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Research Article

Synthesis, Characterization and Catalytic Activity of Azamacrocyclic Transition Metal Complexes

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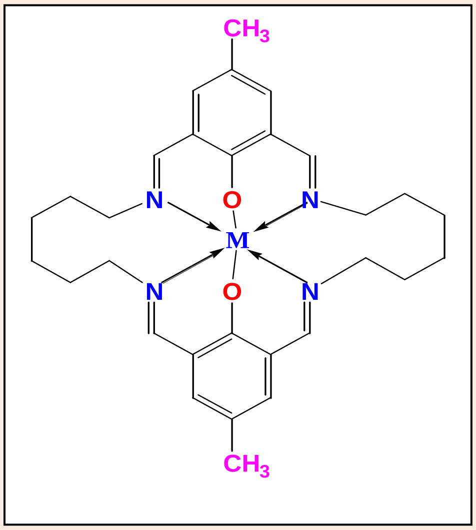
Abstract

New compartmental azamacrocyclic Schiff base were synthesized by the condensation of 2,6–diformyl-4–methylphenol with Hexamethylenediamine. Using azamacrocyclic Schiff base mononuclear metal complexes were synthesized with Cu(II), Co(II), Zn(II) and Ni(II) chlorides. Structural features were determined by analytical and spectral techniques like IR, ^{1}H NMR, UV-VIS, elemental analysis, molar electric conductibility, magnetic susceptibility and thermal studies. The complexes are found to be soluble in dimethylformamide and dimethylsulphoxide. Molar conductance values in dimethylformamide indicate the non-electrolytic nature of the complexes. Spectral studies suggested octahedral geometry around the metal ion. Synthesized Cu(II) complex were screened for catalytic activity which shows oxidation of benzyl alcohol to benzaldehyde.



Keywords: Azamacrocyclic Schiff base, azamacrocyclic transition metal complexes, Characterization, catalytic activity

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Introduction

The design and synthesis of well-arranged metal-containing macrocycles is an interesting field of macrocyclic synthetic chemistry [1]. In addition to their particular structural features, supramolecular species formed by self-assembly of transition metals introduce many special functional and biological properties. The macrocyclic Schiff base ligands have received vital attention not only because of their pharmacological properties [2] and their mixed soft-hard donor character, versatile coordination behavior [3], but also for their capacity for chemical recognition of anions and metals of biochemical, medical and environmental importance [4]. The chemistry of Schiff-base is an important field in coordination chemistry [5].This is due to their ability to react with a range of metal ions forming stable complexes which have applications in different fields [6].

The coordination chemistry of nitrogen donor ligands is an active area of research. A great deal of attention in this area has been focused on the complexes formed by 3d metals with bidentate ligands using both sulfur and nitrogen [7]. The Schiff bases are an important class of ligands in coordination chemistry. The study of structural and binding features of various Schiff base complexes can play an important role in better understanding of the complex biological process. The macrocyclic Schiff bases have been widely studied due to their selective chelation to certain metal ions depending on the number, type and position of their donor atoms, the ionic radius of metal ion and coordinating properties of counter ions [8].

Efforts have been made in the last decades to the design and synthesis of macrocyclic or macroacyclic complexes and to study their physico-chemical properties [9]. These investigations emphasized the great relevance of these systems in basic and applied chemistry. Several synthetic strategies are now days available for the preparation of well organized molecular systems or molecular devices, which exhibit peculiar physico-chemical properties or have well defined properties [10]. Many azamacrocyclic or azamacroacyclic systems containing an appropriate set of donor atoms and a suitable structural configuration are capable of producing new macromolecules which have been used in numerous chemical processes and technologies.

For the synthesis of macrocycles, dicarbonyl precursors and a wide range of diamines have been used [11]. Among these precursors 2,6-diformyl-4-methylphenol was the first one applied for the preparation of the macrocyclic Schiff base by Pilkington and Robson [12] in 1970 via a template method. Since then various polyamines have been concerned in cyclocondensation with 2,6-diformyl-4-substitutedphenol by the template or sometimes non-template method to prepare diamine and tetraimine-typed macrocycles [13,14]. The family of macrocycles obtained from condensation of 4-methyl-2,6 diformylphenol and diamines is an important class of ligands in coordination chemistry [15-17]. Over the years, varieties of related ligands have been used to derive dinuclear and polynuclear compounds having varieties of metal combinations.

Synthesis and studies of coordination compounds derived from new or little explored related azamacrocyclic ligands may therefore be important for more enlightenment.

