



## Complexation behaviour of 3- indole acetic acid with divopositive metal ions and the characterization of the complexes

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### Abstract

On literature review, the studies on carboxylic acids reveal that their coordination chemistry has been studied extensively. However, in view of the absence of reports on the coordination chemistry of substituted acetic acid moieties the present investigation has been undertaken. In the present work, indole acetic acid (IAA) a base moiety was characterized by elemental analysis, Ultra Violet-Visible, FT-IR and <sup>1</sup>H-NMR spectroscopy studies and the interaction of the base IAA with bivalent metal ions like cobalt (II), copper (II) and nickel (II) in non- aqueous media like ethanol was studied. The metal complexes of cobalt (II), copper (II) and nickel (II) ions with IAA are synthesized in solid state and their characterization was done by chemical analysis, electrical conductivity, elemental analysis and spectral measurement (UV-visible, FT-IR, and <sup>1</sup>H-NMR). Magnetic susceptibility values have also been measured for the complexes synthesized.

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

### Introduction

Co-ordination chemistry is a rapidly developing field in chemistry. It has versatile applications in a number of ways. Many naturally occurring substances like chlorophyll (green pigment of plants) and haemoglobin (coloring matter in blood) are co-ordination compounds. The transition metals have a maximum number of vacant d-orbital and can gain considerable stability by accepting electrons from the ligands in the form of dative bonds with the resultant formation of a metal-ligand complex. The tendency of the transition metals to form complex compounds is particularly marked with iron, cobalt and nickel. Excessive accumulation of heavy metals is toxic to most plants. Heavy metals ions, when present at an elevated level in the environment, are excessively absorbed by roots and translocated to shoot, leading to impaired metabolism and reduced growth<sup>[1,2]</sup>

### Material and Methods

A short account of the analytical methods employed in this work is presented in this chapter. Molar conductance, magnetic susceptibility, infrared spectral measurement, ultra-violet spectral measurement, <sup>1</sup>H NMR spectral measurement, elemental analysis and chemical analysis were carried to characterize the synthesized compounds.

Electrical Conductivity Measurement was measured the concentration around 10<sup>-3</sup>M. The infra-red spectra of the ligand NAA and the complexes were taken as KBr pellets in the conventional range of 4000-400 cm<sup>-1</sup>. The <sup>1</sup>H-NMR spectrum was recorded employing TMS as internal reference and DMSO-D<sub>6</sub> and CHCl<sub>3</sub>-D as solvent at 300 K. The <sup>1</sup>H-NMR spectral study has been carried out to elucidate the structure of the organic ligand IAA and its cobalt (II) complex. The electronic spectra of the present ligand and the coloured metal complexes were measured in DMF or DMSO solutions using a double beam UV – visible spectrophotometer Lambda 35. The working range of the instrument was 350 – 1100nm. Magnetic measurements were carried out using a Gouy magnetic balance. The Gouy tube was calibrated using Hg[Co(SCN)<sub>4</sub>] and diamagnetic corrections were made with Pascal's constants. The effective magnetic moments were calculated using Curie's relation,  $\mu_{\text{eff}} = 2.84 [X_M^{\text{corr}} \cdot T]^{1/2}$  B.M, where, T is the absolute temperature at which measurements were done. The metal complexes of naphthalene acetic acid were analyzed for the metal content after decomposing them in conc.HNO<sub>3</sub>. Cobalt (II) and nickel (II) were determined gravimetrically. Copper (II) was determined by the iodometric titration method. The chemical composition of the ligand indole acetic acid

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was determined by analyzing carbon and hydrogen content. Carbon and hydrogen were determined using Vario EL III analyzer.

#### Experimental Techniques

#### Synthesis of metal complexes of Indole acetic acid

##### Preparation of Cobalt (II) Complex

A weight of 1.190g of hydrated Cobalt (II) chloride (0.01 M) was taken in a 100 ml beaker and dissolved in 25ml of hot distilled water. An amount of 5.58 g of IAA (0.03 M) was taken in another 100ml beaker and dissolved in 25ml of hot ethanol. The clear solution of the ligand was added to the solution of the metal salt in small quantities with constant stirring for 10 minutes. A brown coloured solid complex separated from the solution. It was filtered, washed repeatedly with ethanol and finally with solvent ether. The complex was dried and stored in a vacuum desiccator.

The same procedure was adopted for the preparation of Cu(II), Ni(II) complexes.

