Tris(3,5-dimethylpyrazole)copper(II) nitrate: as an oxidation catalyst

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Abstract

Tris(3,5-dimethylpyrazole)copper(II) nitrate (**A**) is a catalyst for mild oxidation of various organic substrates. It acts as catalyst for conversion of benzylamine to benzaldehyde in the presence of hydrogen peroxide. Various benzylic alcohols are converted to corresponding aldehydes and acids by the catalytic amount of the complex (**A**) with hydrogen peroxide at room temperature. The complex also catalyses dimerisation of 2,6-dimethylphenol and thiophenol. The thermal decomposition of tris(3,5-dimethylpyrazole)copper(II) nitrate at 500 °C gives CuO having the monoclinic crystal system. The cyclic voltammogram of the complex tris-(3,5-dimethylpyrazole)copper(II) nitrate shows a quasi-reversible redox cycle at −101 mV ($E_{1/2}$) versus the Ag/AgCl electrode (+ve scan; scan speed 100 mV/s). The ΔE between anodic and cathodic peaks is 110 mV ($i_{pa}/i_{pc} = 1.2$).
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1. Introduction

Copper complexes catalyses various reactions such as electron transfer [1], dioxygen transport [2,3], substrate oxygenation/oxidation [4,5] and reduction of nitrogen oxides [6,7]. In these reactions mononuclear [8–10] or multinuclear copper complex [11,12] may be involved. There are many studies in which pyrazole or imidazole containing binuclear copper complexes are used as catalyst [13,14]. In these studies it is clear that these pyrazole and imidazole based catalysts are very efficient in activating dioxygen for oxidation of primary alcohols. Product selectivity in copper catalysed reactions can be enhanced by variation of the ratio of copper and ligands [15]. Since majority of these complexes involve simple structural features in terms of a five membered heterocyclic nitrogen-donor ligand, we have conducted our study to explore the reactivity of mono-nuclear copper(II) complexes having 3,5-dimethylpyrazole (Fig. 1) as one of the ligand. There can be two advantages in using 3,5-dimethylpyrazole (abbreviated as dmpyz) as a ligand;

and; firstly, 3,5-dimethylpyrazole ligand has ability to form dative bond through one of the nitrogen lone pair [16,17], secondly, the free NH bond of the ring may be utilized to create a supramolecular environment through hydrogen bonding which in turn may provide extra selectivity during a product formation through catalytic reactions.

2. Results and discussion

2.1. Synthesis and characterisation of tris(3,5-dimethylpyrazole)copper(II) nitrate

The copper complex tris(3,5-dimethylpyrazole)copper(II) nitrate (**A**) can be synthesized from the reaction of 3,5-dimethylpyrazole with copper nitrate trihydrate in methanol (Eq. (1a)). The ratio of the copper(II) nitrate trihydrate and 3,5-dimethylpyrazole in 1:2 or 1:3 leads to only tris(3,5-dimethylpyrazole)copper(II) nitrate. On mixing 1:2 molar equivalent ratio of copper(II) nitrate trihydrate with 3,5-dimethylpyrazole we could obtain only tris(3,5-dimethylpyrazole)copper(II) nitrate (**A**); we had also attempted to synthesise bis(3,5-dimethylpyrazole)copper(II)

