



Catalytic oxidation of organosulfides to sulfoxides using two novel Cu(II) and Ni(II) complexes with aqueous H₂O₂: Effect of TMAO promoter on oxidation of organosulfides

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ABSTRACT

Two new copper(II) and nickel(II) complexes [Cu(MeOH)(O-NO₂)(L)](NO₃)·CH₃OH (**1**) and [Ni(L)₂(NO₃)₂]·H₂O (**2**) derived from the 4'-(2-thienyl)-2,2',6',2''-terpyridine (L) were synthesized. The ligand and complexes were characterized with elemental analysis, ¹H and ¹³C NMR, IR spectroscopy and finally the solid structure of complexes were determined by X-ray crystallography. Complexes (**1**) and (**2**) were tested as homogenous catalysts for sulfoxidation of a variety of organosulfide substrates utilizing hydrogen peroxide in the presence of a catalytic amount of trimethylamine *N*-oxide (TMAO). Addition of TMAO to the reaction mixture enhanced the conversion and selectivity.

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1. Introduction

Chemical building blocks containing sulfoxide functional groups are particularly useful for the construction of various important compounds in both bulk and fine chemicals [1–3]. The extensive chemistry of sulfoxides and sulfones makes them very useful reagents in organic synthesis in general and useful synthetic intermediates for the construction of various chemically and biologically significant molecules in particular [4–7]. In this manner metal catalyzed asymmetric oxidation of sulfides, a powerful strategy for the rapid preparation of enantiopure sulfoxides, has garnered extensive attention from the synthetic community [2]. The sulfoxides are usually produced by oxidation of sulfides with several oxidative procedures and a variety of oxidants like molecular oxygen, hydrogen peroxide, urea hydrogen peroxide, *tert*-butylhydroperoxide, iodosyl benzene and sodium hypochlorite [8–11]. Unfortunately most of these reagents are not satisfactory for large-scale synthesis due to the formation of environmentally unfavorable by-products, the low content of effective oxygen, and high cost. Among various terminal oxidants used, hydrogen peroxide has relatively high oxygen content, leaves only water as waste product and has low cost in price than other oxidants. Generally, it is important that to stop the reaction at the sulfoxide step but the reported methods rarely offer

the ideal combination of simplicity of method, good rate, selectivity and high yields of desired sulfoxides. For this reason, the chemistry of the several transition metal complexes with O, N, S and P donor ligands are subject of current interests [12–14]. Recently, many catalytic oxidation of thioethers to the proper sulfoxide catalyzed by Ni(II) and Cu(II) complexes were reported [15–19].

With this background, we describe here the synthesis, spectroscopy and X-ray crystallographic structure determination of Ni(II) and Cu(II) complexes with 4'-(2-thienyl)-2,2',6',2''-terpyridine ligand and the catalytic activity of these novel complexes. Also improvements of the catalytic oxidation of sulfides were investigated in presence of catalytic amount of trimethylamine *N*-oxide.

2. Experimental

2.1. Materials and instruments

The ligand was synthesized according to the previously published procedures with slightly modification [20]. All solvents were obtained from commercial sources and used without further purification unless stated otherwise. If required, solvents were further purified by standard methods. 2-Acetylpyridine, thiophene-2-carboxaldehyde, 28.0–30.0% aqueous ammonia and potassium *tert*-butoxide were purchased from Merck chemicals and were used as received. The hydrated metal salts and TMAO were obtained from Fluka. Melting points are uncorrected and

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were obtained with Electrothermal 9200 melting point apparatus. Infrared spectrums from 250 to 4000 cm^{-1} of solid samples were taken as 1% dispersion in CsI pellets using a Shimadzu-470 spectrometer. ^1H and ^{13}C NMR spectra were recorded at room temperature on a Bruker AVANCE 300 MHz. The NMR spectra are referenced to Me_4Si as external standards. Elemental analysis was performed using a Heraeus CHN-O Rapid analyzer. The course of the reactions was monitored by gas chromatography (Agilent Technologies 6890N Instrument), equipped with a capillary column (19019 J-413 HP-5, 5% phenyl methyl siloxane, capillary 60.0 mm \times 250 mm \times 1.00 mm), and a flame ionization detector.

2.2. Synthesis of ligand (L)

To a solution of 2-acetylpyridine (2.42 g, 20 mmol) in 75 ml absolute ethanol, were added thiophene-2-carboxaldehyde (1.12 g, 10 mmol), potassium *tert*-butoxide (3.09 g, 27.5 mmol) and ammonia solution (30 ml). The reaction mixture was stirred at ambient Temperature for 18 h. After this time, the precipitated impure product was filtered off and successively washed with cold water and cold ethanol–water (50:50) solution and finally with minimum amount of cold diethyl ether. The bright yellow product was dried for 2 days in vacuo over P_2O_5 . The yield was 1.36 g (43%). Physical and spectroscopic properties were consistent with those reported in the literature [21].

