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SOLVOTHERMAL SYNTHESIS AND CHARACTERIZATION OF PENTANUCLEAR Cu^{2+} AND DINUCLEAR Zn^{2+} METAL COMPLEXES WITH DIMETHYL GLYOXIMATE AND PARAPHENYLENEDIAMINE LIGANDS- AN UNFULFILLED ATTEMPT TO PRODUCE METAL ORGANIC FRAMEWORKS

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Solvothermal Synthesis and Characterization of Pentanuclear Cu^{2+} and Dinuclear Zn^{2+} Metal Complexes with Dimethyl Glyoximate and Paraphenylenediamine Ligands-An Unfulfilled Attempt to Produce Metal Organic Frameworks

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ABSTRACT

Polynuclear coordination complexes of the two first row transition elements copper and zinc with the two ligands dimethylglyoxime and paraphenylene diamine, containing nitrogen donor atoms, have been prepared in this paper. This work concerns the synthesis and characterization of the two new synthesized polynuclear complexes (namely CDP and ZDP). The two complexes are derived from Cu(II) and Zn(II) chelates with uni- negative dimethyl glyoximate (DMG) as equatorial ligand and neutral PPD as axial ligand were synthesized in aqueous alcoholic basic media, under reflux conditions. Structural studies based on analytical, FTIR, Electronic, XRD spectral and magnetic data reveal the formation of stable crystalline polynuclear complexes CDP (Cu^{2+}, DMG, PPD) and ZDP (Zn^{2+}, DMG, PPD). In these, the metal ion- DMG (metal dimethylglyoximate) chelates are approximately square planar, in which the planes are connected by PPD ligand. It is proposed that the Cu^{2+} based complex is penta-nuclear with overall octahedral coordination geometry and the Zn^{2+} based complex is di-nuclear with a square pyramidal geometry. This was an unfulfilled attempt to synthesize MOFs, which resulted in di-(Zn^{2+}) and penta-(Cu^{2+}) nuclear complexes.

Key words: MOF, polynuclear complexes, coordination compounds, PPD, DMG, CDP, ZDP.

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DECLARATION

I, the undersigned declare that the results presented in this report entitled" Solvothermal synthesis and characterization of pentanuclear Cu^{2+} and dinuclear Zn^{2+} metal complexes with dimethyl glyoximate and paraphenylene diamine ligands- An unfulfilled attempt to produce Metal Organic Frameworks" were obtained from the investigation done by me under the supervision of my advisors Dr. Yonas Chebude and Professor V. J. T. Raju in the department of chemistry, Addis Ababa University. This was not submitted for publication in any scientific journal or presented in any international conference. All the materials used in this investigation have been properly recognized.

Name: Makida Fanos

Signature: _____

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List of Abbreviations

CDP	Copper based complex
DMG	Dimethylglyoxime
DMSO	Dimethylsulphoxide
FTIR	Fourier transform infrared spectroscopy
PPD	p-phenylenediamine
Uv-vis	Ultraviolet-Visible
XRD	x-ray diffraction
ZDP	Zinc based complex
χ_M	Molar susceptibility
χ_g	Gram susceptibility
M (Mwt)	Molar mass of complex)
n	Number of unpaired electron per metal
μeff	effective magnetic moment
μ_B	Bohr magneton

1. INTRODUCTION

1.1. Definition

Polynuclear complexes are coordination compounds containing two or more metal atoms, or ions and bridging ligands that used to connect the metal ions together through coordination bonding. Mostly divalent transition metals such as copper and zinc are used for the synthesis of polynuclear complexes with bridging ligands. Due to their stability, diverse structure and magnetic interaction between different centers, polynuclear coordination compounds received more attention in different applications like catalysis, antibacterial, antimycotic, cytostatic and cytotoxic activity with different ligands [1, 2].

In this work two new polynuclear complexes, expected to be MOFs, were synthesized, namely CDP and ZDP through solvothermal synthesis method. The structures of synthesized complexes were studied by using Elemental analysis, FTIR, Magnetic susceptibility, Electronic spectroscopy, and XRD instruments.

Metal Organic Frameworks (MOFs) are a class of coordination polymers which are constructed from inorganic metal ions/clusters and organic linkers (typically multidentate). Inorganic metal ions and organic linkers interact through coordination bonding in which inorganic metal ions/clusters form nodes to bind the arms of the organic linkers. This helps to form a repeating Cage-Like structure, which is responsible for the formation of the pore that makes MOFs multipurpose solid porous material [3], general formation of MOF is illustrated below in **figure1**. The term Metal Organic Frameworks was invented in 1995 by Prof. Omar Yaghi [4]. In view of their useful properties (tunable porosity, high surface area, crystal structure, high thermal and chemical stability, non-toxic nature, post synthetic properties) and potential applications (gas/energy storage, drug delivery, adsorption, purification/separation, catalysis, sensor), MOFs have developed into an important area of investigation. Functionally the di- and multi- nuclear metal complexes with 1D, 2D and 3D networking are designated as MOFs.

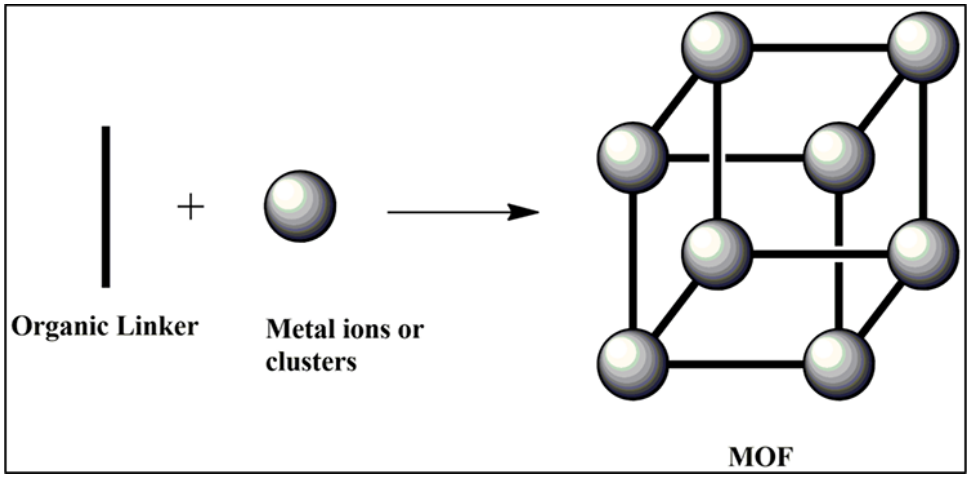


Figure 1: General principle of MOFs synthesis by using suitable method [5].

1.2. Aim of this Work

Transition metals such as; zinc and copper are abundant in our body. Thus Due to their diverse applications especially in biochemistry like; oxygen transportation, cell division, cell growth and other activity, the study of their complexes respecting to their application might be the most important. In this work our aims are:

- ✓ synthesis of CDP and ZDP complexes from metal dimethylglyoximate layers and PPD ligand
- ✓ structural study of the two newly synthesized polynuclear complexes based on analytical, spectral and magnetic studies

1.3. Statement of the Problem

The synthesis and structural study of polynuclear coordination complexes containing N, N-donor bridging ligands with their metal compounds are received more attention due to their catalysis and different biological applications.

As the literature survey indicates the synthesis and characterization of polynuclear coordination complexes that involve divalent copper and zinc metal ions with the organic chelating ligands dimethylglyoxime and paraphenylenediamine have not been studied.

This paper may give good information on the effectiveness of the two nitrogen donor ligands with the divalent metal ions for the formation of stable polynuclear coordination compounds.

1.4. Significance of the Study

Polynuclear complexes have gained attention regarding to their catalysis, biological and other related applications. Especially the study of polynuclear complexes with respect to their magnetic property between different metal centers is more attractive.

1.5. Limitation

- The absence of manual (guidance) to synthesize MOFs
- The absence of conductivity measurement in our laboratory
- The absence of N-absorption machine (to check the porosity of the synthesized compounds) and other significant instruments in our campus.

2. LITERATURE SURVEY

2.1. Background

Polynuclear coordination compounds are complex compound that composed of two or more metal atoms/ions and bridging ligands. The metal atoms/ions may be connected together through direct metal-metal bonds, through bridging ligands, or through both bridging ligands and metal-metal bonds. The general class of coordination compounds or complexes is also extensive and diverse due to their molecular structure, chemical bonding, color, magnetic susceptibility, solubility, volatility, an ability to undergo oxidation-reduction reactions and catalytic activity. Both the transition and main group elements plays a great role in the formation of coordination compounds, or complexes, in which a central metal atom or ion is bonded to one or more bridging ligands through coordinate covalent bonds. Transition metals are known by forming large range of complex ions in various oxidation states, colored complexes, and catalytic properties either as the element or as ions (or both). Coordination compounds can be composed of neutral molecules, positively charged or negatively charged species (ions).