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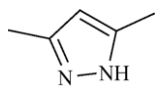 *E-mail address:* juba@iitg.ernet.in (J.B. Baruah).
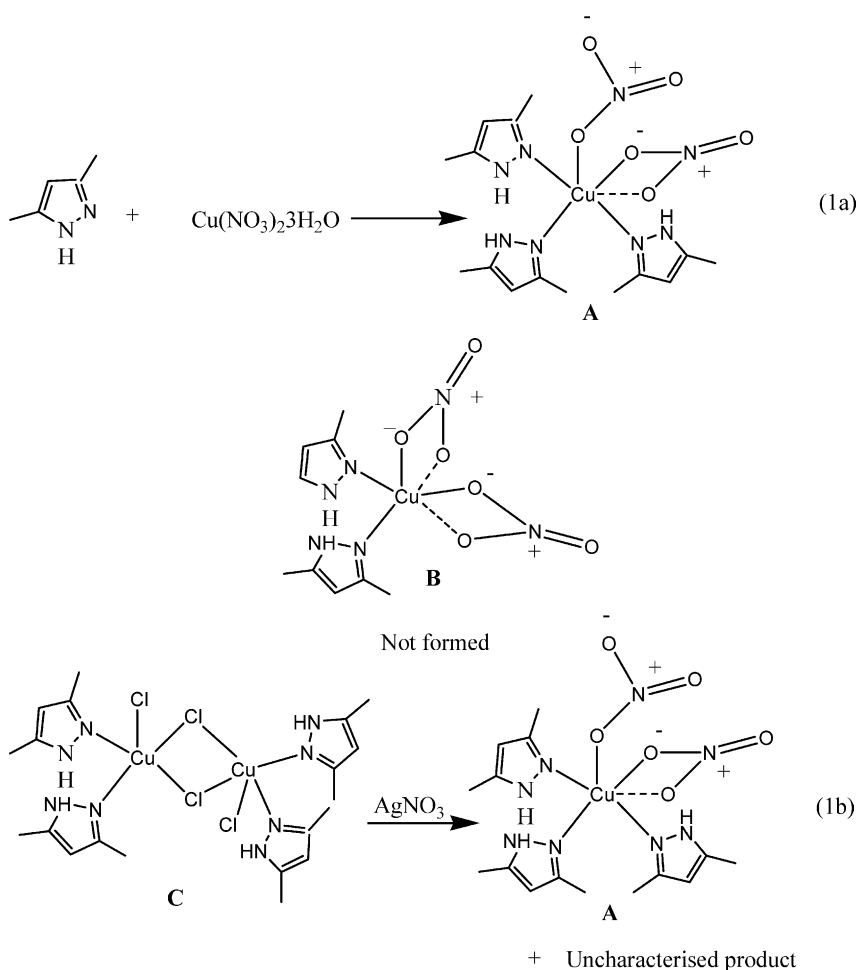
Fig. 1. 3,5-Dimethylepyrazole.

nitrate (**B**) from a preformed 1:2 dimeric adduct by ligand displacement reaction. Thus, the reaction of bis[chloro-bis-(3,5-dimethylpyrazole)copper(II)] (**C**) with AgNO₃ was performed in an anticipation of a simple ligand displacement of chloride by nitrate to give bis(3,5-dimethylpyrazole)copper(II) nitrate (Eq. (1b)) and AgCl. However,

spectrum of the complex shows an absorbance at 700 nm ($\varepsilon = 42.1\,M^{-1}\,cm^{-1}$).

The molar conductance of the complex in water showed another important aspect of the complex. In water its molar conductance was $232\,S\,mol^{-1}\,cm^2$. This corresponds to the presence of ionic nitrato groups in solution as shown in Eq. (2)

$$[Cu(dmpyz)_3(NO_3)_2] \rightarrow [Cu(dmpyz)_3]^{2+} + 2NO_3^- \qquad (2)$$
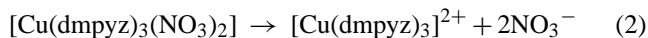
Since water is a good O-donor, it can replace the weakly co-ordinating nitrato group. Therefore the conductance

(1a)

(1b)

+   Uncharacterised product

it was not successful in this regard; in contrast, this reaction also gave tris(3,5-dimethylpyrazole)copper(II) nitrate and AgCl as isolable products.

The complex tris(3,5-dimethylpyrazole)copper(II) nitrate is further characterized by its IR, UV–vis spectra, magnetic moment, thermogravimetry, conductance measurement. The IR spectra of the complex shows a strong absorption at $1383\,cm^{-1}$ which corresponds to the symmetric stretching of the NO₃ group and the other at $1578\,cm^{-1}$ corresponding to the antisymmetric stretching of the same group. Another strong absorption at $3242\,cm^{-1}$ may be attributed to the N—H stretching frequency of the ligand. The visible

