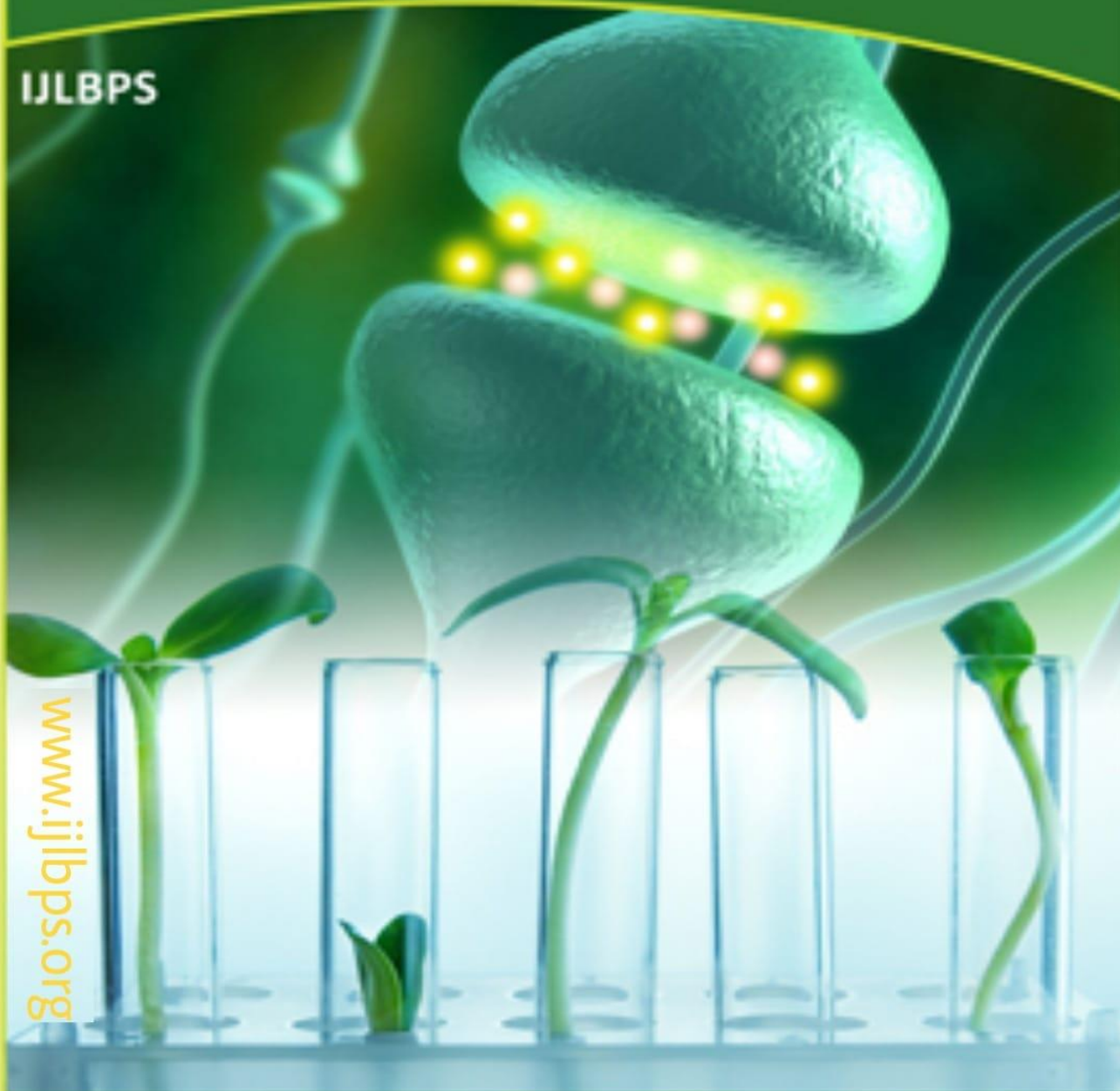




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Characterization of complexes formed between 3-indole acetic acid and divalent metal ions

