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Synthesis and characterization of transition metal complexes of some novel pyrazolo-chalcone derivatives

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ABSTRACT

Some novel pyrazolo-chalcone molecules were synthesized by condensation of pyrzolo aldehyde with appropriate acetophenone. The synthesis of some metal complexes of transition metal was carried out with these pyrazoleo heterocyclic compounds. Each metal complex was synthesized by the reaction of new pyrazolochalcone derivatives with the metal salts such as $Co(CH_3COO)_2 \cdot 6H_2O$, $Ni(CH_3COO)_2 \cdot 6H_2O$, and $Cu(CH_3COO)_2 \cdot 2H_2O$. For the structure elucidation of ligand molecule various spectroscopic techniques such as ^1H NMR, IR and mass has been used. The synthesized metal complexes were subjected to thermal study i.e., TGA and DTA in order to check structural conformation of synthesized metal complexes.

***Keywords*:** Pyrazolochalcone derivatives, Transition metal complexes, Thermal gravimetric analysis

1. INTRODUCTION

Heterocyclic ring contain nitrogen as heteroatom becomes most interesting field of organic chemistry due to their wide range of biological and pharmaceutical activities[1-3]. Pyrazolemoieties show remarkable biological activity such as antibacterial[4], antifungal[5], anti-inflammatory[6, 7], anti-tubercular[8], anticancer[9], analgesic[10], anticonvulsant[11], antidepressant[12] etc. Many natural and synthetic drugs containpyrazole moiety[13].Chalcone is also an important

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class of organic chemistry due to their various activities in medical field[14-16]. Many scientists reported synthesis of chalcone by various methods. In addition, many heterocyclic compounds are synthesized by using chalcone[17].

Due to multifold activity of pyrazole and chalcone, metal complex of some transition metal were prepared by reaction of prazolo-chalcone with selective metal salts such as Co(II), Ni(II) and Cu(II). The structure analysis of pyrazolo-chalocone was carried out by using various analytical techniques such as ^{1}H NMR, IR and mass. The synthesized metal complexes were done by using thermo gravimetric analysis and DSC. It provides qualitative information on the composition and thermal stability of different types of materials[18].These thermo analytical techniques help to understand the molecular structure of materials[19].

The study of thermal behavior of substances at different temperatures provides important information about its practical applicability, their optimum working temperature, environmental conditions for its uses and decomposition rate[20].

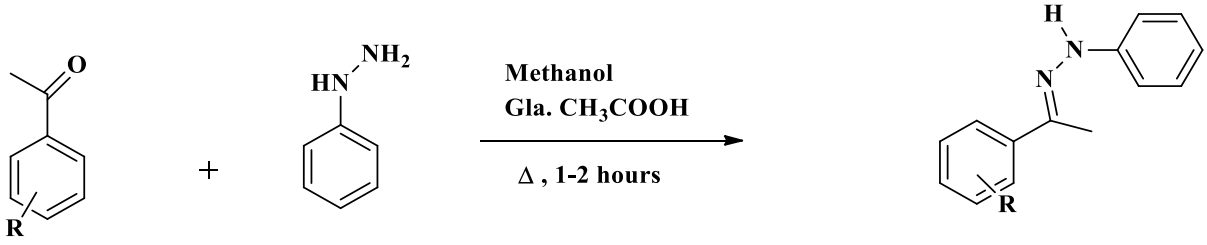
2. EXPERIMENTAL

2. 1. Material and method

All the common reagents used in synthesis of metal complexes were analytical grade reagent provided by Spectro Chem Pvt. Ltd. and used without any further purification. The various solvents likes methanol, *N*,*N*-dimethyl formamide etc., were purchased from LOBA Chemical Pvt. Ltd. The purity of these solvents was checked by GC-MS (SHIMADZU Model-QP-2010) and found to be greater than 95.0 %.

Synthesis of 3 (E)-1-phenyl-2-(1-phenylethylidene)hydrazine derivatives (Int-1)

The methanolic solution of various substituted acetophenone (0.01 mmol) and phenyl hydrazine (0.011 mmol) was refluxed for 1-2 hours in presence of glacial acetic acid as catalyst. The reaction progress was checked by thin layer chromatography using mixture of hexane and ethyl acetate (5:5). After completion of reaction, the obtained reaction mixture was poured into cold water with constant stirring. The product was filtered and washed by cold ether to remove unreacted reagents under vacuum.