Due to their suitability to many applications (such as; adsorption, drug delivery, separation, catalysis and others), porous solid materials have received interesting attention. Porous solid materials are classified into two classes depending on their constituent arrangement (whether they possess regularly ordered arrangement or not): A) amorphous and B) crystalline porous solids. A) Amorphous materials (mostly organic compounds) do not exhibit any ordered arrangement in their structure (eg. Plastics, gels…). They do not reveal high thermal and chemical stability but they are advantageous due to their less expensive and easy to synthesize [6]. Unlike to amorphous, crystalline porous materials (mostly inorganic compounds) exhibit repeating ordered arrangement in their structure (eg. Silica and zeolites) and they are more advantageous due to their crystalline property and tunable porosity [6]. However they have some disadvantages, which can limit their applications (like difficulty of controlling the synthesis condition, lack of flexibility and limited number of structures). General classification of porous solid materials is illustrated in **figure.2**.

Over the past few decades, a new class of porous solid materials known as Metal Organic Frameworks (MOFs) were introduced and gained more attention due to their excellent properties

and helpful applications. Metal Organic Frameworks (MOFs), which are also called coordination polymers are a new class of hybrid materials which composed of inorganic metal ions/clusters and organic linkers through coordination bonding to form well-defined coordination geometry and crystalline structure. Commonly used metal ions like Cu^{2+}, Zn^{2+}, Cd^{2+}…and organic linkers like carboxylates, amines, phosphates, nitrites…play a great role in the synthesis of Metal Organic Frameworks. During the process of MOF polymerization, the formation of coordination bond between metal ions and organic linkers can continue reversibly to allow rearrangement of metal ions and organic linkers. This help MOFs to form highly ordered framework structure [7].

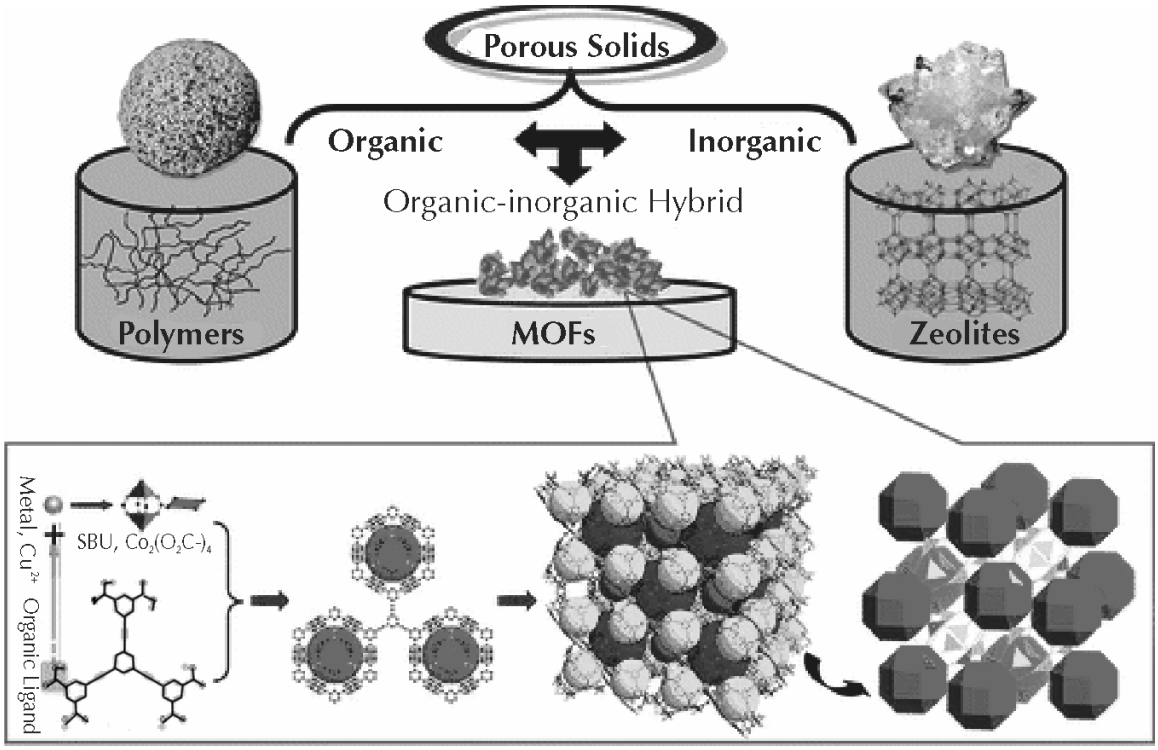


Figure 2: Classification of porous solid materials [6].

2.2. Some Properties of MOFs

MOFs have many fascinating properties including tunable porosity, high surface area, crystalline structure, flexibility/amenability, large range of thermal and chemical stability, post modification properties and non-toxic nature.

1) **Good thermal resistance** MOFs has large range of thermal stability. Among the reported MOFs ZIF family possess high thermal stability greater than 500 °C, Trimeric Cr-based

MIL-88B-NH_2 exhibit 350 °C decomposition temperature and UiO-66 aromatic-based, Co(II) and Ln(III) based compounds display low thermal stability (<200 °C) [8]. Most of the MOFs (including our synthesized compounds) do not melt. In our case both the synthesized MOFs are thermally stable up to 310 °C as melting/decomposition temperature indicate.

2) **Large pore size** is where the guest molecules can be removed and reintroduced reversibly without collapsing framework of the compound [9, 10]. These pores can used to store gases like hydrogen, carbon dioxide, carbon monoxide and others. According to the International Union of Pure and Applied Chemistry, the porosity of crystalline solid materials such as Metal Organic Frameworks is divided in to three categories depending on the diameter of their pore size, such as microporous (pore size <2 nm), mesoporous (pore size 2-50 nm) and macroporous (pore size >50 nm) [6,11].
3) **High surface area** is also among one of the most important properties of MOFs, which can create strong interaction between pores of the MOF and the guest molecules [9].
4) **Crystalline structure** is a very important property which can increase chemical and thermal stability of MOFs.
5) **Flexibility/Amenability** MOFs can be modified through post-synthetic modification in order to fit the ways in which they interact with guest molecules without affecting their pores and structures [12]. Postsynthetic modification is a new synthetic strategy that involves incorporation of active functional groups in to the synthesized framework to use it for the desired applications [6].
6) **Very high sorption behaviors** due to their tunable porosity, MOFs are act as adsorbent for different substances.

2.3. Some Applications of MOFs

Among the classes of porous materials, because of their unique properties, Metal Organic Frameworks are the foremost promising material for various applications including gas/fuel storage, purification/separation, catalysis, sensing, adsorption and drug delivery. Some applications are illustrated in **figure 3:** below.

1) Sensor

Due to their tunable porosity and enormous extent, MOFs are the chosen porous material for sensing application to ward different materials including solvents, gases, small molecules, pesticides, explosives and other biological molecules [7].

2) Gas/Fuel Storage

Due to the fast growth of industrialization and civilization, burning of fossil fuels increasing greenhouse gas emission, which cause serious environmental and global climate change. Hydrogen is taken into account as alternative to fuel because of its pollution free burning and high energy. Due to its low volumetric energy density, the transportation/mobile application at ambient temperature is difficult. To extend its volumetric energy density, compression and liquefaction are suggested. However, because of their harsh operating condition and high storage cost, other alternative techniques are developed. A porous material like Metal Organic Frameworks could be a preferable alternative to store such gases under mild condition because of their non-toxic nature and tunable porosity [13].

3) Catalysts

Metal Organic Frameworks are utilized in catalysis process for various reactions due to their catalytically active, high surface area and tunable porosity. MOFs are used to support homogeneous catalysts, stabilize short-lived catalysts, perform size selectivity and encapsulate catalysts within their pores [14].

4) Adsorption

Environmental pollution may be a global problem that facing person everywhere the globe. Since it require efficient techniques to get rid of hazardous materials (like, Toxic heavy metals, toxic gases and other poisonous substances) from environment. Due to its friendly working system, adsorption is great process to get rid of the hazardous molecules. Metal Organic Frameworks may be used as adsorbent due to their significant physical properties (High expanse and tunable porosity) [14].

5) Purification/separation

Metal Organic Frameworks are utilized in separation/purification process to an excellent extent because of their unique adsorption nature, ultra high and uniform porosity. MOFs show superior performance and selectivity than other solid materials within the process of H_2 purification and hydrocarbon separation [15].

6) Drug delivery/storage

Biologically friendly composition of porous materials is required to use them in drug delivery. Due to their high drug loadings, versatile functionality, non-toxic nature and biodegradability properties, MOFs are considered as a wonderful candidate for drug storage/delivery [16].