Catalysis is an area of research which still continues to be a premier frontier area of chemistry. It plays a key role in modern chemical technology; in fact, it is the backbone of chemical industry. During the last decades, chemists shift their phenomenological approaches towards the structural and mechanistic investigation at the molecular level by a combination of instrumentation, quantum mechanical calculation and computational methods. This renovation has improved the understanding of catalysis.

The oxidation of organic compounds has been considered as a reaction of academic and industrial interest to analyze the catalytic activity of various metal complexes. Traditionally, oxidation of benzyl alcohol to benzaldehyde is performed with stoichiometric amounts of chromium (VI) reagents. These oxidants are not only relatively expensive, but also they generate copious amounts of heavy metal waste. Moreover, the reaction is often performed in environmentally undesirable solvents like chlorinated hydrocarbons. Hydrogen peroxide is a clean oxidant compared to other oxidants [18]. To reduce the harmness and cost of solvents, studies towards solvent free process have been carried out [19, 20]. The Cu(II) [21], Mn(II) [22] and Ru(II) [23] complexes are found to catalyze the selective oxidation of benzyl alcohol to benzaldehyde. Highly selective oxidation of benzylic alcohols to benzaldehydes using active dinuclear manganese (IV) complex as catalyst and hydrogen peroxide or tert-butyl hydrogen peroxide as oxidant is reported [24]. From an economic and environmental perspective, catalytic aerobic alcohol oxidation represents a promising protocol [25]. Considering the important role of copper in enzymatic oxidations, it is hardly surprising that copper is frequently used in oxidation reactions in everyday laboratory practice

This article discusses the oxidation of benzyl alcohol to benzaldehyde, using small amount of synthesized Cu(II) complexes in combination with hydrogen peroxide.

Experimental Section

Materials and methods

All materials were reagent grade and were used as received. 2,6-Diformyl-4-methylphenol was prepared by a modified route from that reported originally by Ullmann and Brittner[26] and then modified by Gagne *et. al.* [27]. The elemental analysis of the compounds was performed on a Perkin Elmer 2400 Elemental Analyzer. IR spectra were recorded on a SHIMADZU model spectrophotometer on KBr disks in the range 4000-400 cm^{-1}. The ^1H NMR spectra were recorded using Bruker DRX 400 spectrometer at 400 MHz with TMS as the internal standard. Mass spectra were obtained with a VG70-70H spectrophotometer. The magnetic moments were measured out using Gouy balance. Purity of the compound is checked by TLC.

Chemistry

Preparation of 2,6-diformyl-4-methylphenol

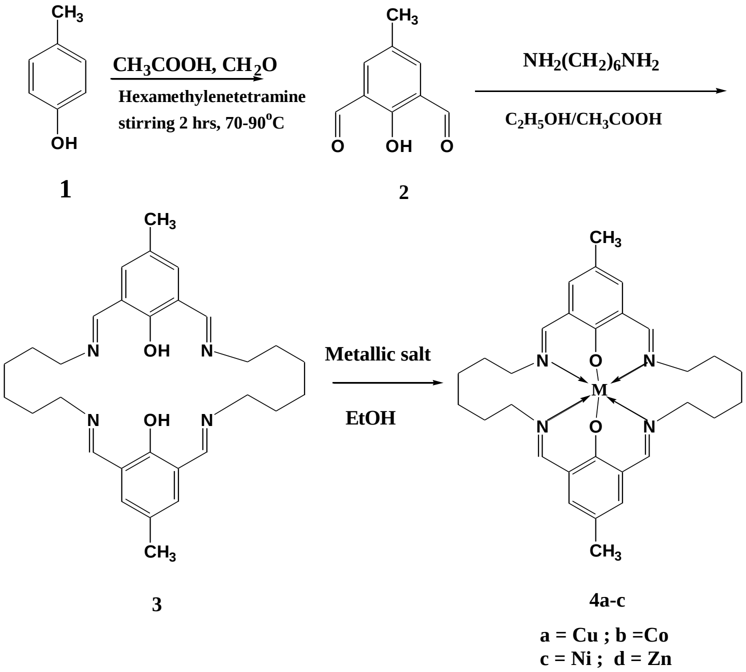
The dialdehyde was prepared by a method as follow. To a solution of p-cresol (10.8g, 10 mmole) in (50mL) acetic acid, hexamethylenetetraamine (28.2g, 20 mmole) and (30g, 100mmole) of paraformaldehyde were added. The mixture was stirred continuously until the light brown viscous solution was obtained then heated to (70-90°C) for two hrs. The solution was cooled to room temperature and concentrated H_2SO_4 (10mL) carefully added. The resulting solution was refluxed for about 30 min and then on treatment with distilled water (400mL) a light yellow precipitate was formed which was stored overnight at (4°C). The yellow product was isolated by filtration and washed in small amount of cold methanol. More pure product was obtained by means of recrystallisation from toluene.