##### Estimation of Cobalt

Cobalt was estimated gravimetrically. Appropriate amounts of mercuric chloride and ammonium thiocyanate were added to the cobalt solution. A blue coloured solid complex  $Hg[Co(SCN)_4]$  separated out. From the weight of the complex the weight of cobalt was calculated.

##### Estimation of copper

Copper was estimated iodometrically.

To the copper solution ammonium hydroxide was added to form pale blue precipitate. It was dissolved in acetic acid and nearly 2g of solid potassium iodide was added and mixed well and then the liberated iodine was titrated against standardised sodium thiosulphate. 2ml of starch solution was added to get the end point. The end point was the disappearance of blue colour. From the titre value the amount of copper was calculated.

##### Estimation of Nickel

Nickel was estimated gravimetrically as follows. To the clear solution 5ml of 1:1 HCl was added and the solution was diluted to 100ml with distilled water. The solution was then heated to about 80 ° C. To the hot solution about 20 ml of 1% alcoholic solution of dimethyl glyoxime reagent was added in drops with constant stirring. Immediately dilute ammonia solution was added drop wise directly to the solution to make it alkaline. A rosy red precipitate of nickel dimethyl glyoximate complex was obtained. The precipitate was digested on water bath for about an hour and the precipitate was allowed to settle. The precipitate was filtered, washed with hot water and dried in an air oven, cooled in a desiccator and weighed. From the weight of the dimethyl glyoximate complex, the weight of nickel was calculated.

#### Results and Discussion

Indole acetic acid (IAA), a new base derived from indole contains two oxygen atoms as potential donor atoms. It is pertinent to study how the IAA binds with the metal atom, when it is interacted with a transition metal salt. Hence, the new base IAA was purchased and used as a ligand.

##### Analytical results

The results of elemental analysis on IAA and its complexes are furnished in Table 1. The percentage compositions of IAA and its complexes indicate their empirical formulae.

Table 1: Analytical Results on IAA and its Metal Complexes

Compound	%C found (expected)	% H found (expected)	% M found (expected)
IAA ( $C_{10}H_9NO_2$ )	76.49 (77.41)	5.32 (5.37)	-
$Co(C_{10}H_8NO_2)_2 \cdot 2H_2O$	62.20 (61.94)	4.62 (4.73)	12.74 (12.68)
$Ni(C_{10}H_8NO_2)_2 \cdot 2H_2O$	62.42 (61.81)	4.82 (4.72)	13.06 (12.86)
$Cu(C_{10}H_8NO_2)_2 \cdot 2H_2O$	61.46 (61.33)	4.96 (4.69)	13.88 (13.53)

##### Characterization of IAA

The commercial product of IAA was purified and then characterized by melting point, elemental analysis, infrared, UV and  $^1H$ -NMR spectra. The results of elemental analysis of IAA are provided in Table 1. The important vibrational frequencies are listed in Table 2. The  $^1H$ -NMR resonance signals are listed in Table 3. A perusal of the IR spectrum shows a medium strong absorption band at  $3389\text{ cm}^{-1}$  which attributed to the carboxylic NH stretching. The absorption band found at  $700\text{-}600\text{ cm}^{-1}$  is ascribed to the aromatic C-H vibration and that at  $1701\text{ cm}^{-1}$  is due to C=O absorption. The absorptions found in the range  $1696\text{-}1510\text{ cm}^{-1}$  may be due to the side chain methylene  $CH_2$  stretching  $2734\text{ cm}^{-1}$ .

The free ligand IAA multiplet signals found at  $\delta 7.966\text{-}7.246\text{ ppm}$  are ascribed to the aromatic protons and the signal seen at  $\delta 7.4\text{-}7.0\text{ ppm}$  is due to the protons of the  $CH_2$  group. The chemical shift due to the carboxylic proton (COOH) is expected to be observed at  $\delta 10\text{-}14\text{ ppm}$ . Since the spectrum was scanned in the  $\delta$  range  $-0.5$  to  $9.5\text{ ppm}$  this particular signal was not located.



