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# An efficient heterogeneous Cu(I) complex for the catalytic oxidation of alcohols and sulfides: synthesis, characterization, and investigation of the catalyst activity

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#### ABSTRACT

A heterogeneous Cu(I) complex was synthesized by reaction of  $C_5H_4NC(O)NHP(O)[NHC(CH_3)_3]_2$  (L) with CuCl and used as a catalyst for green oxidation of aromatic alcohols and sulfides. According to the characterization results obtained from <sup>31</sup>P NMR, UV-Vis, FT-IR, mass, XRD, elemental analysis, and molar conductivity techniques, the chemical formula of the complex (1) was suggested as [CuClL<sub>2</sub>]. Parameters on the catalytic activity (reaction temperature, the substrate to oxidant molar ratio, catalyst amount, and solvent type) were optimized, using  $H_2O_2$  as a green oxidant, and excellent conversion amounts (100%) were achieved under optimal conditions. Moreover, the generality and recyclability of the catalyst were tested and confirmed. A comparison between the oxidation results of the alcohol and sulfide in the presence of 1 with other catalysts indicated that in most cases 1 showed better efficiency, in a more reasonable reaction time and conditions.

#### **ARTICLE HISTORY**

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#### **KEYWORDS**

Cu(I) complex; N-nicotinyl; N',N"-bis(tert-butyl) phosphoric triamide; heterogeneous catalyst; alcohol oxidation; sulfide oxidation



# 1. Introduction

Selective oxidation of alcohol to corresponding carbonyl compounds [1–6] and sulfides to sulfoxide [7–11] are important in organic chemistry. Especially, the production of aldehydes from alcohol reagents is crucial for food additive or fragrance industries.

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This conversion usually needs stoichiometric amounts of toxic metal salts, or catalysts containing expensive transition metals such as gold [12], palladium [13–15], ruthenium, platinum, tungsten [16, 17], or titanium [18]. Manufacturing more efficient catalysts for these reactions are of interest [19–26] and catalytic activities of several metal complexes have been investigated in these oxidation reactions [27–32].

Oxidation of sulfide compounds also has attracted attention. Oxo-vanadium(IV) Schiff base complex (VO(acac)<sub>2</sub>) heterogenized through supporting on mesoporous MCM-41 was utilized in the oxidation of various sulfides and thiols in the presence of urea hydrogen peroxide as the oxidant [33]. Although these catalysts exhibited excellent catalytic activities in solvent-free conditions, their active site still consisted of an expensive transition metal [34]. Among transition metals, copper due to its availability, nontoxic and green aspects has been used as the active site in the oxidation of organic compounds [35–37], but needed ionic liquids to perform its catalytic activity [35] or non-green acids such as periodic acid ( $H_5IO_6$ ) as oxidant [36].

The need for environmentally friendly and cost-effective methodologies for oxidations of alcohols continues to attract attention [16]. Phosphoramide compounds have been used as catalysts in many reactions. Using the first polymer-supported phosphoramide as a catalyst, the aldol reaction between a trichlorosilyl enol ether and various aldehydes was carried out with significant rate enhancements at low temperature [38]. Phosphoramide compounds have been utilized as catalysts for the reduction of acetophenone, obtaining products of modest enantiomeric excess at dramatically increased reaction rates [39]. A series of new tris ( $\beta$ -hydroxy phosphoramide) compounds have been synthesized and used as catalysts of asymmetric borane reduction of ketones [40]. Phosphoric triamide compounds containing -C(O)N(H)P(O)- skeleton are an important group of phosphoramides. This class of compounds has been used for drug, insecticide, growth regulator for plants, fungicide, herbicide, anti-corrosive additive, and antioxidant applications [41]. They have been utilized as N, O-donor ligands in reaction with several metal ions [42-44]. There are few reports about these metal complexes as catalysts in chemical reactions [45, 46].  $[Zn(\mu-Vp)Ln(L)_2(\mu-OAc)]$  and  $[Ni(\mu-Vp)Ln(L)_2(\mu-OAc)]$ Vp)(MeOH)Ln(L)<sub>2</sub>( $\mu$ -OAc)] (L = N-[bis(diethylamino)phosphoryl]-2,2,2-trichloroacetamide, Vp = a Schiff base ligand) have been applied for catalyzing intramolecular transesterification of 2-(hydroxypropyl)-p-nitrophenyl phosphate (HPNP). Kinetic studies exhibited that the rate of hydrolysis is linearly dependent on complex concentration [45].  $MnL_2Cl_2$  (L = N-isonicotinyl, N',N" -bis(pyrrolidinyl) phosphoric triamide) has been reported as an efficient catalyst for olefin epoxidation with H2O2 oxidant. The best yields have been obtained using acetic acid as a co-catalyst at 0°C [46].

