Synthesis and spectral analysis of some metal complexes with mixed Schiff base ligands 1-[2-(2-hydroxybenzylideneamino)ethyl]pyrrolidine-2,5-dione (HL1) and (2-hydroxybenzalidene)glycine (HL2).

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Abstract. In this paper, new metal ions complexes of [chromium (III), iron (III), cobalt(II), nickel(II), copper(II) and cadmium(II)] were prepared from mixed Schiff base ligands 1-(2-aminoethyl) pyrrolidine-2,5-dione ligand which was prepared form the reaction of the succinic anhydride with ethylenediamine then reacted with salicyaldehyde to form a new Schiff base ligand1-[2-(2-hydroxybenzylideneamino)ethyl]pyrrolidine-2,5-dione(HL1). The amino acid (glycine) was reacted with salicyaldehyde to form another new Schiff base ligand (2-hydroxybenzalidene)glycine(HL2). The two types of Schiff bases ligands (HL1), (HL2) were mixed with some metal ions [(Cr³⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺ and Cd²⁺)] to obtain a new metal complexes. The Schiff base ligands were characterized by physic-chemical spectroscopic techniques such as: FT-IR Spectra, UV-Vis. Spectra, mass spectroscopy, ¹HNMR and microanalysis techniques (C.H.N). Which is indicated the purity of Schiff base ligands. The fragments of the prepared free Schiff base ligand (HL1) were identified by mass spectrometer technique. The metal complexes were characterized by spectroscopic techniques such as: FT-IR Spectra, UV-Vis. Spectra, molar conductivity, magnetic moment and microanalysis techniques (C.H.N) and chloride ion percentage. All the analysis of ligands and their metal complexes were in good agreement with the theoretical values which indicated the purity of Schiff base ligands and their metal complexes. From the above data, the molecular structures for all the metal complexes were proposed to be octahedral. The values of magnetic moments showed that all metal complexes are paramagnetic except cadmium (II) complex which is diamagnetic. The values of molar conductivity also appeared that all metal complexes are non-electrolytic nature except iron (III) complex which is electrolytic.

Keywords. Synthesis, metal complexes, Schiff base

1. Introduction

Werner’s classify the coordination compounds according to ligand nature to three types: Amino complexes, aqua complexes and mixed ligand complexes [1, 2, 3]. Mixed ligands are either bidentate or polydentate ligands which contain at least two different types of chemical functional groups capable of binding to metal atom. At this time, the development of these ligands is an increasing interest, as the different features associated with each donor atom confer unique reactivity to their metal complexes [4].
Depending on the number of ligands, attached to the metal ion, the mixed ligand complexes can be bi-ligand, tri-ligand, tetra-ligand or multi-ligand complexes. The formation of the mixed ligand complexes and their properties can be crucial from the point of view of the kinetic effect [5]. The coordination chemistry of transition metal complexes with mixed ligands are of current interest because they can provide new materials with useful properties such as magnetic exchange [6], electrical conductivity [7], photoluminescense [8], nonlinear optical property [9] and antimicrobial activity [10]. The role of mixed ligand complexes in biological process have been well recognized [11]. The biological importance of mixed ligand complexes is that they are sometimes more effective than the free ligands [12]. The stabilities of mixed chelates are of great importance in biological systems as many metabolic and toxicological functions are dependent upon this stability. Many attempts have been made to correlate the stability of the metal-ligand complexes with their antimicrobial activity [13, 14]. It is well established that ternary complexes play a decisive role in the activation of enzymes and also in the storage and transport of active substances [15].

Ogunniran et al. have proved that physical properties and antimicrobial activities are enhanced upon complexation [16]. Amino acids are well known for their tendency to form complexes with metals having biological significance and metabolic enzymatic activities [17]. Many researchers have studied characterization, antimicrobial and toxicological activity of mixed ligand complexes of main transition metals and actinide metal ions [18, 19]. Antitumor activity of some mixed ligand complexes have also been reported [20]. Mixed ligand complexes containing nitrogen and oxygen donors are important owing to their antifungal, antibacterial, and anticancer activities [21]. Mixed ligand complexes also have an important role in numerous chemical and biological systems like water softening, ion exchange resin, electroplating, dying, antioxidant, photosynthesis in plants and removal of undesirable and harmful metals from living organisms. Many of these metal complexes shown a good biological activity against pathogenic microorganisms [22]. The mixed ligand complexes are suitable for mimicking the role of metal ions, detoxification mechanism and drug designing. Some examples on mixed ligand complexes were prepared by Shayma A. Shaker et al. [23], by adding an ethanolic solution of 6-aminopurine to an aqueous solution of metal salts. This is followed by adding an ethanolic solution of theophylline and thiocyanate ion to give complexes with general formula \([\text{M(Tp)}_2(\text{Ad})X_2]\) where \(\text{Ad} = 6\text{-aminopurine}, \text{Tp} = \text{theophylline}, \text{X} = \text{thiocyanate ion and M} = \text{Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)}\) as a 6-coordination complexes.

2. Materials and Methods

2.1. Chemicals
All the Chemicals used in this work were of highest purity available and their supplier without further purification.

2.2. Instrumental Analysis
The infrared spectra of the prepared compounds were recorded using IR Prestige-21, single beam path laser. Fourier transforms infrared spectrophotometer of Shimadzu Company as potassium bromide KBr disc at the wavelength range of (4000-400) cm\(^{-1}\). The spectra were carried out at the laboratories of Ibn Sina State Company.

