

Full Length Research Paper

Synthesis, characterization and thermal analysis of the copper(II) complexes with 2,2'-bipyridyl and 1,10-phenanthroline

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The Cu(II) complexes were synthesized by the addition of Cu(II) acetate monohydrate to ligand in aqueous solution with 1,10-phenanthroline and 2,2'-bipyridyl which led to the precipitation of complexes. The synthesized Cu(II) complexes [Cu(SAla)phen(H₂O)].H₂O, [Cu(SAla)bpy(H₂O)].H₂O were found to be soluble in water, ethanol, methanol and DMSO. The electronic spectra and the magnetic moment support the stereochemistry of the complexes. The electronic spectra of all the complexes display a broad band with maximum at 14765 to 15503 cm⁻¹, which suggested an octahedral geometry of the metal ion. The magnetic moment at the room temperature lying in the range of 1.78 to 2.09 BM corresponds to one unpaired electron which are slightly greater than the spin only value of 1.73 BM, which was expected for one unpaired electron which offer possibility of the paramagnetic nature. The electronic spectra of free ligand shows band at 35651 cm⁻¹ which are intra ligand charge transfer band (INCT). The electronic absorption spectra of the schiff base complexes were recorded using DMSO solvent. The spectrum of Cu(II) complexes display a broad band at 14765 cm⁻¹, which attributed to ²E_g → ²T_{2g} transition, which strongly favours the octahedral geometry around the central metal ion. The thermal gravimetric analysis (TGA), derivative thermogravimetric analysis (DTG), differential thermal analysis (DTA) experiments were carried out to explore the thermal stability of the complexes. The thermal behaviours of all the metal complexes were studied in the temperature range of 0 to 1400°C. The TGA, DTG and DTA studies of complexes reveal that the decomposition proceeds in three steps.

Key words: Copper(II) complexes, 2,2'-bipyridyl, 1,10-phenanthroline.

INTRODUCTION

Organo metallic chemistry has been developed, in the last four decades, to be the largest and important branch as a link connecting the fields of organic and inorganic

chemistry. One of the major applications of the transition metal complexes is its medical testing as antibacterial and antitumor agents aiming toward the discovery of an

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effective and safe therapeutic regimen for the treatment of bacterial infections and cancers. In addition, many Schiff base complexes with metals have also provoked wide interest because they possess a diverse spectrum of biological and pharmaceutical activities, including antitumor and antioxidative activities. Moreover, mixed-ligand complexes are observed in biological systems or in the intermediate chemical reactions with metal ions, which are important to understand the respective chemistry. Investigations concerning 1,10-phenanthroline mixed-ligand chelate systems would provide toward understanding the driving forces that led to the formation of such mixed ligand complexes (Raman and Sobha, 2010).

The copper(II) complexes were characterized by different analytical and spectral methods. The thermal behaviors of the obtained complexes were also investigated. The thermal analysis techniques, such as thermogravimetry (TGA), differential thermal analysis (DTA), and differential scanning calorimetry (DSC), were widely applied in studying the thermal behavior and the structure of metal complexes (Sanghamitra et al., 2014). The results allowed us to acquire information concerning the structure of these compounds, including their thermal behavior and decomposition. Thermal analysis let us also to evaluate the presence of crystallization water molecules in the complexes and to determine the endothermic and/or exothermic effects connected with such processes as: Dehydration, melting, crystallization, and decomposition (Shi et al., 2010). In view of the importance of copper(II) compounds and our interest in the chemistry of coordination compounds involving chelating coumarin base (Liang et al., 2004). Copper complexes have indeed demonstrated a wide range of pharmacological activity such as antibacterial, antifungal, antiviral, anticancer and anti-inflammatory activity (Boerner and Zaleski, 2005). Twenty natural amino acids comprise the building blocks of proteins, which are chemical species indispensable to perform a huge number of biological functions, as exemplified by the role of enzymes. From these twenty amino acids, eight are essential and cannot be produced by the human body. Complexes of transition metals with amino acids in proteins and peptides are utilized in numerous biological processes, such as oxygen conveyer, electron transfer and oxidation. In these processes, the enzymatic active site, which is very specific, forms complexes with divalent metal ions. 1,10-phenanthroline (1,10-phen), 2,2'-bipyridine (2,2'-bipy) and their substituted derivatives, both in the metal-free state and as ligands coordinated to transition metals, disturb the functioning of a wide variety of biological systems. When the metal-free N, N-chelating bases are found to be bioactive it is usually assumed that the sequestering of trace metals is involved, and that the resulting metal complexes are the actual active species. The copper(II) complex with 2,2'-bipyridyl and 1,10-phenanthroline showed antifungal, antibacterial activity

and mosquito larvicidal activity is investigated by the report of Chandraleka et al. (2011). It was found that copper complexes often demonstrate enhanced biological activity than the parent ligand alone. The present paper communicates the synthesis, characterization and thermal analysis of the copper(II) complexes with amino acid L-alanine derived Schiff bases using 2,2'-bipyridyl and 1,10-phenanthroline.

MATERIALS AND METHODS

All chemicals used in the synthesis of the copper complex were analytical grade while L-alanine, salicylaldehyde, copper(II) acetate monohydrate, 1, 10-phenanthroline and 2, 2'- bipyridyl were obtained from Merck Specialities Private Limited.

Preparation of H₂SAla from alanine

To a clean beaker 10 ml of double distilled water and 0.6303 g of potassium hydroxide (0.01 M) was added at room temperature and dissolved completely. To that 1 g of alanine was added and stirred for few minutes. In a separate beaker 1.3721 g of salicylaldehyde (0.01 M) was dissolved in 10 ml ethanol. This salicylaldehyde solution was added to alanine solution at room temperature. The resulting yellow coloured solution was stirred for 30 min using a magnetic stirrer. After stirring the reaction mixture was cooled in an ice bath. The intermediate Schiff base that had formed was reduced with 5 ml of sodium borohydride (0.51 g, 0.01 M) containing few drops of sodium hydroxide solution. The yellow colour slowly discharged and the pH of the solution was adjusted to 3.5 to 5.0 using few drops of concentrated HCl to obtain the solid precipitate. The obtained solid was then filtered and washed with ethanol and diethyl ether and allowed to dry completely at room temperature.

Synthesis of copper(II) complexes

Synthesis of copper(II) complexes using 1,10-phenanthroline

In a clean beaker, 0.2 g of copper(II) acetate monohydrate (1 mM) was taken and dissolved in 15 ml of ethanol. It was stirred for 10 to 15 min. To the royal blue solution formed 0.18 g of 1,10-phenanthroline (1 mM) in 10 ml ethanol was added and mixed well. To this 0.2 g of the corresponding ligand (1 mM) in 10 ml double distilled water with KOH (1 ml, 1 M) was added. The resulting dark green solution was stirred for 2 h at room temperature and then filtered and left for several days. The resulting solid precipitate was dried in a desiccator for few more days to afford the desired product (Koh et al., 1996).

Synthesis of copper(II) complexes using 2,2'-bipyridyl

In a clean beaker 0.2 g of copper(II) acetate monohydrate (1 mM) was taken and dissolved in 15 ml ethanol. It was stirred for 10 to 15 min. To the royal blue solution formed 0.1564 g of 2,2'-bipyridyl (1 mM) in 10 ml ethanol was added and mixed well. To this 0.2 g of the corresponding ligand (1 mM) in 10 ml double distilled water with KOH (1 ml, 1 M) was added. The resulting dark green solution was stirred for 2 h at room temperature and then filtered and left for several days. The resulting solid precipitate was dried in a desiccator for few more days to afford the desired product.