2.3. Synthesis of complex (1)

To a solution of 4'-(2-thienyl)-2,2',6',2''-terpyridine (L) (0.1 g, 0.32 mmol) in CHCl_3 (5 ml) was added a solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.039 g, 0.16 mmol) in methanol (10 ml). The color of the reaction mixture was turned to deep green immediately. After stirring for 30 min at ambient temperature, the green solution was left to evaporate slowly at room temperature. After 1 week, greenish-blue blocks of (1) were isolated (yield 0.07 g, 79.5%, decompose $>298^\circ\text{C}$). IR (CsI, cm^{-1}): 3431b, 3062w, 1761w, 1609s, 1560m, 1480m, 1426m, 1374s, 1292w, 1238w, 1156w, 1096w, 1019m, 843w, 788m, 724m, 644w, 562w, 502w, 415w, 352w. Anal. Calc C, 43.44; H, 3.46; N, 12.66. Found C, 43.47; H, 3.49; N, 12.61.

2.4. Synthesis of complex (2)

To a solution of 4'-(2-thienyl)-2,2',6',2''-terpyridine (L) (0.1 g, 0.32 mmol) in CHCl_3 (5 ml) was added a solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.047 g, 0.16 mmol) in acetonitrile (10 ml). The color of the reaction solution was turned to brownish green. The mixture was stirred for 20 min at room temperature and then was left to evaporate slowly at room temperature. After 5 days, brownish-orange blocks of (2) were obtained (yield 0.113 g, 84.9%, decompose $>322^\circ\text{C}$). IR (CsI, cm^{-1}): 3417b, 3057w, 1607s, 1557m, 1470m, 1425m, 1365b, 1248m, 1157w, 1088w, 1017m, 895w, 844w, 790m, 707w, 637w, 559w, 416w, 215s. Anal. Calc. C, 54.89; H, 3.39; N, 13.48. Found C, 54.92; H, 3.41; N, 13.43.

2.5. General procedure for catalytic oxidation reactions

In a typical experiment, a mixture of 1 mmol of sulfide, 2 mmol of hydrogen peroxide, 0.04 mmol of catalyst and 0.05 mol of TMAO were added to a vessel containing 2 ml CH_3CN at room temperature while the progress of the reaction was monitored by TLC. After 1 h, the reaction mixture was analyzed directly by gas chromatography. In some cases reaction products were identified by injection of pure chemicals, but in other cases confirmed by GC–mass spectroscopy. The yields were calculated from standard curves. Most of

Table 1
Crystallographic and structure refinements data for complexes (1) and (2).

	(1)	(2)
Formula	$\text{C}_{20.5}\text{H}_{19}\text{CuN}_5\text{O}_{7.5}\text{S}$	$\text{C}_{38}\text{H}_{28}\text{Ni}_3\text{NiO}_7\text{S}_2$
Formula weight	551.01	831.51
Temperature/K	150(1)	150(1)
Wavelength $\lambda/\text{\AA}$	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Crystal size/ mm^3	$0.10 \times 0.08 \times 0.08$	$0.20 \times 0.16 \times 0.12$
$a/\text{\AA}$	8.5024(3)	12.6736(7)
$b/\text{\AA}$	9.4502(3)	13.2558(8)
$c/\text{\AA}$	15.5274(6)	14.6113(5)
$\alpha/^\circ$	93.6050(19)	67.122(3)
$\beta/^\circ$	101.8820(17)	79.437(3)
$\gamma/^\circ$	107.6250(18)	63.110(2)
Volume/ \AA^3	1153.04(7)	2016.97(18)
Z	2	2
Density (calc.)/ g cm^{-3}	1.587	1.369
θ ranges for data collection	2.6–27.5	2.6–27.5
$F(000)$	564	856
Absorption coefficient/ mm^{-1}	1.09	0.64
Index ranges	$-11 \leq h \leq 10$ $-12 \leq k \leq 12$ $-19 \leq l \leq 20$	$-16 \leq h \leq 16$ $-15 \leq k \leq 17$ $-19 \leq l \leq 19$
Data collected	13,523	18,777
Unique data (R_{int})	5227, (0.0712)	9141, (0.066)
Parameters, restraints	327, 10	514, 27
Final R_1 , wR_2^a (Obs. data)	0.0649, 0.1578	0.0699, 0.1748
Final R_1 , wR_2^a (All data)	0.1191, 0.1923	0.1349, 0.2039
Goodness of fit on F^2 (S)	1.05	0.98
Largest diff peak and hole/ \AA^3	0.76, –0.91	0.93, –0.86

the reactions were run at least twice and the found values were averaged.

