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Research paper

# Microwave assisted one pot synthesis and characterization of Cesium salt of di-copper substituted phosphotungstate and its application in the selective epoxidation of *cis*-cyclooctene with *tert*-butyl hydroperoxide

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In the present work, we have isolated di-copper substituted phosphotungstate, $Cs_7[PW_{10}Cu_2(H_2O)_2O_{38}]\cdot 9H_2O$, as a single isomer using novel microwave technique from the commercially available $H_3PW_{12}O_{40}$ and $CuCl_2$. The same compound has been synthesized using one pot synthesis method as well. Further, we have shown that our product does not contain any isomer by the virtue of $^{31}P$ NMR spectrum which shows only one signal. Using various physicochemical techniques, we have also shown that the complexes synthesized by both the techniques are the same. The complex was used as a heterogeneous catalyst for the selective epoxidation of *cis*-cyclooctene with TBHP as the oxidant.

## 1. Introduction

Recently, a subclass of polyoxometalates (POMs), transition metal substituted POMs (TMSPOMs), have gained importance as they can be rationally modified on the molecular level, including shape, size, charge density, redox potentials and stability [1,2] which results in their distinctive electrochemical, magnetic, medicinal and catalytic properties [3–5]. Interest in catalytic applications, especially oxidation reactions catalyzed by TMSPOMs has grown extensively and now, various TMSPOMs, especially Mono-TMSPOMs have been synthesized and explored as catalysts for oxidations reactions [6–11]. More recently, di-TMSPOMs, are acquiring significance as there are two transition metals that are substituted, which can alter catalytic activity drastically. A literature survey shows that among di-TMSPOMs, an extensive research has been carried out on synthesis and application of di- transition metal substituted silicotungstates as catalysts for green oxidation reactions [12–16]. To the best of our knowledge, reports on analogous compounds based on phosphotungstates are few and remain mostly unexplored [17–22].

Among di-transition metal substituted phosphotungstates, reports on synthesis of Vanadium [17], Copper [18,19], Titanium [20], Cobalt [21], Nickel [21] and Manganese [22] substituted phosphotungstates are available in art. In 1986, Domaille and Harlow reported synthesis of $\gamma$-$Cs_5[PV_2W_{10}O_{40}]$, consisting of slow addition of solid $Cs_7[P_2W_{10}O_{36}]$ to a preformed solution of $VO_2^+$ at pH 0.8 [17].

In 1993, Casan-Pastor et al. synthesized $K_{5.5}Na_{1.5}[PW_{10}Cu_2(H_2O)_2O_{38}]\cdot 13H_2O$ from the trilacunary $Na_8HPW_9O_{34}\cdot 19H_2O$ and $CuCl_2$ followed by recrystallization for several weeks [18]. The obtained product was characterized by single crystal XRD analysis and the formula of the anion was proposed as $[PW_{10}Cu_2(H_2O)_2O_{38}]^{7-}$. The FT-IR of the synthesized product was found to be similar to that of Finke's thermolytic compound. (In 1987, Finke et al. reported the presence of an unidentified thermolysis product, by FT-IR, during the rational synthesis of $[Cu_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ [19]. They also found that the type of the product obtained depends largely on the experimental conditions such as temperature and time. It was observed as a major product when crystallization was carried at 100 °C for a longer time.) From FT-IR, they concluded the presence of two types of distortions of the $PO_4$ group as a consequence of the presence of two different isomers. Further, they have identified the isomers, relative to the location of the pair of $Cu^{2+}$ ions, by studying the magnetic susceptibility as well as ESR study.

Nomiya et al. reported preparation of $K_7[PW_{10}Ti_2O_{40}]$, by pH-dependent interconversion of its dimeric compound $K_{10}[\alpha,\alpha'$-$P_2W_{20}Ti_4O_{78}]\cdot 12H_2O$ at pH 7.8 [20]. They also reported that during evaporation of the aqueous solution, $K_7[PW_{10}Ti_2O_{40}]$ readily converted to the dimer and thus isolation of analytically pure

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$K_7[PW_{10}Ti_2O_{40}]$ was found to be difficult. Synthesis of $Na_2\{CoHbhep(H_2O)_4\}[PW_{10}Co_2O_{38}\{Hbhep\}_2]$ and $Na_2\{NiHbhep(H_2O)_4\}[PW_{10}Ni_2O_{38}\{Hbhep\}_2]$ has been reported by Cronin et al. [21]. The typical synthesis employs acidification of solution of ligand, individual salts of tungstate and cobalt with nitric acid followed by addition of phosphoric acid. After a long time of reflux (18 h), red crystalline material has been obtained. Recently, Patel et al. established one-pot synthesis of $Cs_7[PW_{10}Mn_2(H_2O)_2O_{38}]\cdot 7H_2O$ by mixing commercially available $H_3PW_{12}O_{40}\cdot 29H_2O$ and $MnCl_2\cdot 4H_2O$ at pH 6.4, followed by reflux and addition of CsCl [22].

A literature survey shows that since last 22 years no study has been carried out on the di-copper substituted phosphotungstates even though copper contains distinct advantages such as unique redox properties, relatively inexpensive and low toxic nature. Our group has been working on substituted polyoxometalates since last five years. We have synthesized and characterized a number of mono transition metal substituted polyoxometalates and studied their catalytic activities for a number of organic transformations. As an extension, it was thought to be of interest to synthesize di-copper substituted phosphotungstate by one pot synthesis method developed by our group [22] and to evaluate its catalytic activity. We have also attempted to develop a new and sustainable synthesis strategy using the microwave route.