Characterization of the copper(II) complexes

Solubility test

The synthesized Cu(II) complexes were tested for their solubility in various polar solvents like water, ethanol, methanol, dimethyl sulfoxide and some non polar solvents like hexane, ethylacetate, chloroform and acetylacetone.

Melting point

The melting point of the synthesized ligands and the complexes were determined in a capillary tube using an Electro thermal melting point apparatus.

CHN analysis

The carbon, nitrogen and hydrogen analyses were carried out using a Heraeus Elemental Analyser.

Structural characterization of Cu(II) complexes

Various techniques are used to elucidate the bonding structure and geometry of the ligands and the complexes prepared. While the ligands are characterized by usual methods such as elemental analysis, UV-visible, magnetic moment, conductivity, Fourier-transform infrared (FT-IR), proton nuclear magnetic resonance ($^1\text{H-NMR}$), electron spin resonance (ESR) spectral techniques and thermal analysis, it differs for complexes depending on the nature of the ligands and the metal ions involved. Ligands on complexation with some metal ions having paired or unpaired electrons give diamagnetic or paramagnetic complexes respectively. Some of the common physicochemical methods adopted by inorganic chemists are discussed subsequently.

Electronic spectroscopy

The UV-Vis spectra of all the complexes were recorded in shimadzu UV 1601 spectrophotometer using the DMSO as solvent in the wave range of 200 to 800 nm.

Magnetic susceptibility

Magnetic susceptibility measurements of the complexes in the solid state were determined by the Gouy balance at room temperature using Cu(II) acetate monohydrate as the calibrant.

Molar conductivity

The molar conductivity was measured with the systronic conductivity bridge using the freshly prepared solution of the complexes in DMSO solvent.

Infrared spectroscopy

The IR spectroscopy is widely used as a characterization technique for metal complexes. The basic theory involved is that the stretching modes of the ligands changes upon complexation due to weakening, strengthening of the bonds involved in the bond formation resulting in subsequent change in the position of the bands appearing in the IR spectrum. The changes in the structural features of the ligands are observed as changes in bands

observed, mainly in the fingerprint region, that is, in the 1500 to 750 cm^{-1} . Nakamoto discusses at length the characterization of metal complexes with the help of IR spectroscopy (Saha et al., 2002). The bands due to the metal ligand bonds are mainly observed in the far IR region, that is, 50 to 500 cm^{-1} . The Infrared spectra in the region 400 to 4000 cm^{-1} were recorded on a Perkin Elmer FT-IR Model Spectrometer at room temperature. Spectra of the solid samples were obtained in KBr pellets.

$^1\text{H NMR}$ spectroscopy

For diamagnetic complexes, NMR spectroscopy still remains as a valuable tool for establishing the structural characterizations. Assignment of protonated carbons were made by two dimensional heteronuclear-correlated experiment using delay values which corresponds to $\delta(\text{C,H})$. The HMQC experiment provides correlation between protons and their attached heteronuclei through the heteronuclear scalar coupling. This sequence is very sensitive (compared to the older HETCOR) as it is based on proton detection (instead of the detection of the least sensitive low gamma heteronuclei). The $^1\text{H NMR}$ spectra were recorded using DMSO solvent and trimethylsilane as internal standard.

ESR spectroscopy

For complexes which are paramagnetic, in addition to the elemental analysis, IR, and electronic spectroscopic techniques, Electron paramagnetic resonance (EPR) spectroscopy acts as an effective and valuable tool to explore the structural features and bonding characteristics of metal complexes. The advances in the ESR spectroscopy have benefited the inorganic chemists with the help of high field and high-resolution spectrometers that helps to resolve the g_{\parallel} and g_{\perp} features of the paramagnetic species.

The information obtainable from a low temperature spectrum of diamagnetically diluted paramagnetic species provides important clues to structural traits and bonding properties of the complexes. The single crystal ESR spectrum measurements are also widely employed to derive more information about the geometry of the paramagnetic species formed. Hathway had extensively surveyed the studies on complexes by using ESR spectroscopy. Various simulation packages are extensively used to simulate the experimental spectrum and hence help to establish the absolute geometry and accurate bonding and structural characteristics of the complexes. ESR spectra were recorded using a Bruker EMX instrument, operating at X-band frequency (9.33 GHz), with 20 mW power, modulation frequency of 100 kHz , using solid samples, at room temperature.

Powder XRD

Powder XRD pattern of all the complexes were recorded on a Rigaku Dmax X-ray diffractometer with CuK α radiation ($\lambda = 1.5404 \text{ \AA}$).

Scanning electron microscopy

SEM images of all the complexes were recorded in a Hitachi SEM analyzer.

Thermal analysis of copper(II) complexes

A simultaneous TGA, DTG and DTA have been obtained by a model NETZSCH STA 409C/CO thermal analyzer. The experiments

were performed in N_2 atmosphere at a heating rate of $10^\circ C \text{ min}^{-1}$ in the temperature range 0 to $1200^\circ C$ using Al_2O_3 crucible. The sample sizes are ranged from 4.5 to 10 mg.

RESULTS AND DISCUSSION

To overcome the general problems of ligand instability for schiff bases of aminoacids and to introduce greater ligand flexibility and model the proton shifted intermediate of transamination reactions; an *in situ* reduction was carried out on salicylaldehyde and aminoacid mixture. In the present study ligand alanine (H_2SAIa) was prepared by the addition of respective aminoacids with salicylaldehyde. Totally two Cu(II) complexes were synthesized by the addition of Cu(II) acetate monohydrate to ligand in aqueous solution with 1,10-phenanthroline and 2,2'-bipyridyl which led to the precipitation of complexes. The complexes were named as copper-salicylaldehyde-alanine-1,10-phenanthroline $[Cu(SAIa)phen(H_2O)].H_2O$, copper-salicylaldehyde-alanine-2,2'-bipyridyl $[Cu(SAIa)bpy(H_2O)].H_2O$. All the complexes were found to be stable at room temperature.

Physicochemical characteristics of $[Cu(SAIa)phen(H_2O)].H_2O$ and $[Cu(SAIa)bpy(H_2O)].H_2O$ complexes

Solubility test

Solubility is often said to be one of the "characteristic properties of a substance," which means that solubility is commonly used to describe the substance, to indicate a substance. In the present study the synthesized Cu(II) complexes were dissolved in some polar solvents like water, ethanol, methanol, ethyl acetate, dimethyl sulphoxide and some non polar solvent like hexane, ethyl acetate, chloroform. The synthesized metal complexes $[Cu(SAIa)phen(H_2O)].H_2O$, $[Cu(SAIa)bpy(H_2O)].H_2O$ were found to be soluble in water, ethanol, methanol and DMSO. The solubility of metal compounds in water and other solvents was of great toxicological importance because it was one of the major factors influencing the availability and absorption of metals. The solubility of metal compounds depends on numerous factors such as pH, presence of other ions, oxidation state of the metal and the rate of oxidation and reduction conversions (Pratviel et al., 1998).