Preparation of the macrocyclic Schiff base ligand

The macrocyclic ligand were synthesized by the condensation of 2,6-diformyl-4-methylphenol with Hexamethylenediamine in 2:2 molar ratios in ethanol and refluxed with stirring with few drops of glacial acetic acid. The completion of reaction was monitored by TLC. The yellow solid precipitate of Schiff base obtained was filtered, washed with distilled water, dried and recrystallized from ethanol.

General synthesis of the complexes: (Scheme: 1)

To a boiling solution of metal(II)chloride (2 mmol) and 4-methyl-2,6-diformyl phenol (0.45 g, 4 mmol) in ethanol (20 cm^3), an ethanolic solution of diamine (4 mmol) was added slowly with constant stirring and the mixture was boiled under reflux for 4 h when a brown compound separated out. The product was filtered out, washed with ethanol and dried in air. The yields were 70-78%.



SCHEME-1

Catalytic studies of metal complexes

The catalytic activity study towards the oxidation of benzyl alcohol was carried out in a 50 mL two necked RB flask fitted with a water cooled condenser. In a typical reaction benzyl alcohol (1.56 mL, 15 mmol) and 30% H_2O_2 (2.4 mL, 22.5 mmol) were mixed and the reaction mixture was heated in an oil bath with continuous stirring. An appropriate amount of catalyst (15 mmol) was added to the hot mixture and the reaction was continued. The progress of the reaction was determined by analyzing the reaction mixture by withdrawing small aliquots of the reaction mixture at specific interval of time.

Results and discussion

The template condensation of 2,6-diformyl-4-methylphenol with Hexamethylenediamine in 2:2 molar ratios in the presence of metal chloride in ethanol (**Scheme 1**) yields light and dark brown complexes. All the complexes are stable at room temperature, soluble in DMSO and DMF. The yield, elemental analysis and molar conductance data of metal complexes are presented in **Table 1.** The elemental analysis data of the complexes are in good agreement with theoretical values. The molar conductance of all the complexes shows that they are non-electrolytes**.** Thin layer chromatographic analysis confirmed the purity of the complexes.

Table 1 Elemental analysis of ligand and its metal(II) complexes and their molar conductance data.

Compound	**Molecular formula**	**Color**	**Yield %**	**Found (calcd) in %**				**Molar conductance $\Omega^{-1}cm^2mol^{-1}$**
				C	H	N	M	
L	$C_{30}H_{40}N_4O_2$	yellow	70 %.	73.13 (73.74)	8.05 (8.25)	11.30 (11.47)	----	----
4a	$C_{30}H_{42}CuN_4O_4$	Pale Brown	71 %	61.10 (61.41)	7.10 (7.16)	9.45 (9.55)	10.25 (10.84)	12.5
4b	$C_{30}H_{46}CoN_4O_6$	Brown	74 %	58.15 (58.29)	7.20 (7.45)	9.02 (9.07)	9.53 (9.53)	15.8
4c	$C_{30}H_{42}\ N_4NiO_4$	Brown	72 %	61.75 (61.93)	6.98 (7.22)	9.55 (9.63)	10.05 (10.10)	16.5
4d	$C_{30}H_{38}N_4O_2Zn$	Brown	75 %	64.98 (65.27)	6.66 (6.94)	10.00 (10.15)	11.20 (11.85)	14.8

Molar conductivity of metal chelates

The conductivity measurements commonly employed in the determination of charge type of the complexes at infinite dilution of the complexes. The stoichiometry of the metal complexes was confirmed by conductometric measurement [28]. The molar conductance of the synthesized mixed ligand complexes were measured using 10^{-3} M DMF solvent. The conductance values are in the range of 12-17 $ohm^{-1}mol^{-1}cm^2$ and the values are listed in **Table 1**. These values are too low to account for any dissociation of the complexes in DMF. Hence these complexes can be regarded as non-electrolyte. The results were compared with the literature values in arriving at this conclusion [29].

Infrared Spectra

The IR spectra of the complexes were recorded to confirm the binding mode of donor atoms with metal ions. The position and/or the intensities of these peaks are expected to change upon chelation. The vibration frequencies and their tentative assignments of the transition metal complexes are listed in **Table 2**. The ligand and metal complexes were characterized mainly using the imine and phenolic bands.

Upon comparison, it was determined the IR spectra of the free ligand shows a band in the region 3435 and 3450 cm^{-1} due to ν(OH) stretching vibration [30]. The absence of O-H stretching and δ (O-H) vibration in the spectra of the complexes indicated deprotonation of the -OH groups.

