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Synthesis and Characterisation of Cr(III) and Co(II) Schiff Base Complexes

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Abstract

Co(II) and Cr(III) metal complexes of Schiff bases were synthesized from the condensation reaction between 4-(dimethylamino)benzaldehyde and 4-amino-3-hydroxy-naphthalene-1-sulfonic acid. Their structures were investigated by elemental analysis, molar conductance measurements, infrared spectroscopy, electronic spectroscopy, and ^{1}HNMR spectroscopy. The elemental analysis data suggested a 1:1 [M:L] ratio for the complexes. The molar conductance measurements of the complexes indicate their electrolytic nature in DMSO as a solvent. The absorption bands in the electronic spectra verified an octahedral environment around the metal ions in the complexes.

Keywords

Schiff Base, Ligand Complexes, ^{1}HNMR Spectra

1. Introduction

Schiff bases have been extensively studied for their synthetic flexibility, selectivity, and sensitivity to the central metal atom; their structural similarity to natural biological compounds and the presence of the azomethine group (–N=CH–), which is important in the biological elucidation of transformation and racemization reaction mechanisms [1]. Schiff bases are an important class of organic compounds, which have a wide range of applications in the fields of analysis, biology, and inorganic chemistry [2]. Some of these compounds are used as corrosion inhibitors [3] and as catalysts in polymers [3] [4] and dyes [5]. Furthermore, Schiff bases have become important in medicine and pharmaceuticals due to their wide range of biological activities [2]-[17]. Schiff bases readily coordi-

nate with metal ions under different reaction conditions. Researchers are still interested in the chemistry of metal complexes with Schiff base ligands with oxygen and nitrogen as donor atoms. To understand the structure and biological processes of biomolecules, Schiff base transition metal complexes have been used as biological models. Manganese, cobalt, nickel, copper, and zinc are important metal elements with biological activity when combined with certain proteins, participating in oxygen transport, electron transfer reactions, or ion storage [18]. Amer *et al*. reported the synthesis and characterisation of Cr(III) and Fe(II) complexes containing Bis(2-methoxybenzylidene)biphenyl-4,4'-diamine Schiff base. All prepared compounds were analysed using elemental analysis, IR, 1H NMR and mass spectroscopy [19]. Bennour *et al*. presented the synthesis and spectral studies of a Schiff base. Its structure was confirmed by IR, NMR and as well as by X-ray diffraction. The different metal complexes were fully characterised using elemental analysis, molar conductivity, infrared and electronic spectra [20]. In the present work, we present the synthesis and spectral studies of a Schiff base (Z)-4-((4-(dimethylamino)benzylidene)amino)-3-hydroxynaphthalene-1-sulfonic acid (L). The Cr(III) and Co(II) complexes were fully characterised using elemental analysis, molar conductivity, infrared and electronic spectra.

2. Experimental

2.1. Material

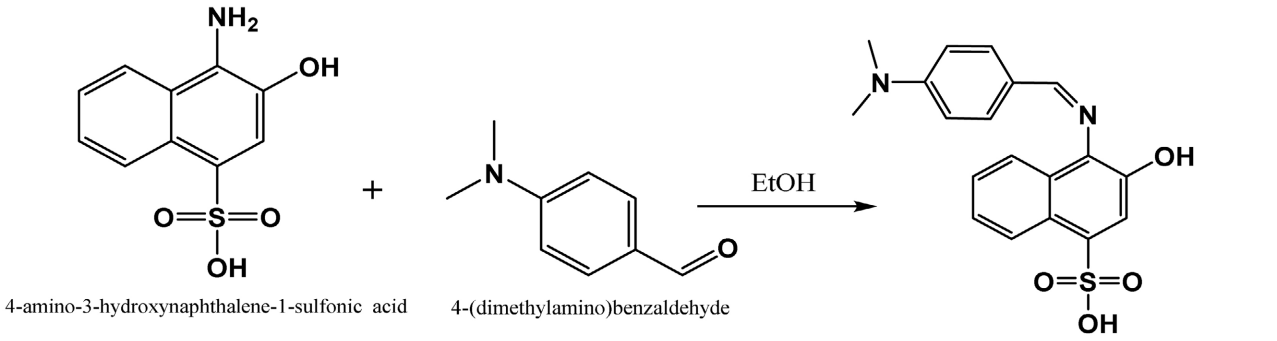
Chemicals were purchased from Sigma-Aldrich and used without further purification. Methanol, and ethanol, were of HPLC grade and were purification using standard methods described in the literature [21].