Melting point

The melting point of a substance is the temperature at which the material changes from a solid to a liquid state. Determining the melting point is a simple and fast method used specially to determine the purity of a substance. This is because even small quantities of impurities

change the melting point, or at least clearly enlarge melting range of compounds. In the present study melting point of ligands and metal complexes were determined. The melting point range of the complexes has minimum range of $110^\circ C$ to a maximum of $212^\circ C$ (Table 1).

UV-visible spectroscopy

The spectra of transition metal complexes depend on the transition of unpaired electrons from the ground state to an excited state. Most of the transition metal complexes are colored and the color is observed due to d-d transition in the visible region. The atomic overlap in metal ligand bond allows d-electrons to penetrate from the central atom to the ligand (Saha et al., 2002). In these spectra there is an intense band at 240 to 300 nm due to $\pi-\pi^*$ transition (Table 2). The transitions are affected by the effect of ligands on the energies of the d orbital of the metal ions. Cu(II) complexes are usually blue or green due to the presence of d-d absorption bands in the 200 to 900 nm region of the spectrum.

Electronic absorption spectra, magnetic susceptibility and conductivity

The electronic spectra and the magnetic moment support the stereochemistry of the complexes. The electronic spectra of all the complexes display a broad band with maximum at 14820 to 15503 cm^{-1} , which suggest an octahedral geometry of the complexes. The magnetic moment at the room temperature lying in the range of 1.78 to 2.09 BM correspond to one unpaired electron which are slightly greater than the spin only value of 1.73 BM, which is expected for one unpaired electron which offer possibility of the octahedral geometry.

$[Cu(SAIa)Phen(H_2O)].H_2O$

The electronic spectra of the Cu(II) complexes were recorded in DMSO solvent. The absorption in the ultraviolet region is attributed to transition within ligand orbital and those in the visible region are probably due to allowed metal to ligand charge transfer transition. The spectra of Cu(II) complex show broad band in the visible region at $15,337 \text{ cm}^{-1}$ which are assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ transition which attributed to an octahedral geometry around the central metal ion.

The broadness of the band can be taken as an indication of Jahn-Teller distortion from the regular symmetry. The observed magnetic moment of the complexes were found to be 1.82 BM which is slightly greater than the spin only value and offers possibility of an octahedral geometry.

Table 1. Physical properties of the Cu(II) complexes.

S/N	Name of the complexes	Empirical formula	Molecular weight	mp 0°C	Colour	BM μ_{eff}	Yield %	Composition analysis (%)				
								C	H	Cu	N	O
1	H ₂ SAla	C ₁₀ H ₁₁ NO ₃	193.199	116	Colourless	-	42.42	62.17(62.11)	5.74(5.69)	-	7.25(7.24)	24.84(24.39)
2	[Cu(SAla)phen(H ₂ O)].H ₂ O	C ₂₂ H ₁₉ CuN ₃ O ₄	452.949	118	Green	1.82	83.05	58.34(58.29)	4.23(4.19)	14.03(13.93)	9.28(9.28)	14.13(14.12)
3	[Cu(SAla)bpy(H ₂ O)].H ₂ O	C ₂₀ H ₁₉ CuN ₃ O ₄	428.929	212	Green	1.78	45.30	56.00(55.95)	4.46(4.43)	14.82(14.68)	9.80(9.80)	14.92(14.91)

mp - Melting Point (0°C), BM- Bohr magneton (magnetic moment).

Table 2. Electronic absorption spectra of Cu(II) complexes.

S/N	Name of the complex	Absorption (cm ⁻¹)	Band assignment	Solvent	Geometry
1	H ₂ SAla	35714	INCT	DMSO	Octahedral
2	[Cu(SAla)phen(H ₂ O)].H ₂ O	15337	² E _g → ² T _{2g}	DMSO	Octahedral
3	[Cu(SAla)bpy(H ₂ O)].H ₂ O	15240	² E _g → ² T _{2g}	DMSO	Octahedral

INCT- Intra ligand charge transfer.

[Cu(SAla)bpy(H₂O)].H₂O

The electronic spectra of the Cu(II) complexes showed band at 15420 cm⁻¹. This position typically was expected for an octahedral geometry and may be assigned to 10 Dq corresponding to the transition ²E_g→²T_{2g}. The broadness of the band can be taken as an indication of Jahn-Teller distortion from the regular symmetry.

The magnetic moment value was found to be 1.78 BM, This was slightly greater than the spin only value of 1.73 BM which is expected for one unpaired electron and offer possibility of octahedral geometry.

Conductivity

The molar conductivity of the complexes was measured in DMSO solvent with 10⁻³ M concentration. The complex showed the molar

conductivity in the range of 12 mho cm⁻² mol⁻¹. The low value of molar conductance indicating the non electrolytic nature of the complexes in DMSO (Chan and Wong, 1995).

FT-Infrared spectroscopy

The IR spectra of the complexes are compared with that of the free ligand to determine the change that might take place during complexation (H₂SAla) shows a broad band at 3432 cm⁻¹ which could be assigned due to OH group. The intense band in the 1104 cm⁻¹ region and band at 1365 cm⁻¹ are assigned to phenolic ν (C-O) and ν (COO⁻) respectively (20).

[Cu(SAla)phen(H₂O)].H₂O

The broad band at 3432 cm⁻¹ observed in the case

of the ligand was shifted at 3440 cm⁻¹ for 1,10 phenanthroline copper complexes which was attributed to ν (OH) of coordinated water molecule. This was further supported by band at 990 and 720 cm⁻¹ due to OH bond rocking and wagging vibration of the water molecule respectively. The band in the region of 1411 cm⁻¹ (Sym COO⁻ stretching vibration) suggests that the amino acid's carboxyl group was involved in the complex formation (Patil et al., 2010). In comparison with complex the band appeared in the region 1112 cm⁻¹ for [Cu(SAla)phen(H₂O)].H₂O due to phenolic ν (C-O) indicates the coordination of phenolic oxygen via deprotonation. The higher side shift to ν (C-O) in the metal complexes due to the expected high mesomeric interaction in the complexes that is probably activated by presence of the metal ion (21). Two topical bands in the region 850 and 773 cm⁻¹ were assigned to ν (C=N) of phenanthroline. The broad band in the 3440 cm⁻¹ region is due to OH stretching which