A medium band corresponding to the phenolic oxygen ν(C-O) is observed at 1275-1297 cm^{-1} for the free ligand [31]. The band in the range 1616 cm^{-1} are observed due to ν(C=N) which has been shifted towards lower region at around 1606-1610 cm^{-1} in the complexes indicating the participation of the azomethine group in the complexes formation [32,33] this shift is also due to reduction of double bond character of carbon-nitrogen bond of azomethine group[34]. The IR spectra of complexes shows additional absorption band at 518-566 cm^{-1} range due to ν (M-O) band [35]. The coordination of nitrogen to the metal atom is supported by the appearance of a new band in the region 440-489 cm^{-1} assignable to (M-N) vibration [36]. It confirms the involvement of nitrogen in coordination.

Table 2 The important infrared frequencies (in cm^{-1}) of ligand and Metal(II) complexes.

Compound	ν (C=N)	ν (O-H)	ν (M-N)	ν (M-O)
L	1616	3450	---	----
4a	1610	---	469	518
4b	1605	---	440	530
4c	1608	---	450	566
4d	1610	---	489	525

^{1}H-NMR spectra

The ^{1}H NMR spectrum of ligand recorded in DMSO showed a peak at δ 2.49 (s, 6, $2\times ArCH_3$) due to methyl group at 4-position on the phenol rings. Twenty four methylene protons have resonated between δ 1.29- 3.34 (m, 24, $12\times CH_2$) and the four azomethine protons have resonated as a singlet at δ 8.51 (s, 4, 4×CH=N-). Two protons due to phenolic -OH have appeared at δ 12.06 (s, 1H) as a singlet whereas the four aromatic protons have resonated at δ 7.23 (s, 4, $2\times ArH_2$) as a singlet.

The ^{1}H NMR spectrum of Zn(II) complex of ligand recorded in DMSO showed a peak at δ 2.12 (s, 6, $2\times ArCH_3$) due to six methyl protons at 4-position of phenyl rings. Twenty four methylene protons have resonated between δ 0.9-3.13 (m, 24, $12\times CH_2$) and four aromatic protons of the phenyl ring have resonated as a singlet at δ 7.1 (s, 4, $2\times ArH_2$) respectively. Four azomethine protons have appeared at δ 8.16 (s, 4, CH=N-) as a singlet. The signal observed at δ12.06 due to the protons of phenolic -OH group, in case of ligand has disappeared indicating coordination of the phenoxide ions to the metal ions via deprotonation [37]. These observations reveal that the involvement of phenolic –OH groups in the complexation with the metal ions via deprotonation indicated by the disappearance of the signals due to –OH groups in the Zn(II) complex. Further, the changes in the chemical shifts of azomethine function and aromatic protons in the Zn(II) complex suggest coordination of the azomethine nitrogen with metal ions.

Mass spectral studies

The mass spectroscopy is one of the most useful analytical techniques used for the structural elucidation of compounds. This technique provides a means for interpretation of the structures of the macrocyclic ligand and its complexes.

The mass spectra of azamacrocyclic ligand and its Cu(II), Co(II), Ni(II), and Zn(II) complexes have been recorded. All the spectra exhibit parent peaks due to molecular ions (M^+). The proposed molecular formula of these complexes was confirmed by comparing their molecular formula weights with m/z values. The mass spectrum for the azamacrocyclic ligand shows a molecular ion peak at m/z = 488. The molecular ion (M^+) peaks obtained for various complexes are as follows: (1) m/z = 586[Cu(II) complex], (2) m/z = 618[Co(II) complex], (3) m/z = 582 [Ni(II) complex] and (4) m/z = 552 [Zn(II) complex]. This data is in good agreement with the proposed molecular formula for these complexes.

Magnetic susceptibility and electronic spectral studies

The electronic spectra of the Schiff base ligand and their Cu(II), Co(II), Ni(II) and Zn(II) complexes have been measured in DMF solution between 200-800 nm at room temperature. The electronic absorption spectra are often very helpful for structural investigation. The electronic spectral measurements were used for assigning the geometry of metal ions in the complexes based on the positions and number of d-d transition peaks.

In the spectra of the Schiff base ligand the absorption band observed at 260-290 nm were assigned to a $\pi \rightarrow \pi^*$transition and the band at 360-390 nm were assigned due to $n \rightarrow \pi^*$ transition associated with the azomethine chromophore (-C=N). The new bands in complexes near 440-489 nm can be assigned to L→M charge transfer band. The UV spectral data of all the complexes were given in **Table 3**.