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Abstract

Research shows that carboxylic acids' coordination chemistry has been investigated extensively, as shown by a survey of the relevant literature. However, the current study was prompted by the dearth of published information on the coordination chemistry of modified acetic acid moieties. The present study characterized the base moiety indole acetic acid (IAA) using elemental analysis, UV-Visible, FT-IR, and ¹H-NMR spectroscopy, and investigated its interaction with cobalt (II), copper (II), and nickel (II) in non-aqueous media such as ethanol. Chemical analysis, electrical conductivity, elemental analysis, and spectral measurement (UV-visible, FT-IR, and ¹H-NMR) were used to characterize the solid-state synthesized metal complexes of cobalt (II), copper (II), and nickel (II) ions with IAA. The synthesized complexes' magnetic susceptibility was also tested.

Key-Words: Indole acetic acid, Bivalent metal ion Copper, Cobalt, Nickel

Introduction:

The chemical subfield of "coordination" is expanding quickly. It may be used in a wide variety of contexts. Co-ordination compounds are common in nature and include things like the green pigment chlorophyll found in plants and the red pigment hemoglobin found in blood. Accepting electrons from the ligands in the form of dative bonds results in the creation of a metal-ligand complex, which provides a great deal of stability to the transition metals since they have a maximum number of unoccupied d-orbital. Iron, cobalt, and nickel are more prone to forming complex compounds among the transition metals. Most plant

life cannot tolerate even small amounts of heavy metals in the soil. Roots that are exposed to high concentrations of heavy metal ions absorb them and transport them to the shoot, where they disrupt metabolism and stunt development. [1,2] Substances and Techniques This chapter provides a concise summary of the analytical approaches used in this study. The synthesized compounds were characterized by their molecular conductance, magnetic susceptibility, infrared spectral measurement, ultraviolet spectral measurement,

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¹H NMR spectral measurement, elemental analysis, and chemical analysis. Conductivity of electricity. The concentration was estimated to be approximately 103 M. KBr pellets were used to collect the infrared spectra of the ligand NAA and the complexes in the standard range of 4000-400 cm⁻¹. First, a 300 K ¹H-NMR spectra was obtained using DMSO-D₆ and CHCl₃-D as solvent and TMS as the internal standard. The organic ligand IAA and its cobalt (II) complex have been investigated using ¹H-NMR spectroscopy in order to clarify their structure. To determine the electronic spectra of the current ligand and the colored metal complexes, a Lambda 35 spectrophotometer was used to analyze solutions of DMF and DMSO. The gadget could measure wavelengths from 350 to 1100 nanometers. A Gouy magnetic balance was used for the magnetic measurements. Hg[Co(SCN)₄] was used for the calibration of the Gouy tube, and Pascal's constants were used for the diamagnetic corrections. To get the effective magnetic moments, we used Curie's relation, $\chi = 2.84[XM \text{ corr.} T] / 2B.M$, where T is the measured absolute temperature. The metal content of naphthalene acetic acid metal complexes was determined by degrading the complexes in concentrated nitric acid. The weight-to-charge ratios of cobalt (II) and nickel (II) were calculated. Iodometric titration was used to identify copper (II). Indigo acetic acid, the chemical make-up of the ligand carbon and hydrogen content analysis resulted in the conclusion that. Hydrogen and carbon content were measured by means of a Vario EL III analyzer.

Methods of Experimentation

Indole acetic acid metal complex synthesis. Cobalt (II) Complex Fabrication Cobalt (II) chloride (0.01 M), weighing 1.190 g, was dissolved in 25 ml of hot distilled water in a 100 ml beaker. 5.58 grams of IAA (0.03 M) were measured out and dissolved in 25 milliliters of hot ethanol in a separate 100 milliliter beaker. The metal salt solution was slowly added to the clear ligand solution while being stirred for 10 minutes. A brownish solid complex precipitated out of the solution. It was filtered, washed many times in ethanol, and then ultimately washed in solvent ether. A vacuum desiccator was used to dry the complex before storing it. Cu(II), Ni(II) complexes were also prepared using the same method.