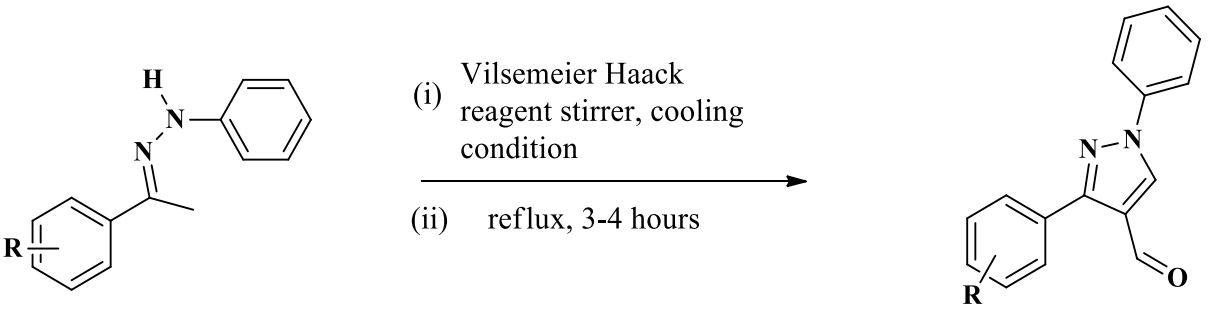


Int-1

Synthesis of 1,3-diphenyl-1H-pyrazole-4-carbaldehyde derivatives (Int-2)

A solution of INT-1 (0.06 mmol) was prepared in anhydrous DMF and the resultant mixture was cooled in ice bath. In this solution, Vilsemeier-Haack reagent (mixture of phosphorus oxychloride ($POCl_3$, 0.18 mmole) and *N*, *N*-dimethyl formamide (DMF, 0.06 mmol) was added drop wise with constant stirring in cool condition. After complete addition

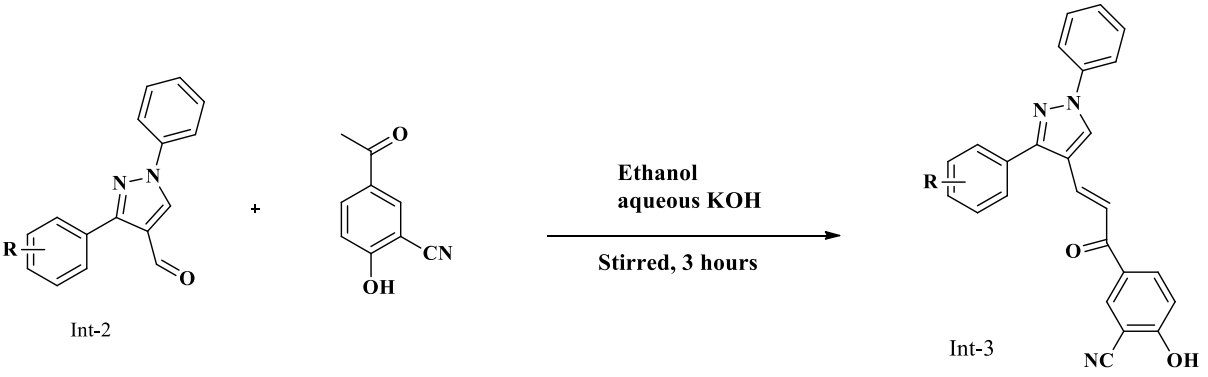
of reagent, the resultant mixture was stirred for 2 hours in ice bath and refluxed for 3 hours in water bath. The progress of reaction was checked by TLC using (4:6 -hexane: ethyl acetate) as a mobile phase. The reaction mixture was poured into crushed ice and stirred for 3-4 hours. The solution was neutralized with 20% Na_2CO_3solution. The obtained solid was filtered and dried under vacuum.



Int-1 Int-2

Synthesis of (Z)-5-(3-(1,3-diphenyl-1H-pyrazol-4-yl)acryloyl)-2-hydroxybenzonitrile derivatives (Int-3)

Equimolar mixture of Int-2 (0.01 mmol) and acetophenone (0.01 mmol) was prepared in ethanol and 5 ml aqueous solution of potassium hydroxide (30 % w/v) was added drop wise. After complete addition of alkali solution, the mixture was stirred for 3 hours at room temperature. The progress of reaction was checked by TLC using 3:7- hexane: ethyl acetate as mobile phase. After the reaction mass was poured into cold water and neutralized with dilute hydrochloric acid. The product was filtered and washed with cold water and dried under vacuum.