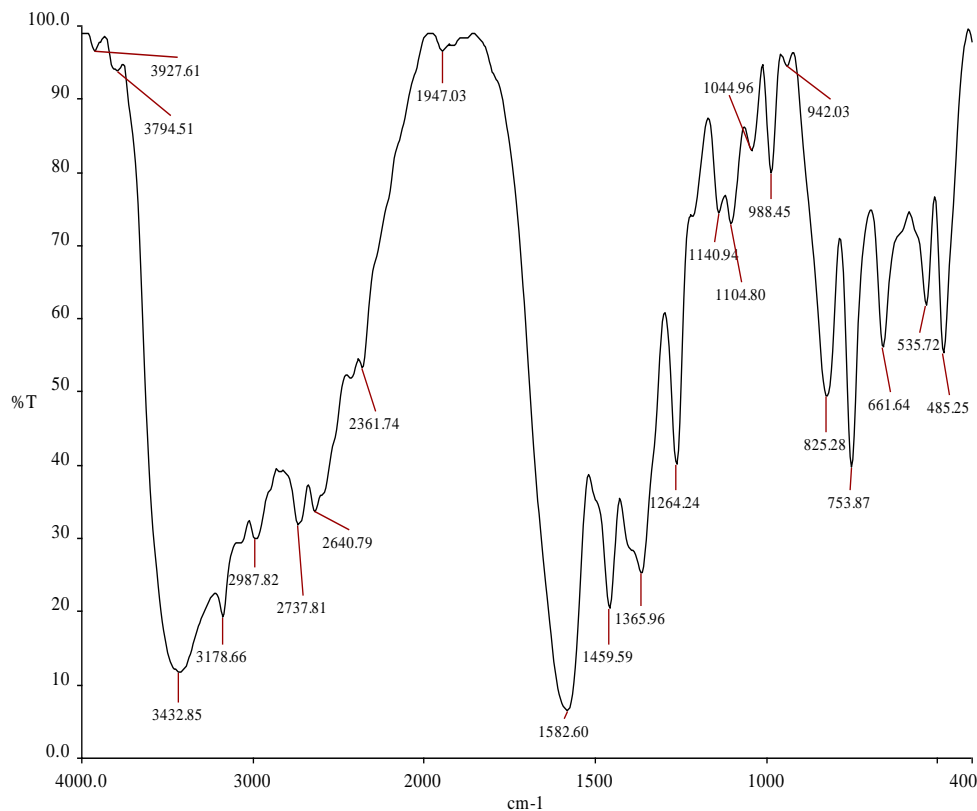


Figure 1. FT-IR of ligand H₂SAla.

confirm the presence of water molecule coordinated to the metal ion (22) and it is confirmed by TGA. In the far IR region, the complexes showed band around 600 to 400 cm⁻¹. That may be assigned to (Cu – N) and (Cu – O) groups (23).

[Cu(SAla)bpy(H₂O)].H₂O

The IR spectrum of this compound has a band at 3476 cm⁻¹ due to the water molecule of the copper complex. The phenolic (C-O) stretching vibration was observed in the 1037 cm⁻¹ region as broad absorption. The bands in the region of 1416 cm⁻¹ (Sym COO⁻¹ stretching vibration) suggest that the amino acid's carboxyl group was involved in the complex formation. The band at region of 2990 to 2730 cm⁻¹ indicates for CH₃ and CH₂ group in the complexes. ν (C-H) of uncoordinated 2,2'- bipyridine observed at 831 to 737 cm⁻¹ respectively shifted to 757 cm⁻¹ in the mixed ligand complexes. The coordinated water in copper(II) complex with 2,2'-bipyridine present at different peak at 930.1 cm⁻¹ (rocking) and 757 cm⁻¹ (wagging) where as none of the vibration appear in the spectra of the uncoordinated ligand. A new strong metal dependent absorption was found at about 600 to 400 cm⁻¹. This band may probably be assigned to ν (Cu - O) and

(Cu – N) of stretching vibration (Raman et al., 2009) (Figures 1 to 3).

¹H NMR

Nuclear magnetic resonance is a powerful spectroscopic technique for investigating molecular structure and dynamics. It involves reorientations of nuclear spins with respect to an applied static magnetic field. ¹H NMR spectra of the prepared ligands have been recorded in DMSO-d₆. The assignment of every signal has been achieved by comparing the ¹H NMR spectra of the ligands reported in literature (Karmakar et al., 2005). Each type of signal has a characteristic chemical shift range that can be used for initial assignment. The ligands H₂SAla shows a significant chemical shift of the aromatic protons in the region 6 to 8.5 ppm indicating the formation of ligand. Thus the overall shifts of the NMR spectra of the ligands confirm the formation of ligands and its possibility of coordination with the ligand (Figure 4). Yield, 42.42%, mp 116°C, ¹H NMR DMSO-d₆ δ (ppm) 1.51-1.28 (d, 3H, J= 9.2Hz), 3.24 (q 1H J= 9.2 Hz), 4.46-4.52, (m, 2H, J= 24Hz), 6.31-6.50 (m, 2H), 6.75-6.88 (m, 2H).

In the ¹H NMR spectrum of the schiff base observed as

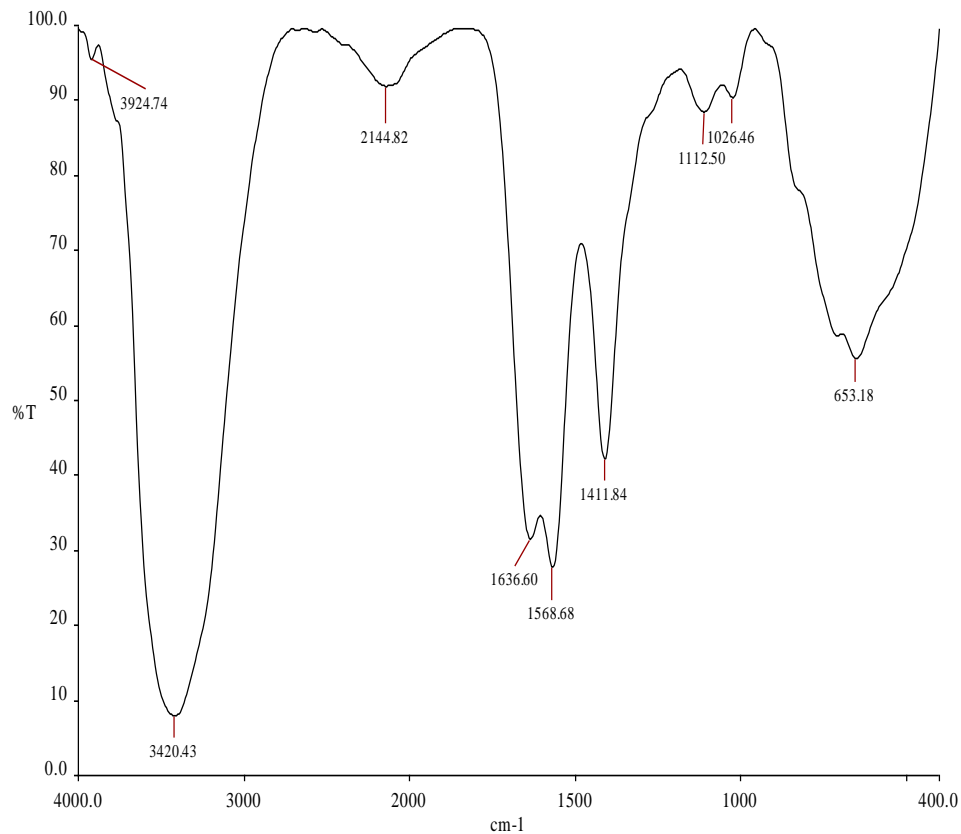


Figure 2. FT-IR of [Cu(SAla)phen(H₂O)].H₂O.