Table 2: Infrared Spectral Bands of IAA Complexes (cm<sup>-1</sup>)

Compound	$\nu_a$ (CO <sub>2</sub> <sup>-</sup> )	$\nu_s$ (CO <sub>2</sub> <sup>-</sup> )	$\Delta$	$\nu$ (MO)	$\nu$ (H <sub>2</sub> O)
Free IAA <sup>-</sup>	1701	1100	601	-	-
Co(IAA <sup>-</sup> ) <sub>2</sub> .2H <sub>2</sub> O	1711	1021	690	523	3432
Ni(IAA <sup>-</sup> ) <sub>2</sub> .2H <sub>2</sub> O	1621	1018	603	540	3107
Cu(IAA <sup>-</sup> ) <sub>2</sub> .2H <sub>2</sub> O	1721	1022	699	511	3397

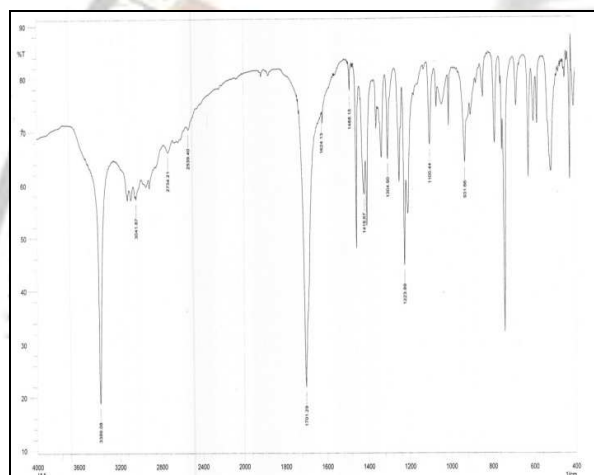


Fig. 1: IR Spectrum of IAA

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

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

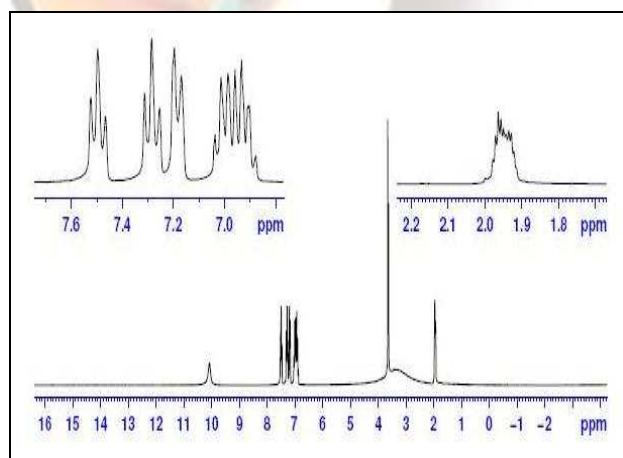


Fig. 2: <sup>1</sup>H-NMR Spectrum of IAA

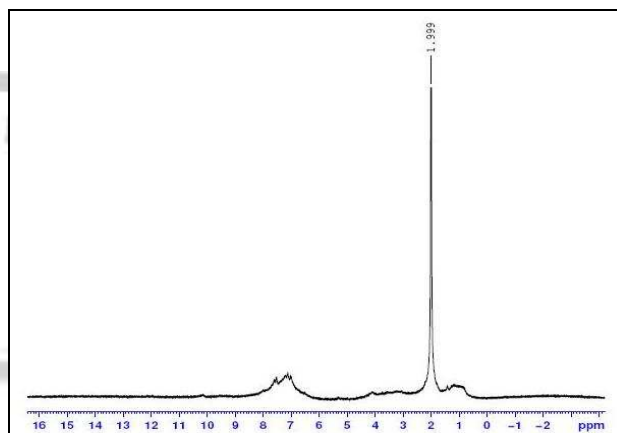


Fig. 3: <sup>1</sup>H – NMR Spectrum of Co(C<sub>10</sub>H<sub>8</sub>NO<sub>2</sub>)<sub>2</sub>.2H<sub>2</sub>O

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

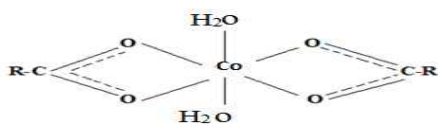
Complex	$\mu_{eff}$ (BM) (Colour)	Absorption bands (cm <sup>-1</sup> )	Electronic transition
Co (IAA <sup>-</sup> ) <sub>2</sub> .2H <sub>2</sub> O	4.80 (Brown)	19058 15356 33670	<sup>4</sup> T <sub>2g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P) <sup>4</sup> T <sub>2g</sub> (F) → <sup>4</sup> A <sub>2g</sub> (F) Charge transfer.
Ni (IAA) <sub>2</sub> .2H <sub>2</sub> O	2.84 (Green)	24814 13405 9814	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (P) <sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (F) <sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>2g</sub> (F)
Cu (IAA) <sub>2</sub> .2H <sub>2</sub> O	1.45 (Green)	11509 32159	<sup>2</sup> E <sub>g</sub> → <sup>2</sup> T <sub>2g</sub> (F) Charge transfer