A literature survey also shows that no catalytic study has been carried out for any of the di-substituted phosphotungstates. So, it was thought to be of interest to evaluate the catalytic activity of the said compound. Epoxidation of *cis*-cyclooctene was selected for the same. The reason for the selection are (i) epoxides are important intermediates for the manufacture of many bioactive molecules and fine and bulk chemicals for polymer synthesis [23] and (ii) our expertise for carrying out oxidation reactions.

The present paper reports synthesis of Cs salt of di-copper substituted phosphotungstate by the reaction of $H_3PW_{12}O_{40}$ and $CuCl_2$ in $H_2O$, followed by the addition of CsCl by two procedures: (1) direct one pot synthesis and (2) microwave synthesis. Both the products have been analyzed by various spectroscopic techniques such as FT-IR, $^{31}P$ NMR, ESR and CV. We have also compared the FT-IR, ESR, $^{31}P$ NMR and CV data of the products obtained by both the synthetic techniques and have found that the products obtained in both the methods are the same. However, we have been unable to get good quality crystals so far for single crystal analysis. Work is still in progress for the same. A detailed study was carried out to explore the use of synthesized complex for the oxidation of *cis*-cyclooctene with *tert*-butyl hydroperoxide (TBHP) as the oxidant under mild reaction conditions.

## 2. Experimental section

### 2.1. Materials

All chemicals used were of A.R. grade. $H_3PW_{12}O_{40}\cdot 29H_2O$, $CuCl_2\cdot 2H_2O$, CsCl and dichloromethane were obtained from Merck. *cis*-cyclooctene was obtained from Spectrochem Pvt. Ltd., Mumbai. $NaHCO_3$ was obtained from SRL, Mumbai. All chemicals were used as received.

### 2.2. One pot synthesis of di-copper substituted phosphotungstate

2.88 g (1 mmol) of $H_3PW_{12}O_{40}\cdot nH_2O$ was dissolved in 10 mL of water and the pH of the solution was adjusted to 6.4 using supersaturated $NaHCO_3$ solution. The solution was heated to 100 °C with stirring. To this hot solution, 0.32 g (2 mmol) of $CuCl_2\cdot 2H_2O$ dissolved in minimum amount of water, was added. The solution was refluxed for 2 h at 100 °C (Scheme S1). This was filtered hot, then 0.5 g solid CsCl was immediately added. The resulting greenish blue precipitates were filtered, dried at room temperature and designated as $RPW_{10}Cu_2$ (Yield-44.6%).

### 2.3. Microwave synthesis of di-copper substituted phosphotungstate

2.88 g (1 mmol) of $H_3PW_{12}O_{40}\cdot nH_2O$ was dissolved in 10 mL of water and the pH of the solution was adjusted to 6.4 using supersaturated $NaHCO_3$ solution. The solution was heated to 90 °C with stirring. To this hot solution, 0.32 g (2 mmol) of $CuCl_2\cdot 2H_2O$ dissolved in minimum amount of water, was added. The solution was microwaved at 100 °C for 30 s (Onida PC23 Black Beauty, power output – 800 W) with 5 intervals of 10, 5, 5, 5 and 5 s. This was filtered hot, then 0.5 g solid CsCl was immediately added (Scheme S2). The resulting greenish blue precipitates were filtered, dried at room temperature and designated as $MPW_{10}Cu_2$ (Yield-43.8%).

In order to verify the viability of the technique, the same complex was synthesized using copper acetate instead of copper chloride. $Cu(CH_3COO)_2\cdot H_2O$ (0.39 g; 2 mmol) was added in place of $CuCl_2\cdot 2H_2O$ and the material was synthesized using the same procedure as above. Greenish powder was obtained, which was designated as $MPW_{10}Cu_2Ac$.

### 2.4. Catalyst characterization

The materials synthesized by both the reflux and microwave techniques were characterized by Elemental analysis, Thermal analysis (TG-DTA), Fourier transform Infrared spectroscopy, $^{31}P$ NMR Spectroscopy, UV–Visible spectroscopy, Cyclic Voltammetry, Powder X-ray Diffractometry and Electron Paramagnetic Resonance Spectroscopy.

Elemental analysis was carried out using a Perkin Elmer Optima-3300 RL ICP Spectrometer (for Cu and W) and JSM 5610 LV EDX-SEM analyzer (for Cs). TG-DTA was carried out on the Mettler Toledo Star SW 7.01 up to 600 °C. FT-IR spectra of the sample were obtained by using the KBr pellet on the Perkin Elmer instrument. $^{31}P$ solution NMR was carried out in $D_2O$ solvent on a Bruker AVANCE 161.97-MHz instrument. The UV–Vis spectrum was recorded at room temperature on Perkin Elmer 35 LAMDA instrument using the 1 cm quartz cell in range of 200–1100 nm. The powder XRD pattern was obtained by using PHILIPS PW-1830. The conditions were: Cu Kα radiation (1.54 Å), scanning angle from 0° to 60°. ESR spectra were recorded on a Varian E-line Century series X-band ESR spectrometer (Liquid nitrogen temperature and scanned from 2000 to 3000 Gauss). Cyclic voltammetry was performed on CHI660E Electrochemical Workstation, Model 600E Series. A glassy carbon working electrode, an Ag/AgCl reference electrode Pand Pt-wire counter electrode were used.