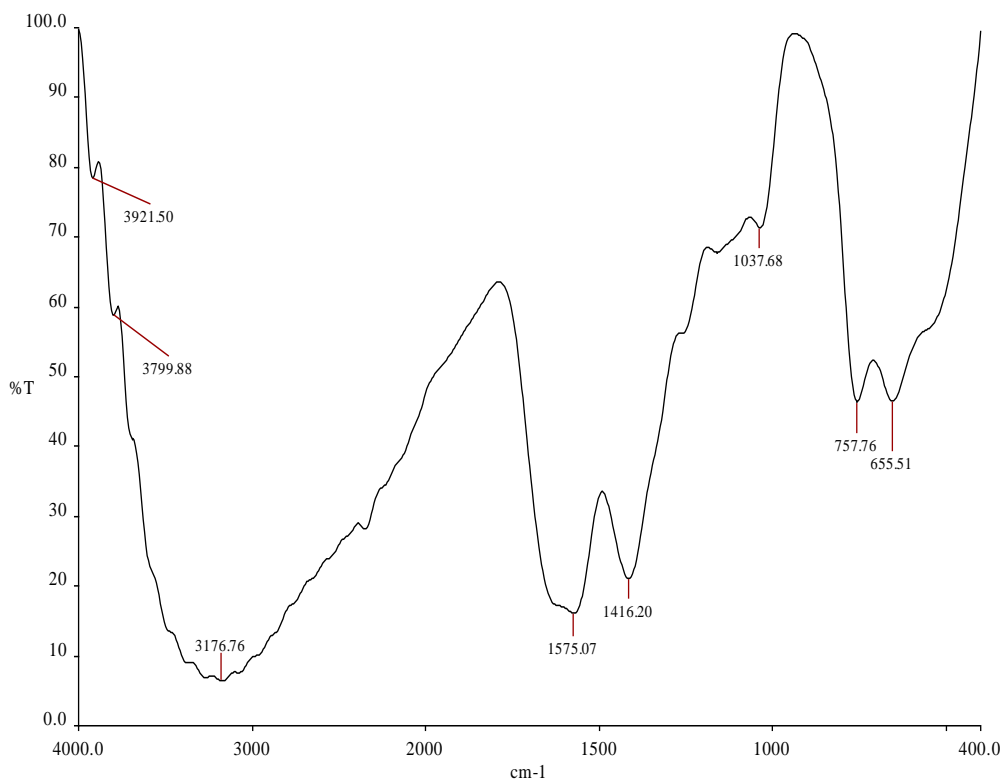


Figure 3. FT-IR of [Cu(SAla)bpy(H₂O)].H₂O.

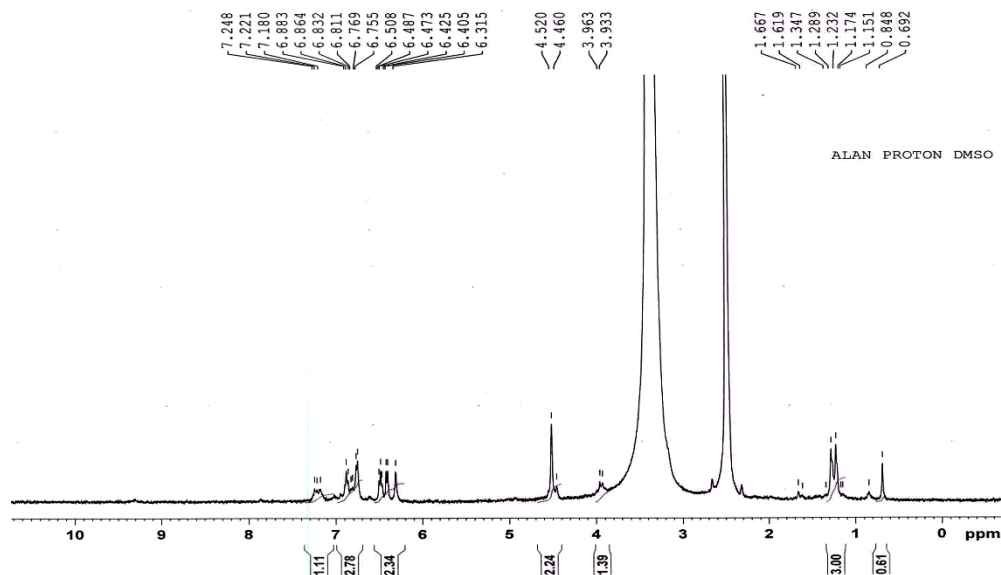


Figure 4. ^1H NMR spectra of H_2SAla .

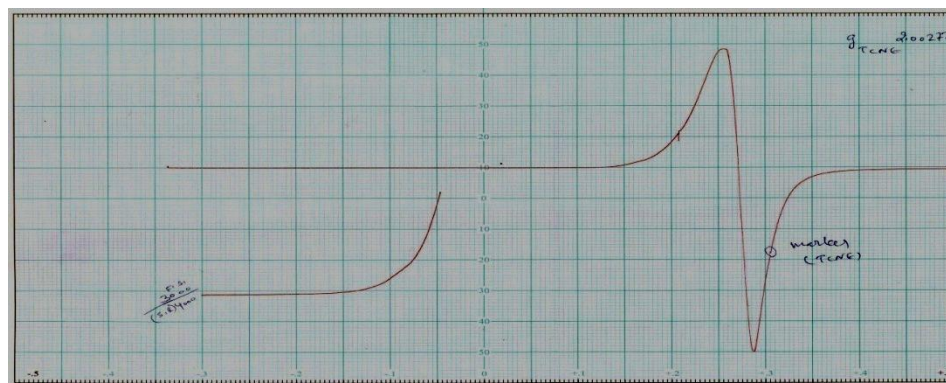


Figure 5. ESR spectral analysis of $[\text{Cu}(\text{SAla})\text{phen}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$.

a doublet in the region 1.51-1.28 (d, 3H) methyl proton, quartet at 3.24 (q, 1H) due to (N-CH) proton, respectively. In addition the signal in the region 6.31-6.88 (m, 4H) were attributed to aromatic proton. A characteristic proton signal at 4.46-4.52 (m, 2H) were assigned to (ph- CH_2).

ESR spectroscopy

ESR spectroscopy is a sensitive technique which is useful in the study of electronic structure of many species including organic free radicals, biradicals, most transition metals and rare earth species. The ESR spectra of the copper complex provide information of importance in studying the metal ion environment.

The ESR spectrum of metal complexes provide information about hyperfine and superhyperfine structure

which are of importance in the study of the environment of the metal ion in the complex, that is, the geometry and the nature of the ligating sites of the schiff base in the metal. The X band ESR spectrum of the polycrystalline copper complex recorded at 100 K shows a well resolved hyperfine splitting and exhibits two intense absorption values, indicating the magnetic anisotropy in the complex (Raman et al., 2009).

The ESR spectral analysis of $[\text{Cu}(\text{SAla})\text{phen}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ complex g_{iso} value was 2.08 and for $[\text{Cu}(\text{SAla})\text{bpy}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ complex g value was 2.087 in present study gives only g_{iso} value in the range of 2.08, 2.087 which was < 2.3 indicating covalent nature of the solid complex. The electronic spectra, magnetic moment value and the relative isotropy of g parameter indicate that the Cu(II) complex shows the octahedral geometry (Figures 5 and 6).

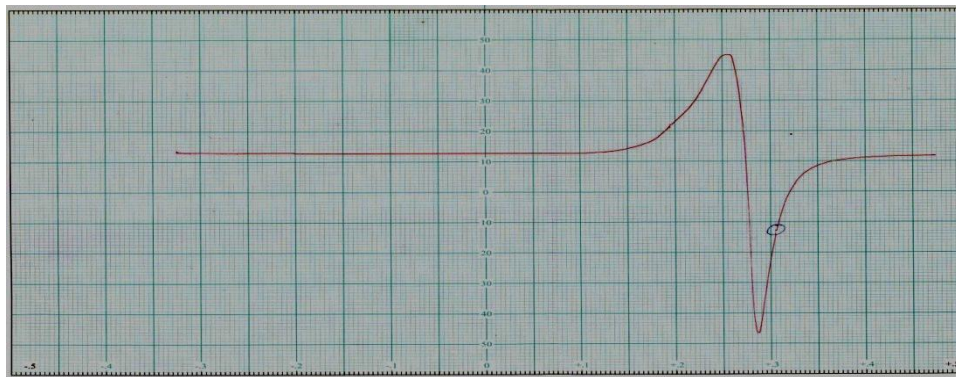


Figure 6. ESR spectral analysis of Cu(SAla)bpy(H₂O)].H₂O.