The electronic spectra of the prepared compounds were obtained using UV-Vis spectrophotometer, UV-160 A Shimadzu using (1.0 cm) quartz cell at room temperature in the range of wavelength (200-900) nm. The prepared ligand and their metal ion complexes were dissolved in dimethyl Sulphoxide (DMSO). These measurements were carried out at the laboratories of Ibn Sina State Company. The metals percentage of the complexes were measured using flame atomic absorption spectrophotometer (Nov AA 350, Germany) for the determination of (Cr\(^{3+}\), Fe\(^{3+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\) and Cd\(^{2+}\)) metal ions in complexes. The measurements were carried out at the laboratories of Ibn Sina State Company. The molar conductivity measurements were obtained using Conduct meter WTW at (25\(^{\circ}\)C) with concentration of \(1\times10^{-3}\) M (DMSO) of the complexes. The measurements were carried out at the
laboratories of Chemistry Department, College of Science for Women, University of Baghdad. Digimelt (MSRS) apparatus were used to measure the melting point of prepared compounds. The measurements were carried out at the laboratories of Chemistry Department, College of Science for Women, University of Baghdad. The magnetic susceptibility values for the prepared complexes were obtained at room temperature using magnetic susceptibility balance of Johnson mathey catalytic system division, England. These measurements were carried out at the laboratories of Chemistry Department, College of Science, Al- Nahrain University. Elemental microanalyses (C.H.N) of compounds were recorded by Euro vector model EA3000, Single V.3.0 single. The measurements were carried out at College of Science, University of Babylon.

The mass spectrum of the Schiff base ligand was carried out by mass spectrometer (GCHS-QP 2010 Ultra Shimadzu) at the laboratories of Chemistry Department, College of Science, Al-Mustansrya University. Proton nuclear magnetic resonance spectrum (¹H-NMR) of the Schiff base ligand was acquired in DMSO-d₆ solution using Brucker AMx 400 MHZ spectrometer with tetra-methylsilane (TMS) as an internal standard for ¹H-NMR analysis. The analysis was carried out at Al-Bayt University, Jordan. Anions analysis (Chlorides %) for the complexes were obtained using on titro processor (Metrohm 686), UV-160A Shimadzu and Turbidity (Hach) respectively. The measurements were carried out in the laboratories of Ibn Sina State Company.

2.3. Synthesis of Amic Acid [1-(2-aminoethyl) pyrrolidione-2,5-dione] Ligand

(0.281 gm., (0.001) mole) from succinic anhydride was dissolved in absolute ethanol (10 ml) with stirring. Ethylenediamine (0.169 gm., 0.001 mole) was dissolved in absolute ethanol (5ml) and added to the succinic anhydride solution were mixed in 1:1 mole ratio. The mixture solution was heated under reflux for (45min). During this period, a white precipitate was formed. The white solid was collected by filtration and then washed with diethyl ether and dried, then kept in desiccator. Weight (0.35), m. p (132-134 °C) and yield (87.5 %). Synthesis can be shown according to the following figure 1.

![Figure 1. Synthesis of 1-(2-aminoethyl) pyrrolidione-2,5-dione ligand.](image)

2.4. Synthesis of Schiff Base Ligand 1-[2-(2-hydroxylbenzylidene amino)ethyl]pyrrolidione-2,5-dione (HL₁) [24]

1-(2-aminoethyl pyrrolidione-2,5-dione ligand (0.230 gm., 0.001 mole) was dissolved in absolute ethanol (17ml) with stirring. Salicylaldehyde (0.198 gm., 0.001 mole) was dissolved in absolute ethanol (7ml), and added to 1-(2-aminoethyl pyrrolidione-2,5-dione solution were mixed in 1:1 mole ratio, and then three drops of glacial acetic acid were added. The mixture was heated with stirring under reflux at temperature (85°C) for (3) hrs. During this period, the colorless solution turned to the yellow solid. The
yellow solid was collected by filtration and recrystallized from absolute ethanol and then dried. Weight (0.298 gm), m. p (106-108 °C) and yield (75%). Synthesis can be shown according to the following figure 2.

Figure 2. Synthesis of Schiff base ligand 1-[2-(2-hydroxylbenzylideneamino) ethyl] pyrrolidine-2,5-dione (HL1).

2.5. Synthesis of Schiff Base Ligand (2-hydroxybenzaldine) glycine (HL2)
Glycine (0.17 gm, 0.001 mole) was dissolved in ethanol/distilled water (15 ml). Salicyaldehyde (0.272 gm, 0.001 mole) was added to the solution of glycine then three drops of glacial acetic acid were added. The mixture was heated under reflux for three hours. During this period, a cream pale yellow solid was formed. The cream solid was then collected by filtration, and then recrystallized from absolute ethanol. Weight (0.33 gm.), m. p. (232-234 °C) and Yield (83%). Synthesis can be shown according to the following figure 3.

Figure 3. Synthesis of Schiff base ligand (2-hydroxybenzaldine) glycine (HL2).
2.6.  Synthesis of The Metal Ion Complexes [Cr$^{3+}$, Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$] from Mixed Ligands of 1-[2-(2-hydroxylbenzylideneamino)ethyl]pyrrolidine-2,5-dione (HL$_1$) and Ligand (2-hydroxybenzaldine)glycine (HL$_2$).