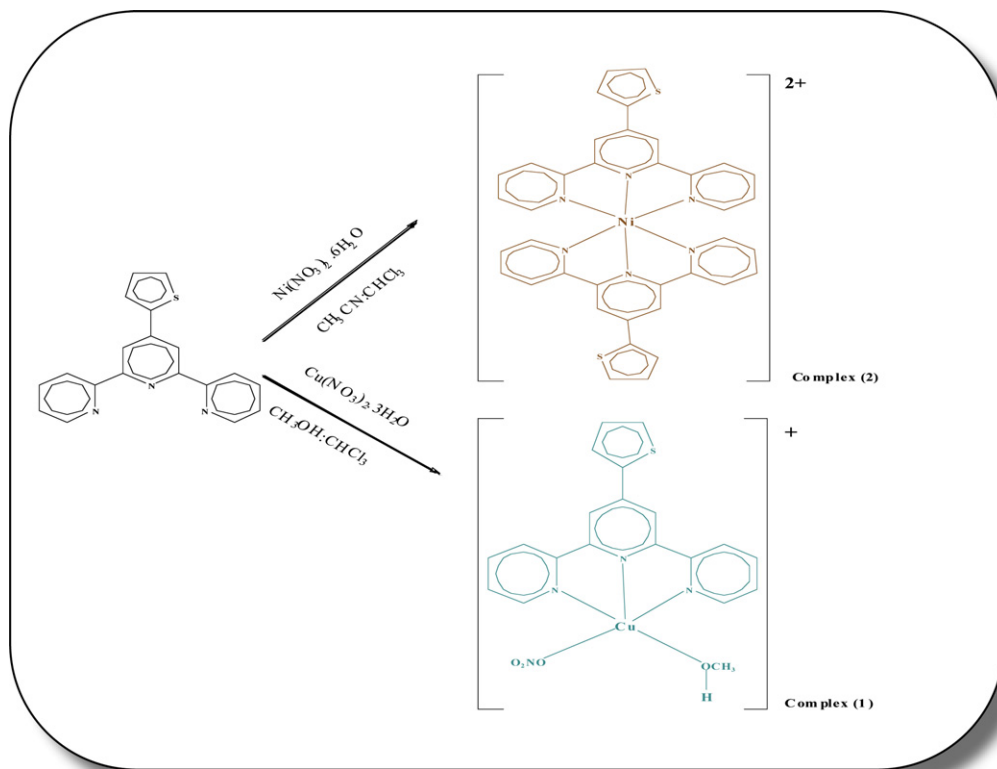
2.6. Crystal structure determination and refinement

The crystallographic data was collected with a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo $K\alpha$ radiation of 0.71073 \AA . For $[\text{Cu}(\text{MeOH})(\text{O}-\text{NO}_2)(\text{L})](\text{NO}_3) \cdot \text{CH}_3\text{OH}$, (1), a greenish-blue block with a dimension of 0.10 mm \times 0.08 mm \times 0.08 mm and for $[\text{Ni}(\text{L})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, (2), a brownish-orange block crystal with a dimension of 0.20 mm \times 0.16 mm \times 0.12 mm was mounted. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 5227 for (1) and 9141 for (2) unique reflections. Data were collected at a temperature of 150(1) K to a maximum 2θ value of 55° for both (1) and (2). The numerical absorption coefficients, μ , for Mo $K\alpha$ radiation are 1.038 and 0.642 mm^{-1} for 1 and 2, respectively. The structures were solved by direct methods [21] and subsequent differences Fourier map and then refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [21]. All of hydrogen atoms were located in a difference Fourier map and then refined isotropically. Cell refinements were performed using the Denzo-SMN crystallographic software package [22]. A summary of the crystal data, experimental details and refinement results is given in Table 1.

3. Results and discussion

3.1. Synthesis of complexes

Two new complexes were synthesized with 4'-(2-thienyl)-2,2',6',2''-terpyridine ligand as depicted in Scheme 1. The ligand was prepared in one pot synthesis from condensation of 2-acetylpyridine, thiophene-2-carboxaldehyde and ammonia in the presence of *t*-BuOK [20]. For preparation of complex (1) and (2), hydrated copper nitrate and nickel nitrate were reacted with lig-



Scheme 1. Reagents and condition for the synthesis of complex (1) and (2) at room temperature.

and in methanol–chloroform and acetonitrile–chloroform mixture, respectively.