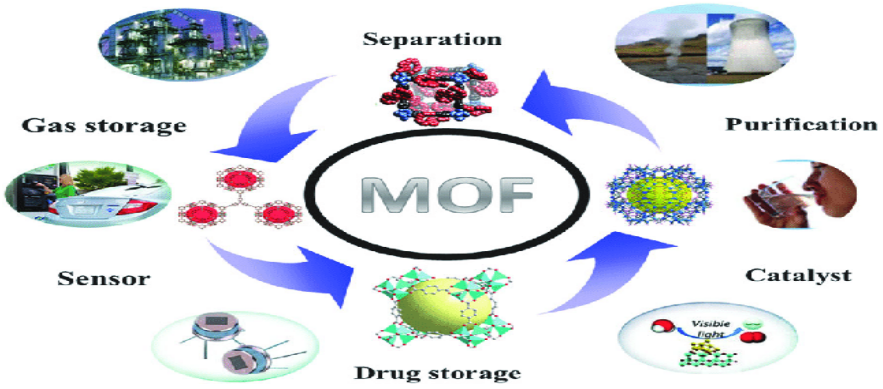


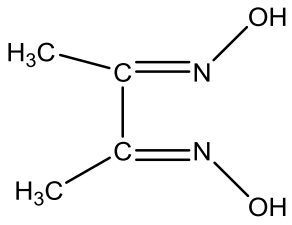
Figure 3: Some Applications of MOFs [17].

2.4. N-Donor Ligands

The construction of Metal Organic Frameworks is often affected by the character of metal ions, organic linkers/ligands and solvent used, which is also similar for polynuclear complexes. Thus, selection of appropriate linker/ligands and metal ions are important. Two N-donor ligands are used during the synthesis of our two polynuclear complexes. DMG was used to form square planar structured layer with copper(II) and zinc(II) ions while PPD was used as axial ligand.

Dimethylglyoxime (DMG)

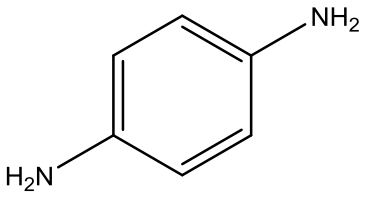
Dimethylglyoxime (N,N'-Dihydroxy-2,3-butanediimine) is an organic compound with the formula CH3C(NOH)C(NOH)CH3. It's the dioxime derivative of the diketone butane-2,3-dione. DMG is employed as gravimetric reagent within the analysis of nickel. DMG can react with many transition metals and form stable complexes [3].Its coordination complexes also are theoretically used as models for enzyme and as catalysts. Structure of DMG is illustrated below in scheme.1.



Scheme 1: Structure of DMG

Paraphenylenediamine (PPD)

Paraphenylenediamine (benzene-1, 4-diamine) is a chemical compound with the formula C6H4(NH2)2. It's aniline derivative compound. It's isomeric with o-phenylenediamine and m-phenylenediamine. It can form covalent bond, due to the unshared electron pair on the nitrogen. It's a binucleophile wont to form variety of compounds. Quinone is made through hydrolysis of P-phenylenediamine; it is often reduced by using anhydrous condition. PPD is especially used as a component of engineering polymers, composites and widely as permanent hair coloring. PPD structure is illustrated in scheme.2.



Scheme 2: Structure of PPD

2.5. Chemistry of Divalent Metal Ion Complexes

2.5.1. Copper (II) complexes

The copper (II) ion is conventionally the more stable oxidation state in aqueous solutions. Compounds of this ion, often known as cupric compounds and they are usually colored. The Copper (II) ion with its d^9 electronic configuration is expected to has one unpaired electron and it has paramagnetic property. Cu^{2+} ion is highly susceptible to distortion in both octahedral and tetrahedral environment. Octahedral complexes with out any distortion supposed to have only one d-d transition $^2E_{2g} \rightarrow {}^2T_{2g}$. In distorted octahedral environment Eg and T2g levels are further split into B_{1g}, A_{1g} and B_{2g} levels. Regular tetrahedral Cu^{2+} complexes are expected to give single band that corresponding to $^2T_2 \rightarrow {}^2E$ transition in near infrared region. Most of the Cu^{2+} complexes have green or blue color due to the single broad adsorption band in the range of 10000-16000 cm^{-1} [18].

2.5.2. Zinc (II) complexes

Almost exclusively in chemical compounds, zinc exhibits +2 oxidation states. The zinc (II) ion with its d^{10} electronic configuration is expected to has dimagnetic property and also no d-d transition expected. Zinc (II) can form 4,5 and 6 coordination number in its complex compound. Zinc (II) complexes usually form tetrahedral geometry because of its fullfilled d-orbital zinc (II) can form stable 18-electron complex through 4-coordination number with its ligands. Zinc is the second most abundant transition metal and essential element in human body. It has role in cell division, cell growth, wound healing, breakdown of carbohydrates and others [19].

2.6. Solvothermal Synthesis Method

Solvothermal method is among the most commonly used methods in the synthesis of chemical compounds. It involves chemical reaction in the presence of solvents on heating. Methanol, ethanol, acetone, and acetonitrile are among the most commonly used organic solvents.

Sometimes mixed solvents are also used to overcome solubility problem with different starting materials. This method is the one used in our polynuclear complexes synthesis by using methanol as a solvent. This method is advantageous due to their easy procedures to run and control the synthesis condition. However, it has limitation like Safety issues during the reaction process [20].

2.7. Characterization Techniques

2.7.1. Elemental analysis

Our solid samples are weighed in containers and loaded into an automatic sampler. The top of the container was pinched with tweezers to seal the sample inside securely. The container was flatted and compressed. Then the sample container was transferred to elemental analyzer and our sample was carried out under Carrier gas flow rate of 120 ml/min, reference flow rate 100 ml/min, oxygen flow rate 250 ml/min; furnace temperature of 900 °C and oven temperature of 75 °C. Sample was run in duplicate and the average values have been taken.

Figure 4: EA 1112 Flash CHNS/O elemental analyzer

2.7.2. *Infrared spectroscopy*

Because of our samples are solid KBr pellet (solid) sample preparation method was used. Firstly, about 100mg of KBr was placed in the mortar and ground until there is no evidence of crystallinity. About 1mg of the synthesized sample was added in mortar which has KBr and continuously ground until the KBr uniformly distributed throughout the sample. The sample was put in the die between the two plates and put into the Qwik Handi-Press. The powder was

pressed for a few minutes under 10 bars to form a pellet. Then the pellet was inserted in FTIR spectrometer and run to produce infrared spectra of the sample in the frequency range of 4000-400cm^{-1}.

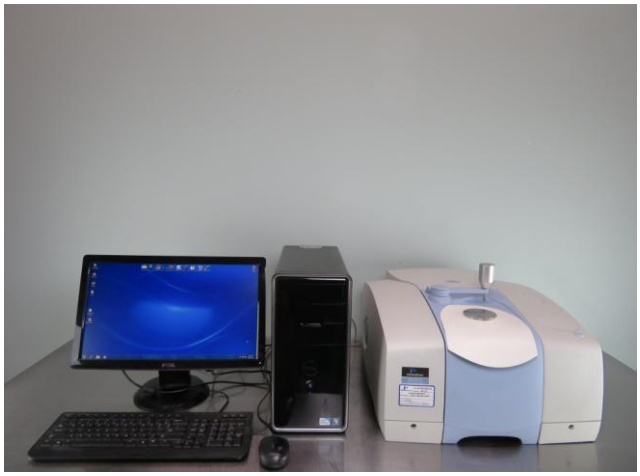


Figure 5: PERKIN ELMER Spectrum 65 FTIR spectrometer

2.7.3. Magnetic susceptibility

The dry sample was weighed and placed in small bottle. The bottle was securely capped and run at 21°C to give gram susceptibility data.

Figure 6: MSB-AUTO magnetic balance

2.7.4. Uv-vis spectroscopy

The sample solution was prepared by dissolving our synthesized compounds in DMSO. Then the prepared solution was poured to the sample holder (cuvette). The cuvette was inserted into the instrument and was run to produce electronic adsorption spectra of the synthesized compounds.

Figure 7: SPECTRONIC GENESYTM 2PC Uv-vis spectrometer

2.7.5. XRD analysis

Our powder sample was dumped onto the sample holder slide. Another clean slide was taken and used to smash the sample to distribute onto the holder. Then the edges were needed to be cleaned. The sample was placed into the instrument and run to produce the XRD pattern of the synthesized compounds.

Figure 8: Rigaku Miniflex600 XRD machine

2.7.6. *Determination of Melting/Decomposition Temperature*

The synthesized compounds were taken and jabbed in to the glass capillary melting point tube, which has one end sealed and the other end open, then the capillary tube containing the sample was inserted into a slot behind the viewfinder of a melting point apparatus. In our case no change was observed on the sample up to 309 ℃, the sample was starting to decompose from 310 °C.