Schiff base ligand (HL$_1$) (0.06gm., 0.0002mole) was dissolved in absolute ethanol (10ml), solution of Schiff base ligand (HL$_2$) (0.14gm, 0.0002mole) and absolute ethanol (10ml) was added to above solution. This is followed by adding (2 mole) of triethylamine and then ethanolic solution of: [Copper(II) chloride (0.04gm, 0.0002mole); Cobalt(II) chloride (0.06gm, 0.0002mole); Nickel(II) chloride (0.04gm, 0.0002mole); Chromium(III) chloride (0.06gm, 0.0002mole); cadmium(II) chloride (0.04gm, 0.0002mole) and iron(III) chloride (0.06gm, 0.0002 mole)] added to the mixed ligand solution of yellow Schiff bases ligands at the mole ratio (1:1:1). The mixture was stirred and heated under reflux for (3) hours at temperature (80-85°C). During this period, the color changed for all complexes. The precipitate was collected by filtration, washed with absolute ethanol, and then recrystallized from absolute ethanol.

The powder collected by filtration and then dried at temperature (70°C) for three hours and then kept in desiccators.

3.  Result and Discussion

The prepared metal complexes were characterized by different techniques; FTIR, UV-VIS and elemental analysis in addition to molar conductivity and magnetic susceptibility. Some physical and analytical data are summarized in tables (1). The molar conductance values of Cr (II), Fe(III), nickel(II), copper(II), and Cd(II) complexes support the non-electrolytic nature for the above complexes.

The magnetic moments for the Ni(II) d$^8$, Cr(III) d$^3$, Cu(II) d$^9$, Co(II) d$^7$, Cd(II) d$^{10}$ and Fe(III) d$^5$, [Ni(HL$_1$)(HL$_2$)(H$_2$O)$_2$], [Cr(HL$_1$)(HL$_2$)(H$_2$O)Cl], [Cu(HL$_1$)(HL$_2$)(H$_2$O)$_2$], [Co(HL$_1$)(HL$_2$)(H$_2$O)$_2$], [Cd(HL$_1$)(HL$_2$)(H$_2$O)$_2$], [Fe(HL$_1$)(HL$_2$)(H$_2$O)Cl] complexes were found to be 2.96, 3.98, 1.78, 3.88, 0.0 and 5.01 B.M. respectively within the expected of spin only values, the above complexes are paramagnetic except the Cd(II) complex is diamagnetic because he electronic configuration of the cadmium (d$^{10}$-system) [25].

The microanalysis (C.H.N) for the prepared metal ions complexes, the results were in a good agreement with the theoretical values, which indicated the identities and purities of all compounds (Schiff base ligands and their metal ion complexes). Also the metal content and the (Chlorides %) ions in complexes were determined and the obtained data were in a good agreement with the theoretical values. All the results were summarized in table 1.
Table 1. Some analytical and physical data of the ligands (HL1), (HL2) and their metal ion complexes.

| Compound and color | M. wt. gm/mol. | Molecular formula | Yield % | m. p. °C | Microanalysis (Calc.) Exp. | M % (Calc.) Exp. | Cl % | Molar Conductance (μs/cm²) | μeff. (B.M) | Ratio M/L |
|--------------------|----------------|------------------|---------|----------|---------------------------|----------------|------|-----------------------------|-----------|----------|
| Schiff base(HL1)   | 246.26         | C₁₃H₁₄N₂O₃      | 75      | 106-108  | (63.40) (5.73) (11.38)    | -               | -    | -                           | -         | -        |
| Shiny-Yellow       |                |                  |         |          |                           |                 |      |                             |           |          |
| Schiff base (HL2)  | 179.17         | C₆H₉N₁O₃        | 83      | 180      | (60.33) (5.06) (7.82)    | -               | -    | -                           | -         | -        |
| Pale-Yellow        |                |                  |         |          |                           |                 |      |                             |           |          |
| [Cu(HL₁)(HL₂)(H₂O)₂] | 523.00         | C₂₂H₂₅N₃O₈Cu    | 87      | 162-164  | (50.52) (4.82) (8.03)    | (12.15)         | -    | 22                          | 1.78      | 1:1:1    |
| Dark-green         |                |                  |         |          |                           |                 |      |                             |           |          |
| [Co(HL₁)(HL₂)(H₂O)₂] | 518.38         | C₂₂H₂₅N₃O₈Co    | 83      | 120-122  | (50.97) (4.86) (8.11)    | (11.37)         | -    | 23                          | 3.88      | 1:1:1    |
| Dark-brown         |                |                  |         |          |                           |                 |      |                             |           |          |
| [Ni(HL₁)(HL₂)(H₂O)₂] | 518.14         | C₂₂H₂₅N₃O₈Ni    | 75      | 200-202  | (51.00) (4.86) (8.11)    | (11.33)         | -    | 21                          | 2.96      | 1:1:1    |
| Orange             |                |                  |         |          |                           |                 |      |                             |           |          |
| [Cr(HL₁)(HL₂)(H₂O)Cl] | 528.88        | C₂₂H₂₅N₃O₇Cl    | 75      | 118-120  | (49.96) (4.38) (7.35)    | (9.83)          | (6.70) | 7.00                        | 3.98      | 1:1:1    |
| Brown              |                |                  |         |          |                           |                 |      |                             |           |          |
| [Cd(HL₁)(HL₂)(H₂O)₂] | 571.86         | C₂₂H₂₅N₃O₈Cd    | 85      | 160-162  | (46.21) (4.41) (7.35)    | (19.66)         | -    | 26                          | 5.01      | 1:1:1    |
| Dark-Off-white     |                |                  |         |          |                           |                 |      |                             |           |          |
| [Fe(HL₁)(HL₂)(H₂O)₂] | 532.37         | C₂₂H₂₅N₃O₇Cl    | 68      | 98-100   | (49.60) (4.35) (7.89)    | (10.48)         | (6.65) | 6.55                        |           |          |
| Cl                 |                |                  |         |          |                           |                 |      |                             |           |          |
| Reddish brown      |                |                  |         |          |                           |                 |      |                             |           |          |
3.1. Mass Spectrometer
The main high resolution mass spectrometer of the prepared Schiff base ligand 1-[2-(2-hydroxybenzylideneamino)ethyl]pyrrolidine-2,5-dione (HL1) which obtained from the reaction of succinic anhydride and ethylenediamine is summarized in figure (1). The molecular ion peak for protonation of the free Schiff base ligand, C_{13}H_{15}N_{2}O_{3} was appeared at m/z = 247(M) which is a good agreement with the theoretical value. The other peaks are detected at m/z = 202, 174, 161, 134, and 120 corresponding to [M(246)+(C_{13}H_{14}N_{2}O_{3})], [M(247)+(C_{13}H_{15}N_{2}O_{3})], [M(202)-(C_{11}H_{10}N_{2}O_{2})], [M(174)-(C_{10}H_{10}N_{2}O)], [M(161)-(C_{9}H_{9}N_{2}O)], [M(134)-(C_{8}H_{8}NO)] and [M(120)-(C_{7}H_{6}O)] respectively. All these fragmentations can be shown in figures 4 and 5.