Here, we synthesized a new Cu(I) complex (1) with N-nicotinyl, N',N"-bis(tert-butyl) phosphoric triamide (L) ligand. Cu(I) as a green catalytic active site in oxidation reactions and L as a phosphor amide ligand bearing catalytic activity created a heterogeneous green catalyst. Characterization of the complex proved that P = O and N<sub>pyridine</sub> participated in coordination. According to CHN, mass analysis, and conductivity measurement, CuClL<sub>2</sub> was proposed as the molecular formula of 1. The complex was applied as a catalyst in the oxidation of aromatic alcohols and sulfides with hydrogen peroxide as a green oxidant. Very good catalytic activities in the oxidation of aromatic alcohols and sulfides were achieved and the catalyst showed good recyclability in the



Scheme 1. Synthesis pathway of 1.

optimum conditions (90% conversion of alcohols in the fourth run and 85% conversion of sulfides in the fifth run). The effects of temperature, catalyst amount, solvent, and substrate to oxidant ratio on the catalytic activity were investigated.

#### 2. Materials and methods

#### 2.1. Materials

The raw materials and solvents were purchased from Merck and Sigma-Aldrich companies.

#### 2.2. Synthesis of Cu(I) complex

N-nicotinyl, N',N"-bis(tert-butyl) phosphoric triamide (L) was synthesized according to the method previously reported [47].

Yield: 72%; m.p. = 273.5 °C. Elemental analysis (%) Calcd: C, 53.85; H, 8.01; N, 17.95. Found: C, 53.86; H, 8.0; N, 17.93. IR (KBr, cm<sup>-1</sup>): v = 3320 (m, NH), 3120 (m), 2950 (m, CH<sub>2</sub>), 1636 (vs, C = O), 1584 (m, v<sub>ring</sub>), 1441 (s,  $\delta_{CH}$ ), 1405 (s), 1287 (m, v<sub>ring</sub>), 1237 (s, P = O), 1205 (s), 1117 (w), 1014 (s, v<sub>ring</sub>), 886 (m), 850 (w), 803 (m), 730 (m), 584 (m), 530 (m), 488 (w). <sup>1</sup>H NMR (500.13 MHz, D<sub>6</sub>-DMSO, 25 °C, TMS):  $\delta = 1.21$  (m, 18H), 4.06 (d, <sup>2</sup>J (PNH) = 7.1 Hz, 2H, NH<sub>amine</sub>), 7.47 (dd, <sup>3</sup>J(H,H) = 7.8 Hz, <sup>3</sup>J (H,H) = 4.8 Hz, 1H), 8.29 (d, <sup>3</sup>J (H,H) = 7.9 Hz, 1H), 8.70 (d, <sup>3</sup>J (H,H) = 4.7 Hz, 1H), 9.07 (d, <sup>5</sup>J (P,H) = 2.1 Hz, 1H), 9.72 (s, 1H, NH<sub>amide</sub>). <sup>13</sup>C NMR (125.76 MHz, D<sub>6</sub>-DMSO, 25 °C, TMS):  $\delta = 31.16$  (d, <sup>3</sup>J (P,C) = 4.9 Hz), 50.35 (s), 123.25 (s), 129.70 (d, <sup>3</sup>J(P,C) = 7.9 Hz, C<sub>ipso</sub>), 135.49 (s), 149.02 (s), 152.23 (s), 166.77 (s, C = O). <sup>31</sup>P NMR (202.46 MHz, D<sub>6</sub>-DMSO, 25 °C, H<sub>3</sub>PO<sub>4</sub> external):  $\delta = 3.66$  (m) [47].

For the synthesis of **1**, 0.312 g (1 mmol) of **L** was dissolved in 2 ml methanol and 0.495 g (0.5 mmol) copper chloride was added to the solution. This mixture was stirred for two weeks at room temperature. The resulting precipitate was separated, washed with methanol, and dried in a vacuum desiccator. The synthesis pathway is illustrated in scheme 1.

Yield: 65%; m.p. = 242 °C. Elemental analysis (%) Calcd: C, 46.51; H, 6.91; N, 15.50. Found: C, 46.64; H, 6.85; N, 15.43. IR (KBr, cm<sup>-1</sup>): v = 3365 (w, NH), 3137 (w), 2973 (m, CH<sub>2</sub>), 1656 (m, C = O), 1604 (w,  $v_{ring}$ ), 1461 (vs,  $\delta_{CH}$ ), 1419 (s), 1409 (s), 1380 (w), 1292 (w,  $v_{ring}$ ), 1220 (vs, P = O), 1203 (vs), 1124 (w), 1022 (s,  $v_{ring}$ ), 892 (w), 852 (w), 813 (w),

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Vilenstiens of		1 [47]
Vibrations of	L (this work)	L [47]
$v_{asNH}, v_{sNH}$	3345, 3131	3320, 3120
V <sub>CH2</sub>	2973	2950
$v_{C=0}$	1643	1636
$v_{C=N}$	1592	1584
δ <sub>CH</sub>	1463	1441
V <sub>P=0</sub>	1243	1237
V <sub>ring</sub>	1021	1041

Table	1	Main	FT-IR	frequencies	of	$(cm^{-1})$	۱
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740 (m), 692 (w), 567 (m, Cu-N), 541 (w), 492 (w), 420 (m, Cu-O). <sup>31</sup>P NMR (202.46 MHz, DMSO-d<sub>6</sub>, 25 °C, H<sub>3</sub>PO<sub>4</sub> external):  $\delta$  = 2.50 (m). UV-Vis in methanol:  $\lambda_{max}$  = 258 nm.