Cu(II) complex

Only one broad band is observed at 625 nm in the electronic spectrum of the Cu(II) complex assigned to $^2E_g \rightarrow {}^2T_{2g}$ transition which is in conformity with octahedral geometry[38]. Though three transitions are expected in this case, they are very close in energy and often appear in the form of one broad band envelope and the broadness of the band is due to Jahn-Teller distortion. These data suggest that the Cu(II) complex have distorted octahedral geometry [39].

An indication of the most probable geometric configuration of the synthesized metal complexes is their magnetic moment values. So, it has been further confirmed by the magnetic moment measurements, room temperature values lie at 1.90 B.M corresponding to the presence of one unpaired electron and it supports a distorted octahedral geometry [40, 41].

Co(II) complex

The electronic spectra of Co(II) complex showed two spin-allowed transitions at 555 and 625 nm assignable to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively, are in conformity with octahedral arrangements for Co(II) ion[42].

The effective magnetic moment (μ_{eff}) of Co(II) complex is 4.82 BM which suggests the high spin six-coordinated octahedral geometry [43, 44] of ligand molecule around the metal ion.

Ni(II) complex

The electronic spectra of the Ni(II) complexes exhibit three absorption bands at of 640 nm, 430 nm and 410nm these bands may be assign to three spin allowed transition: $^3A_{2g}(F)\rightarrow {}^3T_{2g}(F)(\upsilon_1)$, $^3A_{2g}(F)\rightarrow {}^3T_{1g}(F)(\upsilon_2)$, and $^3A_{2g}(F)\rightarrow {}^3T_{1g}(P)(\upsilon_3)$, respectively [45]. This value is indicative to the octahedral geometry.
The Ni(II) complex has magnetic moment value of 2.8 BM at room temperature indicating a spin-free octahedral [46, 47] configuration around the Ni(II) ion.

Zn(II) complex

The Zn(II) complex is diamagnetic. Due to the d^{10} electronic configuration electronic spectra of complex did not show any d-d transition, but only charge transfer absorption is observed at 380-375 nm. By analogy with those described for the complexes containing N_4 donor of macrocyclic ligand and according to the empirical formula and molar conductance of this complex, an octahedral geometry is proposed for this complexes [48].

Table 3 Electronic absorption bands and magnetic values of ligand and their metal(II) complexes.

Ligand/ complexes	Electronic absorption bands and their assignments (nm)			Magnetic Moment μeff, BM
	π-π*	n-π*	d-d transition	
L	260	390	-	-
4a	280	368	448	1.90
4b	261	365	460	4.82
4c	270	360	489	2.8
4d	269	370	450	----

Thermal studies

The TG and DTA studies of the complexes have been recorded in the nitrogen atmosphere at constant heating rate of 10°C/minute. Thermal study on the complexes in controlled nitrogen atmosphere was carried out to understand the stages and temperature range of decomposition. The most probable decomposition pattern of the complexes is proposed on the basis of the careful examination of TG and DTA curves. The thermo analytical data are summarized in **Figure 1** and **Table 4.** The TG of the complexes shows that they are thermally quite stable but to varying degree. The complexes show gradual loss in weight due to decomposition by fragmentation with increasing temperature. Further horizontal constant curve may be due to the presence of metal oxides residue in the remaining part.

The TGA curve and DTG peak temperature of the complexes **4(a-c)** indicates that the decomposition of these complexes takes place in three identical stages. The weight loss in this complexes ranges from 35-215°C in TG curves is termed the first stage of decomposition usually due to loss of moisture. In this case, the weight loss is in the range 7.34-10.50 % is observed, weight loss indicates the loss of lattice water molecules present in the complex [49]. The second step decomposition occurs in the range 210-372°C, which gave the loss of 41.30-44.82 % suggesting the evaporation of ligand. The third step decomposition occurs in the range 372-564°C, which gave the loss of 33.77-35.90 %. The loss in weight corresponds to the remaining organic ligand molecule leaving behind metal oxide as the end product.

While the complex **4d** decomposes in two steps. The first stage of thermal degradation takes place in the range of 230-350°C with the weight loss of 47.46 % due to the decomposition of ligand. The second step decomposition occurs in the range 382-510°C, which gave the loss of 39.50 % due to the decomposition of organic moiety [50].

The experimental values were in full agreement with the percent weight calculated on the basis of stiochiometry proposed for the complexes. The complexes are present in the form of its respective metal oxides above 510°C.