Figure 9: Stuart SMP3 melting point apparatus

3. EXPERIMENTAL

3.1. INSTRUMENTS

Infrared spectra were recorded by using PERKIN ELMER Spectrum 65 FTIR spectrometer in the range of 4000-400 cm^{-1} on KBr pellet. The electronic absorption spectra were measured on SPECTRONIC GENESYTM 2PC Uv-vis spectrometer in the range of 800-200nm regions in DMSO. Rigaku Miniflex600 XRD machine was used to analyze the crystalline phases in the synthesized compounds (to test if the synthesized sample is crystal or not). Magnetic susceptibility measurements were made by using MSB-AUTO magnetic balance at 21°C for the determination of magnetic properties of metals in the obtained products, EA 1112 Flash CHNS/O elemental analyzer was used for determination of carbon, hydrogen and nitrogen in our products. For determination of melting/decomposition temperature, Stuart SMP3 melting point apparatus was used. pH measuring paper was used to adjust pH of solutions.

3.2. CHEMICALS

All chemicals were used from commercial sources without further purification. Methanol (CH_3OH) was used as a solvent and its mixture with water was used to wash up the products while filtering throughout the work. DMG and PPD are bidentate ligands that used in the formation of complexes. $CuCl_2.2H_2O$ (Cu^{2+}) and fused $ZnCl_2$ (Zn^{2+}) were used for complexation. $AgNO_3$ reagent and HNO_3 are used for chloride estimation of the synthesized products. Ammonia was used to maintain the basic condition. Distilled water was also used.

3.3. PROCEDURES

Synthesis was done by refluxing the solution under basic condition to facilitate the deprotonation ($2H^+$) of DMG and magnetic stirrer was used to mix the solution uniformly at 65 °C. The solutions were refluxed until the product separation was complete or until no more product precipitation took place and color change.

1) Synthesis of CDP complex

681.8mg (4mmol) of $CuCl_2 \cdot 2H_2O$ salt, 928.96mg (8mmol) of DMG and 432.56mg (4mmol) PPD were weighed out into a clean 250mL round bottom flask. 120ml of methanol was added to dissolve the mixture. The solution was placed on refluxing setup and refluxed for 7 hours. The product was taken off, cooled at room temperature and filtered by using suction filtration, washed repeatedly with the mixture of methanol and water and then dried at room temperature. Yield: 1.35g, 66.1%.

2) Synthesis of ZDP complex

272.58mg (2mmol) of fused $ZnCl_2$ and 464.64mg (4mmol) of DMG were weighed and placed in a 250ml round bottom flask. 120ml methanol was added and then the contents were refluxed for 2 hours. Then 216.28mg (2mmol) of PPD was added into the hot solution and the refluxing was continued for 5 hours. The product was taken off, cooled at room temperature and filtered by using suction filtration. The product was repeatedly washed with the mixture of methanol and water and then dried at room temperature. Yield: 0.892g, 93.5%. One mole of quinone compound is formed through paraphenylenediamine hydrolysis.

4. RESULTS AND DISCUSSION

4.1 Physical Properties of the synthesized Complexes

Both products are insoluble in water and common organic solvents. CDP is insoluble in cold DMSO, but sparingly soluble in hot DMSO, cold pyridine and hot acetic acid while ZDP is soluble even in cold DMSO, acetic acid and pyridine. They do not melt until 310°C and decompose subsequently.

Table.1. physical properties of the synthesized complexes

Complexes	Color and appearance	Yield (%)	Decomposition temperature (°C)
CDP	shiny black, solid	66.1	313
ZDP	Silver grey, solid	93.5	310

4.2 Characterization of CDP complex

4.2.1 Elemental analysis and composition

The obtained Elemental (C, H, N) analysis (**Table 1:** Elemental analysis of CDP) supports the formation of product with Cu:DMG:PPD mole ratio as 1:2:1, supporting the composition $Cu(DMG)_2(PPD)_{1.2}$ in which DMG represents mono-negative dimethyl glyoximate ion and PPD represents neutral p-phenylenediamine. This composition is in good match with the formation of penta-nuclear complex justifying the real formula as $Cu_5(DMG)_{10}(PPD)_6$.

$$Cu^{2+} + 2DMG + PPD \rightarrow Cu(DMG)_2(PPD)_{1.2}$$

$$5CuCl_2.2H_2O + 10C_4H_8N_2O_2 + 5C_6H_8N_2 \xrightarrow[\text{reflux}]{2CH_3OH,\ 12NH_3} [Cu_5(C_4H_7N_2O_2)_{10}(C_6H_8N_2)_6] + 10HCl + 12H_2O$$

Table 2: Elemental analysis of CDP

CDP/composition	Molecular weight	CHNS percentage (per metal)	Calculated (experimental) value
$[Cu(C_4H_7N_2O_2)_2 (C_6H_8N_2)_{1.2}]$	423.5g/mol	%C	34.5 (34.9)
		%H	4.47 (4.5)
		%N	17 (17.5)

4.2.2 Chloride estimation

CDP was analyzed to check for the presence of chloride ion. 20 mg of the compound was dissolved in hot nitric acid and treated with 1% silver nitrate reagent. Absence of any precipitate formation indicated that, CDP did not include chloride ion in its composition.

4.2.3 FTIR Spectral Studies

The FTIR spectra provide essential information about the nature of functional group present in the synthesized compounds. The FTIR spectrum (**Figure: 10**) of CDP provides evidence for the presence of DMG and PPD and the formation of the complex. The band observed around 3437 cm^{-1} indicates –OH stretching (hydrogen bonded) of the DMG. The intense and sharp bands in the frequency region 3318-3207 cm^{-1} is due to (N-H stretching) of the primary amine of PPD. The absorption bands in the frequency region 2911-2845 cm^{-1} is due to C-H stretching of (sp^2 hybridized) of aromatic PPD and methyl group (sp^3 hybridized) of DMG in the decreasing order of frequency. Coordinated azomethine (C=N) function of DMG is shown at 1607 cm^{-1}. The bands in the frequency region 1460-1396 cm^{-1} indicates asymmetric and symmetric stretching of N-O originating from DMG. Weak bands in the frequency region 580 cm^{-1} are assignable to Cu-

N stretching due to coordinated monobasic bidentate DMG and coordinated neutral ligand PPD. Other related IR assignments are presented in the **table-3** (FTIR Analysis of CDP).

Table 3: FTIR analysis of CDP

Compound class	Group	Absorption (cm^{-1})	Comment
Oxime	O-H	3437	
Aromatic amine	N-H	3318-3207	Doublet (1° amine)
	C-H	2911	sp^2 (aromatic)
		2845	sp^3 (methyl)
DMG	C=N	1607	Azomethine
Aromatic	C=C	1511	
	N-O	1460	Asymmetric
		1396	Symmetric
Aromatic amine	C-N	1314	
	C-C	1064	
	Metal-Nitrogen bond	580	

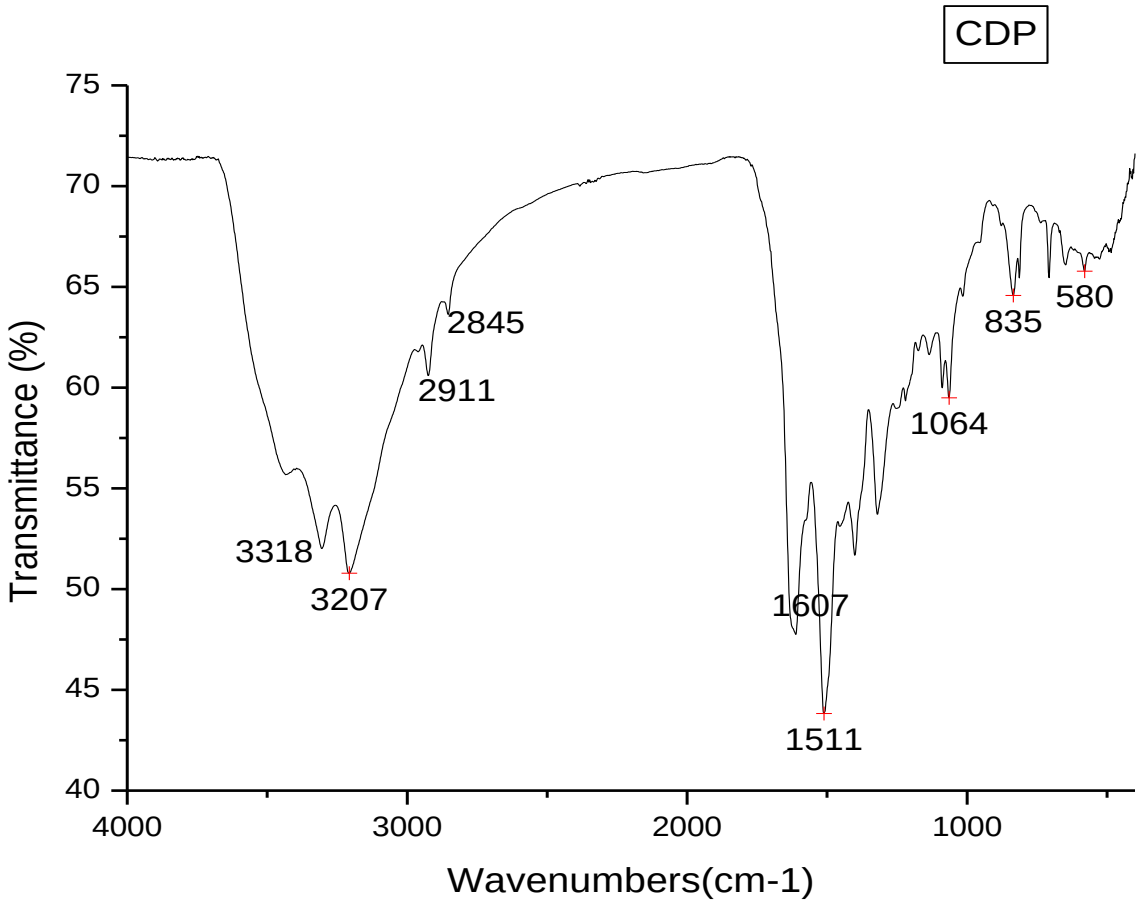


Figure: 10 FTIR spectrum of CDP

4.2.4 Magnetic susceptibility

(χ_g) was measured at 21°C (294.15K) and was used to calculate the number of unpaired electrons of copper in the synthesized CDP complex.

