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# Synthesis, Characterizationand Spectroscopic Studies on Transition Metal Complexes of Isonicotinamide Derivatives

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## Abstract

The ligands such as N, N'- Diisopropylisonicotinamide (DIPIN) and N, N'-Diisobutylisonicotinamide (DIBuIN) have been prepared and characterized by elemental analysis, IR and $^1$H NMR data. From these two ligands the metal complexes such as Co(II), Cu(II)and Zn(II) have been prepared. These complexes have been characterized by elemental analysis,IR, andUV-Visible studies. Single crystal analysis of complex [$Cu(NO_3)_2.3H_2O$(diisopropylisonicotinamide)] has also been carried out.

Keywords:Ligands, metal complexes, elemental analysis, spectral studies, single crystal study.

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## 1. Introduction

Porous materials are very useful in gas storage, adsorption based gas/ vapour separation, shape/ size-selective catalysis, drug storage and delivery, and as templates in the preparation of low dimensional materials[1]. Traditionally, porous materials have been either organic or inorganic materials. In order to take advantage of the properties of organic and inorganic porous materials, porous hybrids which are generally known as metal organic frameworks (MOFs) have been generated which are both stable, ordered and possess high surface areas. MOFs consist of metal ions linked together by organic bridging ligands, and are a new development on the interface between molecular coordination chemistry and materials science. A range of novel structureshave been prepared which feature amongst the largest pores known for crystalline compounds, very high sorption capacities and complex sorption behaviour not seen in aluminosilicate Zeolites[2].MOFs are produced almost exclusively by hydrothermal (method of synthesis of single crystal that depends on the solubility of minerals in hot water under high pressure) or solvothermal techniques.In addition to this standard method, several other synthetic methodologies are described in the literature including the mixture of non-miscible solvents, an electrochemical route, and a high-throughput approach and microwave irradiation.

From a synthetic point of view, it is well know that among various pyridine based ligands, nicotinic acid derivatives such as isonicotinic acid, isonicotinamide are employed for bringing various metal centers in close vicinity through the hydrogen bonding or coordination polymerization or using both[3].Review of the literature[4-7] on the proceeding pages shows that a lot of quality work has been done regarding the self assembly of pyridine based ligands such as pyrazine, 4, 4’-bipyridine, nicotinic acid, isonicotinic acid, nicotinamide and isonicotinamide[8-14].

The work involving nicotinamide and isonicotinamide attract immense importance as they have structural adaptations for forming framework through coordination polymerization and non-covalent interactions such as hydrogen bonding, Pi-Pi interactions etc. However, we have not encountered any studies reported in the literature on the investigations of coordination behaviour of fully substituted amide derivatives of isonicotinamide. Therefore, in the present work, we reported the synthesis, structure and spectral properties of N, N-dialkykisonicotinamide ligands and their complexes with transition metal ions.

## 2. Experimental

### 2.1. Materials and methods

All chemicals were purchased from chemical companies and used as such without any further purification. The UV-Vis spectra of the ligands and metal complexes were recorded using a

JASCO V-530 spectrophotometer. Infrared (IR) spectra in KBr discs were recorded on a SHIMADZU FT-IR 460 plus spectrophotometer. Elemental analyses were performed at SAIF, CDRI, Lucknow. $^1$H-NMR spectrum was recorded in $CDCl_3$ using a Bruker DRX-300, 300MHz NMR spectrometer.

### 2.2. Preparation of Ligands

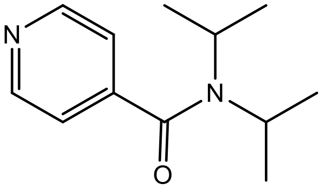
#### 2.2.1. Preparation of N, N- Diisopropylisonicotinamide (DIPIN)

**Step(i):**Isonicotinic acid (20 g) was refluxed with thionyl chloride (50-60mL) in the presence of a few drops of dimethylformamide over a low flame till the acid was distilled. The excess of thionyl chloride was removed azeotropically with benzene using Dean Stark apparatus to give pure isonicotinyl chloride (m.p.155-160).

