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ARTICLE TYPE

An efficient oxidation of alcohols using a new trinuclear copper complex as a reusable catalyst under solvent free condition

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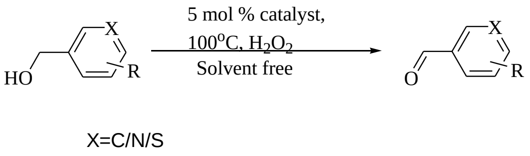
A new trinuclear copper (II) complex $[Cu_3(L)(\mu_2\text{-}Cl)_2(H_2O)_6]$ was synthesized and characterized by various spectroscopic techniques. The trinuclear complex was demonstrated as an efficient catalyst for the selective oxidation of primary, secondary, aliphatic, heteroatomic and conjugated allyl alcohols to the corresponding aldehydes/ketones in good to excellent yields under solvent free conditions using H_2O_2 as an oxidant. The catalyst is easily synthesizable, easy to handle and reusable upto eight runs.

The oxidation of alcohols to aldehydes and ketones is a chemical transformation[1] of primary industrial importance because carbonyl compounds are precursors of a variety of valuable fine chemicals including fragrances, flame retardants and in pharmaceuticals such as vitamins and drugs.[2] Several methods have been developed to accomplish this particular reaction using catalysts from a variety of metals and supports, including chromium reagents,[3] manganese (IV) oxides,[4] activated DMSO,[5] hypervalent iodine reagents,[6] ruthenium reagents,[7] osmium (VI) oxide,[8] metals [9-16] transition metal nitrates on solid supports[17] or NaOCl/TEMPO[8,18], as it was reported in some recent reviews.[19] Although most of these processes offer distinct advantages, but at the same time they suffer from certain drawbacks such as longer reaction time, use of organic solvents, unsatisfactory yields, high costs, use of stoichiometric amounts as well as environmentally toxic catalysts. Thus the development of simple, highly efficient methodologies remains desired.

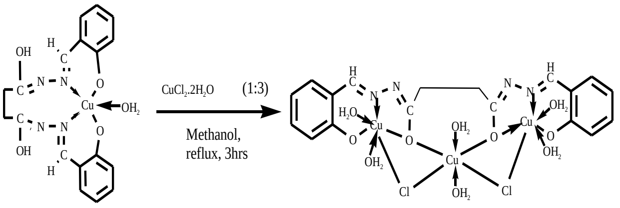
Copper compounds are well known as very important reagent and catalyst[20] in many organic reactions because of their stability, ease of handling,[21] economical and relatively less hazardous nature.[22] Heterogeneous catalysts in the liquid phase offer several advantages as compared to those of homogeneous ones in respect of their recovery, recycling, atom utility and enhanced stability. Literature survey revealed that only a few examples using cheap and “green” copper catalyst and molecular oxygen[23] or hydrogen peroxide[24] are known so far.

Continuing our interest in exploring the catalytic properties of the synthesized complexes,[25] we report herein, a new catalyst-support system for the oxidation of alcohols, which is less expensive than the currently used systems and leads to high yield with high selectivity. The system consists of a copper dihydrazone complex as catalyst, which can be easily prepared and showed excellent tolerance for a broad range of alcoholic substrates and was notably not deactivated by *N/S*- containing heteroatom systems (Scheme 1) under solvent free condition.



Scheme 1 Oxidation of alcohols

The precursor complex $[Cu(H_2L)(H_2O)]$ was synthesized by template method by treating succinoyldihydrazine, $Cu(OAc)_2.H_2O$ and salicyldehyde in 1:1:3 molar ratio in methanol by literature method.[26] The Cu(II) complex on reaction with copper chloride dihydrate in MeOH medium resulted into a dark green precipitate which on the basis of elemental analyses, molecular weight and mass spectral studies was found to have the composition $[Cu_3(L)(\mu_2\text{-}Cl)_2(H_2O)_6]$ (Scheme 2).



Scheme 2 Synthesis of $[Cu_3(L)(\mu_2\text{-}Cl)_2(H_2O)_6]$

The complex is brown in colour and air stable. It is soluble in DMSO and DMF only. The compound is non-ionic in nature, as determined by molar conductance $\Lambda_m = 1.2\ \Omega\ cm^2\ mol^{-1}$.[27] The

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complex has been further fully characterized by spectroscopic techniques viz. IR, UV, EPR and CV (SI, Figs. S1 - S5). The ESI-mass spectrum of the complex show signals at m/z 719.48 [M$^+$] and 741.61 [M+Na-H]$^+$ (Fig. 1).