### 2.5. Catalytic reaction

The oxidation reaction of *cis*-cyclooctene was carried out in a 50 mL batch reactor with a double walled air condenser, magnetic stirrer and a guard tube. TBHP was used as the oxidant. 15 mg of the precatalyst was added. Owing to the fact that there was no aqueous medium, the precatalyst remained heterogeneous. The products obtained were extracted with dichloromethane by repeated extractions. The obtained products were analyzed on a gas chromatograph (Shimatzu-2014), having flame ionization detector, using a capillary column (RTX-5) and were identified by comparison with the authentic samples.

## 3. Results and discussion

### 3.1. Catalyst characterization

Although good quality crystals suitable for single crystal X-ray analysis were not obtained, we have been able to provide enough evidence to show that two Cu(II) centres are present in the lacuna of the phosphotungstate. Tungsten and copper were estimated by Inductive Coupling Plasma-Optical Emission Spectroscopy and Cesium was estimated by Energy Dispersive X-ray Spectroscopy. Their experimental and theoretical values were as follows: Theoretical: W, 49.33; Cu, 3.41; Cs, 24.97. Found ($RPW_{10}Cu_2$): W, 49.82, Cu, 3.64. Found ($MPW_{10}Cu_2$): W, 49.85; Cu, 3.62

The TGA (Fig. S1), shows total weight loss of 5.3% up to 495 °C, in case of $RPW_{10}Cu_2$ and 5.1% in case of $MPW_{10}Cu_2$, corresponding to 11 $H_2O$ molecules. From the elemental as well as the thermal analysis, the chemical formulae of the isolated complexes obtained are $Cs_7[PW_{10}Cu_2(H_2O)_2O_{38}]\cdot 9H_2O$.

It can be seen from Fig. 1, that the FT-IR spectra of $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$ are different from that of $PW_{12}$, but similar to that of $PW_{10}$. This confirms the presence of $PW_{10}$ in the synthesized compounds. As the characteristic P–O vibration is clearly separated and distinct, the central $PO_4$ group can be a good probe for the determination of symmetry in a phosphotungstate [24]. The P–O band of $PW_{12}$ splits into three bands in case of both $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$, which is characteristic of $PW_{10}$ [25,16]. This indicates the presence of di-lacunary phosphotungstate in the compounds synthesized. The three bands also confirm retention of $C_{2v}$ symmetry in the compounds [26,27]. The shift in the P–O band vibrations compared to $PW_{10}$ may be attributed to incorporation of Cu(II) in the lacuna.

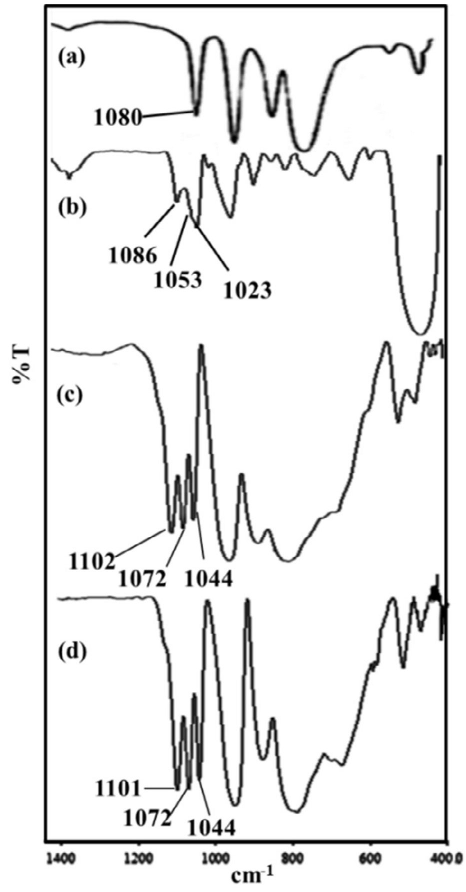

**Fig. 1.** FT-IT spectra of (a) $PW_{12}$, (b) $PW_{10}$ (c) $RPW_{10}Cu_2$ and (d) M $PW_{10}Cu_2$.

Table 1 shows a comparison of the obtained FT-IR data to those reported by Finke et al. [19] (1986) and Pastor et al. [18] (1993). It can be seen that the FT-IR spectrum of the unidentified compound reported by Finke et al. and the FT-IR spectrum of $K_{5.5}Na_{1.5}[PW_{10}Cu_2(H_2O)_2O_{38}]\cdot 13H_2O$, synthesized by Pastor et al. are almost similar to that obtained by us, except the fourth band (at about 1140 $cm^{-1}$ in case of Finke and 1150 $cm^{-1}$ in case of Pastor) which is in the form of a shoulder peak. In our case, it is interesting to note that the compounds synthesized by both, the one pot technique and microwave technique, show only three bands. This indicates the presence of only one isomer, and is in good agreement with Pastor's conclusions [2]. Thus, the FT-IR clearly suggests that we have been able to successfully isolate the unidentified product as a single isomer. This has further been confirmed by $^{31}P$ NMR.