2.2. Measurements

The prepared ligand complexes were subjected to (C, H, and N) elemental analyses using a 2400 Series II CHNS/O elemental analyzer. Molar conductance measurements were carried out in DMSO using CMD650 digital conductivity meter. Electronic absorption spectra were measured in DMSO using a Shimadzu NIR3101PC Uv-Vis spectrometer. Infrared spectra were obtained asKBr disks on a IFS-25 DPUS/IR spectrophotometer (Bruker) in the range of 4000 - 500 cm^{-1}. ^{1}H NMR spectra of the ligands were recorded at 25˚C on a Bruker 600 MHz spectrometer equipped with a cryoprobe.

2.3. Syntheses of Schiff Base (L)

Equimolar amounts of 4-(dimethylamino)benzaldehyde (1.49 g, 10 mmol) and 4-(amino-3-hydroxynaphthalene-1-sulfonic acid (2.39 g, 10 mmol) were mixed together and cooked at reflux for an hour over a water bath. When the combination reached room temperature, a solid of yellow color developed. It was filtered, rinsed with methanol, then crystallized once more in ethanol [22]. Using TLC, the reaction was observed (**Scheme 1**).



4-amino-3-hydroxynaphthalene-1-sulfonic acid

4-(dimethylamino)benzaldehyde

(*Z*)-4-((4-(dimethylamino)benzylidene)amino)-3-hydroxynaphthalene-1-sulfonic acid

Scheme 1. Synthesis of Schiff base.

2.4. Preparation of Complexes

The ligand (Z)-4-((4-(dimethylamino)benzylidene)amino))-3-hydroxynaphthalene-1-sulfonic acid; 3.70 g) was mixed in the same ratio with $CoCl_2 \cdot 6H_2O$ and $CrCl_3 \cdot 6H_2O$ salts to create the ligand complexes in identical amounts (0.01 mol). For three hours, the mixes were refluxed. To change the pH at which the point was, a few drops of an ammonia solution were introduced. The resultant complexes were rinsed with hot ethanol multiple times until the filtrate cleared out. The filtrate was vacuum-dried on anhydrous $CaCl_2$ after first being dried in the air. The yield varied between 79% and 86%. The dried complexes were examined using spectroscopic and elemental analysis. The produced complexes are DMSO-soluble but insoluble in C_2H_5OH. The purity of the ligand complexes was examined using the TLC method.

3. Results and Discussion

3.1. Microanalysis

The elemental analysis data of the ligand complexes shown in **Table 1**, confirm the formation of the 1:1 [M:L] complexes.

3.2. Molar Conductance Measurement

The molar conductance values of the synthesized Cr(III) and Co(II) ligand

Table 1. Some physical properties of mixed ligand complexes.

Chelates	M.Wt	C%	H%	N%	S%	M.C*
L	370	61.20 **(61.61)**	4.95 **(4.90)**	7.70 **(7.56)**	8.73 **(8.65)**	
$[CrL]Cl_2$	564.37	41.20 **(40.44)**	5.12 **(4.47)**	5.23 **(4.96)**	7.53 **(7.30)**	83
[CoL]Cl	535.86	43.10 (42.59)	4.92 (4.70)	5.53 (5.23)	7.83 (7.18)	74

*Unit of molar conductance $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$. ( ) Calculated values in parentheses.

complexes were shown in the Table 1. These values suggest the presence of an electrolyte nature [23]. From the molar conductivity values we come to know of the total number of ions in the complex from which we can arrive at the correct formulation.