Cobalt Estimation

A weight-based estimate of cobalt was made. The cobalt solution was then spiked with the right proportions of mercuric chloride and ammonium thiocyanate. Hg[Co(SCN)₄], a solid combination of mercury and cobalt, was isolated. The amount of cobalt was deduced from the total mass of the structure. Copper price prediction Copper content was calculated using iodometry. When ammonium hydroxide was added to the copper solution, a light blue precipitate formed. Almost 2 grams of solid potassium iodide were added to the acetic acid solution, and after thorough mixing, the resulting freed iodine was titrated against standard sodium thiosulphate. The final result was achieved by adding 2 ml of starch solution. The last stage was the loss of all blue hues. The quantity of copper was determined using the titre value.

Nickel Quantification

The following is a gravimetric approximation of nickel. After diluting the clear solution with distilled water to a volume of 100ml, 5ml of 1:1 HCl was added. Following that, the temperature of the solution was raised to about 80 degrees Celsius. Drop by drop, while continuing to agitate the heated solution, around 20 ml of a 1% alcoholic solution of dimethyl glyoxime reagent was added. To quickly alkalize the solution, a diluted ammonia solution was added drop by drop. The combination of nickel dimethyl glyoximate turned out to be a rosy crimson precipitate. After settling for approximately an hour in a water bath, the precipitate was digested. After being filtered, washed with hot water, dried in an air oven, chilled in a desiccator, and finally weighed, the precipitate was ready for analysis. The amount of nickel was determined by weighing the dimethyl glyoximate complex.

Discussion and Results

The novel base, indole acetic acid (IAA), has two oxygen atoms that may act as donors. It is important to investigate the binding of the IAA to the metal atom in the presence of a transition metal salt. This led to the procurement and subsequent deployment of the novel base IAA.

Conclusions from Analyses

Table 1 provides the elemental analysis data for IAA and its compounds. Empirical formulas may be derived from the percentage makeup of IAA and its complexes.

Table 1: Analytical Results on IAA and its Metal Complexes

Compound	%C found (expected)	% H found (expected)	% M found (expected)
IAA (C ₁₀ H ₉ NO ₂)	76.49 (77.41)	5.32 (5.37)	-
Co(C ₁₀ H ₈ NO ₂) ₂ .2H ₂ O	62.20 (61.94)	4.62 (4.73)	12.74 (12.68)
Ni(C ₁₀ H ₈ NO ₂) ₂ .2H ₂ O	62.42 (61.81)	4.82 (4.72)	13.06 (12.86)
Cu(C ₁₀ H ₈ NO ₂) ₂ .2H ₂ O	61.46 (61.33)	4.96 (4.69)	13.88 (13.53)

Insights about IAA

Melting point, elemental analysis, infrared, UV, and ¹H-NMR spectra were used to characterize the pure commercial IAA product. Table 1 displays the results of an elemental analysis of IAA. Vibrational frequencies of significance are tabulated in Table 2. Tabulated in Table 3 are the ¹H-NMR resonance signals. The NH stretching of carboxylic acids is responsible for a moderately significant absorption band in the IR spectra, seen at 3389 cm⁻¹. The C-H aromatic vibration is responsible for the absorption band at 700–600 cm⁻¹, while C=O absorption is responsible for the band at 1701 cm⁻¹. The side chain

methylene CH₂ stretching at 2734 cm⁻¹ may account for the absorptions seen in the region 1696–1510 cm⁻¹. Multiplet signals for the free ligand IAA may be seen at 7.966 GHz. The signal at 7.4–7.0 ppm is attributed to the protons of the CH₂ group, whereas the signal at 7.246 ppm is attributable to the aromatic protons. It is predicted that a chemical shift of 10–14ppm will be seen because of the carboxylic proton (COOH). When scanning a spectrum, the range is often used. This signal was not detected between -0.5 and 9.5 ppm.