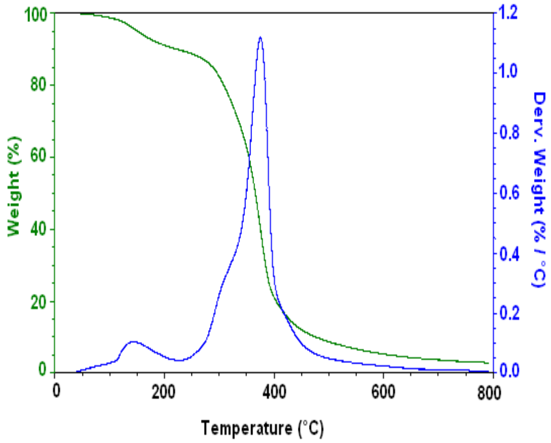


Figure 1 TGA curves of Metal complexes **4**

Table 4 Stepwise Thermal Degradation Data obtained from TGA Curves and their composition.

Complex	Process	Temp. range (°C)	Degradation Products	% Weight loss		No. of Moles	% Residue		Nature
				Calcd	Expt		Calcd	Expt	
4a	I	35-190	H_2O	6.14	7.34	2	13.57	11.96	CuO
	II	210-370	C_9H_7O	44.71	43.80	2			
	III	372-540	$C_6H_{12}N_2$	38.21	35.90	2			
4b	I	40-215	H_2O	11.65	10.50	4	12.12	11.98	CoO
	II	220-372	C_9H_7O	42.42	41.30	2			
	III	379-540	$C_6H_{12}N_2$	36.27	34.25	2			
4c	I	35-209	H_2O	6.19	09.56	2	12.84	11.23	NiO
	II	218-372	C_9H_7O	45.09	44.82	2			
	III	378-564	$C_6H_{12}N_2$	38.50	33.77	2			
4d	I	230-350	C_9H_7O	47.46	46.75	2	14.74	13.10	ZnO
	II	382-510	$C_6H_{12}N_2$	40.57	39.50	2			

Catalytic studies

The catalytic activities of the prepared Cu(II) complex are screened for their activity towards benzyl alcohol oxidation reaction. The catalytic activity was studied using various reaction conditions like temperature, amount of catalyst, time, oxidant to substrate ratio etc in order to find out the optimum conditions for the oxidation reaction. Cu(II) complex showed good activity and the major product of the reaction was found to be benzaldehyde. In the absence of catalyst no significant conversion was observed.

Effect of variation of time

The activity of Cu(II) complex as catalyst for oxidation of benzyl alcohol to Benzaldehyde was affected by reaction time while other parameters kept constant (catalyst: 15mmol, H_2O_2: 2.4mL, benzyl alcohol:1.56mL, temperature: 378K). The conversion increases with increases in time and results are given in the **Table 5.**

Table 5 Effect of variation of time

Time (hrs)	% conversion	% formation of benzaldehyde	Other by products
1	13.45	11.38	2.07
2	16.54	14.55	1.99
3	21.50	19.80	1.70
4	30.65	29.46	1.19

Effect of temperature

The effect of temperature on the oxidation of benzyl alcohol using Cu(II) complex as catalyst was studied at different temperature keeping the other parameters same (catalyst: 15mmol, H_2O_2: 2.4mL, benzyl alcohol:1.56mL, time: 4 hrs). The results given in the **Table 6** shows that conversion increases with increase in temperature.

Table 6 Effect of temperature

Temperature	% conversion	% formation of benzaldehyde	Other by products
318	10.25	8.10	2.15
338	15.60	13.95	1.65
358	25.50	24.10	1.40
378	30.65	29.46	1.19

Effect of amount of catalyst

The reaction when carried out in the absence of catalyst did not yield any products**.** The amount of catalyst has a significant effect on the oxidation of benzyl alcohol. Keeping all the other parameters constant only amount of catalyst changed and the reaction was carried (H_2O_2: 2.4mL, benzyl alcohol: 1.56mL, time: 4 hrs, temperature: 378K). The results revealed that conversion increases with increases in the amount of catalyst and results are given in the **Table 7**.

Table 7 Effect of amount of catalyst

Amount of catalyst (mmol)	% conversion	% formation of benzaldehyde	Other by products
2.5	11.45	9.10	2.35
5.0	14.65	12.55	2.10
10	26.80	24.90	1.90
15	30.65	29.46	1.19

Effect of volume of hydrogen peroxide

The effect of hydrogen peroxide concentration on the rate of reaction was studied by keeping the other parameters constant (catalyst: 15mmol, benzyl alcohol: 1.56mL, time: 4 hrs, temperature: 378K). These studies indicate that the conversion increases with increase in the volume of hydrogen peroxide. The results are given in the **Table 8**.