3.3. ^{1}H NMR Spectrum of Schiff Base

The ^{1}H NMR spectrum of the ligand in $CDCl_3$ (Figure 1) agrees with the suggested structure. The singlets at 9.75 and 7.25 ppm were assigned to the proton of a hydroxyl group (s, H, C—OH) and the proton of an azomethine group (s, H, N=CH), respectively [24]. The chemical shifts observed as singlets at 1.5 ppm (s, H, CH_3) could be responsible for the proton of a methyl group attached to dimethylamino moiety [25]. The aromatic protons of antipyrine moiety appeared at 6.87 - 7.50 ppm. The singlets that appeared at 3.10 ppm (s, H, N—CH_3) were assigned to the proton of the methyl group of dimethylamino moiety [26].

3.4. Infrared Spectra

Figures 2-4 displays the infrared spectrum data for the complexes of Co(II) and Cr(III). The ligand has broad, strong to medium peaks at 1649 and 487 cm^{-1}. These belong to the azomethine group and the phenolic ν(OH) stretching vibration, respectively [27] [28]. By contrasting the IR spectra of the ligands and their

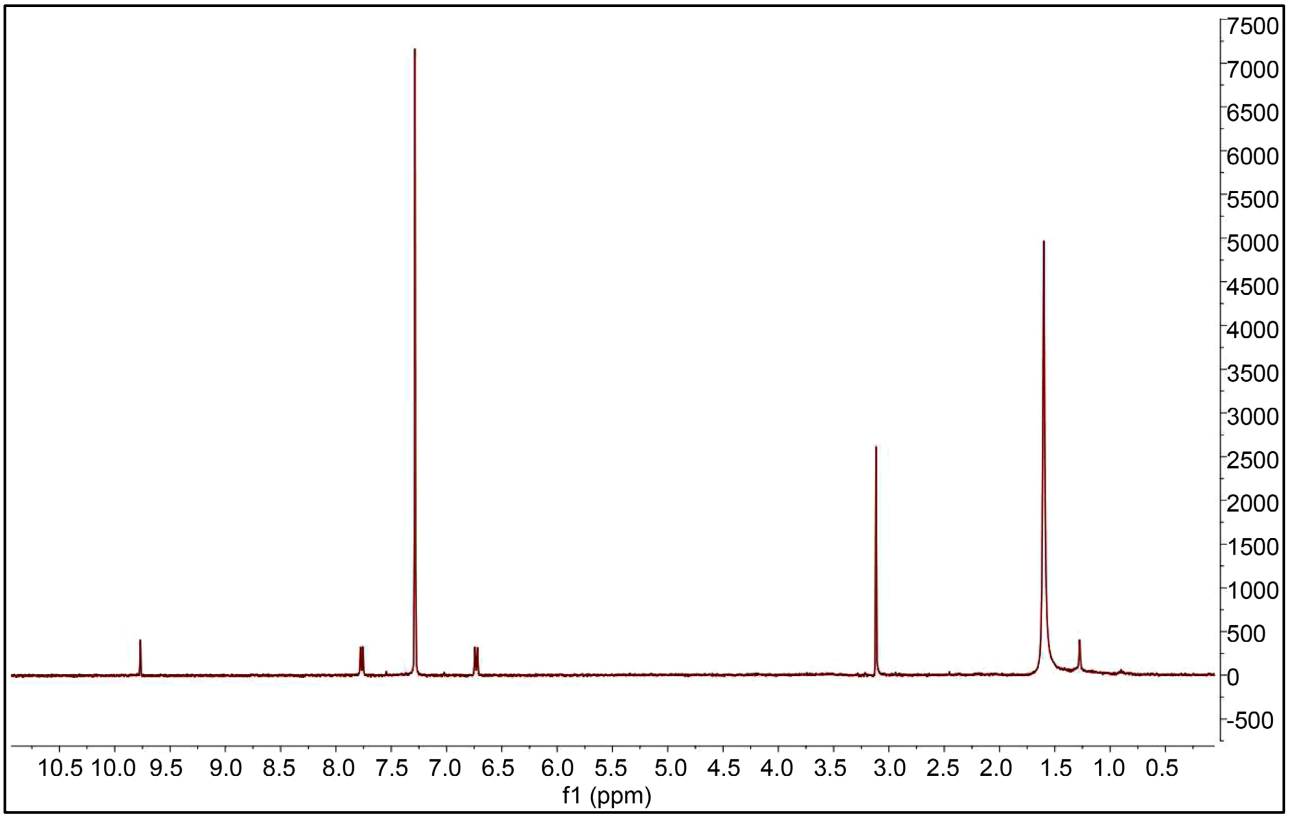


Figure 1. 1H NMR spectrum of Schiff base L.

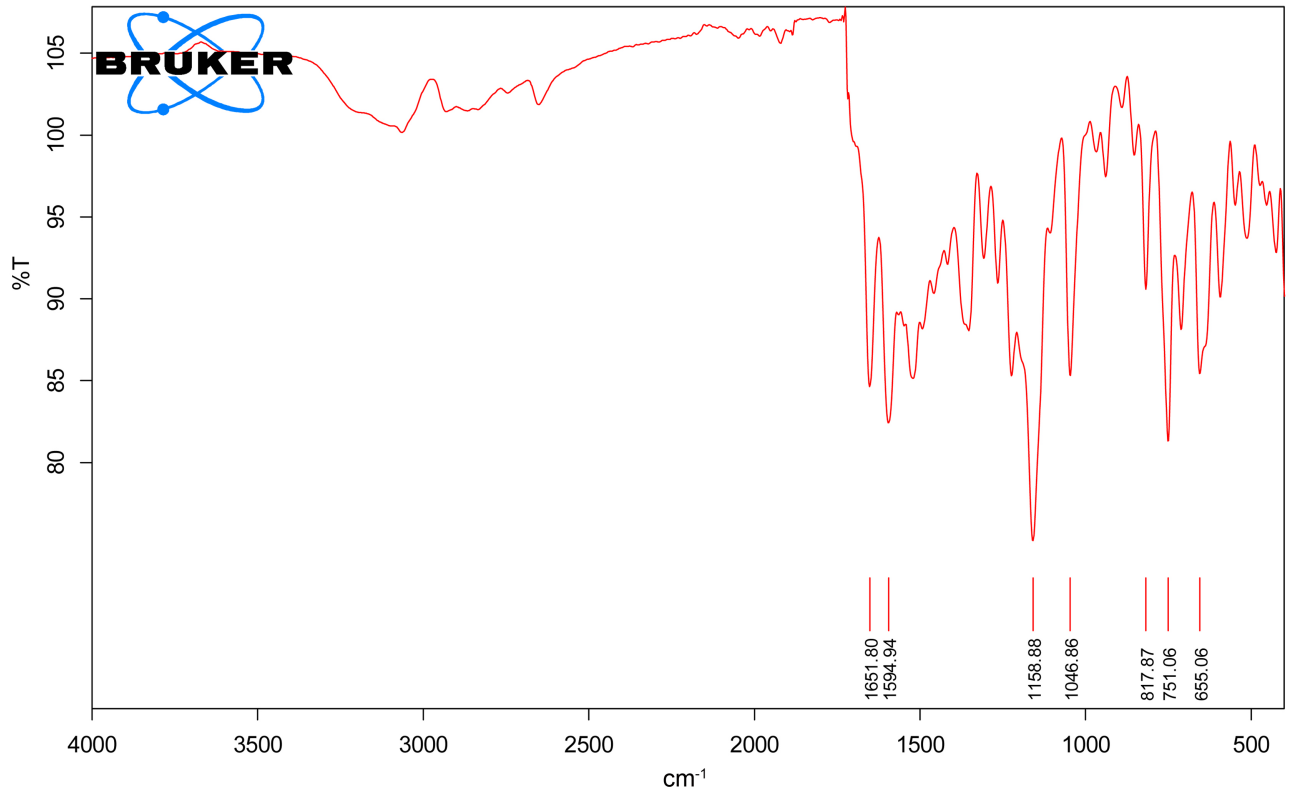


Figure 2. Infrared spectrum of Schiff base.