$^{31}P$ NMR spectroscopy is a useful tool to identify whether there is any change in the environment around the phosphorus moiety. It also helps to indicate presence of isomers if any. It is well established in literature that during the synthesis of disubstituted POMs, obtaining a single isomer is very difficult in aqueous medium, as uncharacterized species result in two or more lines in the spectrum [27]. In the present case, both $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$ give only a single peak confirming the presence of a single isomer. The $^{31}P$ NMR spectra of $PW_{10}$, $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$ are shown in

**Table 1**
Comparison of P–O bands with reported works.

| Band | FT-IR Wavenumbers ($cm^{-1}$) | | | |
|---|---|---|---|---|
| | Finke et al. [19] | Pastor et al. [18] | $RPW_{10}Cu_2$ | $MPW_{10}Cu_2$ |
| P–O | 1140 | 1150 | 1102 | 1101 |
| | 1110 | 1105 | 1072 | 1072 |
| | 1060 | 1070 | 1044 | 1044 |
| | 1040 | 1030 | | |

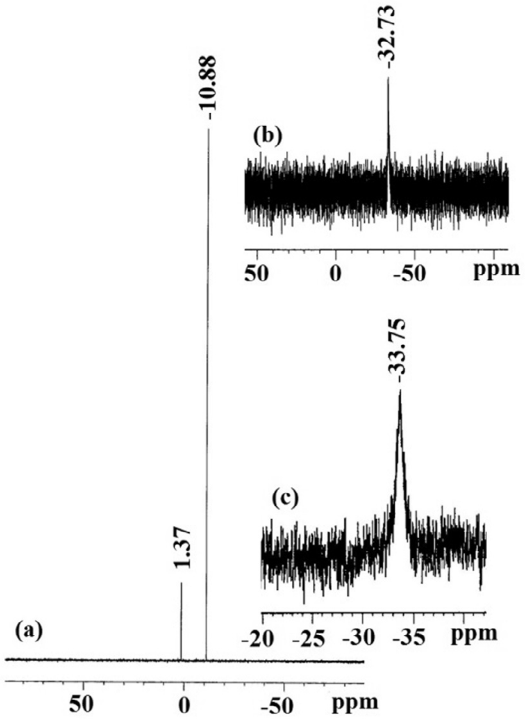

**Fig. 2.** $^{31}P$ NMR spectra of (a) $PW_{10}$ (b) $RPW_{10}Cu_2$ and (c) $MPW_{10}Cu_2$.

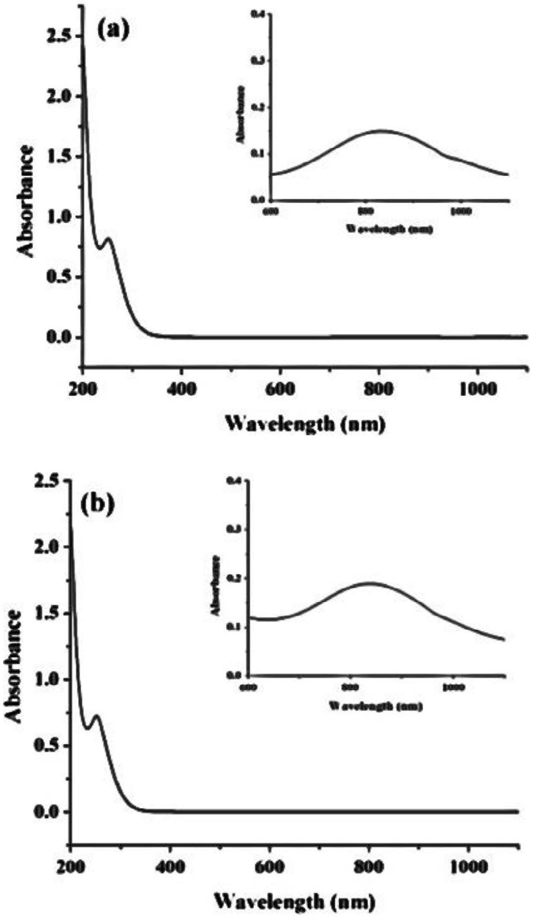

**Fig. 3.** UV–Vis spectra of (a) $RPW_{10}Cu_2$ and (b) $MPW_{10}Cu_2$.

the Fig. 2a–c respectively. The $^{31}P$ NMR for $PW_{10}$ shows a chemical shift value at -10.88 ppm which indicates the formation of $[PW_{10}O_{36}]^{7-}$. Apart from this, one more low intensity peak at 1.37 ppm indicates the formation of another species, $[PW_{10}O_{37}]^{7-}$ [24]. Incorporation of two coppers into the lacuna of $PW_{10}$ results in an upfield shift of the peak. A single peak at −32.73 and −33.75 ppm is seen in case of $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$ respectively. The upfield shift and peak broadening in both the cases may be due to paramagnetic $d^9$ Cu(II) species [12]. Thus, both the synthetic procedures overcome the disadvantage of multiple products that may be formed during the synthesis of desired compound.

The UV–Visible spectra of $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$ are shown in Fig. 3. The peak at 250 nm wavelength indicates presence of the Keggin moiety in the system. In both the cases, the weak broad range peak from 700 to 1100 nm with $\lambda_{max}$ at around 800 nm was obtained, indicating tetragonal distortion for octahedral Cu (II) in the complex [28]. No bands were seen around 600 nm, which is typical of tetrahedral Cu(II). This shows that Cu(II) exhibits a tetragonally distorted octahedral geometry. This is further confirmed by ESR.

ESR Spectroscopy is an excellent technique to understand the symmetry around the transition metal ion. It also gives information about the location and the environmental symmetry of Cu (II) species in the POM. It can tell us whether the metal ion is present in the lacuna or exists as a counter ion [22]. The ESR spectrum of $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$ are shown in the Fig. 4.