# 2.3. Physical measurements

Infrared spectra (4000–400 cm<sup>-1</sup>) were recorded on a Philips 9624 FT-IR spectrophotometer with a KBr disc. Powder XRD pattern was obtained on an EQUINOX 3000 Advance instrument. Mass spectrometric measurement was done with an Agilent 5975 C spectrometer. Elemental analysis (C, H, N) was performed using a Perkin Elmer 2400 elemental analyzer. Hach14d digital conductivity meter was used for measuring the molar conductance of a  $10^{-3}$  M solution in DMSO at room temperature. The melting point was recorded on an Electrothermal type 9200 melting point apparatus. Electronic absorption spectra were done using the Jasco V-570 UV-visible spectrophotometer. <sup>31</sup>P-NMR spectrum was recorded on an Avance 300 (300 MHz) spectrometer in DMSO-d<sub>6</sub>. A Young Lin 6500 gas chromatograph (YL-6500) was used to perform gas chromatography (GC).

# 2.4. Catalytic reaction

Catalytic oxidation of alcohols and sulfides to corresponding acids and sulfoxides by the synthesized copper complex was investigated in the presence of  $H_2O_2$  (28 w%) as oxidant. For each run, a suitable amount of **1** as catalyst (5–15 mol%), the substrate (1 mmol), and  $H_2O_2$  (28 wt%) were reacted in solvent (2 ml). The reactions were performed with different solvents, temperatures, and molar ratio of substrate to oxidant to get to optimal conditions. The oxidation reactions of sulfides were done at ambient temperature. The reactions were monitored by thin layer chromatography. At the end of the reactions, the catalyst was separated, washed with acetone, and dried in a vacuum desiccator to reuse and test the recycling capability.

# 3. Results and discussion

# 3.1. Characterization

# 3.1.1. FT-IR spectroscopy

FT-IR spectra of the ligand were in agreement with those previously reported [47]. The small dissimilarity between the positions of IR bands (Table 1) is due to the differences between FT-IR (here) and IR [47] instruments. FT-IR spectra of **L** and **1** are given in and summarized in Table 2.



Figure 1. The FT-IR spectrum of (a) 1 and (b) L.

Table 2. Main functional groups for FT-IR vibration bands of 1 and L.

Vibrations of	$C_5H_4NC(O)NHP(O)[NHC(CH_3)_3]_2$ (L)	[CuClL <sub>2</sub> ] (1)
V <sub>asNH</sub> , V <sub>sNH</sub>	3345, 3131	3365, 3137
$v_{C=0}$	1643	1656
VC=N	1592	1604
V <sub>P=0</sub>	1243	1220
V <sub>M-O</sub>	—	576
V <sub>M-N</sub>	—	420

The FT-IR spectrum of **1** confirms the presence of **L** in the complex. A comparison between the FT-IR results of **L** and **1** shows that v (PO) has shifted 23 cm<sup>-1</sup> to lower frequencies by forming the complex. The frequency of the carbonyl group in **1** represented a positive shift by complexation. Such a positive shift of v(CO) and a negative shift of v (PO) are observed when a phosphoramide coordinates to a metal ion through the oxygen of its P=O site [48, 49]. The vibration of the pyridine ring in **1** showed a shift to higher frequency relative to **L**, confirming coordinates to a metal center, the frequency of the specific vibrational modes increases, due to coupling with M-N (pyridine) bond vibrations [50, 51]. The two bands at 420 and 576 cm<sup>-1</sup> could also be assigned to Cu-N and Cu-O, respectively [36].

# 3.1.2. <sup>31</sup>P NMR spectroscopy

<sup>31</sup>P NMR spectra of **1** and **L** are shown in Figure 1. Chemical shifts of <sup>31</sup>P are 2.5 ppm and 3.66 ppm, respectively. In both spectra just one peak is observed, so it can be concluded that both materials are pure [52]. There is a significant difference between  $\delta$  (<sup>31</sup>P) of the complex and ligand; this confirms the formation of a new molecule. According to the literature, this difference approves the formation of a metal complex [43].

# 3.1.3. UV-Vis spectroscopy

The UV spectra obtained from **L** and **1** in methanol at room temperature are shown in Figure 2. Two absorption bands observed at 216 and 256 nm in the spectrum of **L** are



Figure 2. The <sup>31</sup>P NMR spectrum of (a) 1 and (b) L.



Figure 3. The FT-IR spectrum of (a) 1 and (b) L.

in agreement with  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions of pyridine derivatives [53–55]. Since the  $\pi \rightarrow \pi^*$  transition bond is more intense in polar solvents [56], the more intense band at 216 nm could be assigned to  $\pi \rightarrow \pi^*$  and the other one to  $n \rightarrow \pi^*$  transitions. Such absorption bands were also observed in the spectrum of 1 which confirms the existence of L in the complex structure. The shifts of these bands from 216 and 256 to 218 and 258 in 1 can be due to the coordination of L to copper [57, 58].



