A catalytic process for the selective oxidation of alcohols by copper (II) complexes

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ABSTRACT

Novel copper (II)–N–(2-pyridyl)–N'–(5-R-salicylidene) hydrazine triphenylphosphine complexes have been synthesized and characterized. The complexes were effective in the catalytic oxidation of primary and secondary alcohols in presence of periodic acid (H_5IO_6) as oxidant. The oxidation reactions were carried out in acetonitrile. Electrochemical electron transfer study reveals Cu^{II}–Cu^{I} reduction in methanolic solutions. A mechanistic study of the above reactions has been proposed.

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The controlled oxidation of alcohols is one of the most important reactions in organic chemistry [1]. In particular, the conversion of primary alcohols to aldehydes is crucial for the synthesis of fine chemicals such as fragrances or food additives [2]. Generally, it either requires stoichiometric amounts of toxic heavy metal salts [3] or expensive catalysts containing transition metals such as palladium, rhodium or ruthenium [4]. Over the last several years, many transition metals such as ruthenium [5], manganese [6], tungsten [7], rhenium [8], iron [9] and vanadium [10] have been used as catalysts for alcohol oxidation.

The Schiff base transition metal complexes are attractive oxidation catalysts because of their cheap, easy synthesis and their chemical and thermal stability. Considerable attention has been paid to the preparation of transition metal complexes of Schiff bases because they are considered to constitute new kinds of potential antibacterial and anticancer reagents. Copper compounds are well known as very important reagent and catalyst in many organic reactions because of their stability and ease of handling.

Copper is an abundant metal on the earth's crust and is found in various metalloproteins, especially in enzymes implicated in the binding of molecular oxygen or in mild and highly selective aerobic oxidation transformations [11,12] Thus, it is surprising that only a few examples using cheap and "green" copper catalysts and molecular oxygen [13] or hydrogen peroxide are known so far [14–18].

This report presents the synthesis of a series of copper triphenylphosphine complexes (**CuL1-3**) containing N–(2-pyridyl)–N'–(5-sub-salicylidene) hydrazine (Scheme 1) and their application as catalysts for the oxidation of alcohols to carbonyl compounds in acetonitrile with periodic acid as co-oxidant.

$[CuCl_2 (PPh_3)_2]$ was prepared by the reaction of $CuCl_2 \cdot 2H_2O$ and triphenylphosphine in absolute alcohol (Merck) [19]. The Schiff bases were prepared in 70–80% yield by condensation reactions of 2-hydrazinopyridine (Aldrich) with the corresponding 5-substituted salicylaldehyde (Loba) in methanolic media [20]. Complexes **CuL1**–**CuL3** were prepared by refluxing a alcohol solution of $[CuCl_2(PPh_3)_2]$ and ligand in a 1:1 molar ratio for 1 h [21].

The isolated solids of complexes are listed in Table 1 together with their elemental analyses, magnetic moments and UV–Vis spectral data. All of the complexes are dark solids insoluble in alcohol, acetone, pyridine, diethyl ether and ethylene chloride, and partly soluble in DMF and DMSO. Elemental analyses of the complexes show 1:1 metal: ligand stoichiometries. The main IR bands and their assignments are listed in Table 2. Significant frequencies were selected by comparing the IR spectra of the ligands with those of the metal complexes. A strong band, typical of ν(C=N) stretching, is found in the 1596–1625 cm^{-1} range in the spectra of the complexes [22,23]. The observed shift in the ν(C=N) stretch after complexation confirms the formation of a coordinate bond from the imine nitrogen to the metal ion [23–25]. The band in the region 1315–1330 cm^{-1} which is assigned to phenolic ν(C–O) in the free ligand, is shifted to higher wave number in the complexes suggesting the coordination of phenolic oxygen to metal ion [26–28]. The N–H stretching frequency occurs around 3100 cm^{-1} in ligands is unaltered in complexes. This factor reveals the non participation of –NH group in coordination [29]. The pyridine vibrations at 610 cm^{-1} (in-plane ring deformation) and 490 cm^{-1} (out of plane ring deformation) in the free ligand were altered in complexes. The band at 530 cm^{-1} in the complex is assigned to ν(M–O). Bands around 1440, 1090, 690 cm^{-1} are assigned for triphenylphosphine moiety [30].