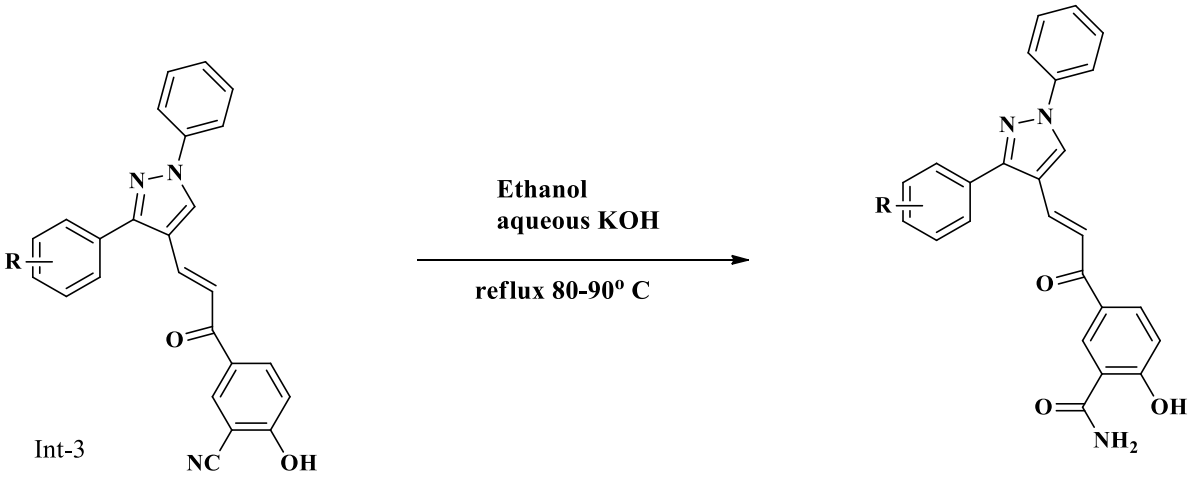


Int-2 Int-3

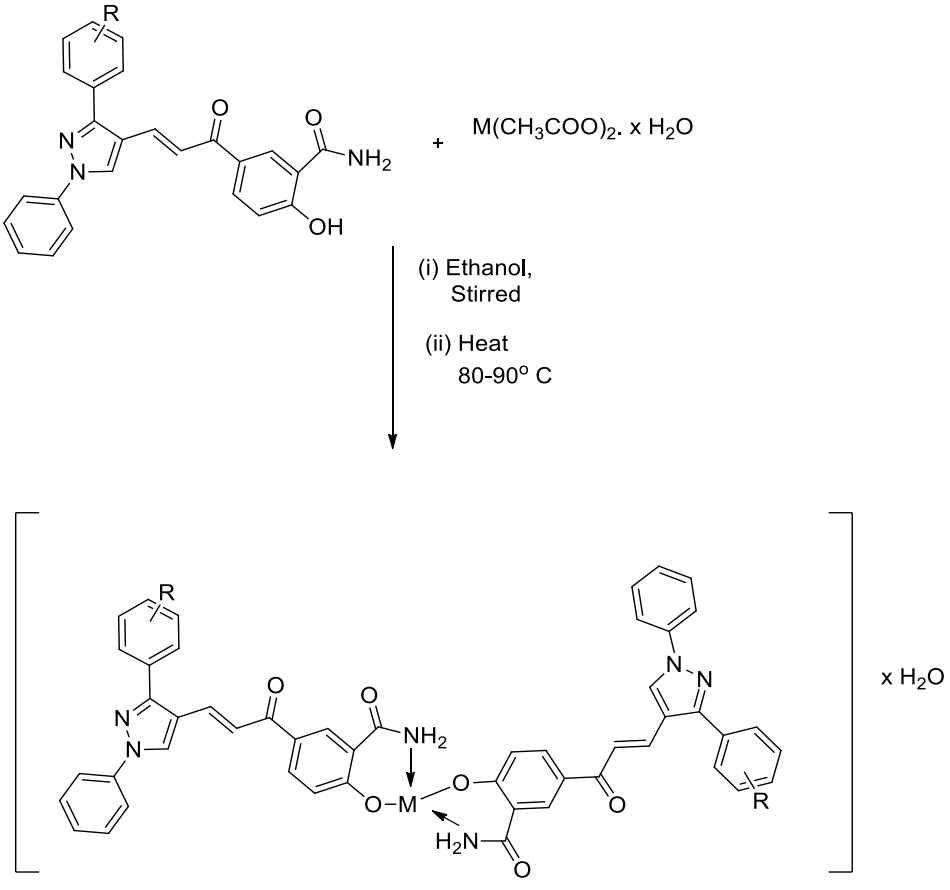
Synthesis of ((Z)-5-(3-(1,3-diphenyl-1H-pyrazol-4-yl)acryloyl)-2-hydroxybenzamide derivatives

Int-3 (0.01 mmol) was dissolved in minimum quantity of ethanol and aqueous KOH (0.10mmol) was added drop wise with constant stirring. After complete addition of alkali solution, the resultant mixture was refluxed in water bath for time. The progress of reaction was checked by TLC using hexane:ethyl acetate-3:7 mixture as mobile phase. The reaction mixture

was poured into cold water and neutralized by dilute acid solution. The obtained precipitate was filtered, washed with cold water and dried under vacuum.



Preparation of metal complexes



M= Cu, Co, Ni
x= number of water molecules in metal complexes
For Cu = 2, Co = 4, Ni = 4

The appropriate metal salt was dissolve in minimum quantity of water and added drop wise into prepared solution of ligand in ethanol. The resultant reaction mixture was heated at 80-90 ºC temperature for 1 hour with constant stirring. The solution was stirred for 2 days at slow rate. The colored precipitate was observed. Once the reaction was complete, extra solvent was removed by using rotary evaporator and the product was filtered, washed and dried under vacuum. The structure confirmation of ligand molecules was by IR, ^{1}H NMR and mass spectral data. The Infra red analysis of lignad was carried out on IRaffinity-1S (SHIMADZU furrier transport infrared spectrophotometer) instrument by solid phase method and in moisture free atmosphere. ^{1}H NMR spectra were taken on a BRUKER AVANCE III at 400 MHz frequency. For ^{1}H NMR spectra, deuterated dimethyl sulfoxide (DMSO-d_6) was used as solvent and tetra methyl silane (TMS) as an internal standard. Mass analysis was carried out by using direct inlet probe method on SHIMADZU GC-MS spectrometer. Thermo gravimetric and differential thermal analysis (TG/DTA) of ligand molecules were taken on SHIMADZU DTG-60H in nitrogen atmosphere with flow rate 10 ml/min. The instrument was calibrated by indium metal prior to analysis. For TGA analysis, sample was placed in open silica pan and was heated from room temperature to 1000 °C with heating rate 10 °C/min. using empty silica pan as reference.