![Figure 4. Mass spectrum of Schiff base (HL1) ligand.](image1)

![Figure 5. The fragmentation pattern of the free Schiff base ligand (HL1)](image2)
3.2. $^1$H-NMR spectrum for the new Schiff base ligand (HL$_1$)

The singlet signal observed at (δ=13.37 ppm) in the spectrum of free Schiff base ligand, was assigned to the proton hydroxyl of phenolic group [26]. The singlet signal showed at (δ=8.9 ppm) was attributed to the proton of azomethine group (HC=N) [27]. The multiplete ranged between (δ=6.909-8.66 ppm) was assigned to the aromatic protons of the ligand [28]. The multiplete at (δ=3.925 ppm) was attributed to (-CH$_2$-CH$_2$). The singlet signal appeared at (δ=2.50 ppm) can be assigned to the solvent (DMSO).

(Singlet, 1H, C-OH)= 13.37 ppm
(Singlet, 1H, N=CH)= 8.9 ppm
(M, 4H, aromatic C-H)= 6.909-8.66 ppm
(M, 8H, CH$_2$-CH$_2$)= 3.925 ppm
(Singlet, DMSO solvent)= 2.50 ppm

The spectrum was summarized in figures [A(2) - B(2)].

![Figure 6a. $^1$H-NMR spectrum of new Schiff base](image)

![Figure 6b. $^1$H-NMR spectrum of new Schiff base](image)
3.3. Infrared Spectra

The FT-IR spectra analyses gave useful information's about the mode of coordination of the ligands to the central metallic ions. The vibration bands of the ligands and their metal complexes as well as their assignments are listed in table (2) and (3). The measurements were carried out for each compound in solid state using KBr in the range (4000-400) cm⁻¹. The spectrum of 1-(2-aminoethyl) pyrrolidine-2,5-dione showed sharp band at (3305) cm⁻¹ attributed to the stretching vibration of (N-H) [28], the band at (3066) cm⁻¹ due to the stretching vibration of (C-H) aromatic. The bands of (2943) cm⁻¹ and (2835) cm⁻¹ assigned to the stretching vibration of (C-H) aliphatic asymmetrical and symmetrical respectively. The band at (1666) cm⁻¹ attributed to the stretching vibration of (C=O) [29]. The sharp bands at (1165) cm⁻¹ and (1099) cm⁻¹ attributed to the stretching vibration of (C-O) and (C-N) respectively [30]. The band at (3305) cm⁻¹ due to the stretching vibration of (N-H) of the spectrum of 1-(2-aminoethyl) pyrrolidine-2,5-dione, was disappeared in the spectrum of the free Schiff base ligand, 1-[2-(2-hydroxybenzylideneamino)ethyl] pyrrolidine-2,5-dione which indicated the formation of Schiff base ligand.

The infrared spectra of 1-[2-(2-hydroxybenzylideneamino)ethyl] pyrrolidine-2,5-dione (Schiff base ligand) (HL₁) appeared characteristic the stretching vibration of (OH) of phenolic group at (3437) cm⁻¹ [31], the band at (3055) cm⁻¹ and (3008) cm⁻¹ can be assigned to (C-H) aromatic stretching vibrations of asymmetrical and symmetrical respectively. The absorption bands at (2900) cm⁻¹ and (2866) cm⁻¹ attributed to (C-H) aliphatic stretching vibrations of asymmetrical and symmetrical respectively [32]. The infrared spectrum of free Schiff base ligand (HL₁) appeared strong sharp bands at (1635) cm⁻¹ and (1577) cm⁻¹ which are due to the stretching vibration of (C=O) and (C=N) respectively [31]. The other strong sharp band at (1496) cm⁻¹ which is due to the stretching vibration of (C=C) of benzene ring [33]. The weak broad absorption band is appeared at (3437) cm⁻¹ for (OH) stretching vibration due to the intramolecular hydrogen bonding [34, 35] which is illustrated in figure 7.