Figure 4. The <sup>31</sup>P NMR spectrum of (a) 1 and (b) L.

To observe the complex color (green) absorption band, the visible spectra of **L** and **1**, obtained from their  $10^{-2}$  M solutions in DMSO, are presented in Figure 3. The shoulder in the visible spectrum of **1** (761 nm) is not observed in the spectrum of **L**. Since copper(I) ion with a d<sup>10</sup> configuration is diamagnetic, no d-d electronic transition was expected for this complex. Since unsaturated ligands with empty  $\pi^*$  orbitals which are coordinated to copper(I) center can act as electron acceptors [59], the observed shoulder could be assigned to MLCT (metal to ligand charge transfer) transition [60].

#### 3.1.4. Powder XRD

X-ray diffraction patterns of **L** and **1** are displayed in Figure 4 recorded in the  $2\theta$  range of  $0-110^{\circ}$ .

The XRD pattern of **1** is very similar to the one for  $Cu_2P_4Cl_2N_4O_2C_{54}H_{52}$ , with COD card no. 4300484, and is different from the ligand pattern. This difference between the XRD patterns of the ligand and complex confirm the formation of the complex [61]. Both compounds illustrate sharp crystalline peaks, pointing to the crystalline nature of both the ligand and the complex. The diffraction data of the complex, angle (2 $\theta$ ), interplanar spacing (d), and the relative intensity (%), are given in Table 3.

Using Debye–Scherrer's method, given in equation 1, the average crystallite size of 1 was 34.6 nm approximately.

$$\mathsf{D} = \mathsf{K}\lambda/\beta\cos\theta \tag{1}$$

K is the shape factor or the average crystallite (usually 0.9),  $\lambda$  is the X-ray wavelength of the instrument (0.154 nm),  $\beta$  is full width at half maximum of the diffraction line (FWHM) in radians and  $\Theta$  is Bragg's diffraction angle.



Figure 5. UV absorption spectrum of (a) L and (b) 1 in methanol.

Table 3. XRD	data of 1.			
Peak No.	<b>2</b> θ (°)	FWHM (°)	d (Å)	Intensity (%)
1	2.0342	1.0752	43.43252	13.31
2	6.5894	0.3456	13.41442	60.89
3	9.1589	0.3072	9.65604	58.23
4	9.7217	0.2304	9.09825	100.00
5	11.2020	0.9216	7.89906	59.46
6	12.1991	0.3840	7.25556	85.05
7	16.4270	0.5376	5.39645	54.84
8	17.3778	0.3072	5.10329	87.63
9	18.3322	0.4608	4.83969	26.21
10	19.3360	0.4608	4.59065	28.08
11	21.5932	0.3840	4.11562	40.54
12	24.3440	0.3456	3.65644	27.61
13	39.7628	0.7680	2.26700	26.23
14	44.6247	0.9216	2.03066	3.60

20: the diffraction angle in degrees; d: the interplanar spacing in angstroms; FWHM: full-width at half-maximum in degrees.



Figure 6. Visible absorption spectrum of (a) 1 and (b) L in DMSO.

Using Bragg's law ( $\lambda = 2d \sin\theta$ ), the d-spacing (distance between crystalline layers or polymeric chains) was calculated. For **L** and **1**, the d-spacing values are 5.25 and 9.09 Å, respectively. By the formation of the complex, the d-spacing increased, which can be related to the coordination of the ligand to the copper center.

#### 3.1.5. Mass spectroscopy and molar conductivity

The mass spectrum of the copper(I) complex (1) is demonstrated in Figure 5. The molecular ion peak at m/z = 723.5 amu, which is the molecular weight of 1, confirms the existence of two L molecules and one Cl in a molecule of 1. The most intense peak at m/z = 57 amu is related to stable tert-butyl cation [62]. The species  $[C_5H_4N]^+$  (pyridine ring) and  $[C_6H_5N_2]^+$  ( $C_5H_4NC(O)NH$ ) are indicated with peaks at 78 and 105 amu, respectively [63]. The peak at 297 amu is due to the presence of  $[C_{13}N_4PO_2H_{22})]^+$ ,  $C_5H_4NC(O)NHP(O)[NHC(CH_3)_3][NHC(CH_3)_2]$ , fragments. In addition, peaks at m/ z = 433 amu and m/z = 340 amu could correspond to  $[CuCl(C_{12}N_4P_2O_4H_{10})]^+$  and  $[CuCl(C_{12}N_4O_2H_{10})]^+$  fragments, respectively.

Conductivity studies were performed to determine whether the chloride is ionpaired or coordinated. Due to the complete solubility of **1** in DMSO, the measurement was done in this solvent. The molar conductivity value of the synthesized complex in DMSO solution was in the range of 7–15 S cm<sup>2</sup> mol<sup>-1</sup>, which indicates that the Cu(I) complex is a non-electrolyte [64], confirming the coordination of the chloride to Cu(I) [65].

Concerning the molar conductivity and mass spectroscopy results, it seems that the structure of **1** is [CuClL<sub>2</sub>].