Table 2: Infrared Spectral Bands of IAA Complexes (cm⁻¹)

Compound	$\nu_{as}(\text{CO}_2^-)$	$\nu_{s}(\text{CO}_2^-)$	Δ	$\nu(\text{MO})$	$\nu(\text{H}_2\text{O})$
Free IAA ⁻	1701	1100	601	-	-
Co(IAA ⁻) ₂ .2H ₂ O	1711	1021	690	523	3432
Ni(IAA ⁻) ₂ .2H ₂ O	1621	1018	603	540	3107
Cu(IAA ⁻) ₂ .2H ₂ O	1721	1022	699	511	3397

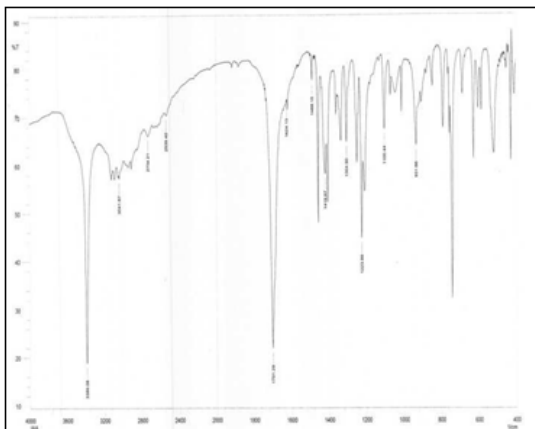


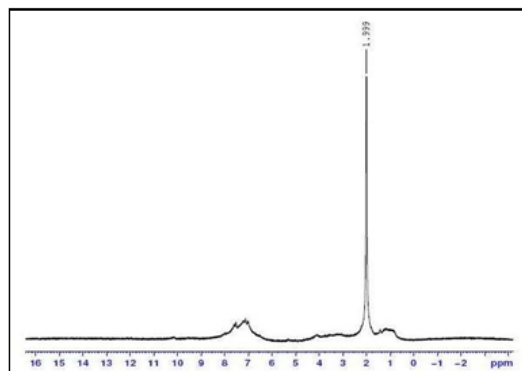
Fig. 1: IR Spectrum of IAA

Table 3: Proton NMR chemical shifts of IAA and its mercury complex (in ppm)

Table 3: Proton NMR chemical shifts of IAA and its mercury complex (in ppm)

Compound	Aromatic Protons	CH ₂ Protons
IAA	7.4-7.0	3.6
Co(C ₁₀ H ₈ NO ₂) ₂ .2H ₂ O	7.6-7.0	1.9

Fig. 2: ¹H-NMR Spectrum of IAA



combine with Co²⁺ to give the pink complex Co(C₁₀H₈NO₂)₂. The elemental analysis (Table 1) and conductivity measured in ~ 10-3M

Fig. 3: ¹H – NMR Spectrum of Co(C₁₀H₈NO₂)₂.2H₂O

Table 4: Magnetic and Electronic Spectral Data on IAA metal Complexes

Complex	μ_{eff} (BM) (Colour)	Absorption bands (cm ⁻¹)	Electronic transition
Co (IAA ⁻) ₂ .2H ₂ O	4.80 (Brown)	19058 15356 33670	⁴ T _{2g} (F) → ⁴ T _{1g} (P) ⁴ T _{2g} (F) → ⁴ A _{2g} (F) Charge transfer.
Ni (IAA ⁻) ₂ .2H ₂ O	2.84 (Green)	24814 13405 9814	³ A _{2g} (F) → ³ T _{1g} (P) ³ A _{2g} (F) → ³ T _{1g} (F) ³ A _{2g} (F) → ³ T _{2g} (F)
Cu (IAA ⁻) ₂ .2H ₂ O	1.45 (Green)	11509 32159	² E _g → ² T _{2g} (F) Charge transfer