measurements were made in acetonitrile and the molar conductance was found to be $93\,S\,mol^{-1}cm^2$. This shows that the nature of the solvent is responsible for ionisation and acetonitrile being a weaker ligand for copper(II) does not cause ionisation of one of the more tightly bound nitrato group. The nitrato complexes having similar five-coordinated copper has generally one of the nitrato group more tightly held due to a chelating mode of interaction [13]. The experimental magnetic moment of the complex was found to be 1.71B.M. which matches well with an expected value of 1.73B.M. These observations suggest that the complex has the structure **A** as shown in Eq. (1a).
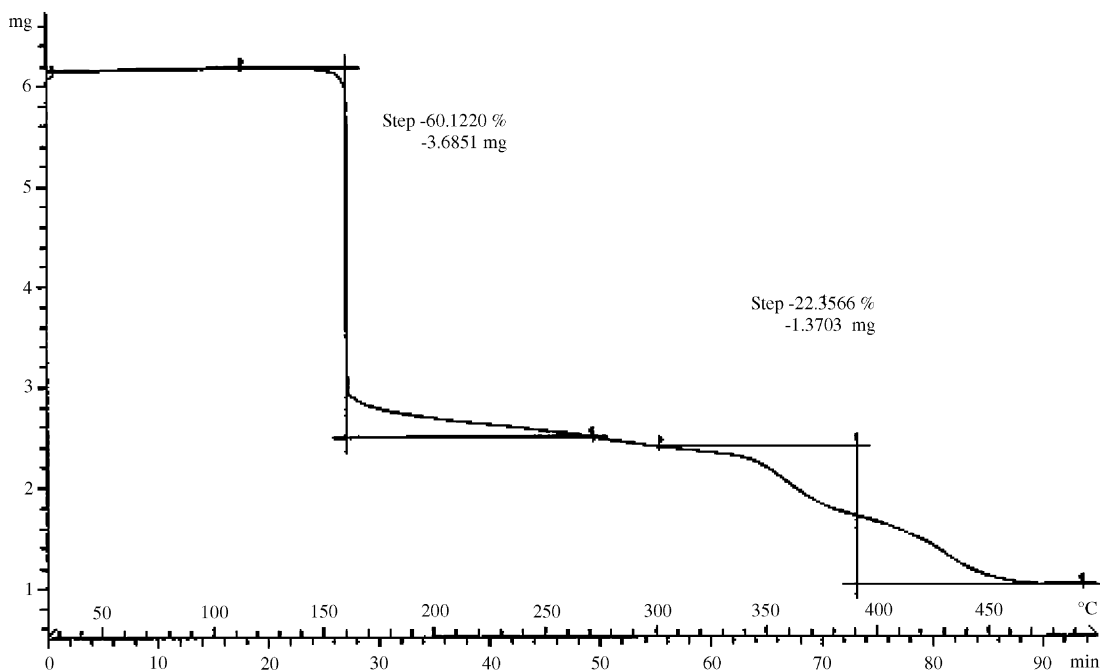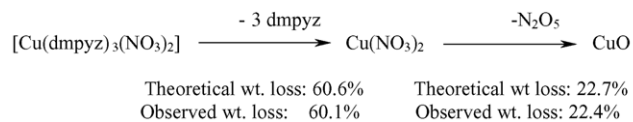
Fig. 2. Thermogram of the complex [Cu(dmpyz)$_3$(NO$_3$)$_2$].

The thermogravimetry of the [Cu(dmpyz)$_3$(NO$_3$)$_2$] complex (Fig. 2) shows an initial loss of 60.1% of the complex in the temperature range of 140–160 °C. This weight loss corresponds to the loss of three 3,5-dimethylpyrazole ligands. The complex then shows a second weight loss in the range of 300–450 °C (a loss of 22.4%) which corresponds to the loss of N$_2$O$_5$, to give a residue of CuO. The sequence of weight losses are shown in Scheme 1.

To confirm that the final residue is CuO, we heated the complex to 500 °C in a controlled manner in a separate experiment. The XRD powder pattern is shown in Fig. 3. It was

$$[Cu(dmpyz)_3(NO_3)_2] \xrightarrow{-\ 3\ dmpyz} Cu(NO_3)_2 \xrightarrow{-N_2O_5} CuO$$

Theoretical wt. loss: 60.6% Theoretical wt loss: 22.7%
Observed wt. loss: 60.1% Observed wt. loss: 22.4%

Scheme 1.

found that the final residue is CuO monoclinic crystal system [18].