Based on all characterization analysis results, the molecular structure for 1 is suggested in Figure 6(b). The structure of L [47] is demonstrated in Figure 6(a).

# 3.2. Investigating catalytic activity of the complex

To investigate the catalytic activity of **1**, it was applied as a catalyst in the oxidation of some aromatic alcohols and sulfides. For this purpose, benzyl alcohol and methyl





Figure 7. X-ray diffraction patterns of (a) 1 and (b) L.

	ОН	catalyst H <sub>2</sub> O <sub>2</sub> (28%) r.t.	ОН
Entry	Solvent	Time (h)	Maximum conversion (%)
1	CHCl₃	17	30
2	n-hexane	22	25
3	CH₃CN	10	95
4	$CH_3CN:H_2O$ (2:1)	12	60
5	Acetone	18	50
6	H <sub>2</sub> O	15	40

Table 4. Optimization of the solvent type in the oxidation reaction of benzyl alcohol.

Reaction conditions: 1 mmol benzyl alcohol, 15 mol% catalyst, 1.5 mmol 28% H<sub>2</sub>O<sub>2</sub>, 2 mL solvent at r.t.

phenyl sulfide were selected as substrates and their oxidation was carried out using hydrogen peroxide (28%  $H_2O_2$ ) as a green and effective oxidant. Parameters such as solvent, catalyst amount, the substrate to oxidant ratio, and temperature were optimized utilizing **1** as the catalyst (given in the following sections). Recyclabilities of **1** in benzyl alcohol and methyl phenyl sulfide oxidations were tested. Different alcohols and sulfides were chosen and their oxidations were done using optimum conditions to study the generality of the catalyst.

#### 3.2.1. Optimization of solvent type in oxidation reactions

Benzyl alcohol and methyl phenyl sulfide oxidation reactions were carried out in several solvents. The solvent, the conversion percentage, and the time, in which the reactions reach their maximum, are given in Tables 4 and 5. For both oxidation reactions the conversion percentage of the substrates is higher in polar solvents (entries 3–6 in Tables 4 and 5) than non-polar ones (entries 1 and 2 in Tables 4 and 5) [66]. The best efficiency of the catalyst was obtained when the solvent was acetonitrile.

The higher catalytic activity of **1** in the oxidation reaction is attributed to the better interaction of the heterogeneous complex in the non-protic polar medium. This finding is confirmed by decreasing conversion upon changing reaction solvent to aceto-nitrile/water (Tables 4 and 5, entries 4 and 6). Due to the high reaction efficiency in acetonitrile, it was selected as an oxidation solvent and was applied in the rest of the reactions that were done to optimize other parameters.

85



4

Table 5. Optimization of the solvent type in the oxidation reaction of methyl phenyl sulphide.

Reaction conditions: 1 mmol methyl phenyl sulfide, 15 mol% catalyst, 2 mmol 28% H<sub>2</sub>O<sub>2</sub>, 2 mL solvent at r.t.

	ОН Н	atalyst $_{2}O_{2}$ (28%) CH <sub>3</sub> CN	ОН
Entry	Catalyst amount (mol%)	Time (h)	Maximum conversion (%)
1	5	14	50
2	10	10	95
3	15	10	95

Table 6. Optimization of the catalyst amount in the oxidation reaction of benzyl alcohol.

Reaction conditions: 1 mmol benzyl alcohol, 1.5 mmol 28% H<sub>2</sub>O<sub>2</sub>, 2 mL CH<sub>3</sub>CN at r.t.

H<sub>2</sub>O

1

2

3

4

5

6

#### 3.2.2. Optimization of the catalyst amount in the oxidation reactions

The use of larger amounts of catalysts usually imposes high costs [67]. In addition, although the rate and efficiency of the reaction increase with increased amount of catalyst, chemo, and stereoselectivity of conversion may be affected [68]. In some cases, the use of high amounts of catalysts causes agglomeration of catalyst, reducing available active sites for the reaction [69]. Therefore, it is necessary to optimize the amount of used catalyst to select the lowest amount that maximizes the conversion percentage and at the same time does not have the mentioned disadvantages. Here we have optimized the catalyst amount for the oxidation reactions of benzyl alcohol and methyl phenyl sulfide. The optimization results are summarized in Tables 6 and 7, respectively. The effect of catalyst amount in both oxidation reactions was tested using 5, 10 and 15 mol% catalysts (values usually used in oxidation reactions [70]), while the reaction solvent was acetonitrile and other conditions stayed unchanged. When 5 mol% of 1 was applied the conversion values were obtained, 50% and 70% for benzyl alcohol and methyl phenyl sulfide oxidation reactions, respectively. The best conversion values, 95% (for benzyl alcohol oxidation) and 97% (for methyl phenyl sulfide oxidation) were achieved using 10 mol% of catalyst. By increasing the amount of the catalyst to 15 mol%, conversion percentage and selectivity were not affected significantly in both alcohol and sulfide oxidation reactions. Hence, all other studies were performed with 10 mol% of catalyst.