$\chi_g = 1.44 \times 10^{-6}$ at 294.15K.

$\chi_M = \chi_g * M$ (M= Molar mass of complex)

$= 1.44 \times 10^{-6} \times 423.5 = 0.61 \times 10^{-3}$

To get number of unpaired electrons we can use the following equation;

$$\chi_M . T = \frac{1}{8} n(n+2)$$

$$0.61 \times 10^{-3} \times 294.15 \times 8 = n^2 + 2n$$

$$n^2 + 2n - 1.435 = 0$$

$$n = 0.56$$

The effective magnetic moment can be calculated as follow:

$$\mu eff = \sqrt{8 \chi_{\cdot M} T}$$

$$\mu eff = \sqrt{(8(0.61 \times 10^{-3} \times 294.15)}$$

$$\mu eff = 1.198 \mu B \approx 1.2 \mu B$$

We know from electronic configuration of Cu^{2+} ($3d^9$) is expected to show one unpaired electron per metal. The experimental value 0.56 is a sub-normal value, which can be correlated with the obtained structure and the experimental data shows that the penta-nuclear structure of CDP allows for metal-metal interactions.

4.2.5 **Electronic spectral studies**

Electronic spectrum of CDP (**Figure:** 11), exhibits a broad multiple band in range of 400-552 nm (25,000- 18,115 cm^{-1}) which has three distinct regions. These regions can be appropriately assigned to $^2E_g \rightarrow {}^2B_2$, $^2E_g \rightarrow {}^2A_1$ and $^2E_g \rightarrow {}^2B_1$ transitions in the increasing order of frequency, supporting distorted octahedral geometry. The intense bands at 320 and 275 nm are intra-ligand bands.

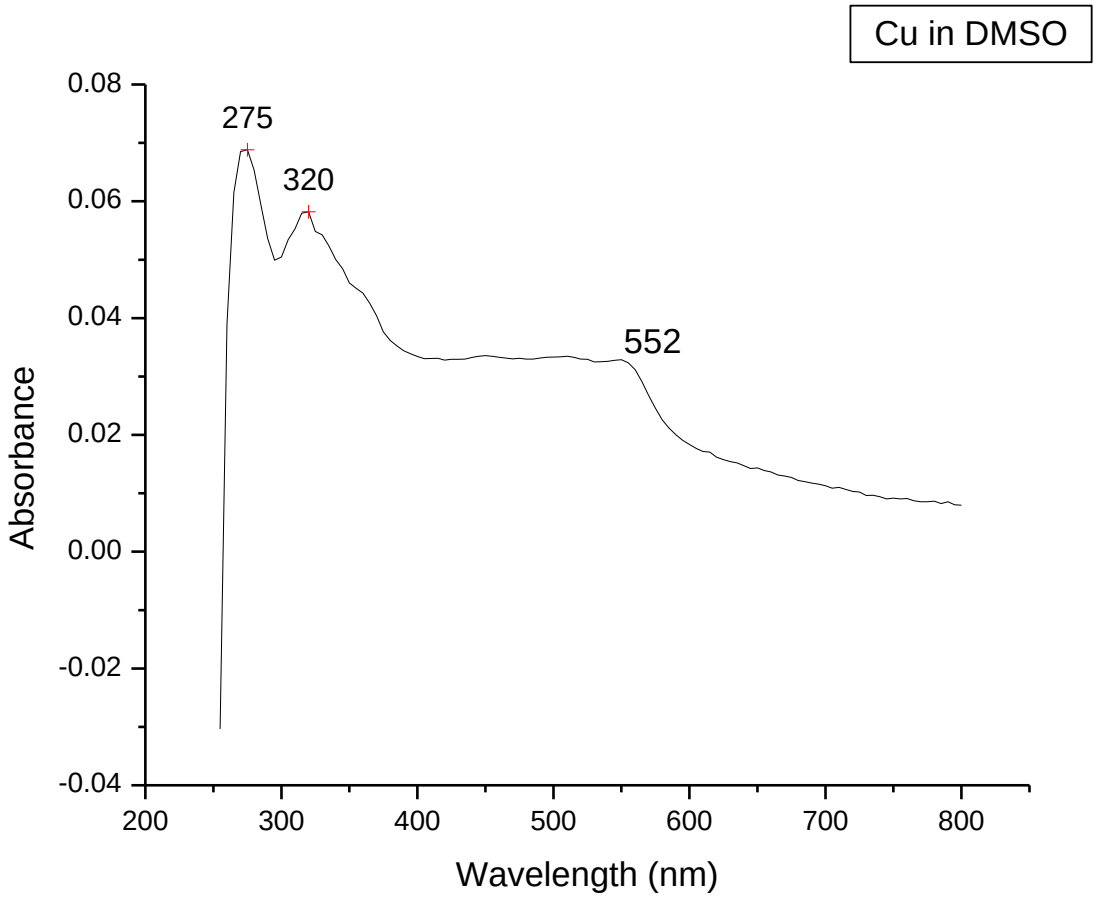


Figure 11: Electronic spectra of CDP

4.2.6 XRD Studies

XRD is an effective and inexpensive method to determine crystalline properties of synthesized compounds. High intensity peaks are observed around 2θ = 15º, 25º, and 27º. It is observed that the powder **XRD spectrum** (**Figure 12 :**) reveals crystallinity of CDP. The crystallite size of the synthesized compound is calculated by using the scherrer equation as follow;

$$D = \frac{\mathrm{K} \times \lambda}{\beta \cos\theta}$$

Where D is crystallite size in nm, K is scherrer constant (0.9), $\boldsymbol{\lambda}$ is wave length of the x-ray sources (0.15406 nm), β is (FWHM) full width at half-height of the diffraction peak in radian and θ is peak position in radians.