![Figure 7. Intramolecular hydrogen bonding in Schiff base ligand (HL₁)](image)

The infrared spectrum of the free Schiff base glycine (2-hydroxybenzaldehyde) glycine ligand (HL₂) appears absorption bands at (3429) cm⁻¹ and (3182) cm⁻¹, which were attributed to (OH) stretching vibration of phenolic and carboxylic groups respectively [34]. The absorption band appears at (3066) cm⁻¹ can be assigned to (C-H) aromatic. The absorption band at (2920) cm⁻¹ attributed to (C-H) aliphatic. The strong sharp bands at (1612) cm⁻¹ and (1519) cm⁻¹ due to the stretching vibration of (C=O) and (C=N) respectively [31]. The absorption band which appeared at (1458) cm⁻¹ attributed to (C=C) stretching vibration [35]. The weak a broad absorption band at (3429) cm⁻¹ is due to the intramolecular hydrogen bonding [36, 37] as shown in figure 8.
Figure 8. Intramolecular hydrogen bonding in the free Schiff base glycine ligand (HL₂).

The absorption band at (1037) cm⁻¹ can be attributed to (C-O) stretching vibration of phenolic group [38] as shown in the figures 9, 10, 11.

Figure 9. Infrared spectrum of 1-(2-aminoethyl) pyrrolidine-2,5-dione

Figure 10. Infrared spectrum for Schiff base ligand (HL₁).
3.4. Infrared spectra of the metal ion complexes derived from mixed of Schiff base ligands (HL1) and (HL2).

The infrared spectra of the metal ions complexes which were derived from the two Schiff base ligands were recorded in the region (4000-400)cm\(^{-1}\) on KBr pellets. The bands at (3437) cm\(^{-1}\) and (3429) cm\(^{-1}\) in the spectra of the two free Schiff bases ligands (HL1) and (HL2) which were attributed to stretching vibration of (OH) phenolic groups disappeared in all the metal ion complexes, which indicated that the oxygen atom is coordinated to the metal ions center of the complexes. These bands in the complexes indicated the deprotonating of phenol proton prior to and indicated the coordination of oxygen of the phenolic group with all the metal ions [39]. The significant resulted from coordination with the central metal ion for the chromium(III), iron(III), cobalt(II), nickel(II), copper(II) and cadmium(II) complexes.

The bands at (1577) cm\(^{-1}\) and (1519) cm\(^{-1}\) in the spectra which are attributed to stretching vibration of the azomethine groups (C=N) of the two Schiff base ligands (HL1) and (HL2) respectively were shifted to higher or lower frequency in the spectra of the chromium(III), iron(III), cobalt(II), nickel(II), copper(II) and cadmium(II) complexes which indicated the participation of the nitrogen atom at the azomethine groups in the coordination [40].

The bands at (1504) cm\(^{-1}\), (1465) cm\(^{-1}\), (1450) cm\(^{-1}\), (1446) cm\(^{-1}\) and (1500) cm\(^{-1}\), can be assigned to (C=C) stretching vibration for the iron(III), copper(II), cobalt(II), chromium(III) and cadmium(II) complexes respectively and appeared very weak band at (1558) cm\(^{-1}\) due to the stretching vibration of (C=C) of nickel(II) complex [41]. The spectrum of Ni(II) and Cd(II) complexes have medium sharp band appeared at (948) cm\(^{-1}\) and (937) cm\(^{-1}\) respectively, which is attributed to the rocking vibration of (OH) of water which indicated the presence of water molecule with the nickel and cadmium ions in the complexes [42], water molecules inside the coordination sphere. In all the spectra of the synthesized complexes the low frequency region observed new medium intensity bands around (509-582) cm\(^{-1}\) and (408-474) cm\(^{-1}\) can be attributed to the frequency of (metal-nitrogen) and (metal-oxygen) respectively [43]. All the infrared spectra data of the metal complexes synthesized from the two free Schiff base ligands are illustrated in the table 2 and figures 12, 13, 14, 15, 16 and 17.
| Compound | $\nu$(OH)$_{\text{Intra}}$ | $\nu$(C-H)$_{\text{Intra}}$ | $\nu$(C=O)$_{\text{Intra}}$ | $\nu$(C=N)$_{\text{Intra}}$ | $\nu$(C-O)$_{\text{Intra}}$ | C(C-N)$_{\text{Intra}}$ | $\nu$(M-O)$_{\text{Intra}}$ | $\nu$(M-N)$_{\text{Intra}}$ | Other bands |
|----------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Amic acid | -                | 2943             | 1666             | -                | -                | 1099             | -                | -                | -                |
| Schiff base (HL$_1$) | 3437            | 3055             | 1635             | 1577             | 1199             | 1111             | 1041             | -                | -                |
| Schiff base (HL$_2$) | 3429            | 3066             | 1612             | 1519             | 1037             | -                | -                | -                | -                |
| $\{\text{Cu (HL}$_1$)(HL$_2$)(H$_2$O)$_2\}$ | 3433            | 3047             | 2951             | 1631             | 1579             | 1192             | 1087             | 509              | 435             |
| $\{\text{Co (HL}$_1$)(HL$_2$)(H$_2$O)$_2\}$ | 3417            | 2978             | 1647             | 1539             | 1199             | 1083             | 516              | 408              | -                |
| $\{\text{Ni (HL}$_1$)(HL$_2$)(H$_2$O)$_2\}$ | 3566            | 3028             | 1683             | 1600             | 1510             | 1087             | 524              | 551              | 435             |
| $\{\text{Cr (HL}$_1$)(HL$_2$)(H$_2$O)Cl\}$ | 3394            | 2997             | 1627             | 1543             | 1033             | 1083             | 528              | 282              | 412             |
| $\{\text{Fe (HL}$_1$)(HL$_2$)(H$_2$O)Cl\}$ | 3375            | 2978             | 1627             | 1543             | 1199             | 1083             | 540              | 455              | -                |
| $\{\text{Cd (HL}$_1$)(HL$_2$)(H$_2$O)$_2\}$ | 3182            | 3035             | 1635             | 1519             | 1199             | 1064             | 520              | 474              | -                |

ar.= aromatic       aliph.=aliphatic    phen.=phenolic    as.= asymmetrical    s.=symmetrical
Figure 12. Infrared spectra for [Cu(HL₁)(HL₂)(H₂O)₂] complex.