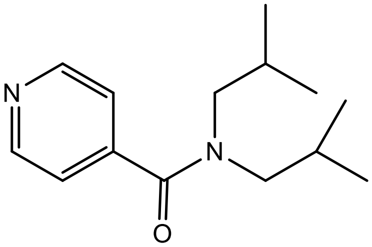
**Step(ii):**Isonicotinic acid (0.15mol) was reacted with thionyl chloride (50-60mL) in the presence of dimethylformamide which gave pure isonicotinyl chloride using Dean and Stark apparatus. Then it was suspended in a mixture of 100mL dry toluene, 0.30mol of pyridine and 0.46mol of diisopropylamine, refluxed and allowed to stand at room temperature overnight. The solid which separated out was removed by filtration and the filtrate was treated with 50% aqueous NaOH solution and chilled. The toluene layer was separated and the alkaline solution was extracted with ether. The combined toluene and ether layer were dried over $Na_2SO_4$ and excess solvent was removed by distillation. The yellow coloured distillation solidified on cooling. The final product was obtained after recrystallization from n-heptane.

#### 2.2.2. Preparation of N, N- Diisobutylisonicotinamide (DIBuIN)

Isoniotinic acid (0.15mol) was reacted with thionyl chloride (50-60mL) to obtain isonicotinyl chloride hydrochloride. It was added to a mixture of about 100mL dry toluene, 0.30mol of pyridine and 0.46mol of diisopropylamine. The mixture was refluxed for 15-20 min and then kept at room temperature overnight. The solid obtained on cooling was removed by filtration and the filtrate was treated with 50% aqueous NaOH solution and chilled. The toluene layer was separated and the alkaline solution was extracted with ether. The combined toluene and ether layers were dried over $Na_2SO_4$ and excess solvent was removed by distillation. The yellow coloured distillate solidified on cooling. The final product was obtained after recrystallization from n-heptane.



**Structure of N,N-Diisopropylisonicotinamide**



**Structure of N,N-Diisobutylisonicotinamide**

## 2.3. Preparation of Metal Complexes

### 2.3.1. [Co $(BF_4)_2.6H_2O$ $(DIPIN)_2$] [1]

This complex was prepared from a reaction mixture containing equimolar amounts of $Co(BF_4)_2.6H_2O$ (489mg, 1.5mmol) and IPIN (591mg, 1.5mmol) dissolved in about 25mL of isopropyl alcohol. The contents were refluxed for 8 h and kept in the refrigerator overnight. On cooling there were no crystals observed in the flask. The contents were filtered to remove any unreacted components and the clear solution (filtrate) was cooled at $4^0$C in a refrigerator. After 3 days, pink coloured fine crystals appeared in the flask. The mother liquor was decanted and the crystalline solid was dried.

### 2.3.2.[Co $(BF_4)_2.6H_2O$ $(DIBuIN)_2$] [2]

This complex was prepared from a reaction mixture containing equimolar amounts of $Co(BF_4)_2.H_2O$(437mg,1mmol) and IbuIN (601mg,2mmol) dissolved in about 25ml of isopropyl alcohol. The contents were refluxes for 8h and then allowed to cool at room temperature. These contents were concentrated using rotary evaporator and then dried on vacuum line, then pink coloured amorphous powder appeared in the flask was collected and stored.

### 2.3.3. $[Cu(CH_3COO)_2H_2O(DIPIN)_2]$[3]

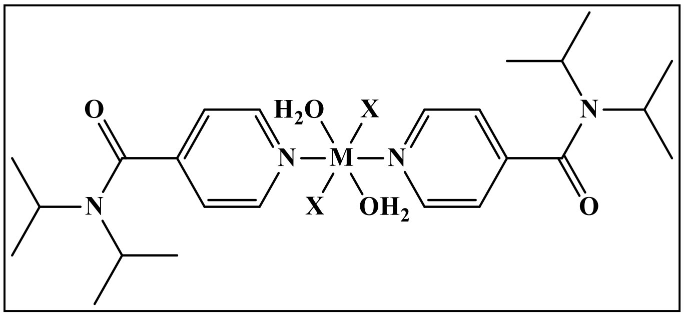
This complex was prepared from a reaction mixture containing equimolar amounts of $Cu(CH_3COO)_2.H_2O$ (343mg,1.5mmol) and IPIN (346mg,1.5mmol) dissolved in about 20 ml of isopropanol. The contents were refluxed for 10 h and then allowed to cool to room temperature. The solution colour changes from light green to blackish blue colour. After a few days, the green coloured crystals appeared in the flask. The sample has been analysed for C H N.