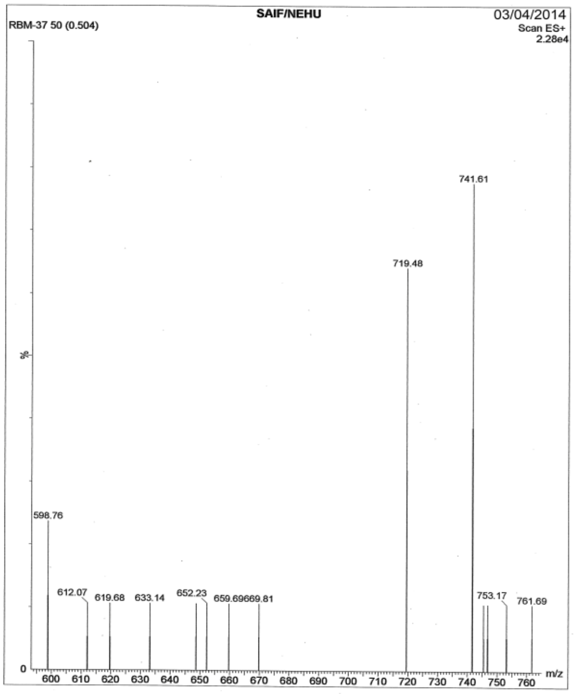


Fig. 1 Mass spectrum of the complex [$Cu_3(L)(\mu_2\text{-}Cl)_2(H_2O)_6$] in DMSO solution

The room temperature magnetic susceptibility measurement shows that the complex is paramagnetic with magnetic moment per empirical formula [$Cu(L_{1/3})(\mu_2\text{-}Cl_{2/3})(H_2O)_2$] containing one copper (II) atom is 1.13 μ_B. This value is much less than the spin - only value of 1.73 BM per copper atom on no-interaction basis. This suggests that there is considerable spin-spin antiferromagnetic interaction between the metal centres.[28] Electron transfer reactions were also studied (Fig. S5) and the electrode reactions may be shown to be as follows:

$$\begin{tikzcd}
{[(L)Cu^{II}Cu^{II}Cu^{III}]^{3+}} \arrow[r, shift left, "+e"] & {[(L)Cu^{II}Cu^{II}Cu^{II}]^{2+}} \arrow[l, shift left, "-e"] \arrow[r, shift left, "+2e"] & {[(L)Cu^{II}Cu^{I}Cu^{I}]} \arrow[l, shift left, "-2e"] \arrow[d, shift left, "+e"] \\
 & & {[(L)Cu^{I}Cu^{I}Cu^{I}]^{-}} \arrow[u, shift left, "-e"]
\end{tikzcd}$$

We also performed geometry optimization of **I** (Fig. 2) using density functional theory (DFT) based (B3LYP)[29] method with the 6-31G** basis set for all atoms except for Cu, for which LANL2DZ basis set along with effective core potential was used.[30] Selected bond distances and angles are listed in (SI, TS1). Frequency calculation was performed to verify that the optimized structure is a minimum energy structure. In the optimized structure of **I**, all the Cu(II) coordinates six atoms to form a distorted octahedral structure. The central Cu(II) is bonded to two oxygen atoms at distances 2.031 and 1.999A$^\circ$ and two bridging chlorides at distances 2.395 and 2.434A$^\circ$. The terminal Cu–N distances are 1.963 and 1.972A$^\circ$ while the Cu-O distances are 1.910, 2.011, 1.919 and 2.043A$^\circ$. The Cu-Cl distances are 2.420 and 2.415A$^\circ$ which are quite close to the distances reported for chloride bridged copper complex with crystal structure.[31] All the three copper atoms are coordinated to two water molecules each. The Cu$\cdots$Cu distances are 3.169 and 3.179 A$^\circ$. The terminal Cu$\cdots$Cu separation is 6.223A$^\circ$ and Cu-Cu-Cu angle is 155.2°.