3. RESULTS AND DISCUSSION

3. 1. Spectral analysis of ligand compound

^{1}H NMR

^{1}H NMR spectrum of ligand molecule shows as Figure 1. It observed that characteristics proton peak of amino group observed at 9.432 δ ppm. The hydroxyl group proton peak in down field at 8.827 δ ppm. Other proton peaks of different groups observed in their appropriate region with appropriate splitting.

IR spectra

Figure 2 the infra-red spectrum of OP-1. The amino group present in molecule showed absorbance at 3456.55 and 3064.99 cm^{-1}. The peak obtained around 3348.54 as broad due to presence of hydroxyl group in molecule. The -CH- stretching and rocking absorbance peaks observed in the region of 3100-3000 cm^{-1} and 1370-1350 cm^{-1} respectively. The carbonyl group present in ligand molecules showed peak at 1766.67 cm^{-1}. The -C=C- stretching peaks observed in range of 1549-1695 cm^{-1}. The characteristics C-N stretching observed at 1066.67 cm^{-1}.

Mass spectra

Table 1. Some physical constants of synthesized compounds.

Code	Substitution	Molecular formula	Molecular weight	% yield	R_f
OP-1	H	$C_{25}H_{19}N_3O_3$	409.14	81	0.78
OP-2	-OCH_3	$C_{26}H_{21}N_3O_4$	439.15	75	0.65

In mass spectrum of OP-1 shown as Figure 3, the molecular ion peak is obtained at 409 m/z.

Table 2. Physical parameters of metal complexes.

Code	Metal	Ligand substitution	Molecular formula	Molecular weight	Melting point
OP-1 Cu	Cu(II)	H	$C_{50}H_{40}CuN_6O_8$	915.43	>300 ºC
OP-1 Ni	Ni(II)		$C_{50}H_{44}NiN_6O_{10}$	946.61	>300 ºC
OP-1 Co	Co(II)		$C_{50}H_{44}CoN_6O_{10}$	947.85	>300 ºC
OP-2 Cu	Cu(II)	p-OCH_3	$C_{52}H_{44}CuN_6O_{10}$	976.49	>300 ºC
OP-2 Ni	Ni(II)		$C_{52}H_{48}NiN_6O_{12}$	1007.27	>300 ºC
OP-2 Co	Co(II)		$C_{52}H_{48}NiN_6O_{12}$	1008.00	>300 ºC

IR spectra of OP-1 Cu

Figure 4 shows infra red spectrum of OP-1 Cu. In lignad molecule, amino group showed absorbance at 3456.55 and 3064.99 cm^{-1} which is shifted at upward in metal complex. In metal complex, absorbance peak of amino group is observed at 3456.55, 3306.54, 3164.06 and 3064.99. The absorbance peak of hydroxyl group is completely disappearing due to bond formation of metal with hydroxyl group. This indicates that the metal is attached with oxygen or oxygen undergoes bond formation with metal. The absorption frequency of carbonyl group is also shifted toward up filed due to metal complex formation with ligand. In infra red spectrum of ligand molecule carbonyl group showed peak at 1766.67 which is shifted toward and observed at 1666.55 cm^{-1}.

Thermo gravimetric analysis

The thermo gravimetric analysis was carried out on Diamond Thermo gravimetric Analyzer and Differential Thermal Analyzer (DTA) in nitrogen atmosphere for all the metal complexes at heating of 10 ºC /min from room temperature to 1000 ºC temperature. During the thermal analysis, metal complex undergo various reaction such as absorption of heat, adsorption, vaporization and sublimation of low melting compounds etc.

TG curves gives information about the temperature at which metal complexes lose moisture or ligand molecule. From the weight loss with the temperature gives degradation pattern of metal complex.

Various thermal properties such as initial decomposition temperature (IDT), the decomposition temperature range and percentage weight loss for all the compounds are determined from thermo gram and are reported in Table 3. The thermal stability of a compound depends on its structure. In the studied compounds, ligand moiety same for all the compounds but central metals are different as shown in Table 2. Hence, in the present study, the variation in thermal stability may be due to nature of different substitutions.

Table 3. Some thermodynamic parameters evaluated from TG thermograms for the studied metal complexes.

Compd. code	Sample amount (mg.)	Initial decomposition temperature (ºC)	Average decomposition range (ºC)	All over % of weight loss	Residual weight loss (mg.)
OP-1 Cu	5.880	120	250-500	90.99	5.350
OP-1 Ni	5.922	160	280-530	91.85	5.439
OP-1 Co	6.841	170	260-520	91.90	6.287
OP-2 Cu	5.523	120	280-570	90.14	4.978
OP-2 Ni	6.744	160	300-590	91.29	6.157
OP-2 Co	4.929	170	280-580	91.50	4.510

From the Figure 5, it observed that the degradation of compound mainly two step process. It observed that up to 150 ºC, approximately 6% weight loss from total weight of sample. This practical weight loss of 6 % is in accordance with the theoretical weight loss of 6.33 %.