Thus, the thermal degradation of [**A**] involves two steps, one is the formation of anhydrous copper(II) nitrate and
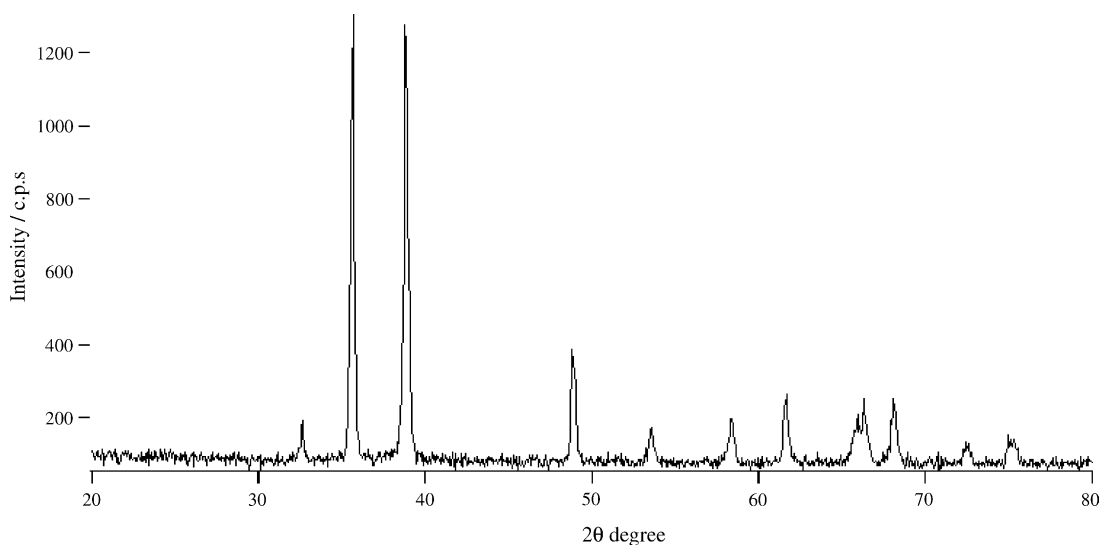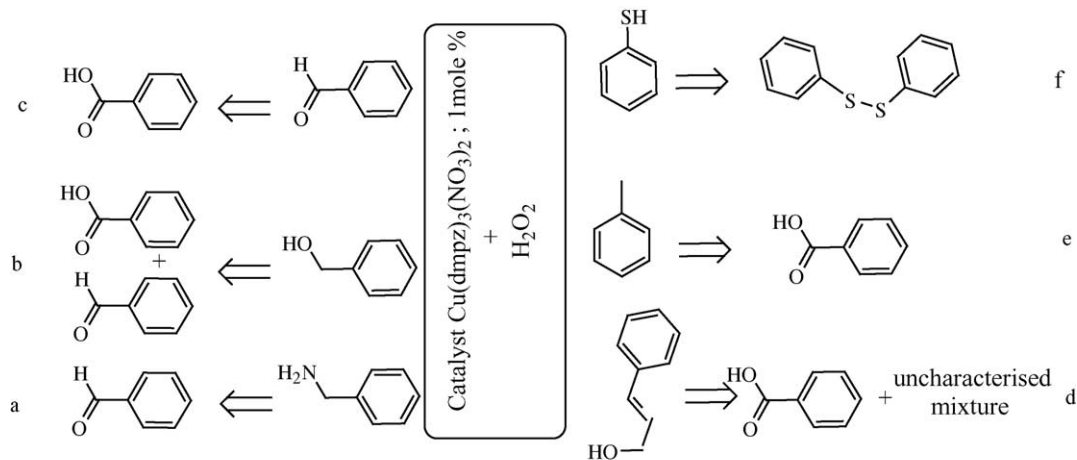

Fig. 3. XRD powder pattern of the residue obtained from [Cu(dmpyz)$_3$(NO$_3$)$_2$] after heating to 500 °C.

Various organic transformations by Catalyst Cu(dmpz)$_3$(NO$_3$)$_2$; 1mole % with H$_2$O$_2$

Scheme 2.

the other is the formation of copper oxide. This is important as direct heating of copper(II) nitrate trihydrate leads to a mixture of products and dehydration is not possible [19]. So, this method also constitutes and a mild method for formation of anhydrous copper(II) nitrate and copper(II) oxide.