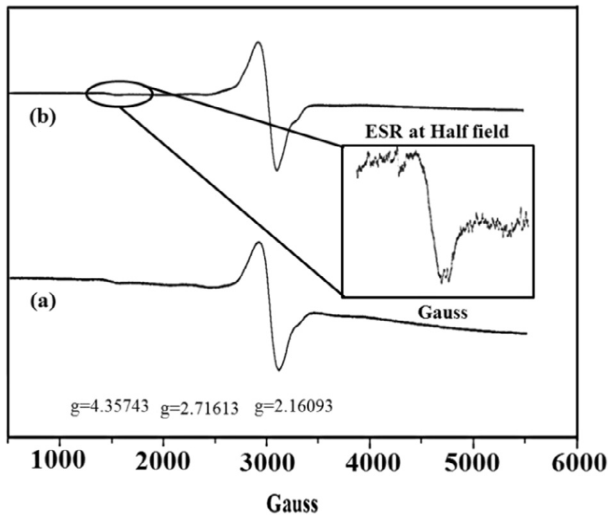

**Fig. 4.** Liquid Nitrogen Temperature ESR Spectra of (a) $MPW_{10}Cu_2$ and (b) $RPW_{10}Cu_2$.

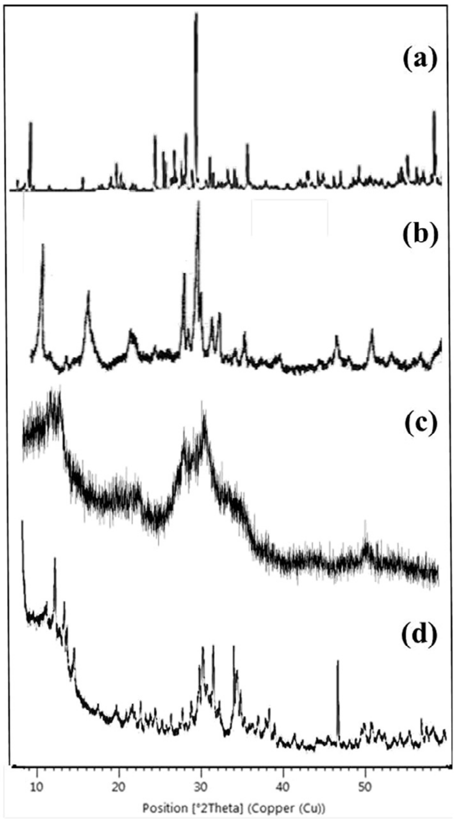

**Fig. 5.** Powder XRD Spectra of (a) $PW_{12}$, (b) $PW_{10}$, (c) $RPW_{10}Cu_2$ and (d) $MPW_{10}Cu_2$.

The first important observation is the presence of a half-field signal at about 1500G in both the cases indicating the presence of two copper centres in the same lacuna [29]. Further, the obtained unresolved hyperfine spectra confirms the presence of Cu in a sixfold tetragonal elongated oxygen coordination, as after the incorporation of Cu(II), the rigid and heavy heteropoly anion is unable to govern the actual geometry surrounding the $Cu^{2+}$ ion, also reported by Gudrun Scholez in 1991 [30]. The observed g-values, $g_{\parallel}(=2.716) > g_{\perp}(=2.161) > 2$ also proves the existence of $Cu^{+2}$ in a tetrahedrally elongated octahedral environment [29]. The higher value of g, i.e., $g > 4$ is an indication of strong