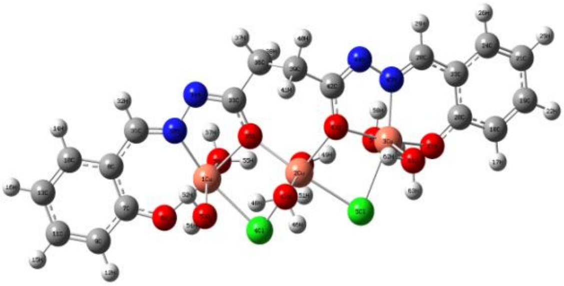
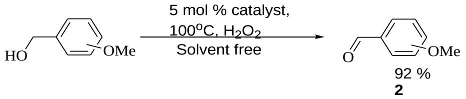


Fig. 2 Optimized structure of the complex [$Cu_3(L)(\mu_2\text{-}Cl)_2(H_2O)_6$]**(I)**

Natural bond orbital (NBO) analysis[32] provide details about the type of hybridization and nature of bonding.[33] According to NBO results, the electronic configuration of Cu1 in [$Cu_3(L^1)(\mu_2\text{-}Cl)_2(H_2O)_6$] is : [core]$4S^{0.32}3d^{9.42}4p^{0.03}5p^{0.01}$, 17.99733 core electrons, 9.73941 valence electrons and 0.04217 Rydberg electrons with 27.77892 electrons as a total electrons and +0.464 as natural charge. Similarly, the electronic configuration for Cu2 is [core]$4S^{0.29}3d^{9.37}4p^{0.02}5p^{0.01}$, 17.99838 core electrons, 9.66412 valence electrons, 0.03821 Rydberg electrons with 27.70071 electrons as a total electrons and +0.273 as natural charge, Cu3 is [core]$4S^{0.33}3d^{9.43}4p^{0.03}5p^{0.01}$, 17.99728 core electrons, 9.76501 valence electrons and 0.04360 Rydberg electrons with 27.80588 electrons as a total electrons and +0.467 as natural charge.

Now, the catalytic properties of copper (II) complex was explored towards the oxidation of alcohols. The oxidation of 4-methoxybenzyl alcohol was considered as a model reaction to optimize the reaction conditions (Scheme 3). Initially, the reaction was carried in presence of 5 mol% catalyst, 30% H_2O_2 at room temperature for 24 h, but yield of product was low (40 %) identified by spectral methods as 4-methoxy benzaldehyde **2**. The presence of singlet at δ 9.20 ppm in ^{1}H NMR and absence of peaks at 4.50 ppm and 2.0 ppm, respectively and bands at 2720, 2820 and 1715 cm^{-1} in IR spectra clearly indicated the formation of **2**.



Scheme 3 Oxidation of 4-methoxy benzyl alcohol

Further, effect of various solvent viz., DCM, CH_3CN, water and toluene on the model reaction was investigated using H_2O_2 (30%) and 5 mol% catalyst. Significant improvement was achieved in

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acetonitrile, but the best results were obtained when the reaction was carried out under solvent free condition (Fig. 3).

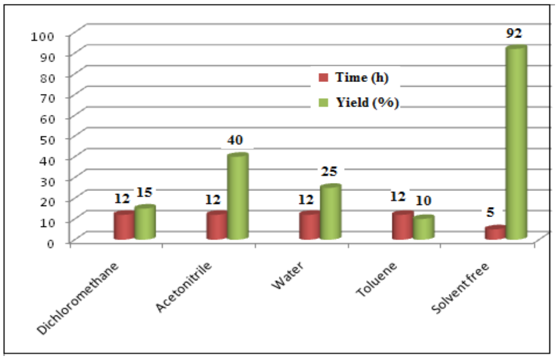


Fig. 3 Optimization of the solvent effect

We turned our attention towards screening of appropriate concentration of catalyst loading. The catalyst loading was varied from 2-15 mol%. The result revealed that when the reaction was carried out at 2 mol% of catalyst it gave lower yield of the product. Best yields were obtained in presence of just 5 mol% of catalyst. On increasing the catalyst loading to 10, 15 mol% the product yield decreased with longer reaction time. The reaction was also carried out in absence of catalyst, but the reaction did not proceed at all and only the starting material was recovered. Thus, the catalyst plays an important role in the success of reaction and product yield (Fig. 4).

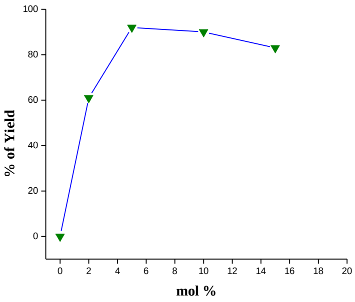


Fig. 4 Effect of catalyst loading on the model reaction

Next, the effect of temperature was also evaluated. It was observed that fast reaction occurred on raising the temperature from 25 °C to 100 °C and the yield of desired product increased considerably. We were pleased to find that the reaction proceeded smoothly and almost complete conversion of reactants was observed at 100 °C to afford the desired product **2** in 92% yield (Table 1, entry 2). However, at room temperature a lower yield of product was obtained even after longer reaction time. Thus, it was concluded that 5 mol% catalyst, H_2O_2 (30 %) without solvent as the optimized reaction condition for this conversion (Fig. 5).