1

2

3



Table 7. Optimization of the catalyst amount in the oxidation reaction of methyl phenyl sulphide.

Reaction conditions: 1 mmol methyl phenyl sulfide, 1.5 mmol 28% H<sub>2</sub>O<sub>2</sub>, 2 mL CH<sub>3</sub>CN at r.t.

# 3.2.3. Optimization of the molar ratio of substrate to oxidant in the oxidation reactions

Although increasing hydrogen peroxide increases the conversion percentage, the oxidant amount needs to be optimized to avoid formation of by-products in the presence of excess H<sub>2</sub>O<sub>2</sub> [71]. In some cases, large amounts of hydrogen peroxide can reduce the reaction efficiency, which can be due to more chemisorption of  $H_2O_2$  and less chemisorption of the substrate on the active site of the catalyst [72]. The oxidation reaction of benzyl alcohol was carried out using three ratios of substrate to oxidant (1:1, 1:1.5 and 1:2) commonly used in similar reactions [73]. When the ratio of the substrate to oxidant was 1:1, the conversion was 70%. Applying the substrate to oxidant molar ratio of 1:1.5, the catalyst amount of 10 mol%, and acetonitrile as a solvent the conversion percentage was 95%, which was the best-obtained result. Increasing the substrate to oxidant ratio from 1:1.5 to 1:2 had no significant effect on the reaction time and conversion percentage.

In the case of the methyl phenyl sulfide oxidation, four ratios of the substrate to oxidant (1:1, 1:1.5, 1:2 and 1:2.5) were applied. Utilizing 1:1 and 1:1.5 ratios of the substrate to oxidant, the attained conversion percentages were 50% and 75%, respectively. The best conversion value (100%) was acquired using a substrate to oxidant molar ratio of 1:2. With increasing the ratio from 1:2 to 1:2.5, the conversion percentage was unaffected. Therefore, other studies in the oxidation of sulfides were done with the substrate to oxidant molar ratio of 1:2.

# 3.2.4. Optimization of the temperature in the oxidation reactions

For temperature optimization of benzyl alcohol oxidation, the reaction was carried out at 25 °C, 50 °C and reflux temperature (78 °C) in optimized conditions (acetonitrile solvent, catalyst amount of 10 mol% and alcohol to  $H_2O_2$  ratio of 1.0:1.5). Results showed that at room temperature, the conversion percentage of substrate oxidation was 95%, and the reaction had no progress after 10 h (Table 8). Completion of the benzyl alcohol oxidation reaction (conversion values = 100%) was achieved after 3 h at 50  $^{\circ}$ C and after 50 min at the reflux temperature (78  $^{\circ}$ C). So, the reflux condition (78  $^{\circ}$ C) (entry 3) was selected as an optimum point because of the shorter reaction time.

Oxidation of methyl phenyl sulfide was carried out at ambient temperature with excellent conversion value and in a reasonable time of 3 h, so no more temperature optimization studies were done for this substrate.



	Table 8.	Effect o	f tem	perature	in	the	oxidation	reaction	of	benzy	a	lcol	hol
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Temperature (°C) Time (h) Maximum conversion (%) Entry 1 10 25 95 2 50 100 3 78 (reflux) 50 (min) 100 3

Reaction conditions: 1 mmol benzyl alcohol, 10 mol% catalyst, 1.5 mmol 28% H<sub>2</sub>O<sub>2</sub>, and 2 mL acetonitrile.



# 3.2.5. Investigating catalyst recycling in the oxidation reactions

Recycling the heterogeneous catalyst after the reaction performance is essential [74]. To investigate the recycling ability of **1** the benzyl alcohol and methyl phenyl sulfide oxidation reactions were performed under optimum conditions. The catalyst was separated, washed, and dried after completion of the reactions. Then it was used further in the oxidation reactions. Results indicated that for benzyl alcohol oxidation the catalyst was recyclable and could be used four times with no significant loss of activity. For methyl phenyl sulfide oxidation the catalyst maintained its catalytic activity up to five runs (Figure 7).

#### 3.2.6. The generality test of 1

The generality of **1** was tested using various substrates. Various alcohols and sulfides were chosen as substrates, and their oxidations were carried out under the optimized reaction conditions. Results are given in Tables 9 and 10. For all of the different alcohols and sulfides **1** catalyzed the reactions with high selectivity to produce the acids and sulfoxides, respectively.

As Table 9 exhibits, different conversion percentages (50%-100%) were obtained using various alcohols as substrates. These differences can be due to the steric and electronic effects [75]. Comparing the oxidation results of benzyl alcohol (entry 2) with 4-methoxybenzyl alcohol (entry 3), in Table 9, indicates that with substituting an electron-donating group (-OMe) in the *para*-position of benzyl alcohol, the completion time of oxidation (conversion amount = 100%) was reduced from one hour to

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Scheme 9.