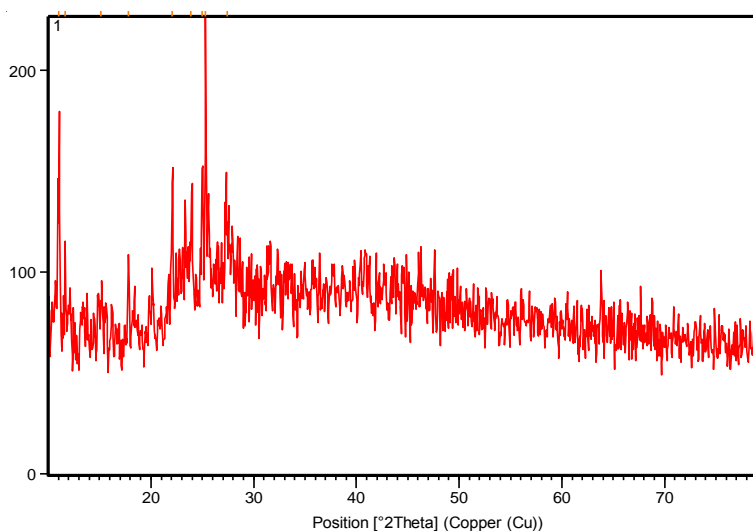


Figure 7. XRD pattern of [Cu(SAla)phen(H₂O)].H₂O.

$$g_{\text{iso}} = \frac{B \text{ marker} \times g \text{ marker}}{B_{\text{iso}}}$$

$$B_{\text{iso}} = \frac{30.7 \times 75.37}{100}$$

$$g_{\text{iso}} = \frac{24.26 \times 2.0027}{23.138}$$

$$g_{\text{iso}} = 2.100$$

$$g_{\text{iso}} < 2.3 \text{ (Covalent nature)}$$

XRD and SEM study

The XRD pattern of [Cu(SAla)phen(H₂O)].H₂O,

Cu(SAla)bpy(H₂O)].H₂O complexes (Figures 7 and 8) showed well defined crystalline peaks indicating that the complex was amorphous in nature. It has specific 'd' values which can be used for its characterization. The crystallite size of the complex d_{XRD} could be estimated from XRD patterns using the Scherrer's formula:

$$d_{\text{XRD}} = 0.9 \lambda / \beta (\cos\theta)$$

Where λ is the wavelength, β is the full width at half maxima and θ is the diffraction angle. The XRD shows that the [Cu(SAla)phen(H₂O)].H₂O, Cu(SAla)bpy(H₂O)].H₂O complexed had the average crystallite size of 51.65 nm and 51.93 nm respectively confirming the nanocrystalline nature of the complex. The surface morphology of [Cu(SAla)phen(H₂O)].H₂O, Cu(SAla)bpy(H₂O)].H₂O complexes are shown in Figures 9a and b. From the SEM images of the complexes, it was inferred that the amorphous, in agreement with powder

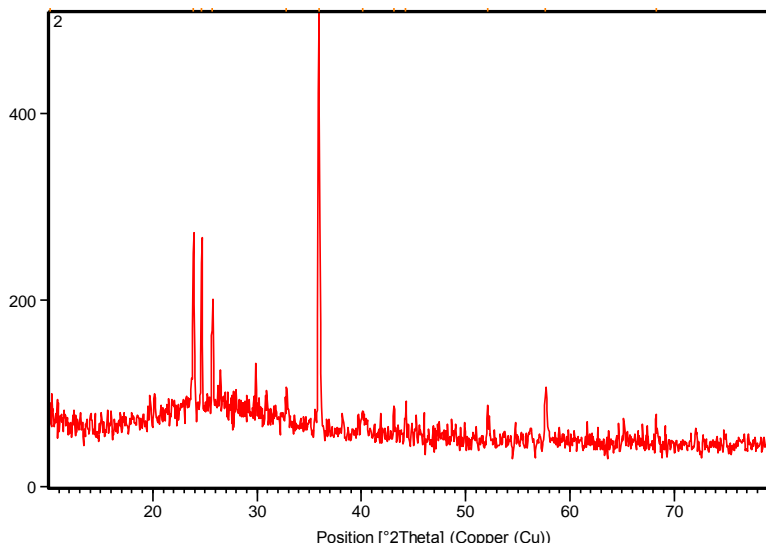


Figure 8. XRD pattern of Cu(SAla)bpy(H₂O).H₂O.

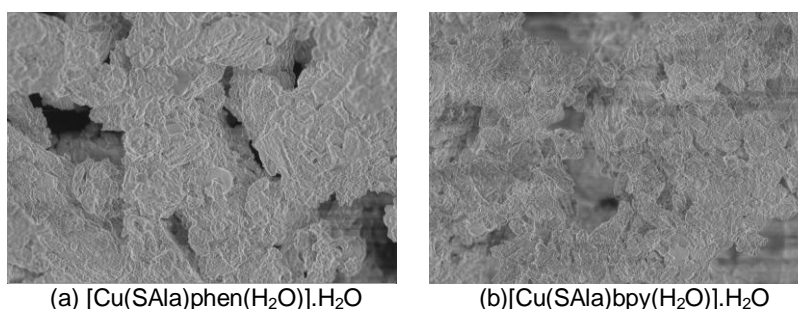


Figure 9. SEM Images of Cu(II) complexes.

XRD results. The particle size of the above complexes was in the diameter range of nano region. Based on the above spectral data, the structure of [Cu(SAla)bpy(H₂O)].H₂O and [Cu(SAla)phen(H₂O)].H₂O complexes assigned as shown in the Figure 12.

Thermal analysis of copper(II) complexes

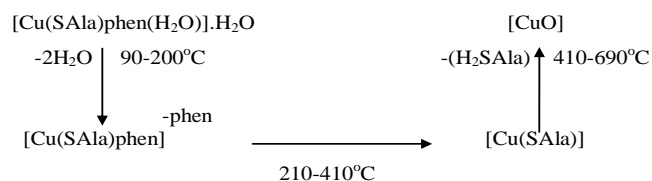
The thermal behavior of the synthesized complexes has been studied to establish different decomposition process and to confirm the proposed stoichiometry. The results of such analysis have been summarized in Table 3 indicating a good correlation between calculated and found weight loss values. The thermal behavior of synthesized complexes was characterized on the basis of TGA / DTG and DTA method. Thermal analysis plays an important role in studying the stability, melting point, structure and decomposition properties of the metal complexes. TGA was studied from room temperature to 1400°C in nitrogen atmosphere. TGA curve was drawn

as percentage mass loss (Vs.) temperature.

[Cu(SAla)phen(H₂O)].H₂O

TGA / DTG and DTA curve of the complex were represented. The thermal decomposition of the compound [Cu(SAla)phen(H₂O)].H₂O takes place in three stages. In the first stage of thermal dehydration of the complex takes place in a single step that is between 90 and 200°C with mass loss of 20.3%

The water molecule was removed in this step. The maximum rate of mass loss was indicated by DTG peak at 120°C.