Characterization of Co (C₁₀H₈NO₂)₂.2H₂O

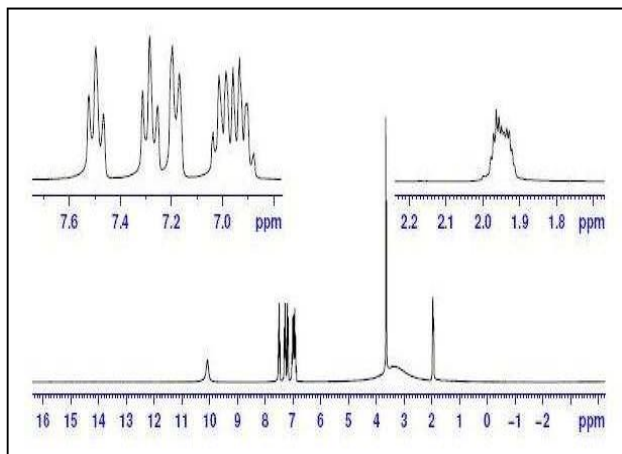
This brown coloured complex having 1:2 metals: ligand stoichiometry may have Co²⁺ oxidation state. During the interaction Co^{II} chloride with IAA the

carboxylic acid might have ionized to give the carboxylate anion which

DMF solution confirm the same.

The free acetate ion (CH_3COO^-) shows absorption at 1711 and 1021cm^{-1} which are attributed to ν_a (COO^-) and ν_s (COO^-) respectively. Considering the IAA^- ion, the band at 1624cm^{-1} may be due to symmetric ν_s (COO^-) vibrations. In the case of the cobalt (II) complex

these respective absorption bands are observed at 1711 and 1021cm^{-1} . The difference (Δ) between the asymmetric and symmetric bands of free IAA^- is at a much higher value of 189cm^{-1} where as in the complex spectrum, Δ is much lower at 100cm^{-1} indicating bidentate chelation of the carboxylate ligand to Co(II) ion.



A perusal of the electronic spectrum of the Co(II) complex shows several bands due to $d-d$ transition, charge transfer and ligand origin. A very weak absorption at 524.7nm (19058cm^{-1}) may be attributed to $4T_2g(F) \rightarrow 4T_1g(P)$ transition. Another very weak absorption band found at 651.2nm (15356cm^{-1}) is attributed to $4T_2g(F) \rightarrow 4A_2g(F)$ transition. A strong band

found at 297nm (33670cm^{-1}) may be due to charge transfer transition. The effective magnetic moment measured at room temperature for the Co^{2+} ion is 4.8 B.M. . Hence, on the basis of chemical analysis, infrared and electronic spectra and magnetic moment the cobalt (II) complex is proposed to have an octahedral stereochemistry.

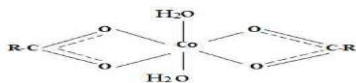
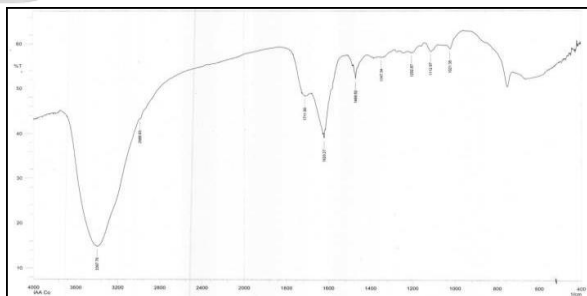


Fig. 4: Structure of $\text{Co}(\text{C}_{10}\text{H}_8\text{NO}_2)_2 \cdot 2\text{H}_2\text{O}$

The infrared absorptions observed at 3407 , 1620 , 800 and 625cm^{-1} are attributed to the ν (OH), δ (HOH),

ρ_r (HOH) and ρ_w (HOH) vibrations of coordinated water molecules respectively.



Characterization of Ni (C₁₀H₈NO₂)₂·2H₂O

The green coloured nicked (II) complex on elemental analysis is found to have 1:2 stoichiometries. Very low electrical conductivity value indicate the complex to be a non-electrolyte. An examination of IR spectrum of

this shows the appearance of ν_a (COO⁻) at 1621cm⁻¹ and that ν_s (COO⁻) at 1018 cm⁻¹. The difference between the symmetric and anti symmetric absorption is at 100 cm⁻¹ which much less than the free ion (IAA⁻) value (189cm⁻¹) this spectral feature indicates the bidentate chelation of the carboxylate ligand. Also the far IR absorption band seen at 2377cm⁻¹ may be due to ν (Co-O). The IR spectrum also shows bands at