Table 8 Effect of hydrogen peroxide

H_2O_2 mL	% conversion	% formation of benzaldehyde	Other by products
0.6	12.44	10.58	1.86
1.2	16.54	14.55	1.99
1.8	22.30	21.25	1. 05
2.4	30.65	29.46	1.19

Conclusion

All the synthesized complexes were characterized by elemental analysis, molar conductance, IR, ^{1}H-NMR, mass, electronic spectra and thermal studies. An octahedral geometry was proposed for all metal (II) complexes with N, O as donor atoms which was supported by magnetic and electronic spectral studies. Thermal studies suggested that metal complexes 4(a-c) show three steps thermal degradation where as 4d with two steps which confirms the absence of water molecule. Mass spectrum of the complex confirms the proposed structure.

Synthesized Cu(II) complex can be used as a good catalyst for the conversion of benzyl alcohol to benzaldehyde. At an optimum temperature of 378°K it shows maximum conversion of 29.46%.

Conflict of Interest

The authors declare that they have no conflicts of interest with respect to the content of the manuscript.

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References

[1] T. Fekner, J. Gallucci, M.K. Chan, *J. Am. Chem. Soc.* **2004**,126, 223.; R. A. Sheikh, S. Shreaz, L. A. Khan, A. A. Hashmi, *J. Chem. Pharm. Res.*, **2010,** 2, 274.

[2] R. A. Shiekh, I. A. Rahman, M. A. Malik, S. M. Masudi, N. Luddin, *Int. J. Electrochem. Sci.*, **2012**, 7, 12829.; R. A. Sheikh, S. Shreaz, L. A. Khan, A. A. Hashmi, *J. Chem. Pharm. Res.*, **2010**, 2, 172.; A.M. Asiri, S.A. Khan, *Molecules.*, **2010**, 15, 6850.

[3] P. Sengupta, R. Dinda, S. Ghosh, W.S. Sheldrick, *Polyhedron.* **2003**, 22,477.; R.R. Fenton, R. Gauci, P.C. Junk, L.F. Lindoy, R.C. Luckay, G.V. Meehan, J.R. Price, P. Tumer, G. Wei, *J. Chem.Soc. Dalton Trans.*, **2002**, 2185.

[4] E. Labisbal, A. Sousa, A. Castineiras, A. Gracia-Vazquez, J. Romero, D.X. West, *Polyhedron*, **2000**, 19,1255.; M.K. Srivastava, B. Mishra, M. Nizamuddin, *Ind. J. Chem.*, **2001**, 40B, 342.

[5] K. B. Shiu, S. A. Liu, G. H. Lee, *Inorganic Chemistry*, **2010,** 49, 9902.

[6] H. A. Habib, B. Gil-Hernandez, K. Abu-Shandi, J. Sanchiz, and C. Janiak, *Polyhedron*, **2010,** 29, 2537.

[7] A. Choudhary, R. Sharma, M. Nagar, M. Mohsin. *Journal of Enzyme Inhibition and Medicinal Chemistry*, **2011,** 26, 394.

[8] R. Hernandez-Molina, A. Mederos, in: J.A. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II, vol. 1, Elsevier, **2004**, Chapter 19.

[9] D. E. Fenton, U. Casellato, P.A. Vigato, M. Vidali, *Inorg. Chim. Acta* **1984**, *95*, 187.

[10] P. Zanello, S. Tamburini, P.A. Vigato, G. A. Mazzocchin, *Coord. Chem. Rev.* **1987,** *77*, 165.

[11] P.Guerriero, P. A. Vigato, D. E. Fenton, Hellier, P. C. *Acta Chem. Scand.* **1992**, 46, 1025.

[12] N. H. Pilkington, R. Robson, *Aust. J. Chem.* **1970,** 23, 2225.

[13] P. Zanello, S.Tamburini, P. A. Vigato, G. A. Mazzocchin, *Coord. Chem. Rev.* **1987**, 77, 165.

[14] Lu, T., Ph.D. Dissertation, Nanjing university, **1988**.

[15] B. Dutta, P. Bag, B. Adhikary, U. Flörke, K. Nag, J. *Org. Chem.* **2004**, 69, 5419.

[16] J.C. Byen, W.H. Lee, C.H. Han, *Inorg. Chem. Commun.* **2006**, 9, 563.

[17] J.C. Byen, C.H. Han, K.J. Kim, *Inorg. Chem. Commun.* **2006**, 9, 171.

[18] H.R. Mardani, H.Golchoubian, *Tetrahedron Lett.* **2006,** 47, 2349.

[19] V.Srivamurugan, G.A. Rajkumar, B. Arabindoo, V. Murugesan, *Indian J. Chem. Sec. B.* **2005**, 44, 144.

[20] P.Gogoi, D. Lonwar, *Org. Biomol. Chem.* **2005**, 3, 3473.

[21] T. Naota, H. Takaya, S.I. Murahashi, *Chem. Rev.* **1998,** 98, 2599.