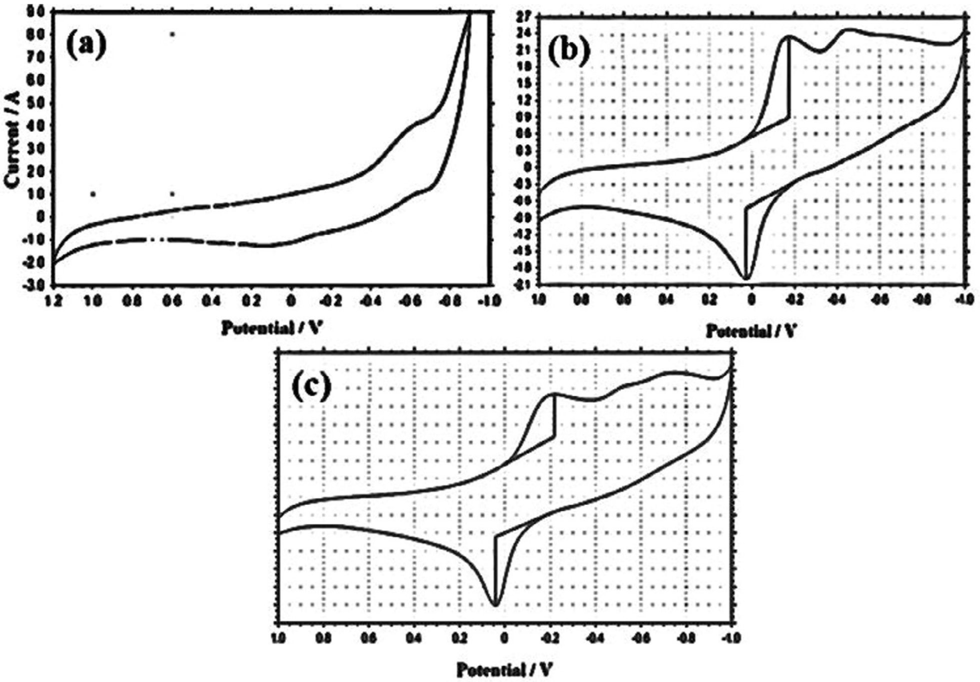

**Fig. 6.** Cyclic Voltammograms of (a) $PW_{10}$, (b) $RPW_{10}Cu_2$ and (c) $MPW_{10}Cu_2$.

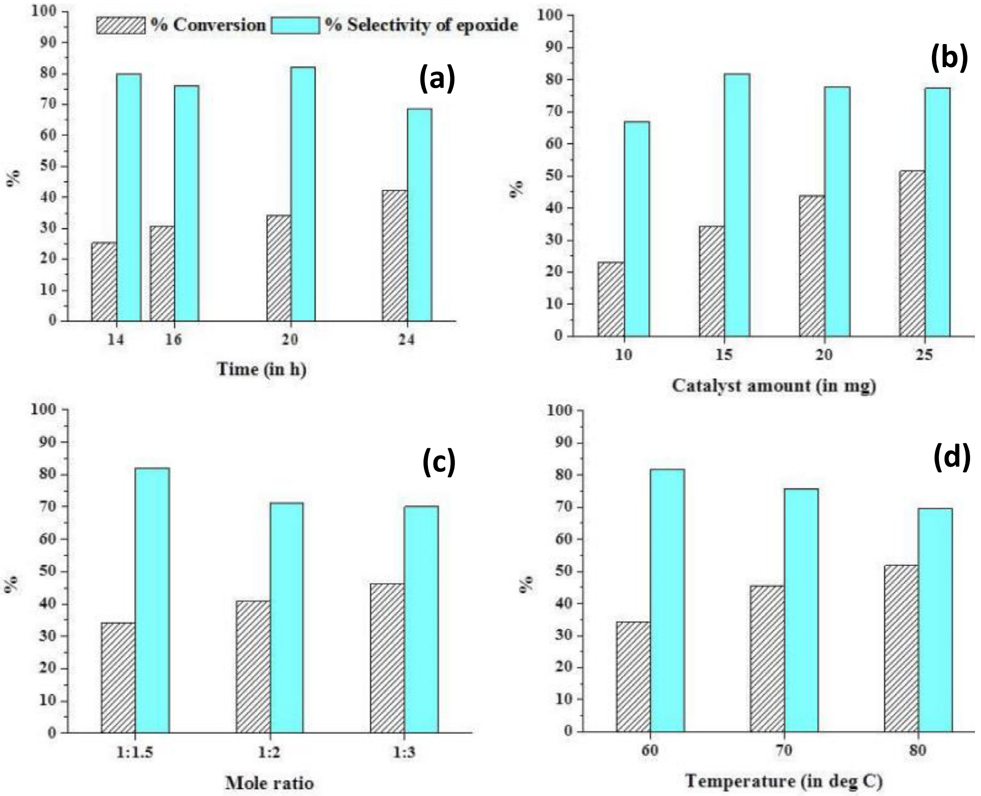

**Fig. 7.** Optimization of parameters for oxidation of *cis*-cyclooctene (a) Effect of time: mole ratio (*cis*-cyclooctene to TBHP) (1:1.5), amount of precatalyst (15 mg), temp. (60 °C); (b) Effect of precatalyst amount: mole ratio (1:1.5), temp. (60 °C), time (20 h); (c) Effect of mole ratio: amount of precatalyst (15 mg), temp. (60 °C), time (20 h); (d) Effect of temperature: mole ratio (1:3), amount of precatalyst (15 mg), time (20 h).

dipole-dipole contribution than exchange coupling interactions [18]. It also suggests that the local tetragonal axis is aligned parallel or slightly misaligned and consistent with $d_{xy}^2$ ground state [31]. In the present case, the calculated value of G is also greater than 4 (4.614), indicating that spin-exchange interaction is negligible [32,18] because, the local tetragonal axis is misaligned.

Since the obtained product was not suitable for single crystal XRD, it was subjected to powder XRD. The powder XRD for $PW_{12}$, $PW_{10}$, $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$ are shown in the Fig. 5. It can be seen, that the powder XRD spectra of $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$ are similar to that of $PW_{10}$ and not $PW_{12}$. This indicates the formation of $PW_{10}$ moiety.

Thus, though the starting material used for the synthesis is $PW_{12}$, formation of $PW_{10}$ species is confirmed. The slight variation in peak intensity may be attributed to the incorporation of Cu into the system. It can be seen that $MPW_{10}Cu_2$ shows crystalline nature, while $RPW_{10}Cu_2$ does not. This also indicates that the product formed by microwave technique may be better when compared to that synthesized by the reflux technique.

Cyclic Voltammetry of 1 mM solution of $PW_{10}Cu_2$ was recorded in buffer medium of pH 5 (acetate buffer) using glassy carbon electrode as working electrode, Ag/AgCl as reference electrode and Platinum wire as a counter electrode.

The Cyclic Voltammograms of $PW_{10}$, $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$ are shown in the Fig. 6. $PW_{10}$ shows reversible redox process and its Epa and Epc peaks are at −0.65 V and −0.6 V respectively. In case of both $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$, show reversible redox couples at approximately −0.7 V. This indicates presence of $PW_{10}$ moiety.

The shift may be due to incorporation of Cu(II) in the lacuna. The incorporation of Cu(II) is further confirmed by a quasireversible wave with an anodic peak at 0.03V and a cathodic peak at −0.2 V and an irreversible process at −0.5 V.

$MPW_{10}Cu_2Ac$ was also characterized using FT-IR, UV and CV, all of which showed results similar to that of $MPW_{10}Cu_2$. The UV for $MPW_{10}Cu_2Ac$ gave a broad range peak with $\lambda_{max}$ at 800 nm along with a shoulder peak at 923 nm which is a clear indication of tetragonal distortion in the octahedral environment of Cu(II) in the system. Cyclic Voltammogram also showed a quasireversible wave with an anodic peak, a cathodic peak and an irreversible process as in the case of $MPW_{10}Cu_2$.