The cyclic voltammogram of the complex [Cu(dmpyz)$_3$-(NO$_3$)$_2$] in acetonitrile with tetrabutylammonium perchlorate as supporting electrolyte shows a quasi-reversible redox cycle at -101 mV ($E_{1/2}$) versus the Ag/AgCl electrode (+ve scan; scan speed 100 mV/s). The ΔE between anodic and cathodic peaks is 110 mV ($i_{pa}/i_{pc} = 1.2$). This is attributed to a Cu(II)–Cu(I) quasi-reversible redox cycle. As change in the oxidation state from +2 to +1 involves change in ligand environment of the copper center from trigonal pyramidal to tetrahedral geometry and this slow process makes ΔE far greater than ideal 90 mV of the Fe^{2+}/Fe^{3+} reversible couple of ferrocene [20].

2.2. Catalytic oxidation by tris(3,5-dimethylpyrazole)copper(II) nitrate

The complex tris(3,5-dimethylpyrazole)copper(II) nitrate (**A**) catalyses various oxidative reactions of organic substrates in the presence of hydrogen peroxide as an oxidant. The representative reactions are shown in Scheme 2 and the results of different substrates are listed in Table 1. Benzylamine reacted with catalytic amount (1 mol%) of copper complex (**A**) in the presence of hydrogen peroxide gave benzaldehyde in good yield (Table 1, entry 1).

The oxidation of benzylic alcohols led to the corresponding aldehydes and carboxylic acids; however, the carboxylic acids were the major products (Scheme 2c) in all the reactions. Since it is possible that the benzylic alcohol first transforms to aldehyde followed by its further oxidation to carboxylic acid, the reactions of the corresponding aldehydes were carried out. These reactions led to the formation of the

Table 1
Results of [Cu(dmpyz)$_3$(NO$_3$)$_2$] catalysed oxidation reactions

Entry no.	Substrate	Temperature (°C)	Time (h)	Product, yield (%)
1	C$_6$H$_5$CH$_2$NH$_2$	RT	5	C$_6$H$_5$CHO (75%)
2	C$_6$H$_5$CH$_2$OH	RT	8	C$_6$H$_5$COOH (70%), C$_6$H$_5$CHO (30%)
3	p-MeO-C$_6$H$_4$CH$_2$OH	RT	6	p-MeO-C$_6$H$_4$COOH (75%); p-MeO-C$_6$H$_4$CHO (25%)
4	p-NO$_2$-C$_6$H$_4$CH$_2$OH	RT	6	p-NO$_2$-C$_6$H$_4$COOH (85%); p-NO$_2$-C$_6$H$_4$CHO (15%)
5	p-Cl-C$_6$H$_4$CH$_2$OH	RT	6	p-Cl-C$_6$H$_4$COOH (80%); p-Cl-C$_6$H$_4$CHO (20%)
6	p-Me-C$_6$H$_4$CH$_2$OH	RT	6	p-Me-C$_6$H$_4$COOH (82%); p-Me-C$_6$H$_4$CHO (18%)
7	C$_6$H$_5$CHO	RT	1	C$_6$H$_5$COOH (100%)
8	p-MeO-C$_6$H$_4$CHO	RT	1	p-MeO-C$_6$H$_4$COOH (100%)
9	p-NO$_2$-C$_6$H$_4$CHO	RT	1.5	p-NO$_2$-C$_6$H$_4$COOH (100%)
10	CH$_3$CHO	RT	6	CH$_3$COOH (trace)
11	2,6-Dimethylphenol	RT	1	4,4′-Dihydroxy-3,5,3′,5′-tetramethylbiphenyl (98%)
12	CH$_3$C$_6$H$_5$	70 °C	6	C$_6$H$_5$COOH (12%)
13	C$_6$H$_5$SH	RT	0.5	C$_6$H$_5$SSC$_6$H$_5$ (100%)

All the reactions were carried out in acetonitrile (5 ml) with H$_2$O$_2$ (1 ml, 30 vol%) with substrates (5 mmol) and tris(3,5-dimethylpyrazole)copper(II) nitrate (0.05 mmol).

corresponding carboxylic acids (Table 1, entries 7–9). The reaction time required was much less than the corresponding time required for aldehyde formation from benzylic alcohol (cf. Table 1 entries 2–4), suggesting that the conversion of aldehyde to carboxylic acid by the catalyst is rapid and that once aldehyde is formed from benzylic alcohol it gets converted to the corresponding acid under the reaction condition.

