II) > Fe(III) > Cr(III) for Gram-positive and Co(II) > Ni(II) > Th(IV) > Cr(III) > Mn(II) > Cd(II) > Fe(III) > Cu(II) for Gram-negative bacteria. But UO₂ (II) does not have any antibacterial activity. Co(II) and Ni(II) complexes are found to have antibacterial activity against Gram positive and Gram negative organisms more than the parent Schiff base, while Cr(III) and Th(IV) are found to have nearly the same biological activity. In addition, Mn(II) and Ni(II) complexes

show higher biological activity against Gram positive bacteria more than the parent Schiff base (H₂L²) (Table 11).

Fungus: Schiff base H₂L² shows antifungal activity against *A. Nigar* and *A. Llavus*. It has sensitivity toward the organisms in the following order *A. Nigar* > *A. Llavus*. But some metal complexes showed antifungal and sensitivity of these complexes toward organisms follow the order Cd(II) > Cu(II) and another metal complexes show any antifungal activity. The Cd(II) complex found to have antifungal activity higher than parent Schiff base (Table 11).

It was demonstrated that the Schiff base and its metal complexes showed a higher effect on *B. Subtilis* and *S. Pyogones* (Gram positive bacteria) than *P. Vulgaris* and *Escherichia coli* (Gram-negative bacteria). It is known that the membrane of Gram-negative bacteria is surrounded by an outer membrane containing lipopolysaccharides. The newly synthesized Schiff base and its metal complexes seem to be able to combine with the lipophilic layer in order to enhance the membrane permeability of the Gram-negative bacteria. The lipid membrane surrounding the cell favours the passage of only lipid soluble materials; thus the lipophilicity is an important factor that controls the antimicrobial activity. Also the increase in lipophilicity enhances the penetration of Schiff base and its metal complexes into the lipid membranes and thus restricts further growth of the organism [41,42]. This could be explained

by the charge transfer interaction between the studied molecules and the lipopolysaccharide molecules which lead to the loss of permeability barrier activity of the membrane. The Schiff base and its metal complexes could enhance the antimicrobial effect on both strains probably by the pyridyl and azomethine nitrogens and thiol group [43]. The Schiff base and its metal complexes are more toxic on *B. Subtilis* and *S. Pyogones* than on *Escherichia coli*, probably due to the thiol, COOH, S and phenyl groups, which might interact with the double membrane.

The activities of all the tested complexes may be explained on the basis of chelation theory; chelation reduces the polarity of the metal atom mainly because of partial sharing of its positive charge with the donor groups and possible p electron delocalization within the whole chelate ring. Also, chelation increases the lipophilic nature of the central atom which subsequently favors its permeation through the lipid layer of the cell membrane [44].

4. Conclusions

The results of this investigation support the suggested structures of the metal complexes. It is obvious from this study that only mononuclear complexes are obtained. Cr(III), Fe(III) and Th(IV) complexes have octahedral geometry while Co(II), Ni(II), Cu(II), Cd(II) and UO₂(II) complexes are trigonal bipyramidal except Mn(II) complexes, they have trigonal bipyramidal and octahedral geometry with H₂L¹ and H₂L², respectively. The biological activities of the Schiff bases under investigation and their complexes against bacterial and fungal organisms are promising which need further and deep studies on animals and humans.

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