Magnetic moments of the copper complexes lie between 1.41 and 1.94 B.M. (Table 1) which agrees with the expected value for the S = 1/2 system and lie in the reported range for penta coordinated

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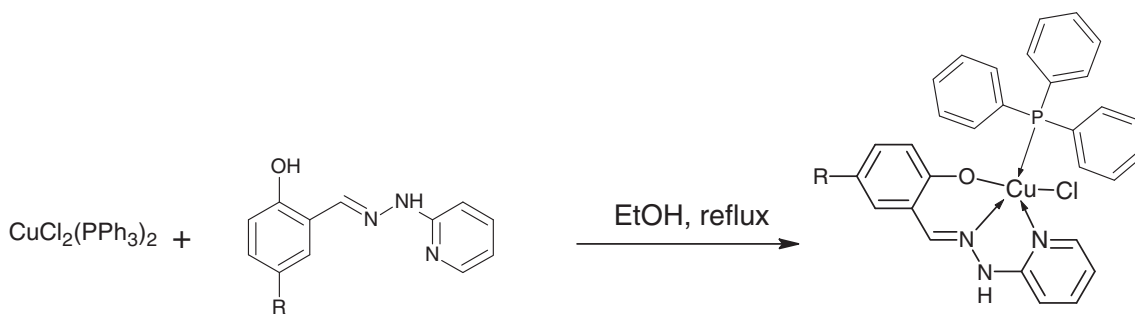
Scheme 1. Synthesis of Copper (II) complexes. (**L1**: R=H, **L2**: R=Cl, **L3**: R=Br).
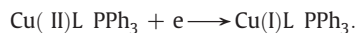
Table 1
Analytical data, magnetic moments and UV–Vis spectral data of the synthesized complexes.

Complex	% Found (calculated)			μ_{eff} (BM)	UV–Vis Spectral Data (cm^{-1})	
	C	H	N		d–d bands	Intraligand and C.T.
CuL1	62.77(62.83)	4.32(4.39)	7.18(7.33)	1.69	12478, 16949, 22727	30303, 41666, 46511
CuL2	59.08(59.27)	3.86(3.98)	6.75(6.91)	1.83	12405, 16915, 22752	30298, 41605, 46498
CuL3	55.15(55.23)	3.65(3.71)	6.32(6.44)	1.94	12450, 16901, 22767	30259, 41701, 46551

structure. The magnetic moments of the complexes exhibit less than the spin only value (1.73 B.M.). This may be due to an anti ferromagnetic effect, influence of the spin-orbital coupling in the ground state for spin doublet species [31]. The bands at 12,478, 16,949 and 22,727 cm^{-1} of the **CuL1** complex are assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions of penta coordinated disposition of the copper ion. The transitions for all the other complexes are given in Table 1. ESR spectra of copper (II) complexes were also recorded in acetonitrile–toluene mixtures at room temperature. Typical spectra with g >g observed are indicative of a five coordinated structure and the unpaired electron is in the $d_{x^2-y^2}$ orbital (Fig. 1). The observed low A values (Table 3) of the order of 132–160×10^{-4}cm^{-1} are also consistent with a typical monomeric distorted five coordinated structure [32]. However the quotient g /A is helpful for indexing

and identifying a distortion towards five coordinated structure [33,34]. The quotient should range from 145 to 175 cm^{-1} for a regular five coordinated structure and the observed results (140–170 cm^{-1}) are indicative of square-pyramidal geometry.

The electroactivity of the complexes was studied in MeOH solutions using cyclic voltammetry and coulometry at platinum working electrodes. A one-electron reductive response is observed, presumably due to the electrode reaction shown as follows:

$$Cu(II)L\ PPh_3 + e \longrightarrow Cu(I)L\ PPh_3.$$

The electrode process in the CV is reproducible in the potential range of 0.08 to −0.08 V with no trace of decomposition as reflected in a smooth cyclic voltammogram. The one-electron stoichiometry of

Table 2
Infra red spectral data of the synthesized complexes.

Complex	ν_{N-H}	$\nu_{C=N}$	ν_{C-O}	Bands due to pyridine	Bands due to PPh$_3$	ν_{M-O}	ν_{M-N}
CuL1	3105	1589	1370	625, 475	1433, 1095, 691	528	457
CuL2	3099	1594	1384	630, 471	1435, 1096, 693	532	455
CuL3	3115	1588	1356	631, 475	1434, 1093, 695	527	455

Table 3
ESR spectral data of the Cu^{II} complexes.