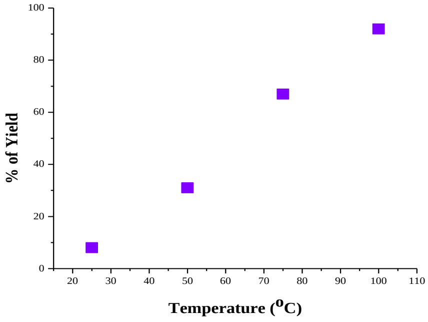
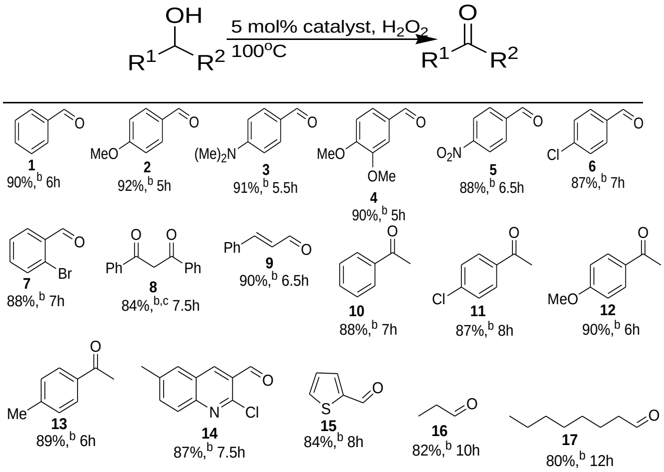


Fig. 5 Effect of temperature on the model reaction

The above optimized protocol was further extended for oxidation of different primary, secondary and hetero-aromatic alcohols. The feasibility of employing aliphatic alcohols instead of aryl alcohols in the reaction was also investigated (Table 1). Benzyl alcohol with substituents of varying electronic properties smoothly converted to the corresponding aldehydes (Table 1, 1-7). Electron donating substituents gave higher yields (2-4) whereas electron withdrawing substituents slightly lowered the yields (5-7). Benzyl alcohol and phenyl ethanol also gave good yields (1 and 10). Electron donating and withdrawing substituents on phenyl ethanol also oxidized to the corresponding ketones in good to excellent yields (10-13). It follows from Table 1 that both aromatic primary and secondary alcohols worked well, giving excellent yields of products with high purity. It was found that benzil was obtained in good yields from benzoin (8) and cinnamaldehyde from cinnamyl alcohol giving yield up to 90 % (9). The conversion proceeded smoothly even in the presence of heteroatoms such as *N* and *S* in the substrates (14 and 15). Oxidation of primary aliphatic alcohols to the corresponding aliphatic aldehydes is difficult using most heterogeneous catalysts, thus the low conversion of these alcohols (16 and 17) is understandable because of its low reactivity.[34] Hence, our catalyst oxidized various alcohols in good to excellent yields. Further, scope of the catalyst is currently underway in our laboratory.

Table 1 Oxidation of alcohols to aldehydes and ketones[a]



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[a]reaction condition: catalyst (5 mol %), alcohol (5 mmol), H_2O_2 (30%) were stirred at 100 °C for appropriate time. [b]isolated yield. [c]benzoin used as substrate

The reusability of catalyst is important for catalysis reactions. Therefore, the reusability of our prepared catalyst was also examined. It was found that the catalyst can be reused for another eight consecutive runs under similar reaction conditions. After each run, the catalyst was filtered and washed with DCM and dried in oven for 30 minutes and reused for the next run. The yields of product decreased slightly with reuse of catalyst over eight consecutive runs (Fig. 6).

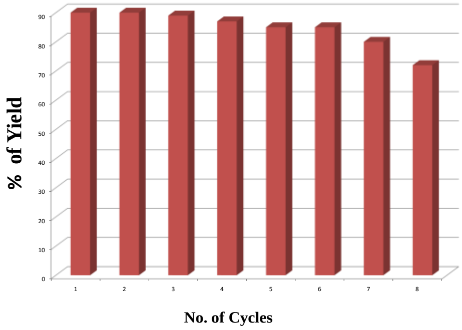

Fig. 6 Reusability of catalyst

Conclusion

In conclusion, a new trinuclear copper (II) complex $[Cu_3(L)(\mu_2\text{-}Cl)_2(H_2O)_6]$ was synthesized and used as a general catalyst for the efficient oxidation of a broad range of alcoholic substrates including heteroatom systems with hydrogen peroxide as an oxidant to give the corresponding aldehydes/ ketones in good to excellent yields under solvent free condition. The main advantage of our protocol is that expensive noble metals are not required for this transformation and the catalyst could be easily synthesized from simple starting materials with reusability upto eight runs without any significant loss of catalytic activity.