### 2.3.4. $[ZnCl_2(DIPIN)_2]$ [4]

This complex was prepared from a reaction mixture containing equimolar amount of $ZnCl_4$ (412mg, 1mmol) and IPIN (272mg, 1mmol) dissolved in about 25 ml of isopropanol. The contents were refluxes for 8 h and then allowed to cool to room temperature. The solution colour change to off white. The precipitate obtained was concentrated using rotary evaporator and then dried on vacuum line and off white amorphous powder was collected.

**2.3.5. $[Cu(NO_3)_2.3H_2O(DIPIN)_2]$ [5]**This complex was prepared from a reaction mixture containing $[Cu(NO_3)_2.3H_2O]$(246mg,1mmol) and IPIN (413mg,2mmol) dissolved in about 20 ml of acetonitrile. The contents were refluxed for 7 h and then allowed to cool to room temperature.

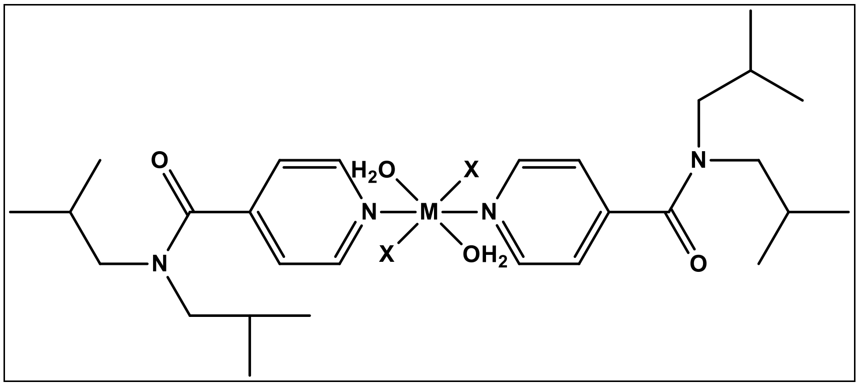
After two days, it was filtered using filter paper. The filtrate was then allowed to cool. After a few days, the green coloured crystals appeared in the flask. Single crystal X-Ray analysis was also performed.



**Where,** **$M^{2+}$** **$X^-$**

Complex 1$Co^{2+}$ $BF_4$
Complex 3 $Cu^{2+}$ $CH_3COO^-$
Complex 4 $Zn^{2+}Cl$
Complex 5 $Cu^{2+}$ $NO_3$

**Schematic representation of chemical structure of metal complexes 1, 3, 4 and 5**



Where, $M^{2+}$ is Co and X is $NO_3^-$

**Schematic representation of chemical structure of metal complex 2**

## 3. Results and Discussion

The isonicotinamide ligands possess two potential donor sites in the form of pyridine nitrogen and carbonyl oxygen atoms. As amonodendate ligands, the bonding may involve only one of these donor atoms. It has been observed that coordination to the metal ion takes place in a monodentate fashion through pyridine nitrogen atom in preference to the carbonyl oxygen atom. However in a few cases, the ligands use both pyridine nitrogen and carbonyl oxygen atoms to coordinate in a bidendatebriding manner between successive metal centres to form coordination polymers.

Complexes **1-4**have been isolated in good yield by stirring the appropriate metal(II) salt with the corresponding N,N-dialkylisonicotinamide ligand in a 1:2 mol ratio. Complexes 1 and 2 are pink in color while 3 and 5 are green in color and complex 4 is off white in color. In all the complexes from 1 to 5 downward shift of$\upsilon_{CO}$isobserved as compared to corresponding values in the respective neat ligands, indicating coordination to the metal center through nitrogen and the carbonyl oxygen as well. The electronic absorption spectra of the complexes 3 and 5 were recorded in methanol. These complexes present a relatively broad band in the visible region, with maxima centered at about 717nm and 767nm, indicating a distorted octahedral geometry of the complexes.