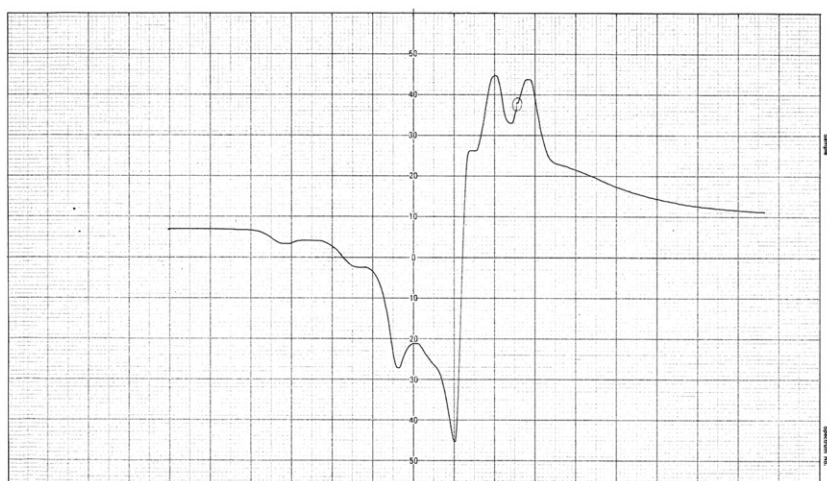| Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel} \times 10^{-4}$cm^{-1}	$A_{\perp} \times 10^{-4}$cm^{-1}	α^2	β^2
CuL1	2.369	2.074	158.00	16.8	0.75	0.69
CuL2	2.414	2.088	147.00	18.2	0.87	0.86
CuL3	2.322	2.106	146.00	20.4	0.66	0.71

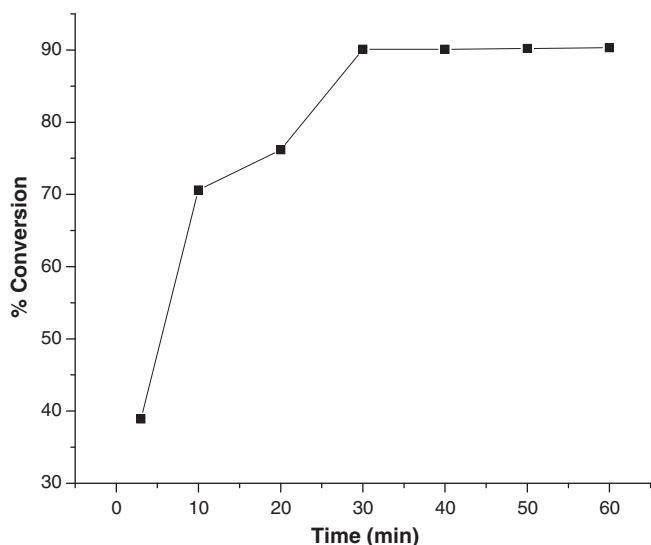**Fig. 1.** ESR spectrum of **CuL1**.

Fig. 2. Effect of time with % conversion.

the couple was confirmed from the comparison of current height with that of a standard [35] copper(II)–copper (I) couple, since attempted coulometry at potentials more cathodic than E_{pc} gave a continuous coulomb count due to some unidentified side reactions [36]. The similar pattern in electron transfer behavior of all the complexes at about same potential once again corroborates the closely similar structure of the cationic units.

The present work describes the catalytic oxidation of primary and secondary alcohols by the synthesized copper (II) complexes in acetonitrile–periodic acid system [37]. All the complexes oxidize primary and secondary alcohols to corresponding aldehydes and ketones respectively. The aldehydes or ketones formed were determined by GC using the internal standard method [38].

Benzyl alcohol was selected as a model substrate for optimization of the reaction conditions. In order to study the effect of time on the activity, the product analysis was done at regular intervals of time under similar reaction conditions (Fig. 2). It was found that the total reaction time required was 30 min in CH_3CN–H_5IO_6 system. The oxidation occurred only in poor yield by simply bubbling molecular oxygen through reaction mixture under similar reaction conditions (Table 4, entry 2). To evaluate the catalytic effect of **CuL1**, the oxidation of benzylalcohol was carried out under similar reaction conditions in the absence of catalyst and no conversion was observed (Table 4, entry 3). Further, when the oxidation of benzylalcohol was carried out using less amount of **CuL1**, the yield was low (Table 4, entry 4). Also the reaction was carried out using low amount of oxidant under same conditions and was observed that the yield was low (Table 4, entry 5).

Table 4
Oxidation of benzylalcohol to benzaldehyde[a] in CH3CN–H5IO6 system.

Entry	Reaction time (min)	% Conversion
1	30	92.2
2[b]	360	<20
3[c]	360	NR[d]
4[e]	30	50.6
5[f]	30	61.2

[a] Unless otherwise indicated, all reactions were carried out with 1.08 g (1 mmol) of benzylalcohol with (0.01 mmol) of **CuL1** catalyst, 1 mmol of H_5IO_6.
[b] The reaction was carried out under an atmosphere of O_2 instead of H_5IO_6.
[c] The reaction was carried out without Cu(II) catalyst.
[d] NR: reaction did not occur.
[e] The concentration of Cu(II) catalyst was decreased to 0.005 mmol.
[f] The concentration of the oxidant was decreased to 0.5 mmol.