**Characterization of Co (C<sub>10</sub>H<sub>8</sub>NO<sub>2</sub>)<sub>2</sub>.2H<sub>2</sub>O**

This brown coloured complex having 1:2 metals: ligand stoichiometry may have Co<sup>2+</sup> oxidation state. During the interaction Co<sup>II</sup> chloride with IAA the carboxylic acid might have ionized to give the carboxylate anion which combine with Co<sup>2+</sup> to give the pink complex Co(C<sub>10</sub>H<sub>8</sub>NO<sub>2</sub>)<sub>2</sub>. The elemental analysis (Table 1) and conductivity measured in ~ 10<sup>-3</sup>M DMF solution confirm the same.

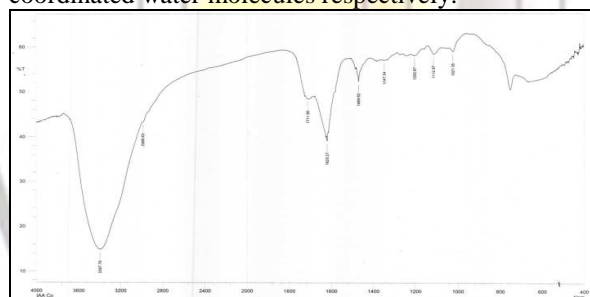
The free acetate ion (CH<sub>3</sub>COO<sup>-</sup>) shows absorption at 1711 and 1021cm<sup>-1</sup> which are attributed to  $\nu_a$  (COO<sup>-</sup>) and  $\nu_s$  (COO<sup>-</sup>) respectively. Considering the IAA<sup>-</sup> ion, the band at 1624 cm<sup>-1</sup> may be due to symmetric  $\nu_s$  (COO) vibrations. In the case of the cobalt (II) complex these respective absorption bands are observed at 1711 and 1021 cm<sup>-1</sup>. The difference ( $\Delta$ ) between the asymmetric and symmetric bands of free IAA<sup>-</sup> is at a much higher value of 189cm<sup>-1</sup> where as in the complex spectrum,  $\Delta$  is much lower at 100cm<sup>-1</sup> indicating bidentate chelation of the carboxylate ligand to Co<sup>II</sup> ion.

A perusal of the electronic spectrum of the Co<sup>II</sup> complex shows several bands due to d-d transition, charge transfer and ligand origin. A very weak absorption at 524.7nm (ie19058 cm<sup>-1</sup>) may be attributed to <sup>4</sup>T<sub>2g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(P) transition. Another very weak absorption band found at 651.2nm (15356cm<sup>-1</sup>) is attributed to <sup>4</sup>T<sub>2g</sub>(F) → <sup>4</sup>A<sub>2g</sub>(F) transition. A strong band found at 297nm (33670cm<sup>-1</sup>) may be due to charge transfer transition. The effective magnetic moment measured at room temperature for the CO<sup>2+</sup> 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.

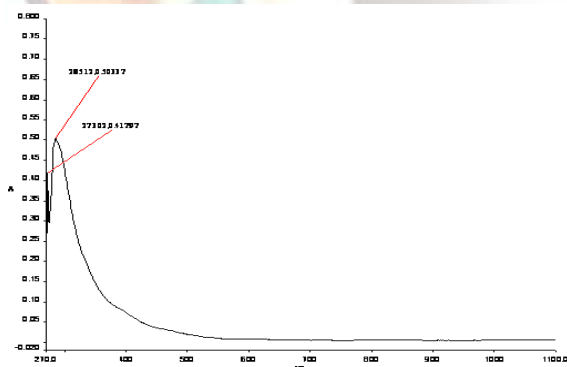


**Fig. 4: Structure of Co (C<sub>10</sub>H<sub>8</sub>NO<sub>2</sub>)<sub>2</sub>.2H<sub>2</sub>O**  
 The infrared absorptions observed at 3407, 1620, 800 and 625cm<sup>-1</sup> are attributed to the ν (OH), δ (HOH),

ρ<sub>r</sub>(HOH) and ρ<sub>w</sub>(HOH) vibrations of coordinated water molecules respectively.