3107(ν_r), 1631, 801, and 625 cm⁻¹ which are attributed to the presence of coordinated water molecules. The band found at 540 cm⁻¹ is ascribed to the (Ni- O) stretching vibration. The electronic spectrum of the Ni II complex shows an absorption at 24814 cm⁻¹ (403 nm) which is attributed to $3A_{2g}(F) \rightarrow 3T_{1g}(P)$ transition, another band at 13405CM⁻¹ (746 nm) due to $3A_{2g}(F) \rightarrow 3T_{1g}(F)$ and a third band at 9814 CM⁻¹ (1019 nm) due to $3A_{2g}(F) \rightarrow 3T_{1g}(F)$ transition. These absorption bands are indicative of an octahedral symmetry of Ni II in the complex. The μ_{eff} value measured at 2.84 B.M is also supportive of octahedral geometry. Hence, based on analytical conductivity and magnetic data and IR and UV-visible spectroscopy a bidentate chelation of the organic ligand and octahedral stereochemistry is proposed to this complex.

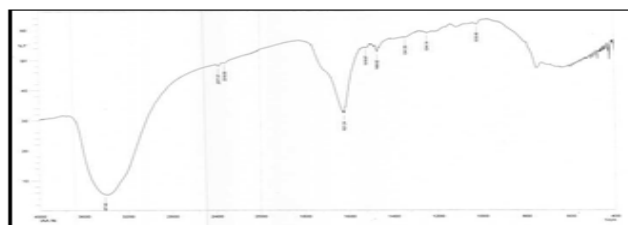
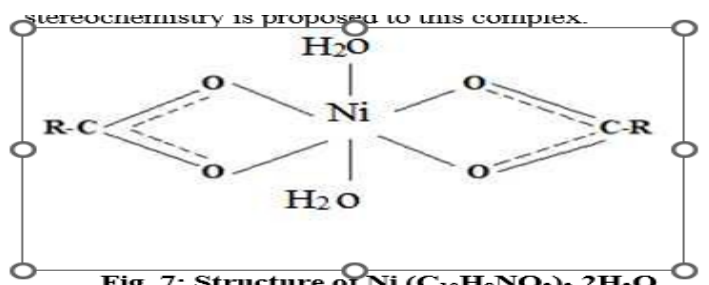


Fig. 8: IR Spectrum of Ni (C₁₀H₈NO₂)₂·2H₂O

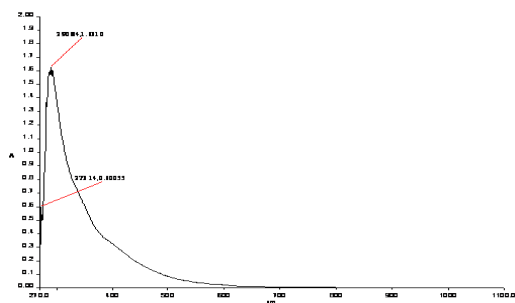


Fig. 9: UV-Spectrum of Ni(C₁₀H₈NO₂)₂·2H₂O Characterization of Cu (C₁₀H₈NO₂)₂·2H₂O

On the basis of chemical and elemental analysis this complex is given 1:2 stoichiometry. The very electrical conductance measured for this complex reveals that the complex is non-ionic. The IR spectrum indicates the presence of ν_a (COO⁻) and ν_s (COO⁻) vibrational frequencies at 1721 and 1022 cm⁻¹ respectively. The difference between these two is much higher than expected for bidentate chelation mode of coordination

of IAA- ligand. Presence of water in the coordination sphere is indicated by IR bands at 3432 (ν), 2379, 700 (split) and 600 cm⁻¹. The band at 511 cm⁻¹ also points to the binding of Cu and O atoms. The green coloured CuII complex

measures an electronic absorption band at 11509 cm⁻¹ (868.86 nm) which is attributed to $2E_g \rightarrow 2T_2g$ (F). It also exhibits another band at 32159 cm⁻¹ (310.95 nm) which may be due to charge transfer transition. The complex has a μ_{eff} value of 1.45 B.M per Cu atom at room temperature. The very low value of μ_{eff} may be due to a coupling of the unpaired electrons one on each Cu II ion. Hence, based on chemical and elemental analysis, conductivity, magnetic moment, IR and electronic absorption spectra, this complex is given a carboxylato bridged binuclear structure where there is antiferromagnetic interaction between two copper ions.