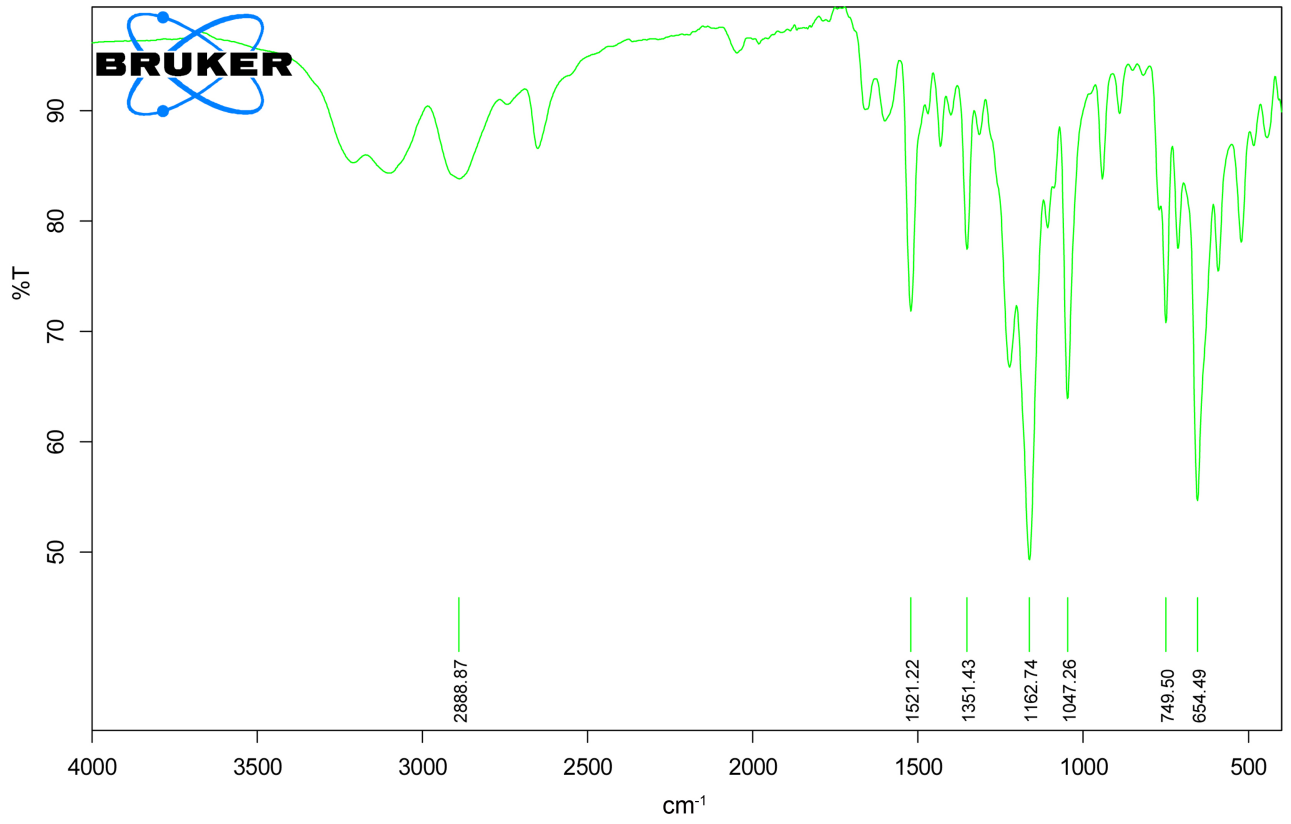


Figure 3. Infrared spectrum of Cr(III) complex.