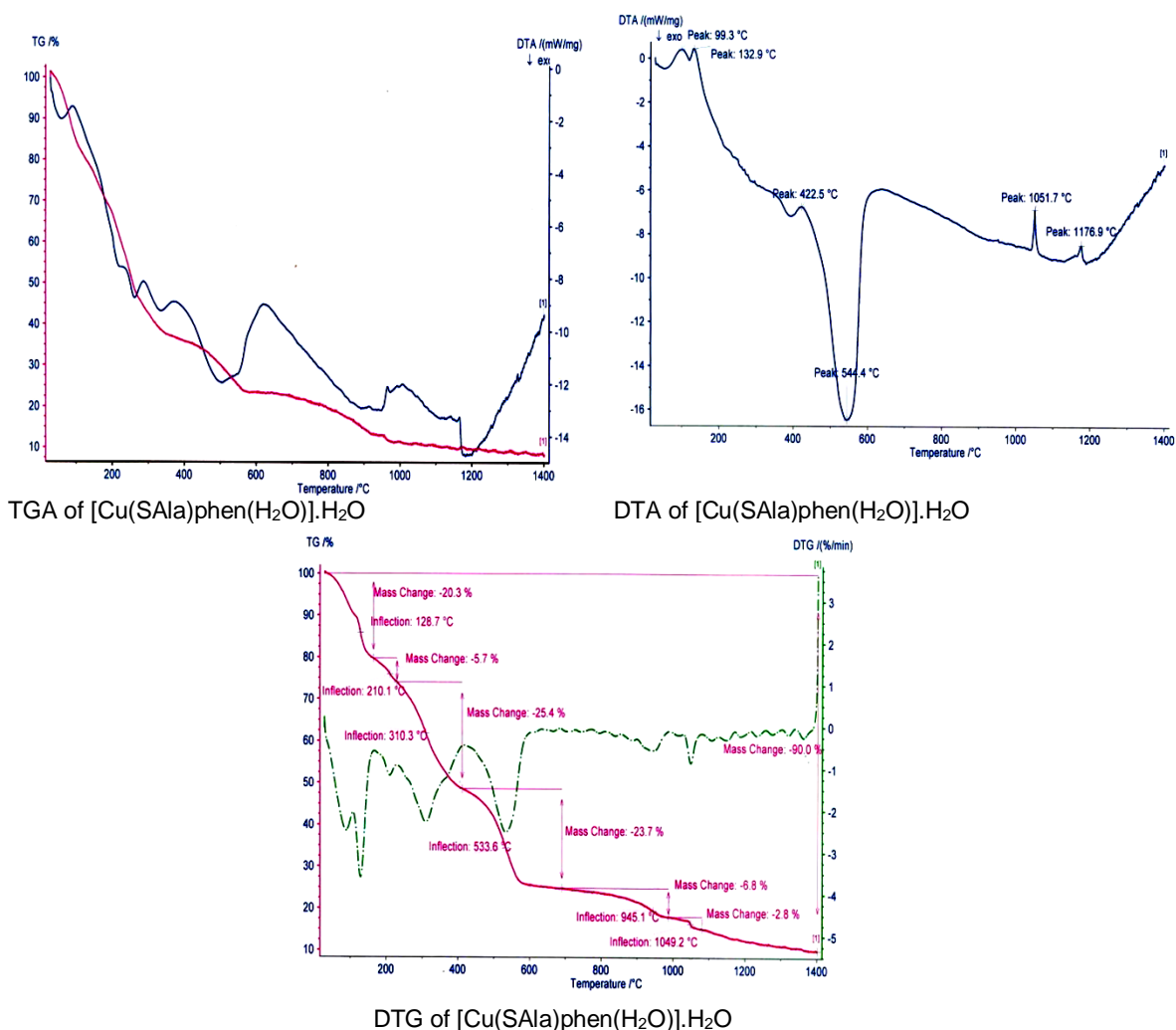


Figure 10. Thermal analysis of $[\text{Cu}(\text{SAla})\text{phen}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$.

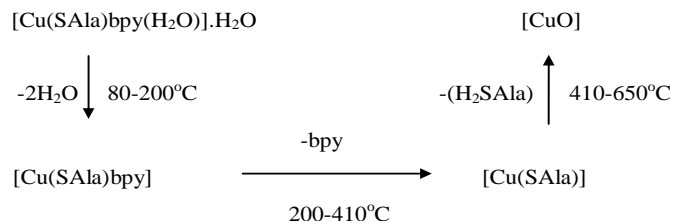
In the second stage which occurs in the temperature range 210 to 410°C with DTG peak observed at 310°C, this range corresponds to the decomposition of phenanthroline ligand and the observed mass loss was recorded as 25.4%. The third stage was the decomposition of schiff base ligand (H_2SAla) in the temperature range 410 to 700°C with the DTG peak observed at 550°C

The overall mass loss observed was 90% and it was compared with theoretical mass loss value which was found correct. The end product estimated was CuO . The observed mass and the calculated mass were almost equal (Figure 10 and Table 3).

$[\text{Cu}(\text{SAla})\text{bpy}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$

The thermal dehydration of this complex in the first stage which accounts for a mass loss of 30.2% was attributed

to the loss of water leaving behind the non hydrated complex takes place between 80 to 200°C. The maximum rate of mass loss was indicated by the DTG peak at 81.6°C:

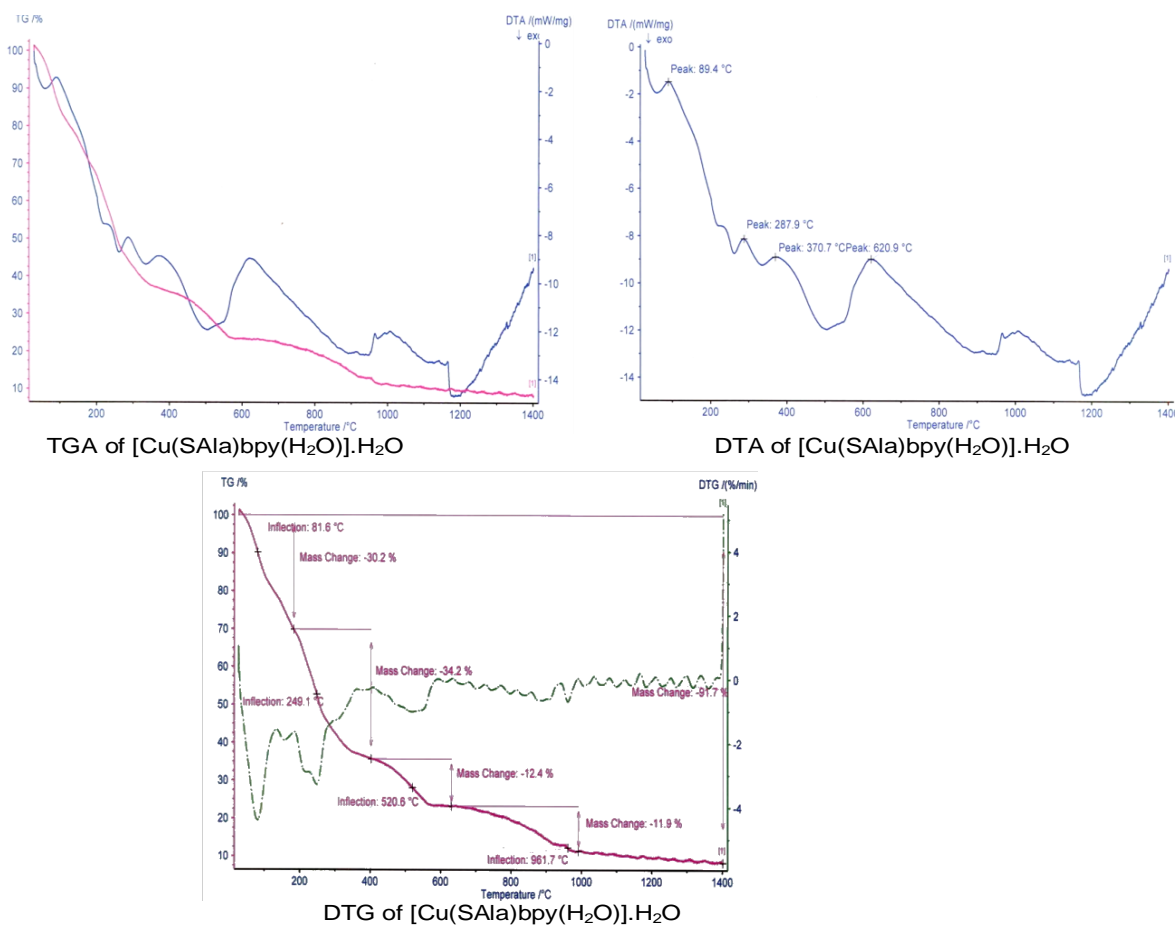


The remaining complex begins to decompose from range 200 to 410°C with DTG peak observed at 249.1. This range corresponds to the decomposition of bipyridyl ligand for DTA peaks observed at 287.9 which clearly shows that at least unstable intermediates are also formed during this degradation stage. The observed

Table 3. Thermal analysis of Cu(II) complexes by TGA, DTA and DTG method

S/N	Name of the complexes	TGA range (°C)	Stage	Mass loss (%)	DTA (°C)	Process	DTG	Evolved moiety
1	[Cu(SAla)Phen(H ₂ O)].H ₂ O	90-210	I	5.7	(+)132.9	Endo	120	Dehydration of H ₂ O
		210-410	II	25.4	(+)300.10	Endo	310	Partial decomposition of Phenanthroline
		310-690	III	23.7	(+)544.4	Exo	533.6	Removal of (H ₂ SAla)
		>690	Residue	9.6	1051	Endo	945.1	Leaving CuO
2	[Cu(SAla)bpy(H ₂ O)].H ₂ O	80-200	I	30.2	89.4	Endo	81.6	Dehydration of H ₂ O
		200-400	II	34.2	287.9	Endo	249.1	Removal of bipyridyl
		400-650	III	12.4	510	Exo	520.6	Removal of (H ₂ SAla)
		>650	Residue	11.9	960	Endo	961.7	Leaving CuO

TGA, Thermogravimetric analysis; DTA, Differential thermal gravimetric; DTG, differential thermogravimetric analysis.

**Figure 11.** Thermal analysis of [Cu(SAla)bpy(H₂O)].H₂O.

mass loss was 34.2%. The third stage was decomposition of ligand (H₂SAla) in temperature range of 410 to 650°C with the DTG peak observed at 520°C and DTA peak observed at 510°C. The overall mass loss observed was 91.7% and it was compared with

theoretical mass loss value.

The end product estimated as CuO and the observed mass and calculated mass were overall equal. As a result the observed product was in good agreement with the metal oxide (Figure 11).

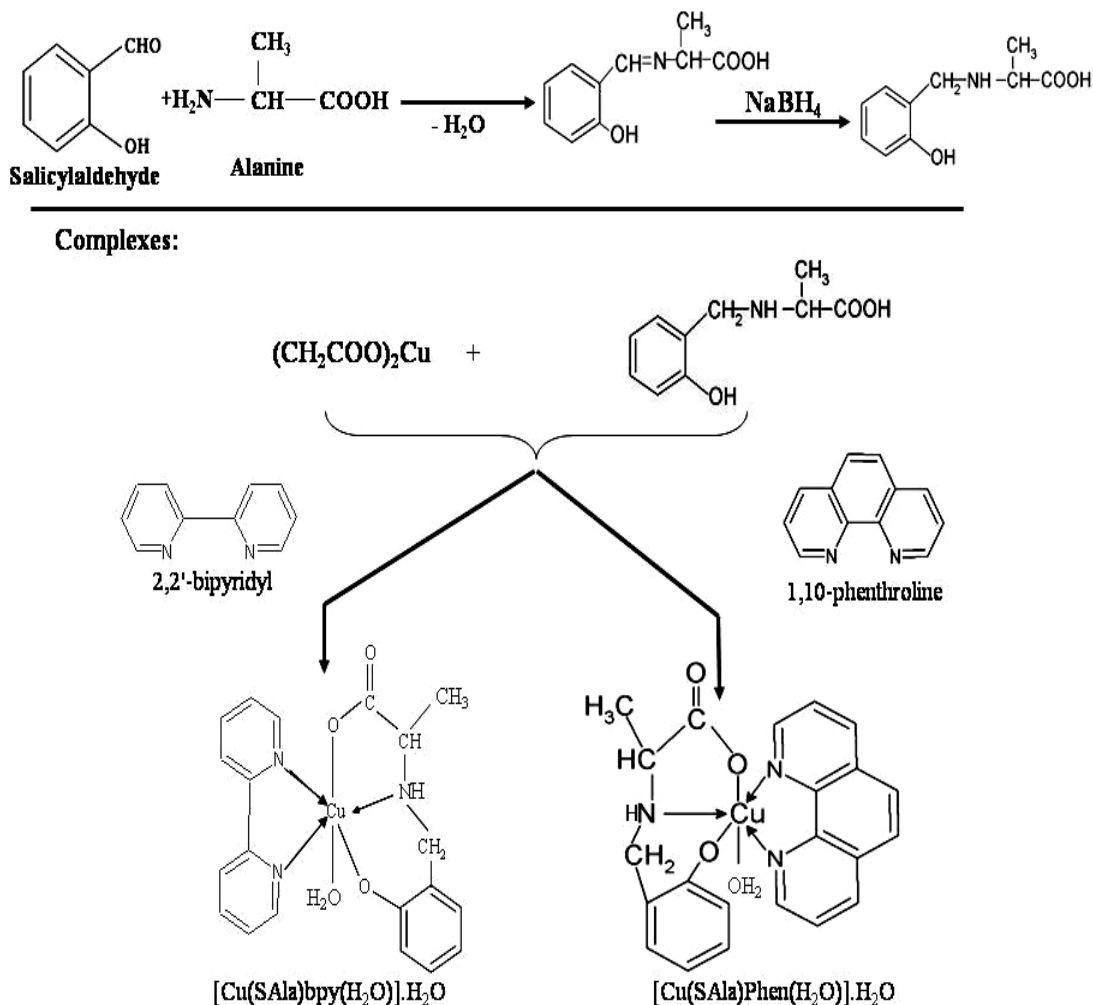


Figure 12. Synthesis scheme and proposed structure of $[\text{Cu}(\text{SAla})\text{bpy}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ and $[\text{Cu}(\text{SAla})\text{phen}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$.

Conflict of Interest

The authors have not declared any conflict of interest.

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