## Tables and figures

**Table 1: Characterization of DIPIN and DIbuIN ligands**

| S.No | Characterization | Ligand 1 | Ligand 2 |
|---|---|---|---|
| 1 | Colour | Yellowish-brown | Yellowish-brown |
| 2 | Melting Point | 97-98º C | 54-56º C |
| 3 | Elemental Analysis | C,69.23;H,8.94;N,13.14(%) | C,71.67;H,9.24;N,11.84(%) |

| | | | |
|---|---|---|---|
| 4 | IR | 1600 ,1595, 1540, 995, 602 and 403cm$^{-1}$ | 1652cm$^{-1}$ |

## Table 2: UV-Vis spectral datafor complexes 1-5

| Complex No | Complex | Wavelength (nm) |
|---|---|---|
| 1 | $[Co(BF_4)_2.6H_2O\ (DIPIN)_2]$ | 367 |
| 2 | $[Co(BF_4)_2.6H_2O\ (DIBuIN)_2]$ | 367 and 505 |
| 3 | $Cu(CH_3COO)_2H_2O(DIPIN)_2]$ | 367 and 717 |
| 4 | $ZnCl_{2.}\ (DIPIN)_2$ | 367 and 505 |
| 5 | $[Cu(NO_3)_2.6H_2O\ (DIPIN)_2]$ | 367 and 762 |

## Table 3: IR spectral data for complexes 1-5

| Complex No | Complex | IR range ($cm^{-1}$) |
|---|---|---|
| 1 | $[Co(BF_4)_2.6H_2O\ (DIPIN)_2]$ | 1590.97 |
| 2 | $[Co(BF_4)_2.6H_2O(DIBuIN)_2]$ | 1600.75 |
| 3 | $Cu(CH_3COO)_2H_2O(DIPIN)_2]$ | 1574.27 |
| 4 | $ZnCl_{2.}\ (DIPIN)_2$ | 1594.15 |
| 5 | $[Cu(NO_3)_2.6H_2O\ (DIPIN)_2]$ | 1633.32 |

## Table 4: C,H,N analysis of complexes 1- 5

| Complex No. | Complex | % of N *Expt (Theo) | % of C *Expt (Theo) | % of H *Expt (Theo) |
|---|---|---|---|---|
| 1 | $[Co(BF_4)_2.6H_2O\ (DIPIN)_2]$ | 7.85 (7.83) | 40.24 (40.25) | 5.74 (5.75) |
| 2 | $[Co(BF_4)_2.6H_2O(DIBuIN)_2]$ | 8.22 (8.21) | 48.86 (48.85) | 6.76 (6.77) |
| 3 | $Cu(CH_3COO)_2H_2O(DIPIN)_2]$ | 8.34 (8.35) | 42.23 (42.25) | 5.20 (5.21) |
| 4 | $ZnCl_{2.}\ (DIPIN)_2$ | 8.42 (8.43) | 42.23 (42.24) | 5.74 (5.75) |
|  |  | 14.44 |  |  |

| | | | | |
|---|---|---|---|---|
| 5 | [$Cu(NO_3)_2.6H_2O$ (DIPIN) $_2$] | (14.43) | 47.34<br>(47.35) | 5.91<br>(5.92) |