Figure 13. Infrared spectra for [Co(HL₁)(HL₂)(H₂O)₂] complex.

Figure 14. Infrared spectra for [Ni(HL₁)(HL₂)(H₂O)₂] complex.
Figure 15. Infrared spectra for [Cr(HL₁)(HL₂)(H₂O)Cl] complex.

Figure 16. Infrared spectra for [Fe(HL₁)(HL₂)(H₂O)Cl] complex.

Figure 17. Infrared spectra for [Cd(HL₁)(HL₂)(H₂O)₂] complex.
3.5. **Electronic Spectra of (Amic acid), free Schiff base ligands [(HL, and (HL,)] and their metal complexes.**

The ultraviolet-Visible Spectrum of the white 1-(2-aminoethyl) pyrrolidine-2,5-dione (Amic acid), figure 18 showed strong sharp and high intensity absorption band at (236nm, 42372 cm⁻¹) and (300nm, 35000 cm⁻¹) which are attributed to (π→π*) and (n→π*) electronic transitions respectively for carbonyl group. The electronic absorption Spectrum of the shiny yellow 1-[2-(2-hydroxybenzylideneamino)ethyl] pyrrolidine-2,5-dione (HL, figure 19 appeared two sharp and high intensity absorption band at (269nm, 37174 cm⁻¹) and (282nm, 35460 cm⁻¹) are assigned to (π→π*) and (n→π*) electronic transition of benzene ring and azomethine group respectively (44,45). The weak intensity absorption band at (236nm, 42372 cm⁻¹) has electronic transition of Schiff base azomethine group [46, 47].

The U.V-Vis Spectrum of the yellow (2-hydroxybenzaldine)glycine ligand (HL, figure 18) exhibited three absorption bands, the first and second are very strong and sharp appeared at (215nm, 46511 cm⁻¹) and (250nm, 40000 cm⁻¹) were assigned to (π→π*) electronic transition of benzene ring and azomethine group [48]. The third absorption band revealed as slightly broad and low intensity at (325nm, 30769cm⁻¹) could be assigned to (n→π*) electronic transition of the Schiff base azomethine group [49, 50].

![Figure 18. The electronic spectrum for Amic acid.](image1.png)

![Figure 19. The electronic spectrum for Schiff base (HL,) ligand.](image2.png)

For complexes, the bands are classified into two distinct groups: These belong to ligand transitions appeared in the ultraviolet region, while d-d transitions appeared in the visible region; these transitions are assigned in relevance to the structures of complexes. Complexes of Schiff base ligands with metal
ions caused either bathochromic hypochromic shifts of ligand bands. The intensities and positions of new observed bands related to charge transfer (C.T) and (d-d) electronic transitions are mainly depending on the oxidation numbers and the position of the metal ion in the periodic table, stereochemistry of complexes and ligand field strength [51]. The UV-Vis spectrum of nickel(II) complex in dimethylsulphoxide (DMSO) display new bands at (276nm, 36231cm⁻¹), (386nm, 25906cm⁻¹), (321nm, 31152cm⁻¹), (408nm, 24509cm⁻¹), (485nm, 20618cm⁻¹) and (844nm, 11848cm⁻¹) which are assigned respectively to (π→π*) electronic transition type, (n→π*) electronic transition, charge transfer (C.T), \(3\{\text{A}_2\text{g}_\Gamma\rightarrow\text{3T}_1\text{g}_\Gamma(\upsilon_3)\}\), \(3\{\text{A}_2\text{g}_\Gamma\rightarrow\text{3T}_1\text{g}_\Gamma(\upsilon_2)\}\) and \(3\{\text{A}_2\text{g}_\Gamma\rightarrow\text{3T}_2\text{g}_\Gamma(\upsilon_1)\}\) of the nickel(II) complex.

The bands related to (π→π*) electronic transition in the complex shifted compared with these observed at the free Schiff base ligands (HL₁) and (HL₂). This attributed to the coordination of the ligands to the central metal of the complex. The bands at (316nm, 31645cm⁻¹) and (325nm, 30769cm⁻¹) which belong to (HL₁) and (HL₂) respectively were shifted to higher or lower wavelength in the nickel(II) complex. This explained on the bases of stabilizes of non-bonding ion pair of azomethine group nitrogen atom as a result of donation of this non-bonding ion pair to the nickel ion through the coordination [52]. The spectrum of the nickel(II) complex displayed new bands at (386nm, 25906cm⁻¹), (408nm, 24509cm⁻¹) due to the charge transfer, \(3\{\text{A}_2\text{g}_\Gamma \rightarrow\text{3T}_1\text{g}_\Gamma (\upsilon_3)\}\) electronic transitions, the other new bands appeared at (485nm, 20618cm⁻¹) and (844nm, 11848cm⁻¹) can be assigned to \(3\{\text{A}_2\text{g}_\Gamma \rightarrow\text{3T}_1\text{g}_\Gamma (\upsilon_2)\}\) and \(3\{\text{A}_2\text{g}_\Gamma \rightarrow\text{3T}_2\text{g}_\Gamma (\upsilon_1)\}\) electronic transitions respectively.