Experimental section

Melting points were recorded in open capillaries and are uncorrected. A Perkin-Elmer 2400 series II CHN analyzer was used to collect micro analytical data (C, H and N). The APCI mass spectrum of the complex was recorded on a Water ZQ 4000 Micro mass spectrometer in DMSO solution. The copper content of the complex was determined by standard literature procedure.[35] Conductance measurement was made at 1 KHz using Wayne Kerr B905 Automatic Precision Bridge. A dip-type conductivity cell having a platinized platinum electrode was used. The cell constant was determined using a standard KCl solution. Room temperature magnetic susceptibility measurement was made on a Sherwood Magnetic Susceptibility Balance MSB-Auto. Diamagnetic correction was carried out using Pascals Constants.[36] The standard used in the magnetic moment studies was a sealed sample of Manganese Chloride solution in a standard sample tube. The tube is labelled with the reading C_{std} = 1192, R_o = -35 and T °C = 21, where C_{std} = reading taken in a calibrated instrument using a tared standard sample tube, R_o = reading of the empty tube, T °C = temperature at which the measurement was taken. Firstly, an empty sample tube of known weight (g) was placed into the tube guide and the reading R_o was taken. A small amount of solid was introduced into the weighing sample tube, and the bottom of the tube was gently tapped on a wooden bench a number of times to settle the solid particles. This procedure was repeated until a sufficient amount of sample was added, corresponding to a sample length, *l*, in the range 1.5 cm – 2 cm. Then the sample mass (m) in grams and the sample length, (*l*), in cm was noted. Packed sample tube was then placed into the tube guide and the reading R was taken. The Mass susceptibility, χ_g in cgs, was calculated using χ_g = C x *l* in cm x $(R\text{-}R_o) / 10^9$ x Mass of sample in tube in g; χ_g x Molecular mass = Molar susceptibility (χ_M); $\mu_{eff} = 2.84\sqrt{\chi_M}$ x T, T = temperature at which the measurement was taken. The magnetic moment for the complex per copper (II) atom was calculated using the empirical formulation for the complex i.e. $[Cu(L_{1/3})(\mu_2\text{-}Cl_{2/3})(H_2O)_2]$. The empirical formula for the complex is taken as one third of the molecular formula $[Cu_3(L)(\mu_2\text{-}Cl)_2(H_2O)_6]$. The FT-IR spectrum of the complex was recorded on a Perkin-Elmer FT-IR system, Spectrum BX, infrared spectrophotometer using KBr pellets. UV-Visible Spectra of the complex was recorded in DMSO solution at ~10^{-3} M concentration on a Perkin- Elmer Lambda-25 spectrophotometer. Electron paramagnetic resonance spectrum of the complex was recorded at X-band frequency on a Varian E-112 E-Line Century Service EPR spectrometer using TCNE (g=2.0027) as an internal field marker. Variable temperature experiments were carried out with a Varian Variable Temperature accessory. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Avance - 400 spectrometer and Jeol – 300 and 500 spectrometers.

Typical procedure for one pot conversion of alcohols to aldehydes catalyzed by $[Cu_3(L)(\mu_2\text{-}Cl)_2(H_2O)_6]$:

All of the reactions were carried out at 100 °C under reflux in a 25ml flask equipped with a magnetic stirrer. 30% H_2O_2 solution was added to a mixture of alcohol (5 mmol) and the catalyst (5 mol %). The reaction solutions in all cases were vigorously stirred using magnetic stirrer and an oil bath was used to achieve the desired reaction temperature. After completion (TLC), the reaction mixture was cooled to room temperature and filtered. Filtrate was extracted with ethyl acetate (3x10 ml) and the combined organic extract was washed with water (3x10ml), brine (10 ml) and dried over anhydrous Na_2SO_4. After removing the solvent the crude product was purified by column chromatography over silica gel (60-120 mesh) using ethyl acetate and hexane as eluent to afford the pure products **1-17**.

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Graphical Abstract

An efficient oxidation of alcohols using a new trinuclear copper complex as a reusable catalyst under solvent free condition

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A new copper complex has shown efficacy as a catalyst for the selective oxidation of different alcohols using H_2O_2 as an oxidant under solvent free condition.

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