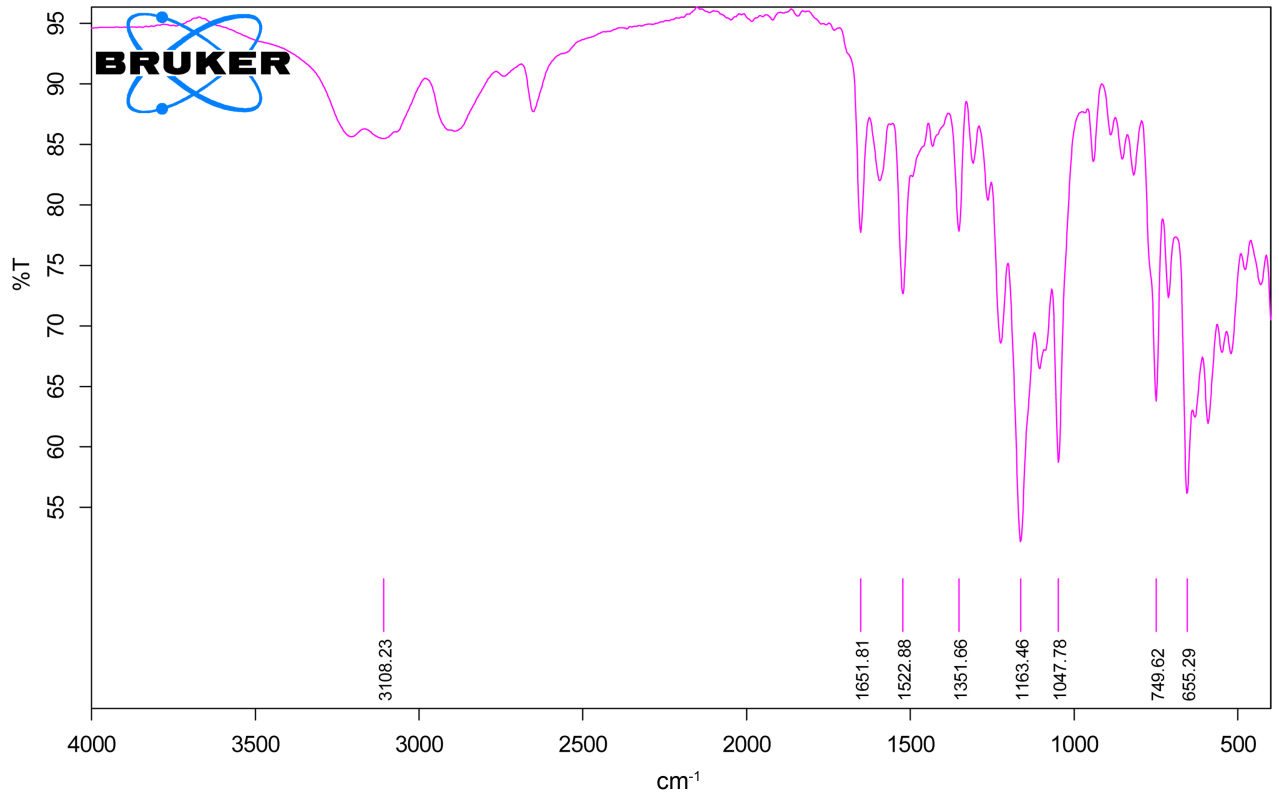


Figure 4. Infrared spectrum of Co(II) complex.

complexes, the bonding behavior of the ligand was determined. Through a deprotonated hydroxyl group and the ligand's azomethine nitrogen atom, L coordinates with the metal ion to behave as a bidentate ligand, as demonstrated by this comparison [29].