This decomposition amount is approximate to the loss of two lattice H_2O molecules. It also confirms that the water molecule in metal complexes in non-bounded form. Hence, in first step of degradation of sample, water molecules are evaporated. In second step of degradation, various heterocyclic rings present as ligand in metal complex may be dissociated into small molecules and evaporated.

Hence, in second dissociation step, stepwise degradation observed up to 450º C. At 1000 ºC temperature almost 91% molecules evaporated and approximate 9% was remained in sample pan. From the pattern of the graph / thermogram, it is clear that metal complex synthesized successfully and also it having two non-bounded water molecules.

4. CONCLUSION

In the present study, metal complexes of transition metals such as Cu(II), Co(II), and Ni(II) were prepared with some synthesized pyrazolo-chalocne derivatives. The structure conformation of ligands compounds was carried out by different spectroscopic techniques.

The synthesized metal complexes were also subjected for thermal gravimetric analysis (TGA) and DTA in order to find out degradation step of metal complexes. The TGA analysis suggested that Cu(II) form tetravalent metal complexes while Ni(II) and Co(II) form hexavalent metal complexes with ligand molecules.

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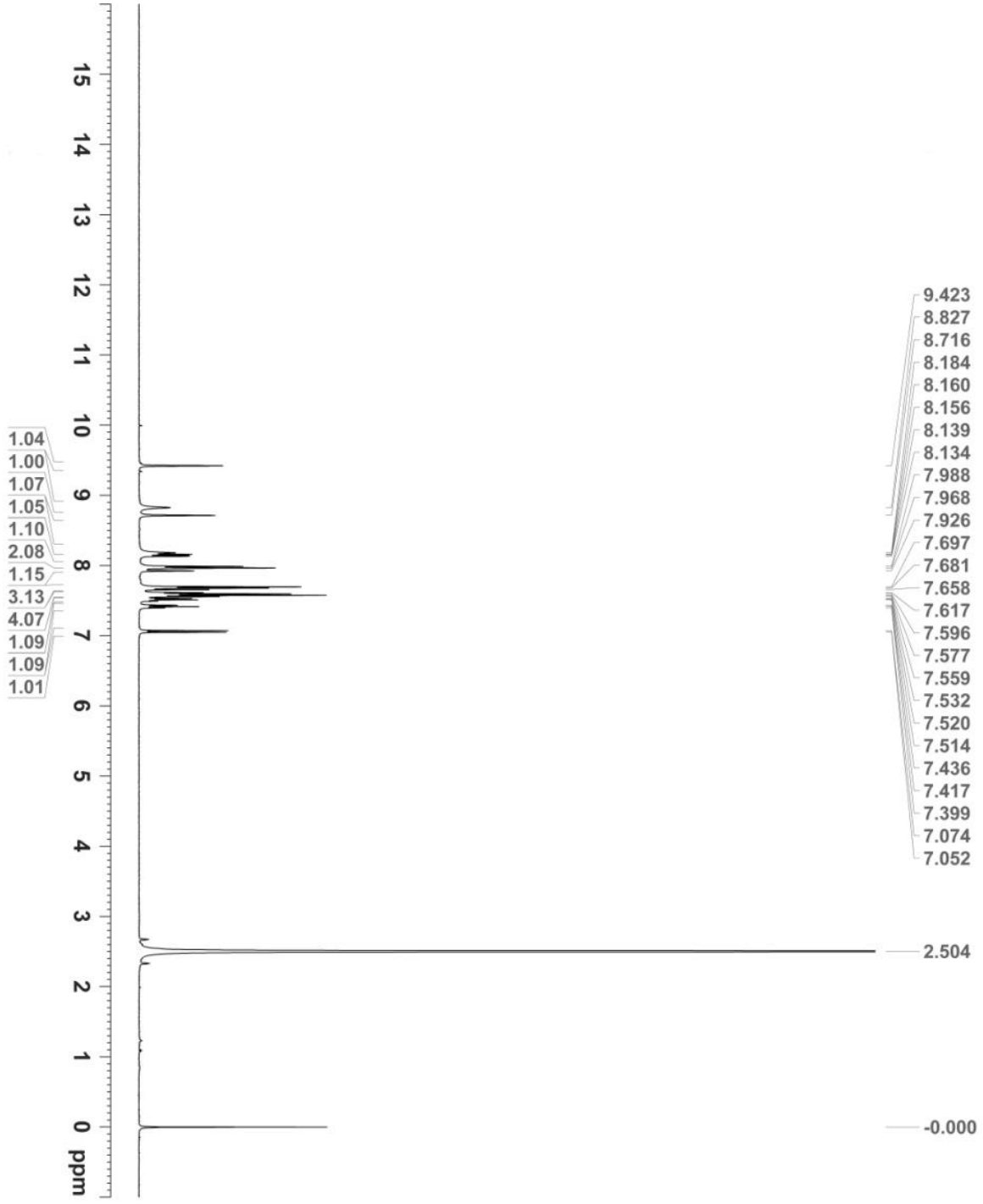