$$D = \frac{0.9 \times 0.15406}{0.007\cos 0.236}$$

$$D = 19.81nm$$

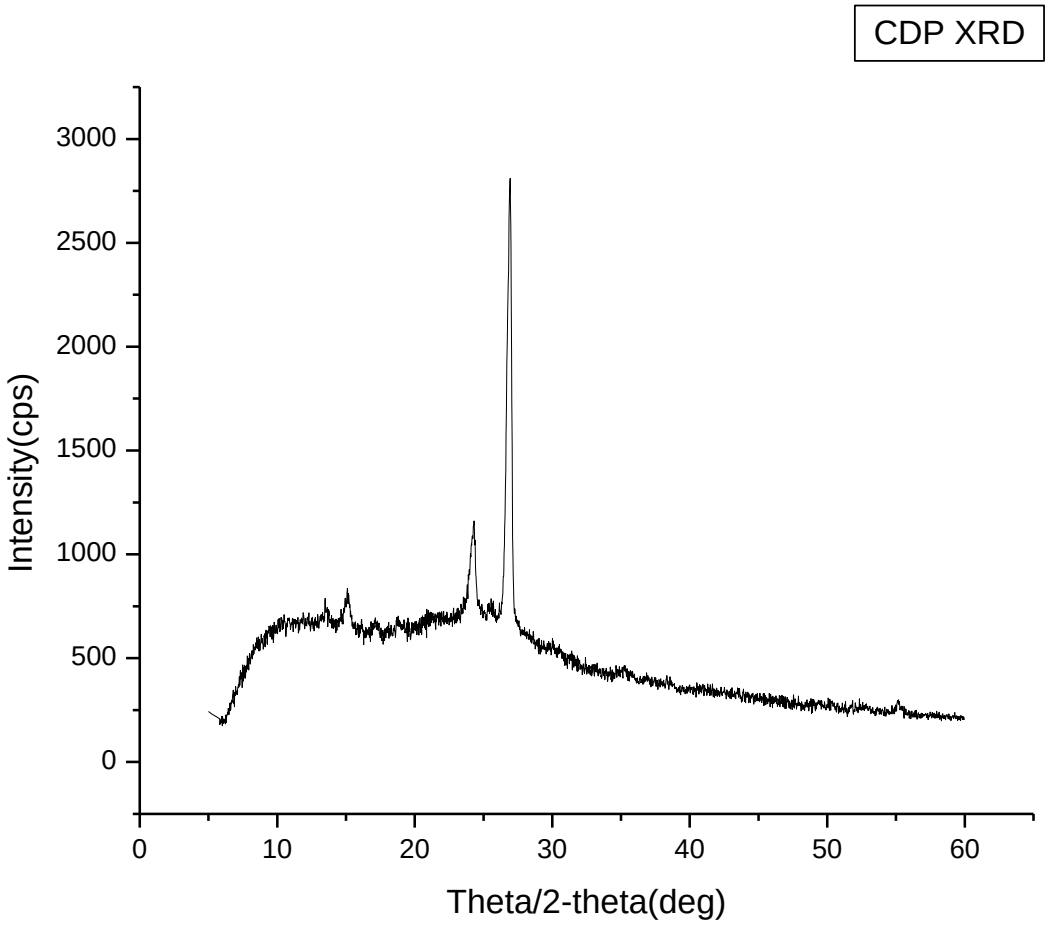
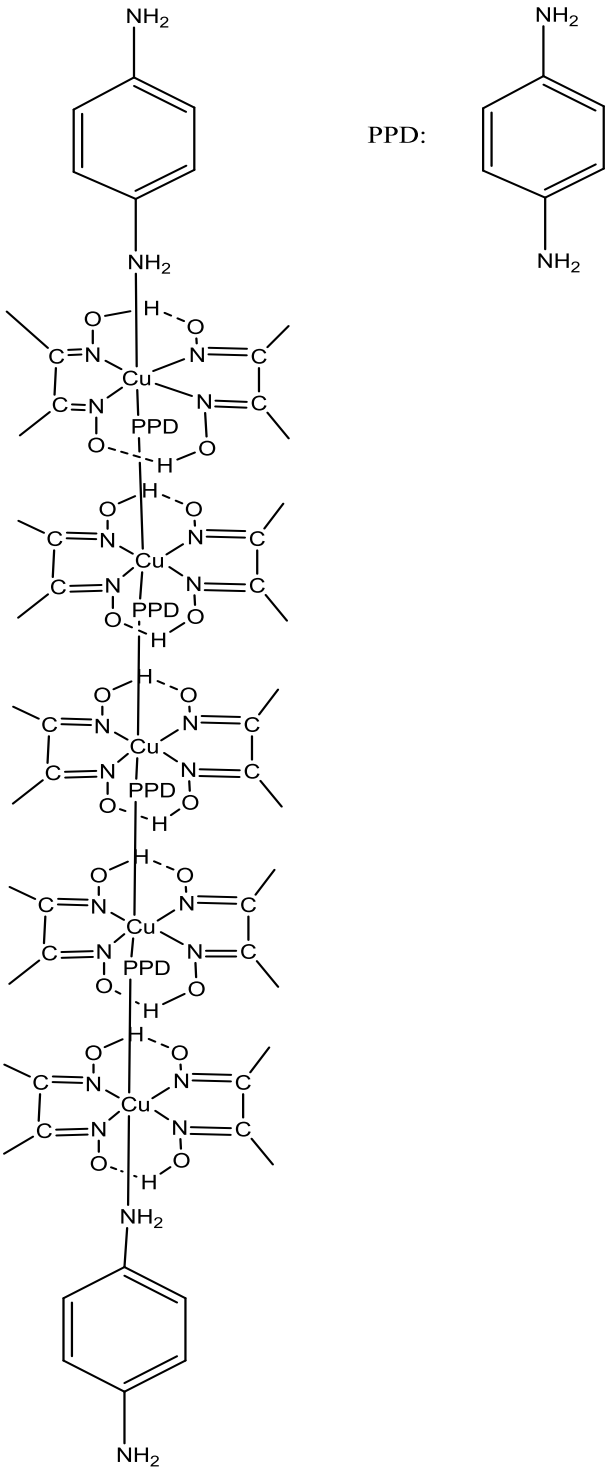


Figure 12: XRD pattern of CDP

4.3 CONCLUSION

Based on the analytical, FTIR spectral, magnetic susceptibility, Electronic spectra and XRD spectral studies it may be concluded that CDP formed a penta-nuclear structured complex with well defined octahedral geometry of Cu(II) due to uni-negative dimethyl glyoximate ion chelation in the equatorial plane and neutral PPD ligand in the axial plane. The proposed structure is given in **scheme 3**.



Scheme 3: The proposed structure of CDP complex

4.4. Characterization of ZDP

4.4.1 Elemental analysis and composition

Elemental (C, H, N) analysis (**Table 4:** Elemental analysis of ZDP) supports the formation of product with Zn:DMG:PPD mole ratio as 1:2:0.5., supporting the composition $Zn(DMG)_2(PPD)_{0.5}$. This composition is in good match with the formation of a di-nuclear complex justifying the real formula as $Zn_2(DMG)_4(PPD)$, in which DMG represents mono-negative dimethyl glyoximate ion and PPD represents neutral p-phenylenediamine. The experimental data further supported the inclusion of 4mol of water and 2mol of methanol molecules per metal in the composition.

$$Zn^{2+} + 2DMG + PPD \rightarrow Zn(DMG)_2(PPD)_{0.5}\bullet 2CH_3OH\bullet 4H_2O$$

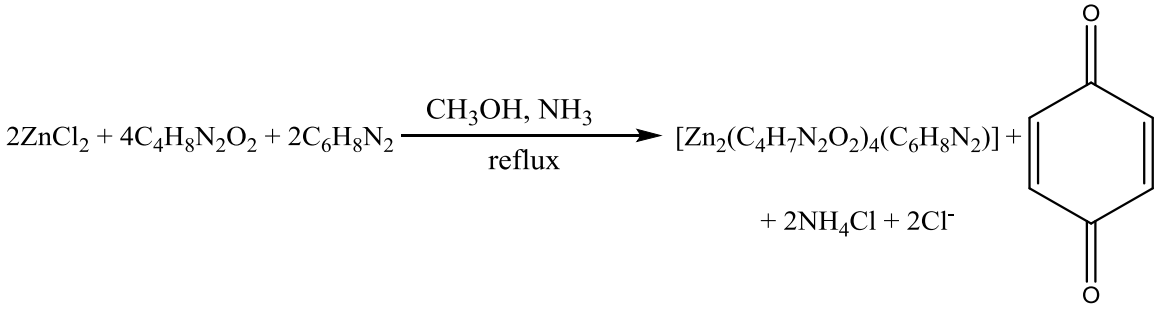


Table 4: Elemental analysis of ZDP

ZDP/composition	Molecular weight	CHNS percentage (per metal)	Calculated (experimental)value
$[Zn_2(C_4H_7N_2O_2)_4(C_6H_8N_2)](CH_3OH)_4(H_2O)_8$	1113.66g/mol	%C	28 (28.98)
		%H	6.1 (6.09)
		%N	12.5 (12)

4.4.2 Chloride estimation

The synthesized ZDP complex showed similarity with CDP in the absence of chloride ion in its composition.

4.4.3 FTIR spectral Studies

The **FTIR spectrum** (**Figure 13 :**) provides evidence for the presence of DMG and PPD and the formation of complex. ZDP show a broad band at 3437cm^{-1} frequency is assignable to the overlap of O-H stretching in water and methanol molecules. These molecules may be present inside as well as outside the structure. The coordination geometry around Zn(II) may be more open to accommodate the solvent molecules. As such, five coordinated square pyramidal geometry is proposed for ZDP complex. The absorption band observed in the frequency range 3271-3125 cm^{-1} indicate (N-H) stretching of primary amine of PPD. The absorption bands in the frequency region 3025-2923 cm^{-1} is due to C-H stretching of (sp^2 hybridized) of aromatic PPD and methyl group (sp^3 hybridized) of DMG in the decreasing order of frequency. Azomethine (C=N) function is indicated by band at stretching frequency 1584 cm^{-1}. The bands in the frequency region 1233-1214 cm^{-1} indicates asymmetric and symmetric stretching of N-O originating from DMG. Other related assignments are presented in the (**Table-5** FTIR analysis of ZDP).