The same spectra, however, show the bands at 1595 cm^{-1} caused by the ligand's υ(CH=N) azomethine group (1450 cm^{-1}) and the potent band of phenolic C-O stretching vibration at 1158 cm^{-1}. As the complex forms, these bands shift, showing that they participated in coordination with the Cr(III) and Co(II) ions. The free ligands allocated to the υ(M-O) and υ(M-N) vibrations lack another band in the ranges of 610 - 630 cm^{-1} and 545 - 575 cm^{-1}. The presence of this vibration provides evidence that chelation involves the coordination groups –O–, –CH=N, and water [30].

3.5. Electronic Spectra

In DMSO solution, the electronic spectrum was captured. The glossy yellow (Z)-4-((4-(dimethylamino)benzylidene)amino))-3-hydroxynaphthalene-1-sulfo nic acid (L) displayed two distinct, highly intense absorption bands at 275 nm, (36363 cm^{-1}) and 288 nm, (34722 cm^{-1}). These belong to the benzene ring's ($\pi \rightarrow \pi^*$) and the azomethine group's ($n \rightarrow \pi^*$) electronic transitions, respectively [27]. The electronic transition of the Schiff base azomethine group is attributed to the weak intensity absorption band at 237 nm (42194 cm^{-1}) [28]. The spectral absorption data of the [CoL]. Cl complex shows several bands at (288 nm,

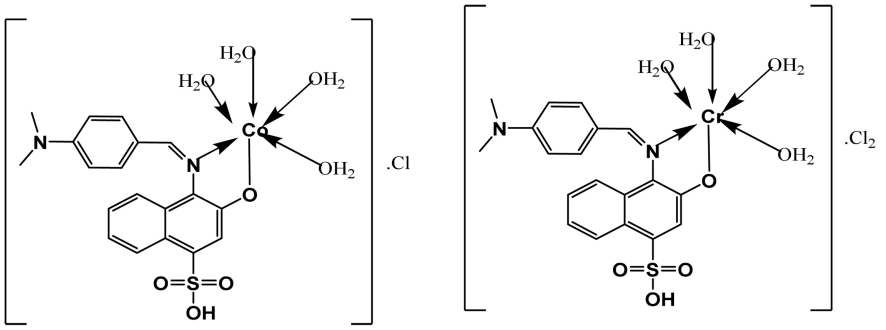


Figure 5. Chemical structures of Cr(III) and Co(II) Schiff bases complexes.

34,722 cm^{-1}), (365 nm, 27397 cm^{-1}) and (720 nm, 13889 cm^{-1}) attributed to an intra-ligand π-π* transition (phenyl ring), a charge transfer band, and $^4T_1g(F) \rightarrow {}^4T_2g(F)$, $^4T_1g(F) \rightarrow {}^4T_1g(P)$ and $^4T_1g(F) \rightarrow {}^4A_2g(F)$ transitions, which indicate an octahedral structure [31]. A low intensity broad band found in the electronic spectra at wavelengths of 410 and 570 nm is attributed to the Cr(III) ion's d-d transitions. In this complex, two transition bands $^4T_2g \leftarrow {}^4A_2g$, and $^4T_1g \leftarrow {}^4A_2g$, as well as a third transition $^4T_1g(P) \leftarrow {}^4A_2g(F)$ are seen. The transitions' associated energies are 17,544 and 24,390 cm^{-1}, respectively. The complex's shape appears to be octahedral around the central Cr^{3+} ion, according to the spectrum changes [32].

4. Conclusion

In this study, we developed a specific method for synthesizing bidentate Schiff bases and their complexes. In spectroscopic investigations, the deprotonated hydroxyl group and azomethine nitrogen atom of the ligand (L) complexes were utilized to describe the structure of the Schiff base ligand (L) coordinates with metal ions (**Figure 5**). These formations are all octahedral in shape. Every complex has an electrolytic nature. Based on molar conductance measurements, IR, Vis-Uv and ^{1}HNMR spectroscopy, as well as elemental studies (C, H, N, and S), we may propose the following chemical formulae for the produced ligand complexes.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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