[22] J.Brinksma, M.T. Rispens, R. Hage, B.L. Feringa, *Inorg. Chim. Acta.* **2002**, 75, 337.

[23] J.U. Ahmad, P.J. Figiel, M.T. Raisanen, M. Leskela, T. Repo, *Appl. Cat. A* **2009,** 17, 371.

[24] C.Zondervan, R. Hage, B.L. Feringa, *Chem. Commun.* **1997**, 419.

[25] P. Gamez, I. Arends, R.A. Sheldon, J.Reedijk, *Adv. Synth. Catal.* **2004,** 346, 805.

[26] F. Ullmann, K. Brittner, *Chem. Ber.*, **1909**, 42, 2539.

[27] R. R. Gagne, C. L. Spiro, T. J. Smith, C. A. Hamann, W. R. Thies, A. K. Shiemke, *J. Am. Chem. Soc.*, **1981**, 103, 4073.

[28] Sangamesh, A. Patil, Vinod, H. Nalik, Ajaykumar, D. Kumar, D. Kulkarni, prema S. Badami, *Spectrochim.Acta.A.*, **2010,** 75, 347.

[29] E. Tas, M. Aslanoglu, A. Kilic, O. Kaplan, H. Temel, *J. Chem. Res.* (S), **2006,** 4, 242.

[30] M. Usama, Gomaa, A. Ibrahim, Sbbahm, S. Rabie, *Newyork Sci.J.*, **2012**, 5(4).

[31] A. Ahmed El-Asmy, A.Z. Al-Abdeen, W.M. Abo El-Maaty, M.M. Mostafa, *Spectrochim. Acta Part A*, **2010,** 75, 1516.

[32] K. Karaoglua, T. Barana, I. Degirmencio glub, K. Serbesta, *Spectrochim, Acta Part A*, **2011,** 79, 867.

[33] R.Olar , M. Badea , D. Marinescu, M. Carmen Chifiriuc , C. Bleotu, M. Nicoleta Grecu, E. E. Iorgulescu, V. Lazar, *Eur. J. Med. Chem.*, **2010,** 45, 3027.

[34] M .Ravanasiddappa, T. Sureshg, K. Syed, S. C. Radhavendray, C. Basavaraja, S. D. Angadi, *E J.chem.*, **2008**, 5(2), 395.

[35] P. A. Kulkarni, S. I. Habib, M. M. Deshapande, D. V. Saraf, *J. Basic. Appl. Chem.*, **2012,** 2(2), 12.

[36] R. Jain, A. P. Mishra, *J.Serb. chem. soc.*, **2012,** 77, 1.

[37] R. Malhotra, K. Sudhir, Jyoti, H. R. Singal, K. S. Dhindra, *Indian J. Chem.*, **2000**, 39A, 421.

[38] N. Raman, S. Ravichandran, C. Thangaraja, *J. Chem. Sci.*, **2004,** 116(4), 215.

[39] K. Abe, K. Matsufuji, M. Ohba, H. Okawa, *Inorganic Chemistry*, **2002,** 41(17), 4461.

[40] E. Tas , A. Kilic , N. Konak , I. Yilmaz, *Polyhedron*., **2008,** 27, 1024.

[41] B. K. Das, S. J. Bora, M. Chakrabortty, L. Kalita, R.Chakrabarty, R. Barman, *J. Chem. Sci.*, **2006,** 118(6), 487.

[42] S. Thakurta , R. J. Butcher , G. Pilet , S. Mitra, *Journal of Molecular Structure*., **2009**, 929, 112.

[43] N. Raman, V. Muthuraj, S. Ravichandran, A. Kulandaisamy, *Proc. Indian Acad. Sci.* (*Chem. Sci.*), **2003,** 115(3), 161.

[44] G. G. Mohamed, *Spectrochim Acta Part A.*, **2006,** 64, 188.

[45] A.P. Mishra, R. K. Mishra, S. P. Shrivastava, *J. Serb. Chem. Soc.*, **2009,** 74 (5), 523.

[46] E. Canpolat, M. Kaya, *Turk J Chem.*, **2005,** 29, 409.

[47] G. G. Mohamed, M. M. Omar, A. M. Hindy, *Turk J Chem.*, **2006,** 30, 361.

[48] A.S. Shayma, K. Hamid, M.A. Hapipah. *Chem. Papers.*, **2011**, 65, 299.

[49] K.R. Surati, *Spectrochim. Acta A*, **2011,** 79, 272.

[50] L. S. Kumar, K. S. Prasad, H. D. Revanasiddappa. *Eur Jour of Chem.*, **2011,** 2, 394.

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