*Expt-Experimental, Theo -Theoretical

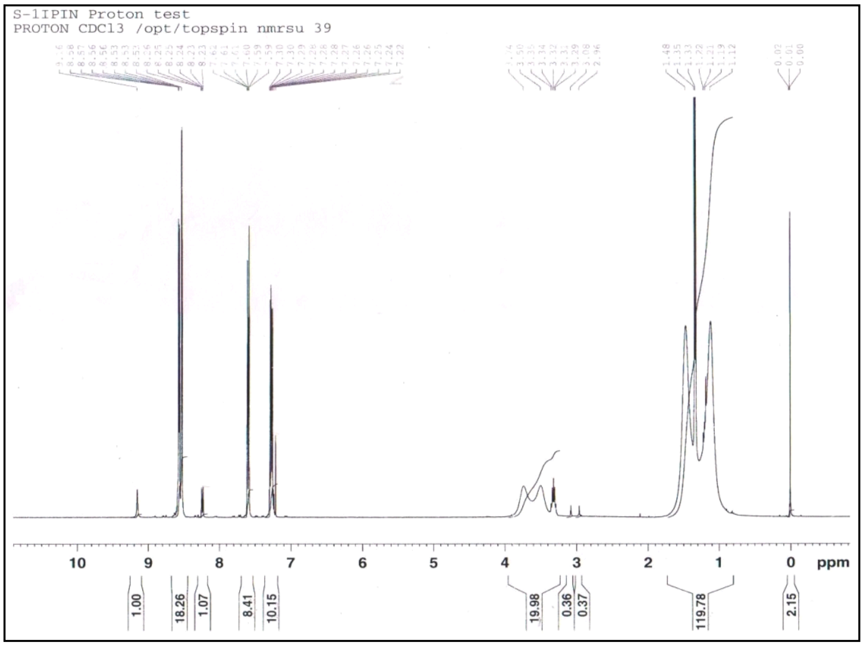


Figure 1: $^1$HNMR spectrum of DIPINligand

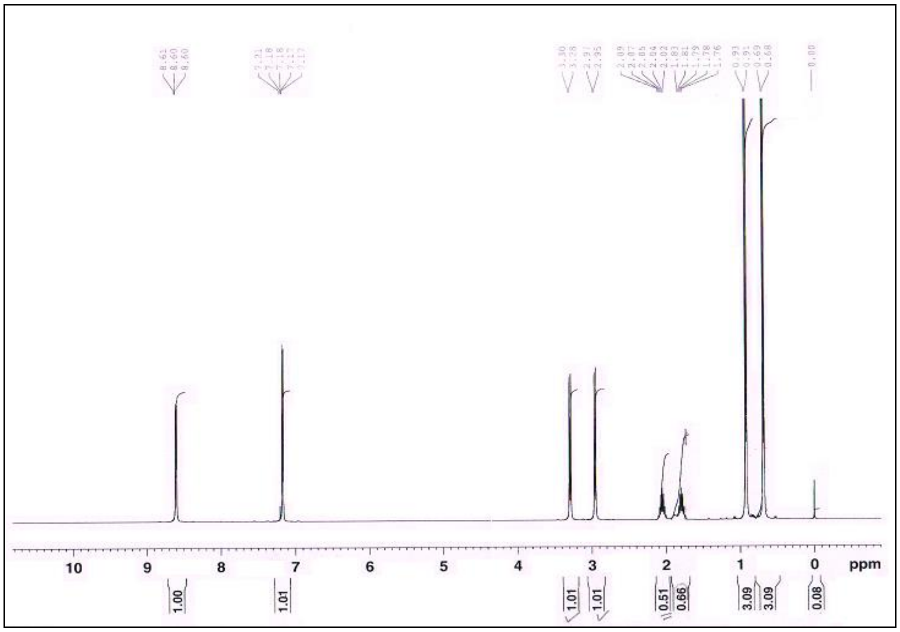


Figure 2: $^1$H NMR spectrum of DIBuIN ligand

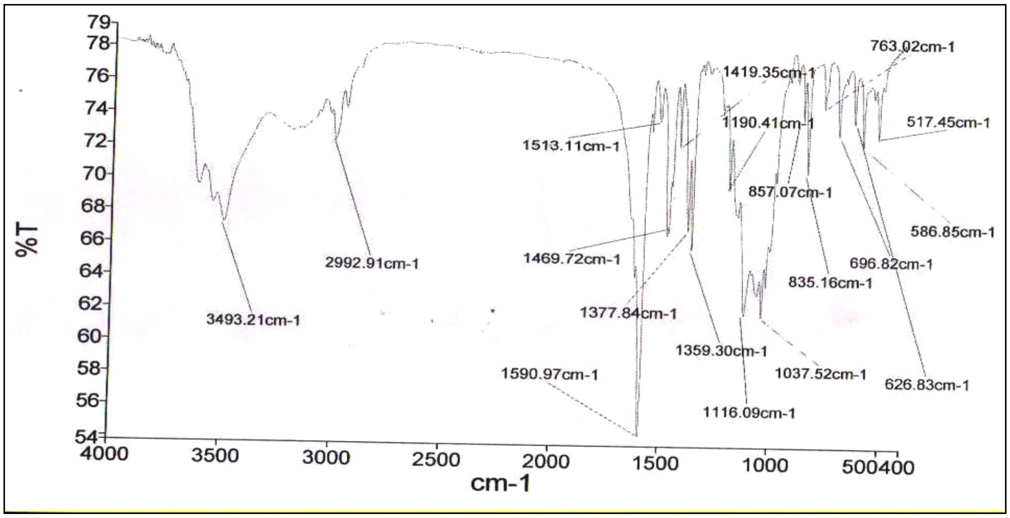


Figure 3: IR spectrum of complex**1**

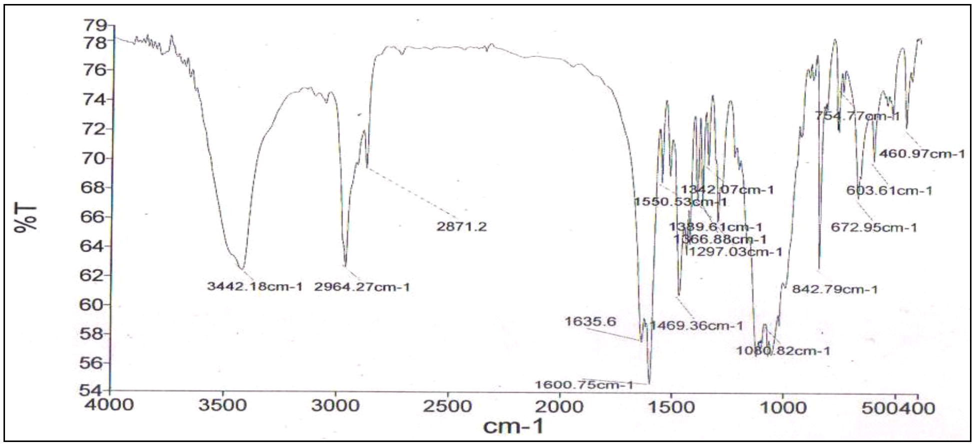


Figure 4: IR spectrum of complex **2**

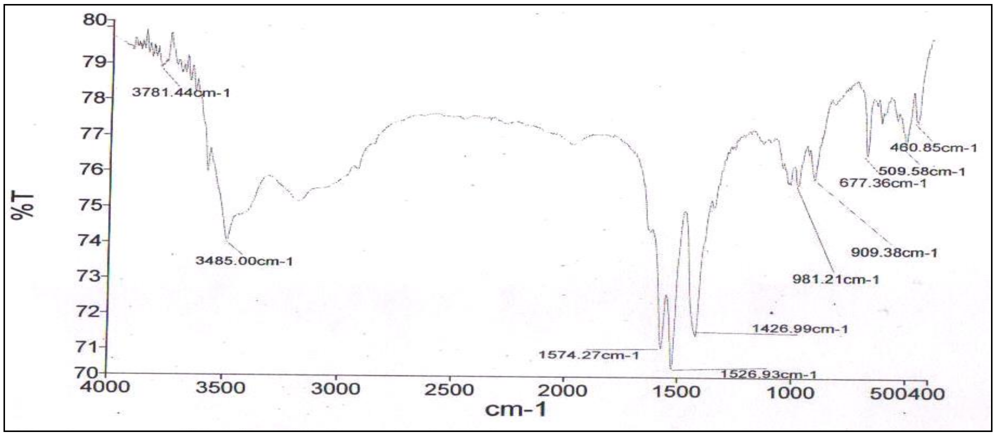


Figure 5: IR spectrum of complex**3**

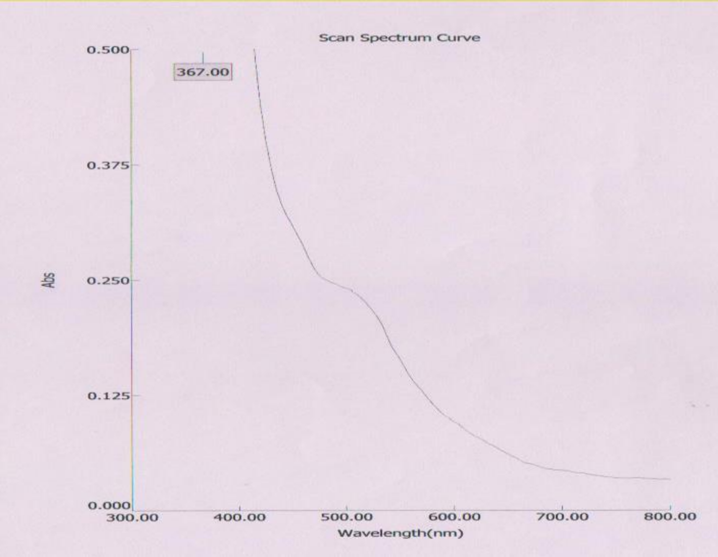


Figure 6: UV-Vis spectrum of complex**1**