			Maximum	<b>-</b> , (1)
Entry 1	Alcohol O2N OH	O <sub>2</sub> N OH	conversion (%) 65	11me (h) 5
2	ОН	ОН	100	1
3	Н3СО ОН	H <sub>3</sub> CO	100	0.5
4	OH	OH	60	5
5	OH CH3	CH3	65	3.5
6	OH OH		70	6.5
7	CH <sub>3</sub> OH	CH <sub>3</sub>	50	4
8	ОН	ОН	70	4

Reaction conditions: 1 mmol alcohol, 10 mol% catalyst, 1.5 mmol 28% H<sub>2</sub>O<sub>2</sub>, 2 mL acetonitrile and reflux condition.

30 minutes. On the contrary, the presence of an electron-withdrawing group  $(-NO_2 \text{ in entry 1})$  in this position reduced maximum conversion to 65% and the time of oxidation to 5 h. In the case of alcohols 6–8, it seems that the steric factor plays a greater role than the electronic effect. A comparison between the oxidation results of benzyl alcohol (entry 2) and benzoin (entry 6) shows that with increasing the steric hindrance (entry 6) the maximum conversion decreased to 70% and the time of oxidation was prolonged to 6.5 h.



Table 10. Oxidation results of various sulfides to sulfoxides using 1.

Reaction conditions: 1 mmol sulfides, 10 mol% catalyst, 2 mmol 28% H<sub>2</sub>O<sub>2</sub>, 2 mL acetonitrile.

Results of oxidation reactions of various sulfides (Table 10) indicated that 1 could catalyze the oxidation reaction of various sulfides to produce their corresponding sulfoxides, without a trace amount of sulfones. The main reason for the difference between the resulted conversion amounts for these reactions is the steric effects. A comparison between the results of 1-4 (Table 10) shows that as the sulfides become bulkier, the amount of maximum conversion becomes less (1 > 2 > 3 > 4).

Table 11 illustrates some examples from previous studies on benzyl alcohol oxidation reactions with various catalysts. Comparison between conversion and time of reaction of 1 and other listed catalysts indicates that the activity of 1 is in a moderate to good range, confirming **1** as an efficient catalyst. As can be seen from Table 11, in the presence of 1, the oxidation of benzyl alcohol is carried out at a lower reaction time and with a higher conversion percentage relative to other reactions. In the case of [RuH(CO)(py-NP)(PPh<sub>3</sub>)<sub>2</sub>]Cl catalyst (entry 9), with conversion of 100%, higher temperature and reaction time have been applied relative to the mild conditions of 1. Another advantage of 1, besides the mild conditions, is its good selectivity to one product (see the results of entries 1 and 2).

Table 12 shows a comparison between our results for methyl phenyl sulfide oxidation, using 1, with other catalysts reported. The conversion percentage of 100% was obtained in a short time in the presence of 1 using mild conditions, while in most of the other reactions (entries 1-9) such conversion has not been achieved even in longer reaction times. However, there also are cases in which the oxidation reaction of methyl phenyl sulfide has been performed with a good conversion percentage in a shorter time than ours (entries 11 and 12). Concerning the high cost of the Ti derivatives, it seems that our catalyst could be more economical than these two catalysts.

Table 1	1. Comparison between the effic	iency of 1 with reported catalyst	s for benzyl alcohol oxidat	ion reaction.			
						Recycling	
Entry	Catalyst	Conditions	Conversion (%)/yield (%)	Time (h)	Type of catalyst	runs	Ref.
-	[Mn <sub>2</sub> (μ <sub>1,3</sub> -6-CH <sub>3</sub> -2-NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COO) <sub>2</sub> (biv) <sub>4</sub> ](CIO <sub>4</sub> ) <sub>2</sub>	CH <sub>3</sub> CN, H <sub>2</sub> O <sub>2</sub> , 70°C	37.4 (Benzaldehyde) 42.8 (Benzoic acid)	24	Homogenous	0	[76]
2	Excited flavinium salt	CH <sub>3</sub> CN, O <sub>2</sub> , 40 °C	63	16	Homogenous	0	[77]
ŝ	Manganese(II) complex	CH <sub>3</sub> CN: H <sub>2</sub> O, H <sub>2</sub> O <sub>2</sub> , 30 °C	59 (Benzaldehyde)	18	Homogenous	0	[78]
	(Mn(Me <sub>2</sub> EBC)Cl <sub>2</sub> )	1	11 (Benzoic acid)		ı		
4	PW <sub>11</sub> Zn@MCM-41-Im	CH <sub>3</sub> CN, H <sub>2</sub> O <sub>2</sub> , reflux	94	10	Hybrid	4	[62]
5	Fe304@SiO2-Schiff base-Co(II)	CH <sub>3</sub> CN, O <sub>2</sub> , reflux	94	9	Hybrid	I	[80]
9	[CuL <sup>2</sup> (OH)]-Y <sup>[a]</sup>	CH <sub>3</sub> CN, TBHP, reflux	79	7	Homogenous	0	[72]
7	[Ru <sub>3</sub> (CO) <sub>8</sub> (C <sub>5</sub> H <sub>4</sub> NCO <sub>2</sub> ) <sub>2</sub> ]	Water, NaOH, isopropanol, 98 °C	90	12	•		[81]
8	[Ru(L)X(CH <sub>3</sub> CN) <sub>2</sub> ].X <sup>[b]</sup>	Water, CsOH, reflux (argon)	82	24	Homogenous	0	[82]
6	[RuH(CO)(py-NP)(PPh <sub>3</sub> ) <sub>2</sub> ]Cl <sup>[c]</sup>	Water, NaOH, 110 °C	100	6-24	Homogenous	0	[83]
10	Complex 1	CH <sub>3</sub> CN, H <sub>2</sub> O <sub>2</sub> , 78°C	100	-	Heterogeneous	4	This work
[a]: 2-eth	yl-4-methyl 5-(2hydroxybenzylideneami	no)-3-methylthiophene-2,4-dicarboxylat	ie.				
[b]: L = 2	,6-bis (benzimidazol-2-yl), $X = OTF$ .						
[c]: py-NF	$^{2} = 2 - (2 - pyridyl) - 1,8 - naphthyrid.$						