The reaction of cinnamyl alcohol, at 60 °C for 12 h resulted in C–C bond cleavage to give benzoic acid (25% with 1 mol% of catalyst) and several side products which could not be characterised. The exact nature of the reaction process involved in this reaction is not clear. We obtained only cinnamic acid from oxidation of cinnamdehyde. Moreover it was also found that cinnamic acid did not undergo decarboxylation under similar reaction condition. This led us to assume that in the case of cinnamyl alcohol oxidation there may be intermediacy of β-ketocarboxylic acid, which underwent further oxidation. Further study on the mechanistic part of this reaction is underway. A phenolic compound having substituents at 2- and 6-positions of the ring, namely 2,6-dimethylphenol undergoes dimerisation to give 4,4′-dihydroxy-3,3′,5,5′-tetramethylbiphenyl in high yield.

The catalytic C–H activation reactions of side chain carbon adjacent to an aromatic substrates was also carried out with the complex. The C–H activation of toluene gave several products; only benzoic acid could be characterized in a pure form. The reaction of diphenylmethane gave benzophenone (4% isolated) as one of the products in the reaction with catalytic amount of **A** (1 mol%) in the presence of hydrogen peroxide at 60 °C for 8 h.

Control experiments suggest that none of 3,5-dimethylpyrazole, hydrogen peroxide alone and a mixture of the two together causes these transformations under identical reaction conditions; thus, copper(II) complex (**A**) is the essential catalyst in these transformation. We have also tested the catalytic activity of copper(II) nitrate trihydrate with hydrogen peroxide in acetonitrile for similar oxidation reactions; this combination did not lead to the formation of desired products under identical condition, either. However, the oxidation reactions with a lower yield can be effected from a mixture of copper(II) nitrate trihydrate and 3,5-dimethylpyrazole along with hydrogen peroxide in very low yield. Since, during the synthesis of tris(3,5-dimethylpyrazole)copper(II) nitrate irrespective of the ratio of 3,5-dimethylpyrazole and copper(II) nitrate trihydrate only the tris(3,5-dimethylpyrazole)copper(II) nitrate is formed; the active catalyst is believed to be derived from the ionised species of tris(3,5-dimethylpyrazole)copper(II), as shown in Scheme 3, which anchors a peroxide unit similar to the five-coordinated intermediates described in the literature [21]. The driving force for such intermediate formation is reflected in the quasi-reversible couple present in the copper complex which facilitates oxidation of hydrogen peroxide to give a copper(I) species and followed by formation of the reactive intermediate as shown in Scheme 3.

In conclusion we have demonstrated that tris(3,5-dimethylpyrazole)copper(II) nitrate is a good catalyst for various organic transformation in the presence of hydrogen peroxide and it also serves as a precursor for synthesis of CuO monoclinic crystal system.