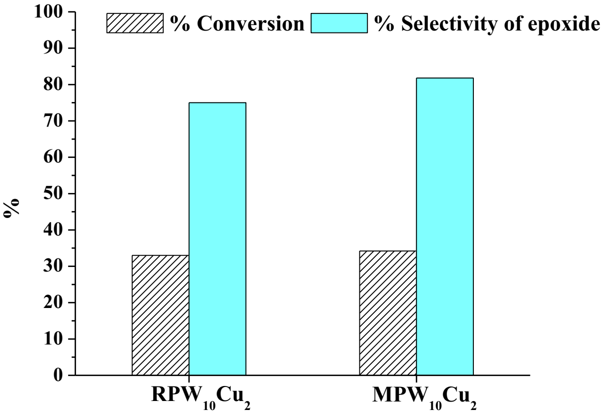

**Fig. 8.** Percentage conversion of *cis*-cyclooctene and selectivity of *cis*-cyclooctene oxide using $MPW_{10}Cu_2$ and $RPW_{10}Cu_2$ (Precatalyst amount-15 mg; Mole ratio 1:1.5; Temperature–60 °C; Time–20 h).

### 3.2. Catalytic reaction

A preliminary study was conducted for the oxidation of *cis*-cyclooctene using $MPW_{10}Cu_2$ as precatalyst and $H_2O_2$ as the oxidant. Since this reaction did not proceed significantly, TBHP was thought to be used as the oxidant. A detailed study of oxidation of *cis*-cyclooctene was then carried out using $MPW_{10}Cu_2$ as precatalyst and TBHP as the oxidant, varying various parameters. The major product was cyclooctene-oxide while small quantities of cyclooctanone and *tert*-butyl alcohol were also formed as by-products.

The effect of reaction time was studied by varying the time and keeping all other parameters constant. With increase in time from 14 h to 20 h, there is a steady increase in conversion and selectivity of the epoxide. But, with increase in time to 24 h, the conversion increases, but selectivity of epoxide decreases (Fig. 7a). Hence, time was optimised at 20 h.

The effect of amount of precatalyst was studied by varying precatalyst amount and it was seen that with increase in amount from 10 mg to 15 mg, there is increase in conversion and selectivity. But, with further increase, there is a decrease in selectivity of the epoxide (Fig. 7b). Hence 15 mg precatalyst was taken as optimum.

The ratio of the substrate to oxidant was varied keeping all other parameters constant. It was found that with increase in the ratio from 1:1.5 to 1:3, an increase in conversion of cyclooctene is seen, but there in a decrease in the selectivity of epoxide (Fig. 7c). Hence, 1:1.5 was taken as the optimum ratio.

To know the effect of temperature on catalytic activity, the reaction was carried out at three different temperatures. From 60 °C to 80 °C, there is a linear increase in conversion, but a decrease in the selectivity of cyclooctene oxide with an increase in unwanted products (Fig. 7d). Hence, 60 °C was chosen to be the optimum temperature for the reaction.

Finally, in order to compare the catalytic activities of the precatalysts synthesized by both the techniques, oxidation of *cis*-cyclooctene was carried out under the optimised conditions using $RPW_{10}Cu_2$ as the precatalyst. Both the precatalysts gave comparable results stating that both the synthetic routes gave the same precatalyst. Fig. 8 shows the results of oxidation of *cis*-cyclooctene with both the precatalysts.

### 3.3. Control experiments

Control experiments were carried out with Cesium salt of $PW_{10}$ and $CuCl_2$ and the results are shown in Table 2. It can be seen that in presence of $PW_{10}$, the reaction does not proceed significantly, while in case of $CuCl_2$, the reaction gives comparable results. This shows that copper plays a significant role as a precatalyst in the reaction. The conversion in case of $CuCl_2$ may also be due to the fact that the electron withdrawing nature of chloride stabilizes the reduction of Cu(II), thus facilitating oxidation of the reactant

**Table 2**
Control experiments using $PW_{10}$[a], $CuCl_2$[b] and $MPW_{10}Cu_2$[c].

| Catalyst | % conversion | % selectivity | | Turn over number (TON) |
|---|---|---|---|---|
| | | Cyclooctene oxide | Cyclooctanone | |
| $PW_{10}$ | 4.3 | 78.1 | 21.9 | – |
| $CuCl_2$ | 34.0 | 71.3 | 12.2 | 414 |
| $MPW_{10}Cu_2$ | 34.2 | 81.1 | 18.9 | 851 |

[a] Precatalyst amount-10.67 mg; Mole ratio 1:1.5; Temperature–60 °C; Time–20 h.
[b] Precatalyst amount-1.37 mg (active amount of Cu-0.51 mg); Mole ratio 1:1.5; Temperature–60 °C; Time–20 h.
[c] Precatalyst amount-15 mg (active amount of Cu-0.51 mg); Mole ratio 1:1.5; Temperature–60 °C; Time–20 h.

**Table 3**
Test for Heterogeneity.[a]

| Catalyst | % conversion | % selectivity | |
|---|---|---|---|
| | | Cyclooctene oxide | Cyclooctanone |
| $MPW_{10}Cu_2$ (14 h) | 25.2 | 80.0 | 20.0 |
| Filtrate (16 h) | 25.7 | 80.6 | 19.4 |

[a] Precatalyst amount-15 mg; Mole ratio 1:1.5; Temperature–60 °C.