Table 5: FTIR analysis of ZDP

Compound class	Group	Absorption (cm^{-1})	Comment
	O-H	3437	H_2O, CH_3OH
Aromatic amine	N-H	3271-3125	NH_2 (amine)
	C-H	3025	sp^2 (aromatic)
		2923	sp^3 (methyl)
DMG	C=N	1584	Azomethine
Aromatic	C=C	1515	
DMG	N-O	1233	Asymmetric

		1214	Symmetric
Aromatic amine	C-N	1088	
	C-C	835	
	Metal-linker bond	545	

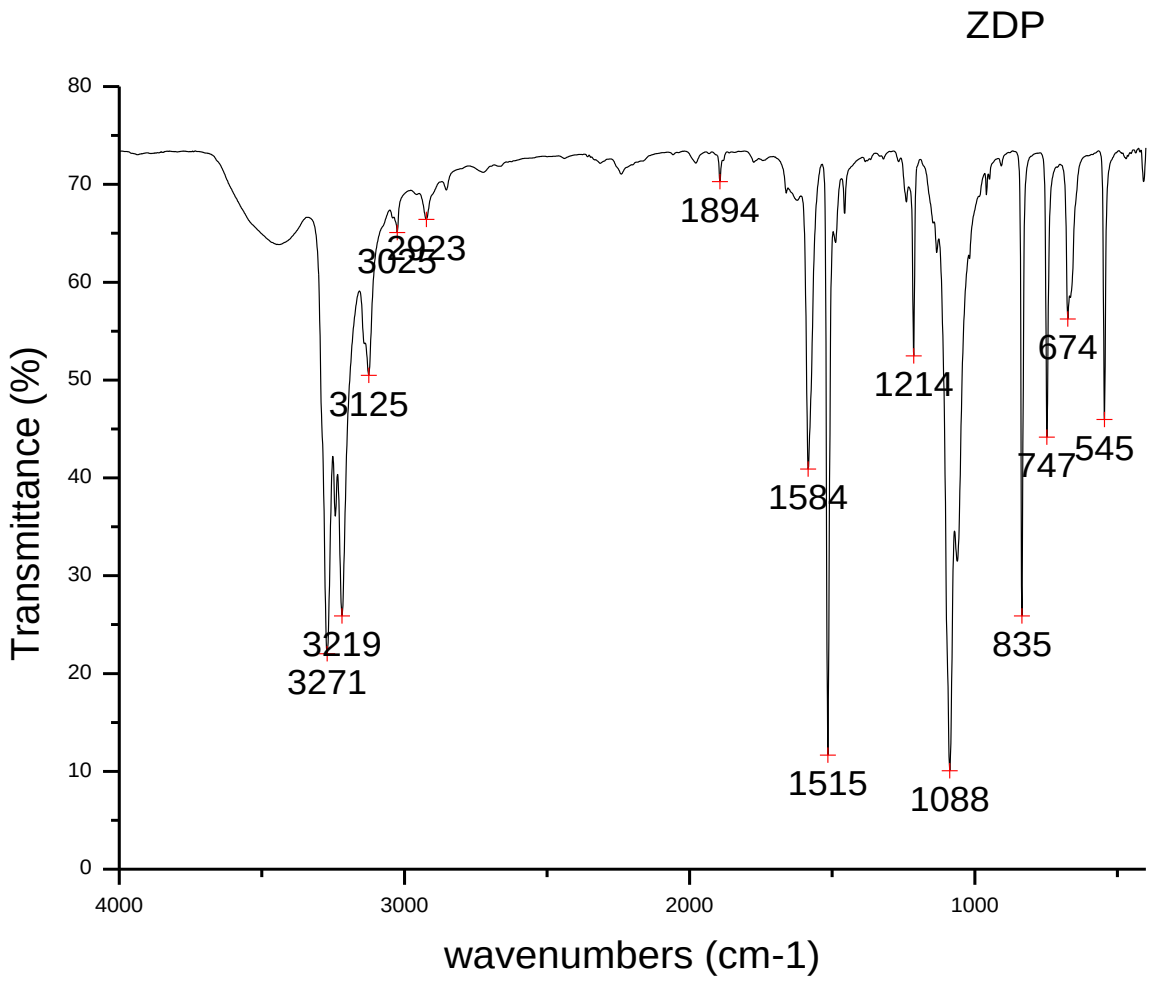


Figure 13: FTIR spectrum of ZDP

4.4.4. Magnetic susceptibility

Because of d^{10} electronic configuration of Zn^{2+}, diamagnetic property is expected. Thus the magnetic measurement data was not recorded for zinc contained complex (ZDP).

4.4.5. Electronic spectral studies

The **electronic spectrum** of ZDP (**Figure 14 :**), show the intense bands at 275, 325, 480 and 500 nm are assignable to intra-ligand π→π*(benzene), n→π*(OH, NH_2) and n→π*, π→π*(C=N) chromophores. Due to d^{10} electronic configuration of Zinc (II) ion, no d-d transitions are expected.

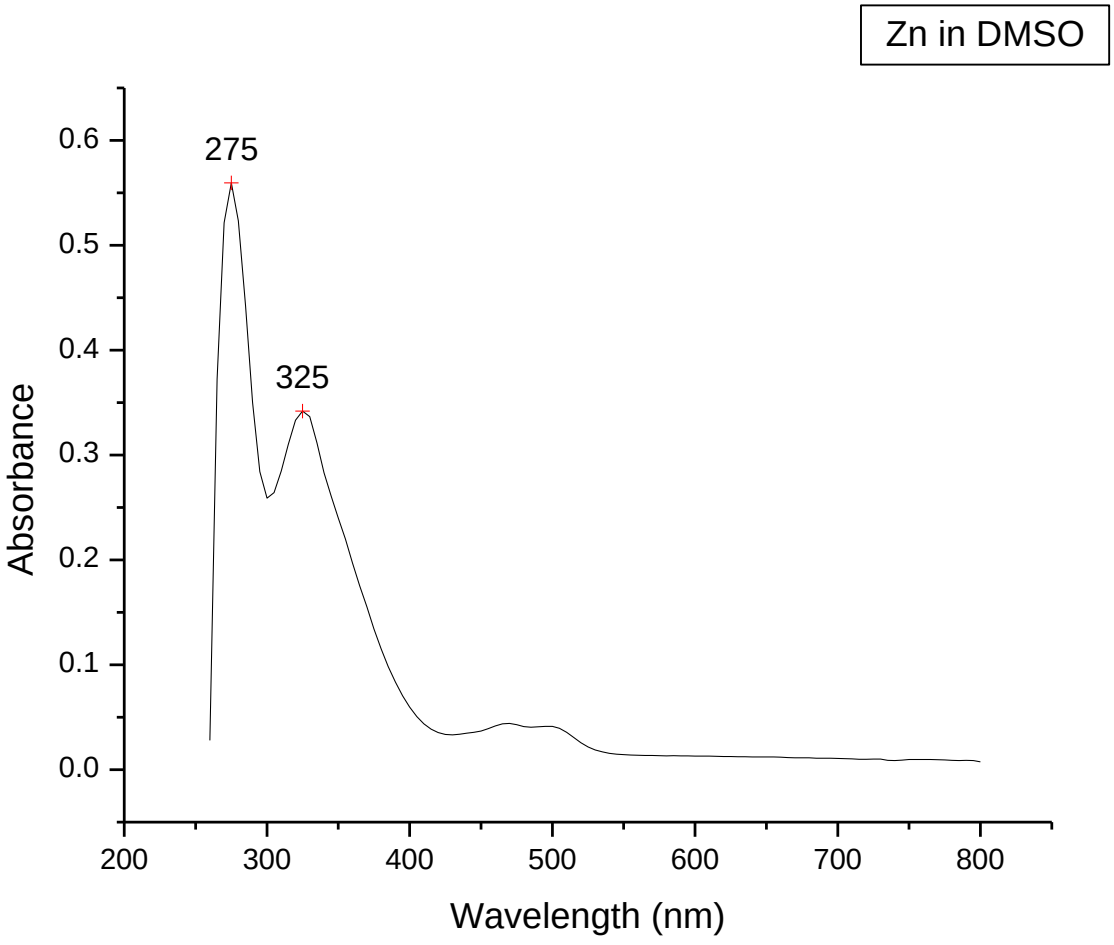


Figure 14: Electronic spectrum of ZDP

4.4.6. XRD analysis

High intensity peaks are observed around 2θ = 12º, 14 º, 16 º, 21 º, 25 º, 26 º, 30 º, 32 º, 35º with few weak intensity peaks in the range of 36 º-55 º. The sharp peaks show repeating unit cell that confirm the crystalline property of the synthesized compound. It is observed that the powder **XRD pattern** (**Figure 15 :**), proves the crystalline property of ZDP.