**Fig. 5: IR Spectrum of Co (C<sub>10</sub>H<sub>8</sub>NO<sub>2</sub>)<sub>2</sub>.2H<sub>2</sub>O**



**Fig. 6: UV-Spectrum of Co(C<sub>10</sub>H<sub>8</sub>NO<sub>2</sub>)<sub>2</sub>.2H<sub>2</sub>O**

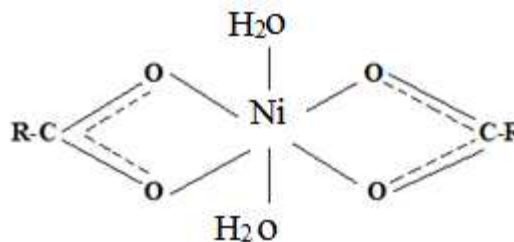
### Characterization of Ni (C<sub>10</sub>H<sub>8</sub>NO<sub>2</sub>)<sub>2</sub>.2H<sub>2</sub>O

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<sub>a</sub> (COO<sup>-</sup>) at 1621cm<sup>-1</sup> and that ν<sub>s</sub> (COO<sup>-</sup>) at 1018 cm<sup>-1</sup>. The difference between the symmetric and anti symmetric absorption is at 100 cm<sup>-1</sup> which much less than the free ion (IAA<sup>-</sup>) value (189cm<sup>-1</sup>) this spectral feature indicates the bidentate chelation of the carboxylate ligand.

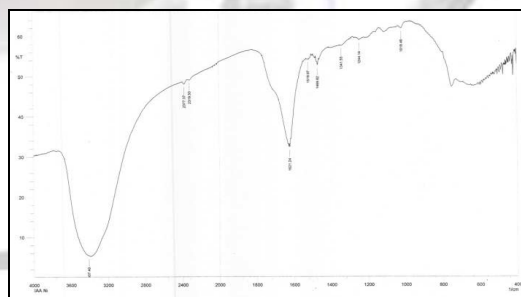
Also the far IR absorption band seen at 2377 cm<sup>-1</sup> may be due to ν(Co-O). The IR spectrum also shows bands at 3107(lr), 1631, 801, and 625 cm<sup>-1</sup> which are attributed to the presence of coordinated water molecules. The band found at 540 cm<sup>-1</sup> is ascribed to the (Ni- O) stretching vibration.

The electronic spectrum of the Ni<sup>II</sup> complex shows an absorption at 24814 cm<sup>-1</sup> (403 nm) which is attributed to <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(P) transition, another band at 13405 CM<sup>-1</sup> (746 nm) due to <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(F) and a third band at 9814 CM<sup>-1</sup> (1019 nm) due to <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(F) transition. These absorption bands are indicative of an octahedral symmetry of Ni<sup>II</sup> in the complex. The μ<sub>eff</sub> value measured at 2.84 B.M is also supportive of octahedral geometry.

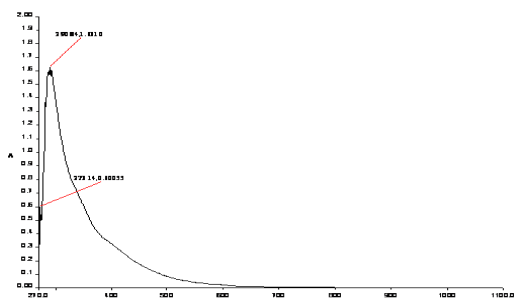
Hence, based on analytical conductivity and magnetic data and IR and UV-visible spectroscopy a bidentate chelation of the organic ligand and octahedral stereochemistry is proposed to this complex.



**Fig. 7: Structure of Ni (C<sub>10</sub>H<sub>8</sub>NO<sub>2</sub>)<sub>2</sub>.2H<sub>2</sub>O**



**Fig. 8: IR Spectrum of Ni (C<sub>10</sub>H<sub>8</sub>NO<sub>2</sub>)<sub>2</sub>.2H<sub>2</sub>O**

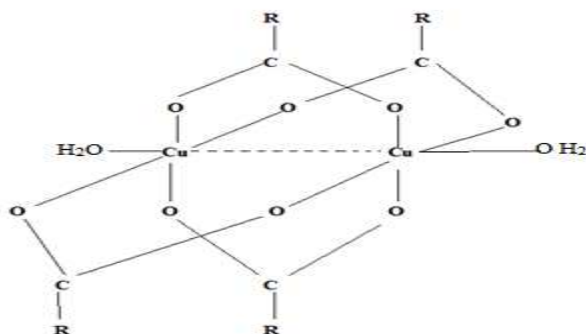


**Fig. 9: UV-Spectrum of Ni(C<sub>10</sub>H<sub>8</sub>NO<sub>2</sub>)<sub>2</sub> · 2H<sub>2</sub>O**  
**Characterization of Cu (C<sub>10</sub>H<sub>8</sub>NO<sub>2</sub>)<sub>2</sub> · 2H<sub>2</sub>O**