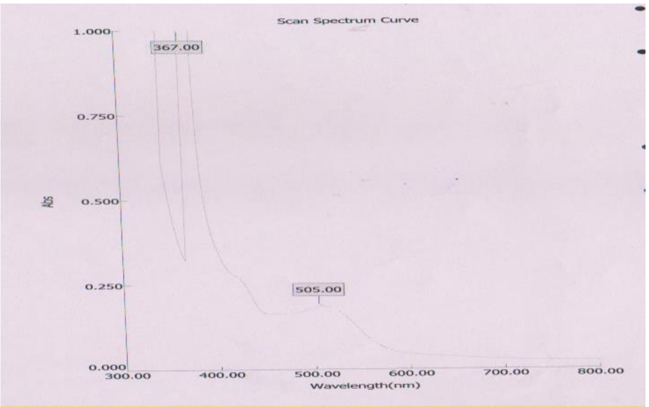


Figure 7: UV-Vis spectrum of complex**2**

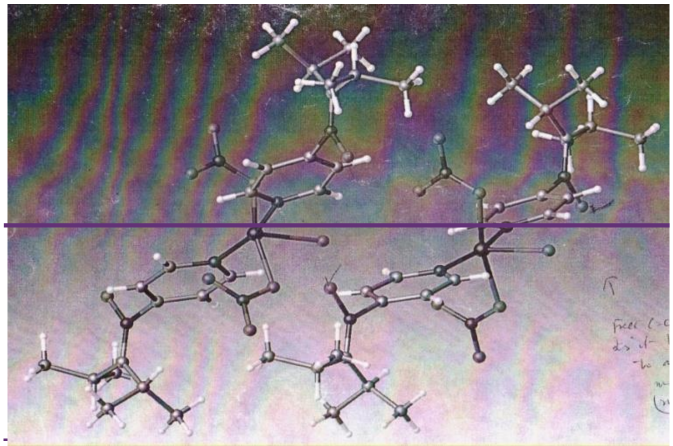


Figure 8: Single crystal structure of complex **5**

## 4. Conclusion

In this work, we have reported the coordination chemistry of N,N-diisoalkylnicotinamide with Co(II), Cu(II) and Zn(II) metal ions containing various anions. The fully substituted amide derivatives of pyridine mono carboxylic acids such that isonicotinic acids provide the necessary rigidity and binding sites that enhance the chances of formation of coordination networks. The ligands N,N'-diisopropyl and N,N'-diisobutylisonicotinamide have been synthesized and characterized by elemental analysis, melting point, IR and $^1$H NMR data. Using these two ligands the metal complexes such as cobalt, copper and zinc have been prepared. These complexes have been characterized by IR, UV-Visible and elemental analysis studies. Single crystal study of complex **5**showed thedistorted octahedral geometry of the complexes.

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