The crystallite size of the synthesized compound is calculated by using the scherrer equation as follow;

$$D = \frac{\mathrm{K} \times \lambda}{\beta \cos\theta}$$

Where D is crystallite size in nm, K is scherrer constant (0.9), $\boldsymbol{\lambda}$ is wave length of the x-ray sources (0.15406 nm), β is (FWHM) full width at half-height of the diffraction peak in radian and θ is peak position in radians.

$$D = \frac{0.9 \times 0.15406}{0.0049 \cos 0.14}$$

$$D = 28.3nm$$

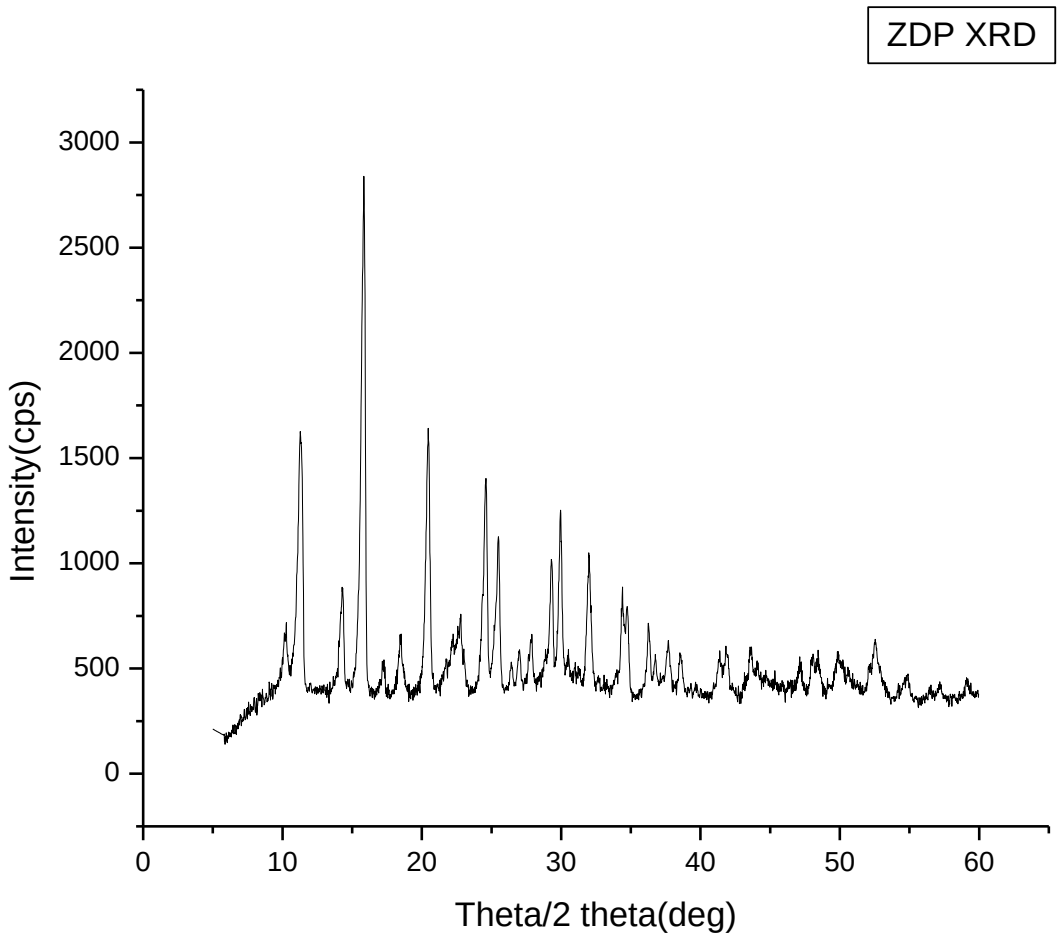
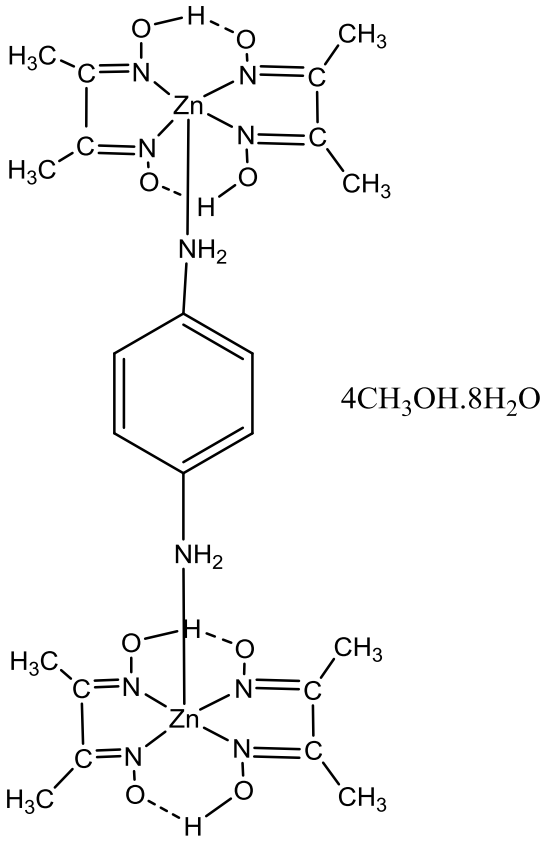


Figure 15: XRD pattern of ZDP

4.5. CONCLUSION

It is concluded that ZDP is a dimeric complex, containing two equatorial $Zn(DMG)_2$ axially connected by one pillared ligand PPD. The synthesized complex is proposed to be structurally more open with five coordinate and square pyramidal geometry around Zn(II). The proposed structure is presented in **scheme 4**.



Scheme 4: The proposed structure of ZDP MOF

5. SUMMARY

Polynuclear coordination compounds are recognized for their useful applications related to catalysis and different biological activities may increases the necessity of more systematic study on polynuclear complexes. Two divalent metal ion containing polynuclear coordination complexes involving potential bis- chelating bidentate NN- donor ligand (mono-negative DMG) providing equatorial ligand and neutral NN- donor functioning PPD as axial ligand were synthesized. Based on chemical, analytical, spectral and magnetic studies penta-nuclear and di-nuclear for Cu(II) and Zn(II) complexes formation was concluded respectively. The geometries around Cu(II) and Zn(II) were proposed as octahedral and square pyramidal respectively.

6. RECOMMENDATION

From this work I suggest that, Synthesis of MOFs in high yields under mild experimental conditions using less harmful/ green solvents and with essential characterization techniques like N-absorption machine will be a welcome requirement in the future investigation. This report is a small attempt this direction further work will be required.

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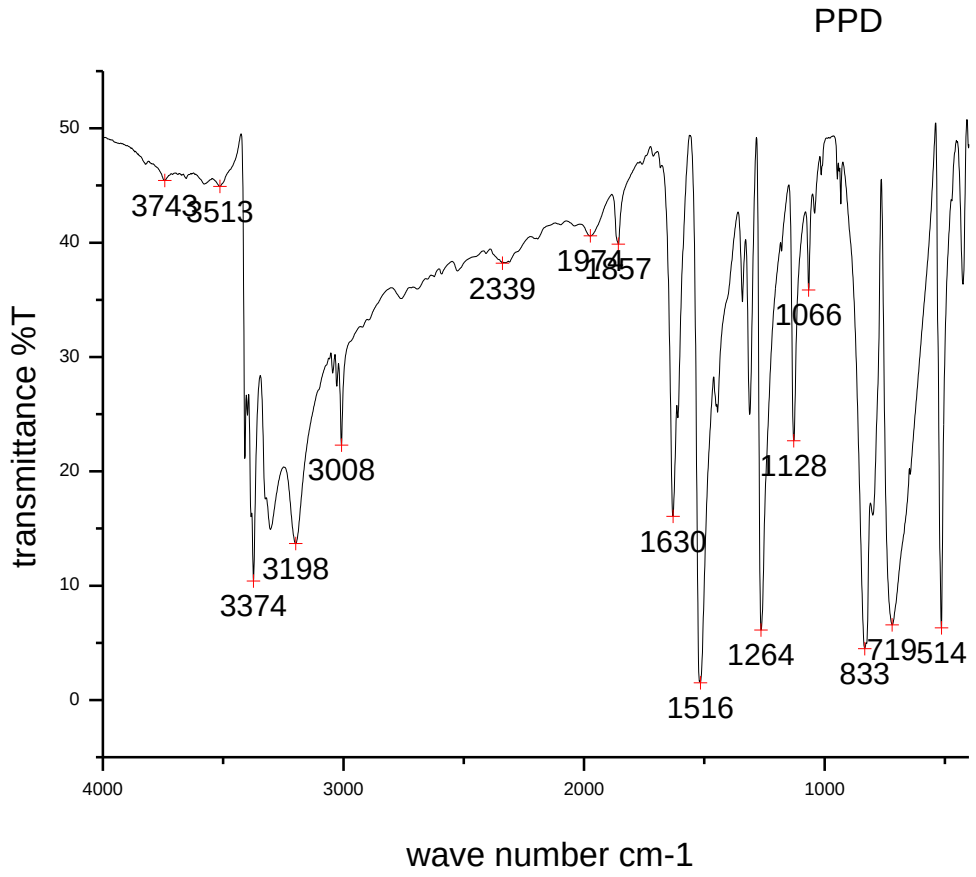
PPD-FTIR SPECTRUM; APPENDIX-I



DMG-FTIR SPECTRUM; APPENDIX-II