Scheme 3.
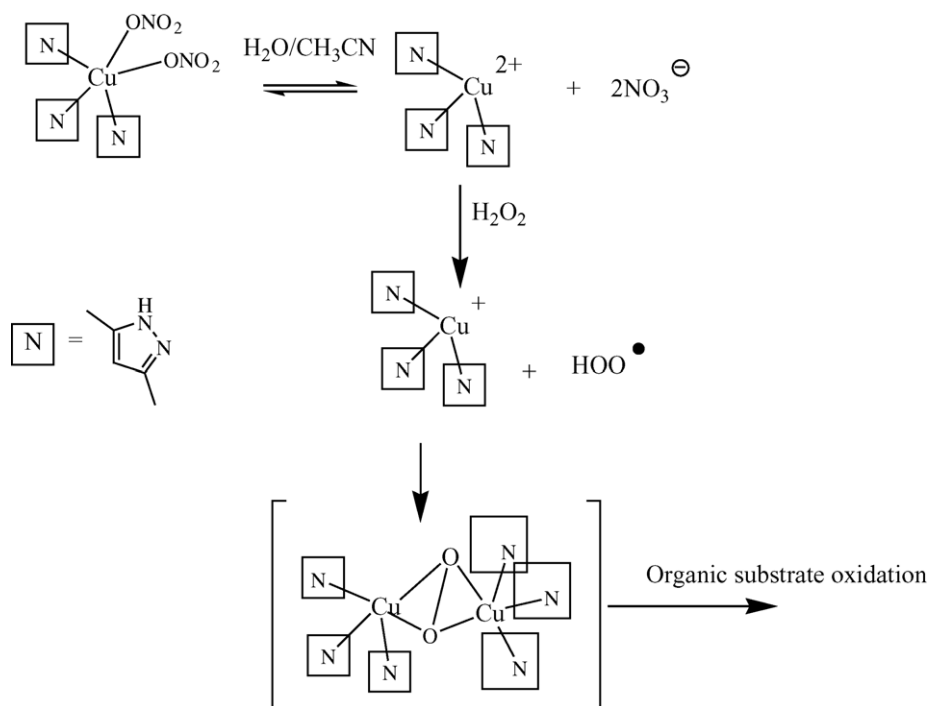
3. Experimental

3.1. Materials

All the reactions were carried out with analytical or laboratory grade chemicals. The solvents used in the reaction and for column chromatography were distilled by literature procedure. All the oxidized products were purified and characterized by comparing their NMR, IR and GC data with those of authentic samples.

Bis-[chloro-bis-(3,5-dimethylpyrazole)copper(II)] was prepared by literature procedure [22].

3.2. Preparation of the [Cu(dmpyz)$_3$(NO$_3$)$_2$]

To a solution of Cu(NO$_3$)·3H$_2$O (4 mmol, 0.967 g) in 5 ml methanol in a round bottom flask, 5 ml methanolic solution of 3,5-dimethylpyrazole (12 mmol, 1.154 g) was added. The colour of the solution changed to dark blue. The solution was stirred for one and half hour at room temperature. Solvent was removed under pressure to give a deep blue coloured solid. The solid was repeatedly washed with diethyl ether to remove any unreacted 3,5-dimethylpyrazole. The crude product was redissolved in dichloromethane (15 ml) and kept at 10 °C to yield regular small needle like crystals after 5 days. Yield: 1.74 g (91%). Elemental analysis: Calcd. for C$_{15}$H$_{24}$N$_8$O$_6$Cu; C, 37.81; H, 5.04; N, 23.53; found: C, 37.63; H, 5.06; N, 23.46. IR (KBr cm^{-1}): 3242(w), 2925(vw), 1578(s), 1470(s), 1383(vs), 1265(m), 1055(m) UV–vis (H$_2$O): $\lambda_{max} = 700$ nm, $\varepsilon = 43.3$ M^{-1} cm^{-1}; magnetic moment (RT): 1.71 B.M; molar conductance (water): 231.66 S mol^{-1} cm^2.

3.3. Procedure for oxidation

Since all oxidation reactions involves similar procedures, two typical oxidation procedures are given below.

3.3.1. Oxidation of benzylamine

To a solution of [Cu(dmpyz)$_3$(NO$_3$)$_2$] (4 mmol, 0.0952 g) in 5 ml of acetonitrile in a round bottom flask, benzylamine (4.5 mmol, 0.4823 g) was added and reaction mixture was stirred to form a homogeneous solution. Then hydrogen peroxide (4 equiv., 2.0 ml) was added dropwise to this solution and stirring was continued at room temperature. The reaction was monitored by TLC time to time. After 4 h the reaction was stopped, solvent was evaporated in a rotary flash evaporator, the catalyst was washed with water and finally the product was isolated by extracting with ether. The product benzaldehyde was obtained (0.334 g, 75%) by column chromatography (silica gel, hexane/ethylacetate).

3.3.2. Oxidation of p-chlorobenzyl alcohol

To a solution of [Cu(dmpyz)$_3$(NO$_3$)$_2$] (0.05 mmol, 0.0237 g) in 5 ml of acetonitrile, 5 mmol, 0.7130 g of p-chlorobenzyl alcohol was added and the reaction mixture was stirred to form a homogeneous solution. Hydrogen peroxide (4 equiv., 2.3 ml) was then added and stirring was continued at room temperature. After 1 h, the reaction was stopped and solvent was evaporated. The crude mixture was then treated with NaHCO$_3$ solution and extracted with dichloromethane. The aqueous layer was neutralized with 2N HCl and extracted with ether to give the corresponding acid (0.556 g, 78%). The identity of the product was ascertained by recording its IR and NMR spectra.

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