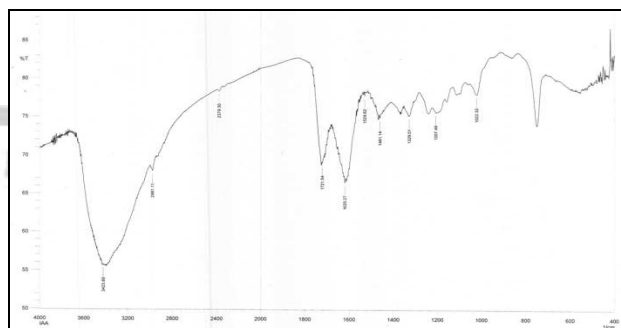
On the basis of chemical and elemental analysis this complex is given 1:2 stoichiometry. The very electrical conductance measured for this complex reveals that the complex is non-ionic. The IR spectrum indicates the presence of  $\nu_a(\text{COO}^-)$  and  $\nu_s(\text{COO}^-)$  vibrational frequencies at 1721 and 1022  $\text{cm}^{-1}$  respectively. The difference between these two is much higher than expected for bidentate chelation mode of coordination of IAA<sup>-</sup> ligand. Presence of water in the coordination sphere is indicated by IR bands at 3432 (br), 2379, 700 (split) and 600  $\text{cm}^{-1}$ . The band at 511  $\text{cm}^{-1}$  also points to the binding of Cu and O atoms.

The green coloured Cu<sup>II</sup> complex measures an electronic absorption band at 11509  $\text{CM}^{-1}$  (868.86 nm) which is attributed to  ${}^2E_g \rightarrow {}^2T_{2g}$  (F). It also exhibits another band at 32159  $\text{cm}^{-1}$  (310.95 nm) which may be due to charge transfer transition. The complex has a  $\mu_{\text{eff}}$  value of 1.45 B.M per Cu atom at room temperature. The very low value of  $\mu_{\text{eff}}$  may be due to a coupling of the unpaired electrons one on each Cu<sup>II</sup> ion.

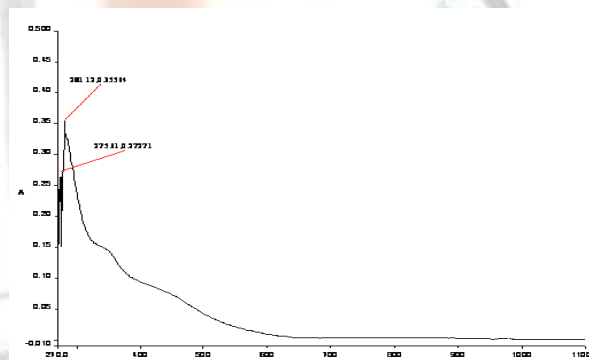
Hence, based on chemical and elemental analysis, conductivity, magnetic moment, IR and electronic absorption spectra, this complex is given a carboxylato bridged binuclear structure where there is antiferromagnetic interaction between two copper ions.



**Fig. 10: Structure of Cu (C<sub>10</sub>H<sub>8</sub>NO<sub>2</sub>)<sub>2</sub> · 2H<sub>2</sub>O**



**Fig. 11: IR Spectrum of Cu (C<sub>10</sub>H<sub>8</sub>NO<sub>2</sub>)<sub>2</sub> · 2H<sub>2</sub>O**



**Fig. 12: UV-Spectrum of Cu (C<sub>10</sub>H<sub>8</sub>NO<sub>2</sub>)<sub>2</sub> · 2H<sub>2</sub>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 metal complexes of carboxylates 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 <sup>1</sup>H 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. All the complexes have 1:2 stoichiometry. All of them have two coordinated water molecules each. In the Co<sup>II</sup>, Ni<sup>II</sup> complexes, the carboxylate ligand acts as a chelating bidentate and in Cu<sup>II</sup> complex, it is bridging bidentate. The very low magnetic moment determined in the case of Cu<sup>II</sup> complex suggests a binuclear bridged structure. The metal ions in all the complexes studied are in an octahedral environment.



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