Figure 1. ^{1}H NMR spectrum of OP-1

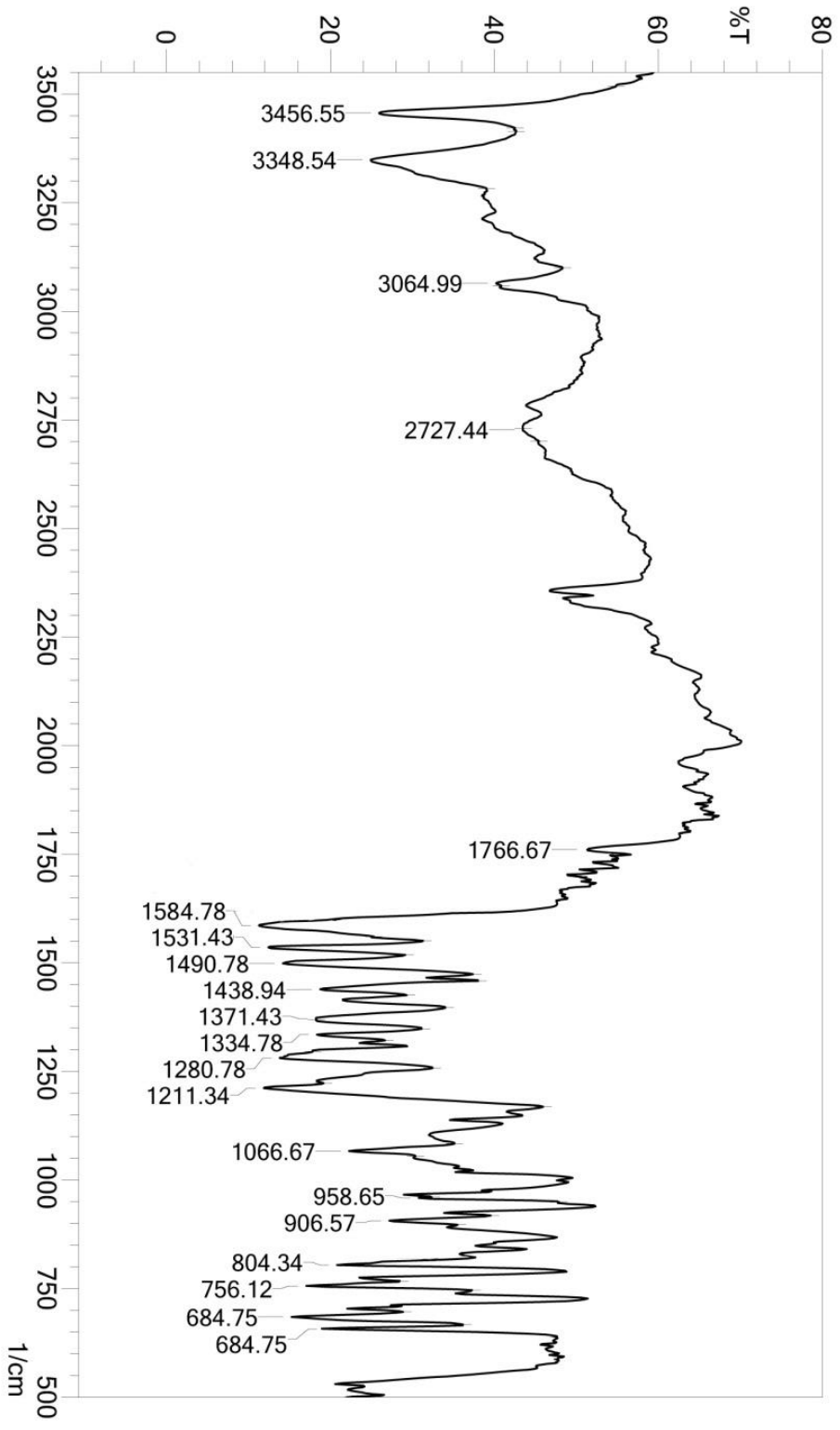

Figure 2. IR spectrum of OP-1