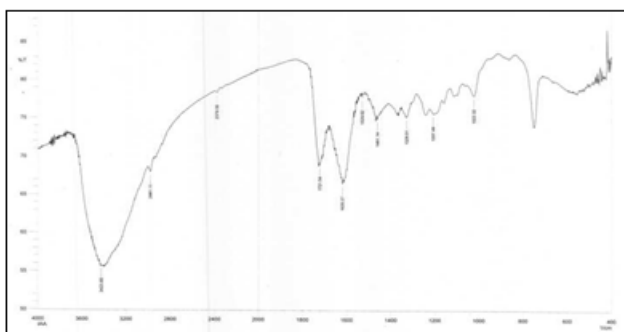
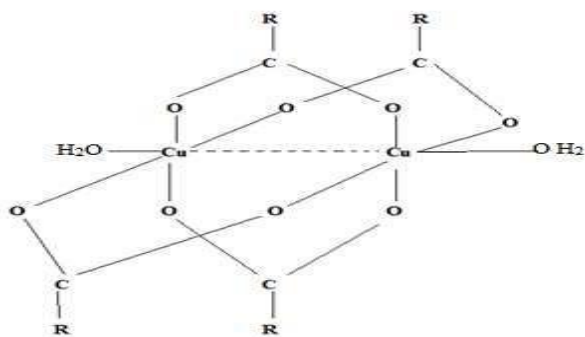


Fig. 11: IR Spectrum of $\text{Cu}(\text{C}_{10}\text{H}_8\text{NO}_2)_2 \cdot 2\text{H}_2\text{O}$

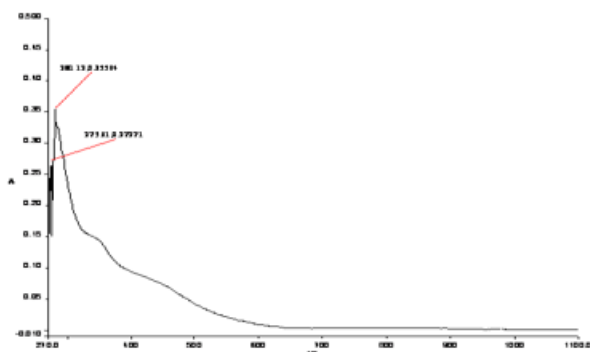


Fig. 12: UV-Spectrum of $\text{Cu}(\text{C}_{10}\text{H}_8\text{NO}_2)_2 \cdot 2\text{H}_2\text{O}$

This work embodies the results on the investigation of coordinating nature of 1- indole acetic acid with transition metals [Co(II), Ni(II), Cu(II)] .It details on transition metal ion complexes with reference to cobalt (II), nickel (II) and copper (II) ions, the biological importance of naphthalene acetic acid and a review on metalboxylates and related compounds. It gives the details of the experimental techniques

employed for the structural characterization of the complexes isolated. The experimental techniques

include electrical conductivity and magnetic measurements, IR, UV-visible and ¹H NMR spectroscopy, elemental and chemical analysis. This work outlines the discussion of the results obtained. On the physico-chemical data obtained the bonding atoms are fixed and the stereochemistry assigned for all the



complexes. The complexes have 1:2 stoichiometry. All of them have two coordinated water molecules each. In the Cu(II) complexes, the carboxylate ligand acts as a

chelating bidentate and in Cu(II) complex, it is bridging bidentate. The very low magnetic moment determined in the case of Cu(II) complex suggests a binuclear bridged structure. The metal ions in all the complexes studied are in an octahedral environment.

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