The value of magnetic moment was 2.96 B.M. This confirms the paramagnetic character of the complex. Depending on all the above results we can suggest this complex which is octahedral around Ni(II) ion [53] as shown in table (3) and figure (16). The electronic absorption spectrum of cobalt(II) complex in dimethylsulphoxide (DMSO) showed the absorption bands at (274nm, 36496cm⁻¹) attributed to (π→π*) electronic transition type, and at (363nm, 37548cm⁻¹) due to (n→π*) electronic transition of the two new absorption bands compared with these related to the free Schiff base ligands (HL₁) and (HL₂) and appeared another absorption bands at (386nm, 25906cm⁻¹) and (460nm, 21739cm⁻¹) due to charge transfer (C.T) and \(3\{\text{A}_2\text{g}_\Gamma \rightarrow\text{3T}_1\text{g}_\Gamma (\upsilon_3)\}\) electronic transition.

The value of effective magnetic moment of this complex is 3.88 B.M. This confirms the paramagnetic character of the complex. According to these results and in addition to others such as atomic absorption, molar conductivity which confirm the neutral nature of this complex and microanalysis (C.H.N) of this complex, we can suggest that the cobalt(II) complex is an octahedral complex geometry around the cobalt(II) ion [54] as shown in table (3) and figure (17). The spectrum of copper(II) complex displays four bands: the first band with high intensity and high molar absorptivity appeared at (273nm, 36630cm⁻¹) attributed to (π→π*) electronic transition, the other three new absorption bands at (363nm, 27548cm⁻¹) attributed to (n→π*) electronic transition and was shifted to higher wavelength, (390nm, 25641cm⁻¹) and (578nm, 17301cm⁻¹) can be assigned to \(3\{\text{A}_2\text{g}_\Gamma \rightarrow\text{3T}_1\text{g}_\Gamma (\upsilon_3)\}\) and \(3\{\text{A}_2\text{g}_\Gamma \rightarrow\text{3T}_1\text{g}_\Gamma (\upsilon_1)\}\) electronic transitions respectively.

The magnetic moment value of the complex is 1.78 B.M. which is in a good agreement with the calculated value, which confirmed the octahedral geometry around the copper(II) ion [55] as shown in table (3) and figure (18). The UV-Vis spectrum of chromium(III) complex, appeared four absorption bands, the first at (272nm, 36765cm⁻¹) can be assigned to (π→π*) electronic transition, the second band at (391nm, 22575cm⁻¹) with high molar extinction coefficient and intensity attributed to \(3\{\text{A}_2\text{g}_\Gamma \rightarrow\text{3T}_1\text{g}_\Gamma (\upsilon_3)\}\) electronic transition, the third band at (520nm, 19230cm⁻¹) attributed to \(3\{\text{A}_2\text{g}_\Gamma \rightarrow\text{3T}_1\text{g}_\Gamma (\upsilon_3)\}\) electronic transition, the fourth band at (688nm, 14535cm⁻¹) can be assigned to \(3\{\text{A}_2\text{g}_\Gamma \rightarrow\text{3T}_2\text{g}_\Gamma (\upsilon_1)\}\) electronic transition, the value of magnetic effective for chromium complex is 3.98 B.M., which is in a good agreement with the theoretical value, which confirmed this complex that is octahedral geometry around the Cr(III) ion [56, 57] as shown in table (3) and figure(19). The spectrum of iron(III) complex, the bands related to (n→π*) electronic transition which is observed in the ultraviolet-visible spectra of the two free Schiff base ligands (HL₁) and (HL₂) at (305nm, cm⁻¹) and (325nm, 30769cm⁻¹) shifted to higher and lower wavelength. This explained on the bases of stabilizes of non-bonding ion pair of azomethine group nitrogen atom as a result of donation of this non-bonding ion pair to iron(III) ion through the coordination [58]. When we compared the bands related to (π→π*)
electronic transition in the two free Schiff base ligands with those observed in the complex spectrum, we shall observe shift to higher wavelength in addition to appeared new bands in the region of the spectrum, all these changes give good indication for complexion by ligands to the iron(III) ion. The spectrum of the complex exhibited new broad bands at (488nm, 2049cm⁻¹), (632nm, 15823cm⁻¹) and (827nm, 12092cm⁻¹) which are assigned to (C.T), [^6A1g→^4T2g(D)] and [^6A1g→^4T1g(G)] electronic transitions respectively.

The value of effective magnetic moment of Fe(III) complex is 5.01 B.M., which is in a good agreement with the calculated value. According to these electronic transitions and the magnetic value and the microanalysis (C.H.N) and atomic absorption, molar conductivity which confirm the neutral nature of this complex and element analysis (C.H.N) and atomic absorption, molar conductivity which confirm the neutral nature of this complex and element analysis (C.H.N) of this complex, we can suggest this complex as an octahedral complex geometry around the iron(III) ion [59] as shown in table (3) and figure (20). The electronic spectrum of cadmium(II) complex, shows three new absorption bands, the first absorption band at (268nm, 37313cm⁻¹) can be assigned to (π→π*) electronic transition, the second absorption band at (302nm, 31152cm⁻¹) attributed to (n→π*) electronic transition and the third absorption band at (408nm, 24509cm⁻¹) is due to metal-ligand charge transfer (C.T) electronic transition [60]. According to these results and in addition to element analysis (C.H.N) and the value of magnetic moment of cadmium(II) complex is 0.0 B.M. which is in a good agreement with the theoretical value. The complex is an octahedral geometry around the cadmium(II) ion [61]. The spectrum data is illustrated in table (3) and figure 21.