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12. Comparison betwee Catalyst Fe <sub>3</sub> 0 <sub>4</sub> /salen of C	(II)	/ or 1 with reported catalysts for Conditions EtOH, H <sub>2</sub> O <sub>2</sub> , 60 °C	Conversion (%)/yield (%) 83	Time (h)	Type of catalyst Hybrid	Recycling runs 8	Ref. [84]
Ni-Salen/MCM-41 EtOH, UF Borax MeOH, H-	EtOH, UF MeOH, H <sub>3</sub>	HP, r.t. 03. r.t.	95 35	2.6 6	Hybrid Heterogeneous	νυν	[85] [86]
Ti(Oi-Pr)4+ Shiff base Dry dichlorometh	Dry dichlorometh	ane, H <sub>2</sub> O <sub>2</sub> , 0°C	92	10	Homogenous	0	[87]
4-phenyl-9H-thioxanthen-9-one MeOH, a	MeOH, a	ir, r.t.	93	ιΩ I	Homogenous	0	88
Schift-base oxo-vanadium complex/Fe <sub>3</sub> O <sub>4</sub> Solvent free,	Solvent free,	H <sub>2</sub> O <sub>2</sub> , r.t.	96	ĿO Y	Hybrid	6	[89]
litanosilicate CH <sub>3</sub> CN, F	CH <sub>3</sub> CN, H	1 <sub>2</sub> 0 <sub>2</sub>	96	4	Hybrid		[06]
CeMe <sub>2</sub> N-PS-SiV <sub>2</sub> W <sub>10</sub> Water, H <sub>2</sub> O	Water, $H_2O$	<sub>2</sub> , r.t.	84.6	9	Hybrid	2	[91]
S <sub>18</sub> -HPV <sub>2</sub> W <sub>10</sub> Water, H <sub>2</sub> C	Water, H <sub>2</sub> C	) <sub>2</sub> , r.t.	23	9	Hybrid	I	[92]
Complex 1 CH <sub>3</sub> CN, H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> CN, H <sub>2</sub> O <sub>2</sub>	», r.t.	100	2	Heterogeneous	5	This work
[Ti <sub>2</sub> (O <sub>2</sub> ) <sub>2</sub> O <sub>2</sub> (OH) <sub>2</sub> (carboxylate)]- Water, H <sub>2</sub> O.	Water, H <sub>2</sub> O	2, r.t.	100	0.3	Hybrid	10	[6]
poly(sodium acrylate)							

# 4. Conclusion

A Cu(I) complex (1) with a phosphoric triamide ligand was synthesized and characterized by various methods. Results indicated that 1 is in a crystalline phase, the ligand is coordinated to copper via P = O and  $N_{pyridine}$ , one molecule of 1 contains one Cu, two molecules of L, and one Cl<sup>-</sup>. According to the characterizations, the proposed formula of 1 is [CuClL<sub>2</sub>].

Additionally, **1** was used as a heterogeneous catalyst for aromatic alcohols and sulfide oxidations, with  $H_2O_2$  as a green oxidant. Solvent, catalyst amount, the substrate to oxidant ratio, and temperature were optimized **1** as the catalyst and benzyl alcohol and methyl phenyl sulfide as substrates. For oxidation of benzyl alcohol the optimum conditions were catalyst amount of 10 mol%, substrate to oxidant ratio of 1:1.5, reflux temperature (78 °C), and acetonitrile as the solvent. For the oxidation of methyl phenyl sulfide to its corresponding sulfoxide, the best results were achieved by 10 mol% of the catalyst, substrate to oxidant ratio of 1:2, ambient temperature, and acetonitrile as the solvent. Recycling experiments showed that **1** could catalyze the oxidation reactions of benzyl alcohol and methyl phenyl sulfide for 4 and 5 runs, respectively.

Moreover, using the optimum conditions, the oxidation of various alcohols and sulfides were investigated. Comparison between the oxidation results of benzyl alcohol and methyl phenyl sulfide in the presence of **1** with other catalysts (under the other previously published conditions) showed that in most cases, **1** had better and more efficient results, in terms of conversion percentage, reaction time, and reaction conditions.

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#### **Disclosure statement**

No potential conflict of interest was reported by the authors.

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