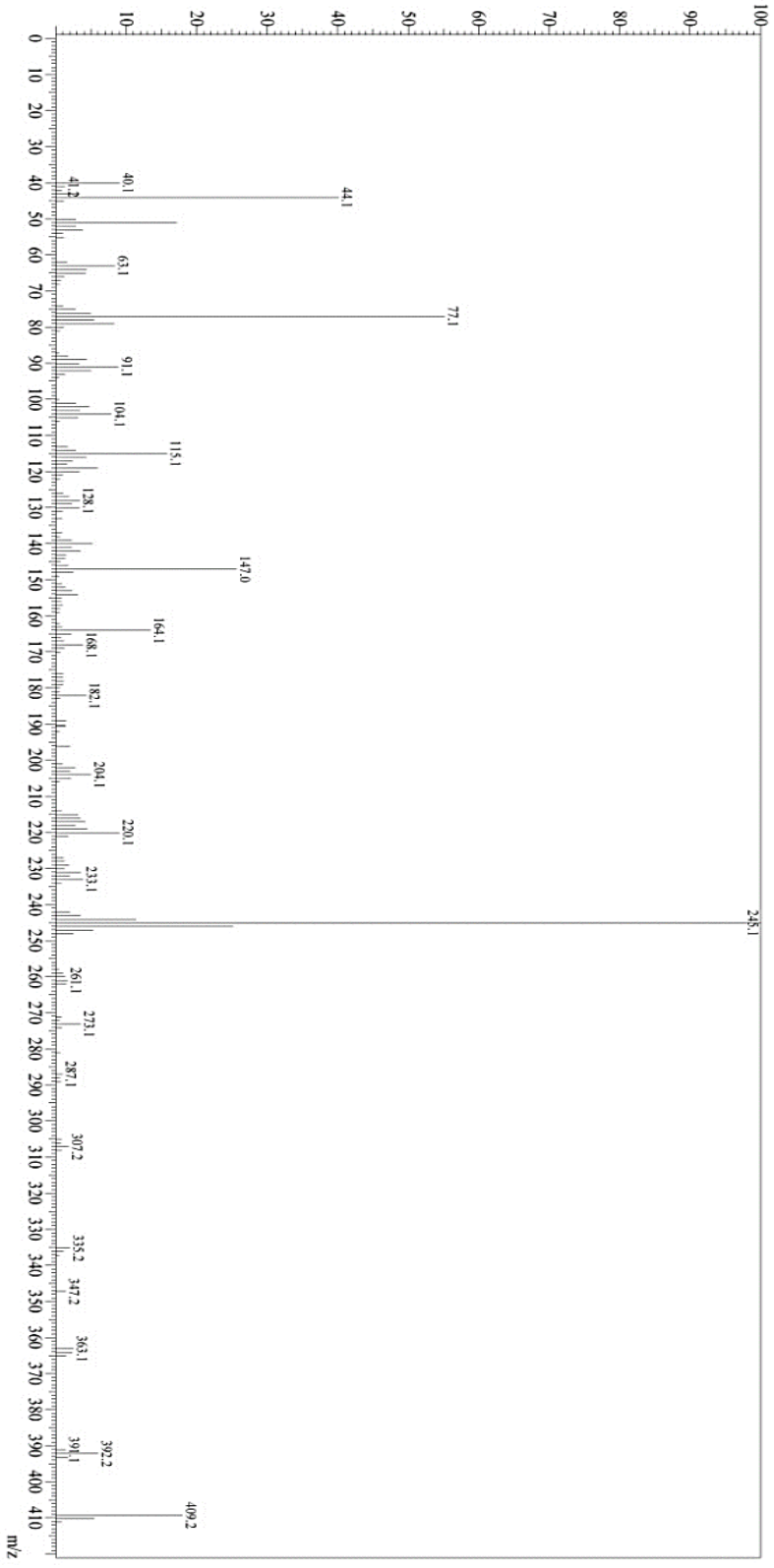

Figure 3. Mass spectrum of OP-1

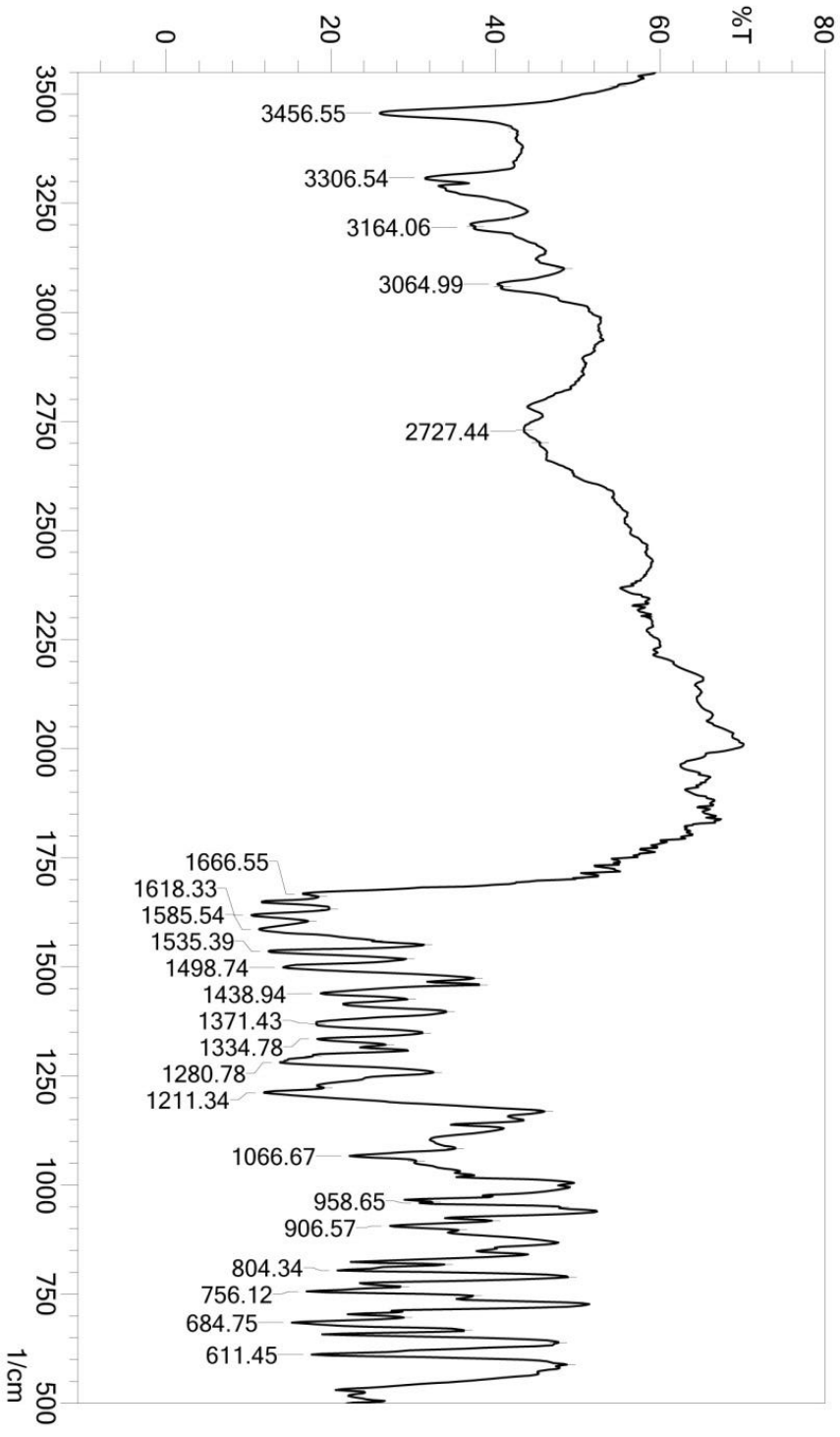