Table 3. Electronic absorption spectra data of Amic acid, free Schiff base ligands (HL₁) and (HL₂) and their metal ion complexes. (part1)

| Compounds             | λmax (nm) | ε max (Molec⁻¹ cm⁻¹) | C max Molec⁻¹ cm⁻¹ | ASSIGNMENT     | Suggested structure |
|-----------------------|-----------|----------------------|--------------------|----------------|---------------------|
| Amic acid             | 236       | 42372                | 335                | 0.335          | π→π*                |
|                       | 296       | 33783                | 2223               | 0.223          | n→π* carbonyl group |
| Schiff base(HL₁)      | 316       | 31645                | 1135               | 1.135          | π→π* benzene        |
| C₁₃H₁₄N₂O₃            | 269       | 37174                | 869                | 0.869          | π→π*                |
|                       | 316       | 31645                | 1135               | 1.135          | n→π* azomethine     |
| Schiff base(HL₂)      | 215       | 46511                | 2087               | 0.208          | π→π* benzene        |
| C₉H₉NO₃               | 250       | 40000                | 2206               | 2.206          | π→π* azomethine     |
|                       | 325       | 30769                | 717                | 0.717          | n→π* azomethine     |
|                       | 321       | 31152                | 1521               | 1.521          | n→π* benzene        |
| [Ni(HL₁)(HL₂)(H₂O)₂]  | 386       | 25906                | 1217               | 1.217          | C.T Octahedral      |
|                       | 408       | 24509                | 1068               | 1.068          | ^3A→^3T₁g(υ₃)       |
|                       | 485       | 20618                | 500                | 0.50           | ^3A→^3T₁g(υ₂)       |
|                       | 844       | 11848                | 1                  | 0.001          | ^3A→^3T₁g(υ₁)       |
|                       | 274       | 36496                | 2166               | 2.166          | π→π* benzene        |
|                       | 363       | 27548                | 2060               | 2.060          | n→π* benzene        |
| [Co(HL₁)(HL₂)(H₂O)₂]  | 386       | 25906                | 1217               | 1.217          | C.T Octahedral      |
|                       | 460       | 21739                | 250                | 0.25           | ^4T₁g(υ₃)→^4T₁g(υ₁)  |
|                       | 273       | 36630                | 2000               | 2.00           | π→π* benzene        |
|                       | 363       | 27548                | 2060               | 2.060          | n→π* benzene        |
| [Cu(HL₁)(HL₂)(H₂O)₂]  | 390       | 25641                | 1751               | 0.751          | C.T Tetrahedral     |
|                       | 578       | 17301                | 31                 | 0.031          | ^2T₂→^2E            |
|                       | 272       | 36765                | 1648               | 1.648          | π→π* benzene        |
| [Cr(HL₁)(HL₂)(H₂O)Cl] | 391       | 25575                | 792                | 0.792          | ^4A→^4T₁g(υ₁)       |
|                       | 520       | 19230                | 46                 | 0.046          | ^4A→^4T₁g(υ₁)       |
$^{4}A_{2g}(F) \rightarrow ^{4}T_{2g}(F) (\nu_1)$

$^{6}A_{1g} \rightarrow ^{6}T_{2g}(D)$

$^{6}A_{1g} \rightarrow ^{6}T_{1g}(G)$

$[\text{Fe(HL}_{1})(\text{HL}_{2})(\text{H}_{2}\text{O})\text{Cl}]$

Octahedral

$[\text{Cd(HL}_{1})(\text{HL}_{2})(\text{H}_{2}\text{O})_{2}]$

Octahedral

Figure 20. The electronic spectrum for $[\text{Ni(HL}_{1})(\text{HL}_{2})(\text{H}_{2}\text{O})_{2}]$ complex.

Figure 21. The electronic spectrum for $[\text{Co(HL}_{1})(\text{HL}_{2})(\text{H}_{2}\text{O})_{2}]$ complex.
Figure 22. The electronic spectrum for $[\text{Cu(HL}_1\text{)(HL}_2\text{)(H}_2\text{O})_2]$ complex.

Figure 23. The electronic spectrum for $[\text{Cr(HL}_1\text{)(HL}_2\text{)(H}_2\text{O})\text{Cl}]$ complex.

Figure 24. The electronic spectrum for $[\text{Fe(HL}_1\text{)(HL}_2\text{)(H}_2\text{O})\text{Cl}]$ complex.
According to above mentioned analysis, the suggested structures for the prepared ligand and its metal complexes are illustrated below:

**Amic acid:** 1-(2-aminoethyl)pyrrolidone-2,5-dione

**Schiff base (1) ligand:** 1-[2-(2-hydroxybenzylideneamino) ethyl]pyrrolidone-2,5-dione (HL1)

**Schiff base (2) ligand:** (2-hydroxybenzaldine)glycine (HBG)(HL2).
[Cr(HL1)(HL2)(H2O)Cl]

[Co(HL1)(HL2)(H2O)2]

[Fe(HL1)(HL2)(H2O)Cl]

[Ni(HL1)(HL2)(H2O)2]

[Cu(HL1)(HL2)(H2O)2]

[Cd(HL1)(HL2)(H2O)2]

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