The oxidation of other benzylic and allylic alcohols was then examined using the optimized reaction conditions. All the synthesized copper (II) complexes were found to catalyze the oxidation of alcohols to corresponding carbonyl compounds. **CuL1** showed better results than all the other complexes (Table 5). This may be due to the fact that the catalytic activity of complexes varies with the size of substituent. It was observed that the activity decreases with increase of bulkiness of the substituents. This may be due to steric hindrance caused by the substituent, which can affect the planarity of the ligand in the complexes [30]. The results for the oxidation of a variety of alcohols

Table 5
Oxidation of alcohols catalyzed by **CuL1**[a] in CH_3CN–H_5IO_6 system.

Entry	Alcohols	Product	Time (min)	% conversion[b]	TON[c]
1			30	92.2	91
2			30	91.6	88
3			30	91.1	86
4			30	90.1	85
5			30	91.0	85
6			30	92.8	91
7			30	91.5	90
8			30	88.9	85
9			30	91.4	90
10			30	90.8	87
11			45	78.3	77
12			45	82.2	74
13			45	78.9	70
14			45	76.5	68
15			45	71.2	72

[a] 1 mmol alcohol, 1 mmol H_5IO_6, 0.01 mmol CuL1, 20 mL CH_3CN, room temperature.
[b] GC yield.
[c] TON = mol of product/mol of the catalyst.
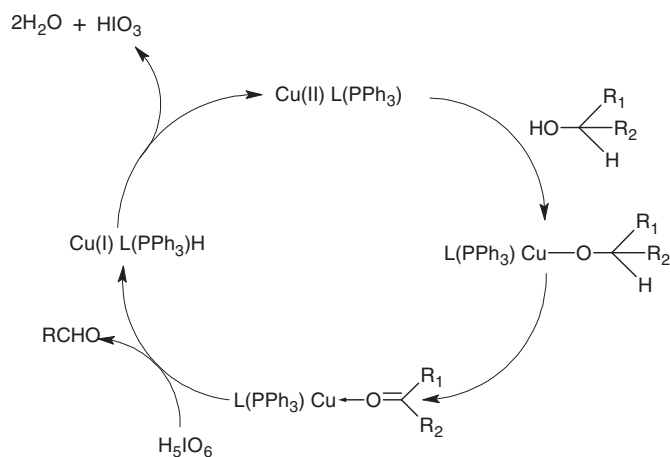
$$2H_2O + HIO_3$$

Fig. 3. Proposed mechanism for the catalytic oxidation of alcohols.

are summarized in Table 5. Further over oxidation to acids was ruled out by co-injecting authentic samples.

A mechanism has been proposed for the above described results (Fig. 3). The mechanistic studies suggest that an initial hydrogen-transfer reaction within the copper-alkoxide, generates the carbonyl-bound copper species [39]. Upon reaction with oxidant, this copper complex then produces the carbonyl compound. Homolytic cleavage followed by hydrogen atom abstraction from the complexed Cu(I) species. With concomitant loss of a water molecule, regenerates the loaded catalyst and initiates a second catalytic cycle.

In conclusion a five coordinated complexes of Cu(II) were investigated as catalysts for the oxidation of primary and secondary alcohols in the presence of periodic acid as co-oxidant. The catalyst can be easily prepared and is therefore extremely cost effective. High conversions and selectivity were observed for all alcohol substrates. Nevertheless, the conversions and selectivities are comparable to those reported with the most active homogeneous metal Schiff-base complexes. The design and synthesis of well-characterized Schiff base complexes containing triphenylphosphine may provide a new class of catalysts for oxidation reactions.

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[37] A solution of copper complex (0.01 mmol) in 20 mL acetonitrile was added to the solution of substrate (1 mmol) and H5IO6 (1 mmol). The mixture was stirred at 70 °C. At the requisite times aliquots of the reaction mixture were removed and the alcohol and aldehyde/ketone extracted with ether. The ether solution was then analyzed by GC.
[38] The reaction product analysis was carried out using gas chromatography (GC) (Shimadzu 2014, Japan); the instrument has a 5% diphenyl and 95% dimethyl siloxane Restek capillary column (30 m length and 0.25 mm diameter) and a flame ionization detector (FID). Nitrogen gas was used as the carrier gas. The retention times for different compounds were determined by injecting commercially available compounds under identical gas chromatography conditions. The oxidation products are commercially available, and were identified by GC co-injection with authentic samples.
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