**Table 4**
Recyclability of the precatalyst.[a]

| Catalyst | % conversion | % selectivity | |
|---|---|---|---|
| | | Cyclooctene oxide | Cyclooctanone |
| $MPW_{10}Cu_2$ | 34.2 | 81.9 | 18.1 |
| Recycled $MPW_{10}Cu_2$ | 32.0 | 81.0 | 19.0 |

[a] Precatalyst amount-15 mg; Mole ratio 1:1.5; Temperature–60 °C; Time–20 h.

[33]. Although $MPW_{10}Cu_2$ and $CuCl_2$ give comparable results, the advantages of $MPW_{10}Cu_2$ are; better selectivity for the epoxide and as $MPW_{10}Cu_2$ is a heterogeneous catalyst, it can be recovered and regenerated easily.

### 3.4. Leaching and heterogeneity test

The leaching of Cu from $PW_{10}Cu_2$ was tested by carrying out UV analysis of the product mixture. The absence of the characteristic Cu absorption band indicates no leaching of the catalyst.

For proof of heterogeneity, a test was carried out in which the precatalyst was filtered out from the reaction mixture after 14 h of the reaction. 2-propanol was added to the filtrate as a radical terminator so that no further reaction occurs via auto-oxidation and the filtrate was allowed to run for further 2 h. The reaction mixtures after 14 h and 16 h were analyzed by GC and the results are shown in Table 3. No significant change in conversion of the substrate indicates that the active species does not leach out and the precatalyst is truly heterogeneous in nature.

### 3.5. Recyclability of the catalyst

The precatalyst was centrifuged from the reaction mixture, washed with methanol and dried. The recovered precatalyst was then used for the same reaction under the optimised conditions and the results are shown in Table 4.

As it can be seen from the table, no appreciable change is seen in the conversion and selectivity of the products, indicating that the precatalyst is stable and can be regenerated for repeated use. The slight reduction in the conversion may be due to loss of the precatalyst during the regeneration. Thus, though we have been able to show only one cycle, the precatalyst can be recycled and reused for multiple cycles.

#### 3.5.1. Characterization of regenerated precatalyst

The regenerated material was characterized using ESR and Cyclic Voltammetry.

From Fig. 9, it can be clearly seen that the ESR spectra of both fresh and recycled $MPW_{10}Cu_2$ are similar. The unresolved hyperfine structure of MPW10Cu2 is obtained back in the recycled complex, indicating the regeneration of the original precatalyst.

The cyclic voltammograms of both fresh and recycled $MPW_{10}Cu_2$ are similar, as seen in Fig. 10. We can clearly interpret that the quasireversible peak is retained in the recycled complex, thereby confirming that the precatalyst is regenerated after the reaction.

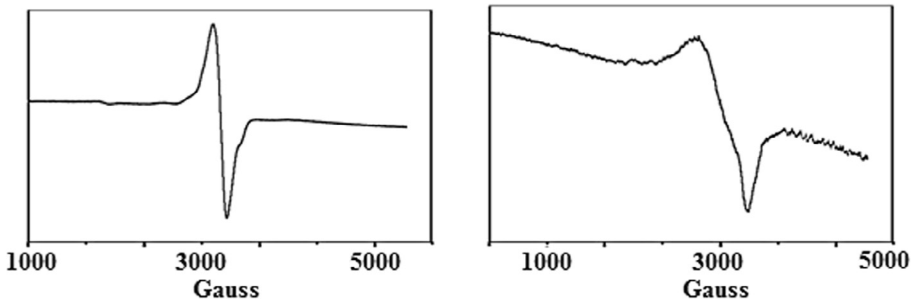

**Fig. 9.** ESR spectra of (a) Fresh $MPW_{10}Cu_2$ and (b) Recycled $MPW_{10}Cu_2$.

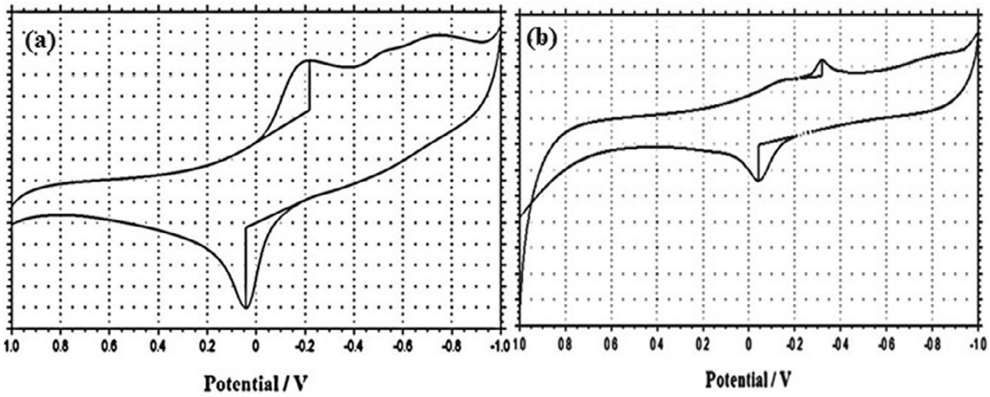

**Fig. 10.** Cyclic Voltammograms of (a) Fresh $MPW_{10}Cu_2$ and (b) Recycled $MPW_{10}Cu_2$.

## 4. Conclusions

We have introduced a novel, green and sustainable microwave method for the synthesis of di-TMSPOMs, which may open up new routes to establish the synthesis of a number of polyoxometalate based compounds. The catalytic activity of the synthesized compound was evaluated for the epoxidation of *cis*-cyclooctene. The catalyst shows excellent selectivity (82%) for the epoxide (active amount of Cu is 0.5 mg). The catalysts was also recycled and reused without any significant loss in the selectivity.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2016.12.031.

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