Figure 4. IR spectrum of OP-1 Cu

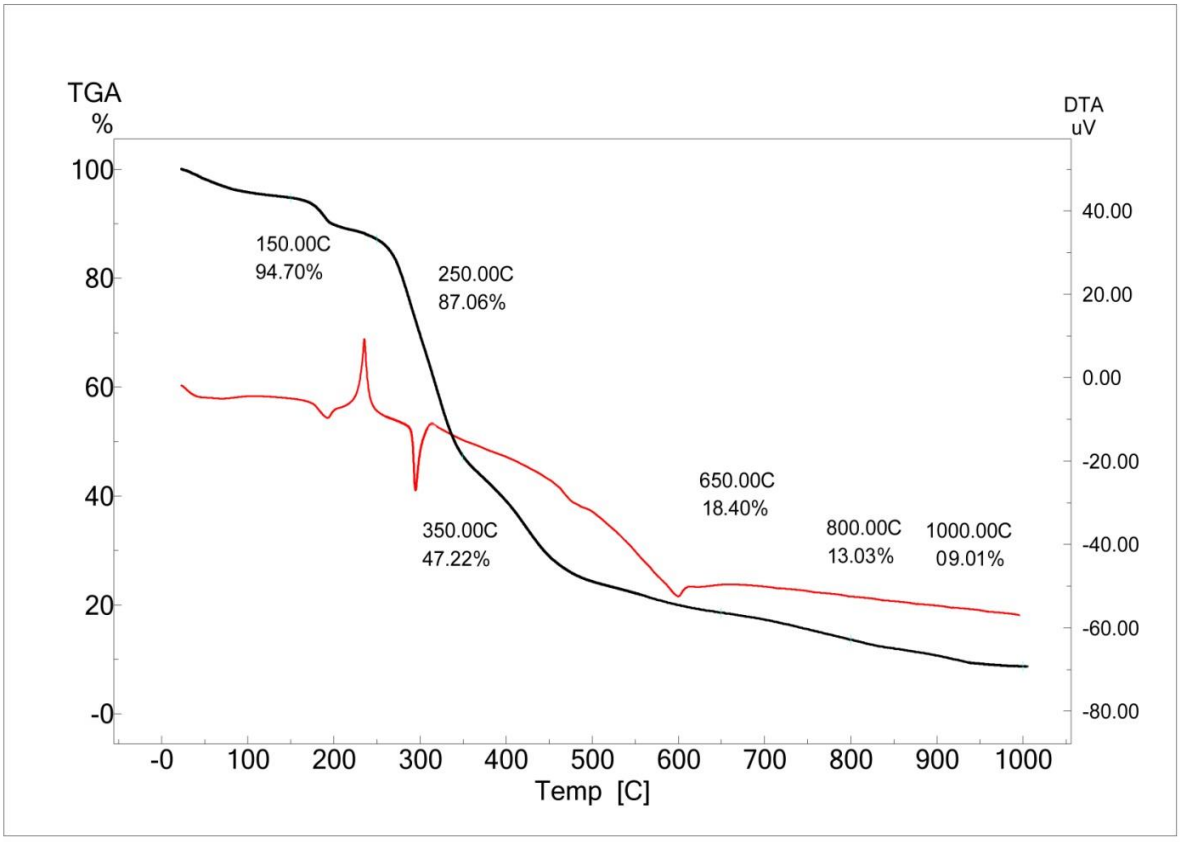

Figure 5. Thermo gram of OP-1 Cu