3.2. Description of the molecular structure of $[\text{Cu}(\text{MeOH})(\text{O}-\text{NO}_2)(\text{L})](\text{NO}_3) \cdot \text{CH}_3\text{OH}$ (1), and $[\text{Ni}(\text{L})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (2)

Recrystallization of micro crystals of complex (1) in methanol and acetonitrile yield greenish-blue and brownish-orange block crystals correspond to (1) and (2), respectively. Crystallographic data for (1) and (2) are given in Table 1. The structure of (1) consists of $[\text{Cu}(\text{MeOH})(\text{O}-\text{NO}_2)(\text{L})]$ cation and nitrate anion accompanying with one methanol molecule (Fig. 1). The copper(II)

environment consists of nitrate ion, one 4'-(2-thienyl)-2,2',6',2''-terpyridine ligand and one methanol molecule giving a distorted square based pyramidal geometry. The Cu–N and Cu–O average bond distances are 1.990(4) and 2.095(3) Å, respectively, both consistent with the range observed for similar copper mixed ligand compounds [23,24]. The unit cell-packing diagram of the complex is presented in Fig. 2. Different hydrogen bonds exist in the structure. One between free nitrate ion and the OH group of coordinated methanol ($\text{O4} \cdots \text{O5} = 2.648(6)$ Å and $\text{O4}-\text{H4}-\text{O5}$ angle of 150.6°) and another one exists between the coordinated nitrate and the free methanol molecule ($\text{O9} \cdots \text{O3} = 3.285(13)$ Å and $\text{O9}-\text{H9}-\text{O3}$ angle of

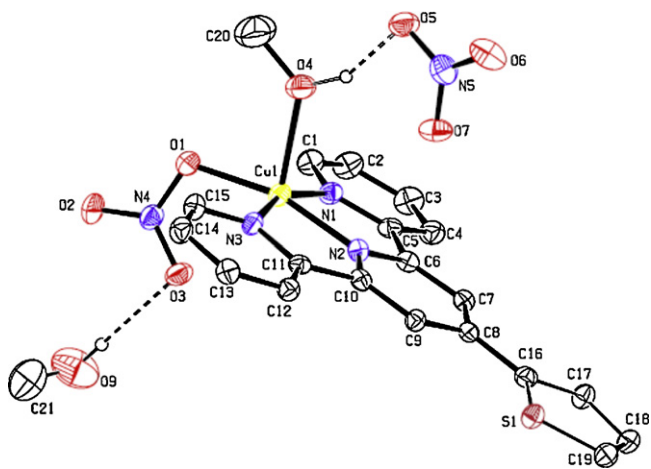


Fig. 1. The labeled diagram of $[\text{Cu}(\text{MeOH})(\text{O}-\text{NO}_2)(\text{L})](\text{NO}_3) \cdot \text{CH}_3\text{OH}$ (1). Thermal ellipsoids are at 30% probability level and hydrogen atoms were omitted for more clarity.

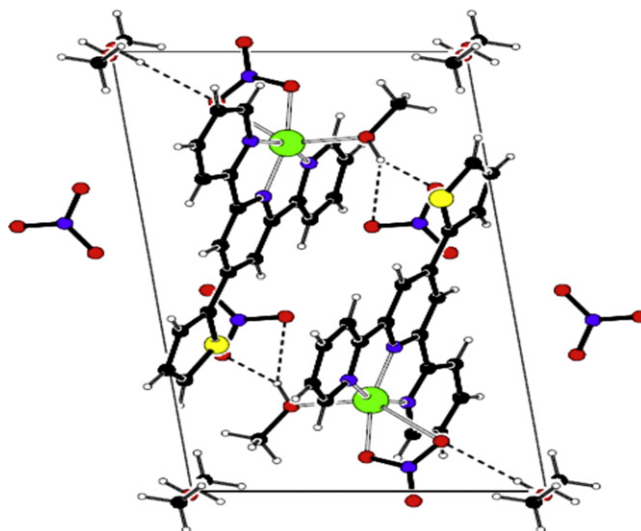


Fig. 2. Crystal packing diagram for $[\text{Cu}(\text{MeOH})(\text{O}-\text{NO}_2)(\text{L})](\text{NO}_3) \cdot \text{CH}_3\text{OH}$ (1). Hydrogen bonds are shown as dashed lines.

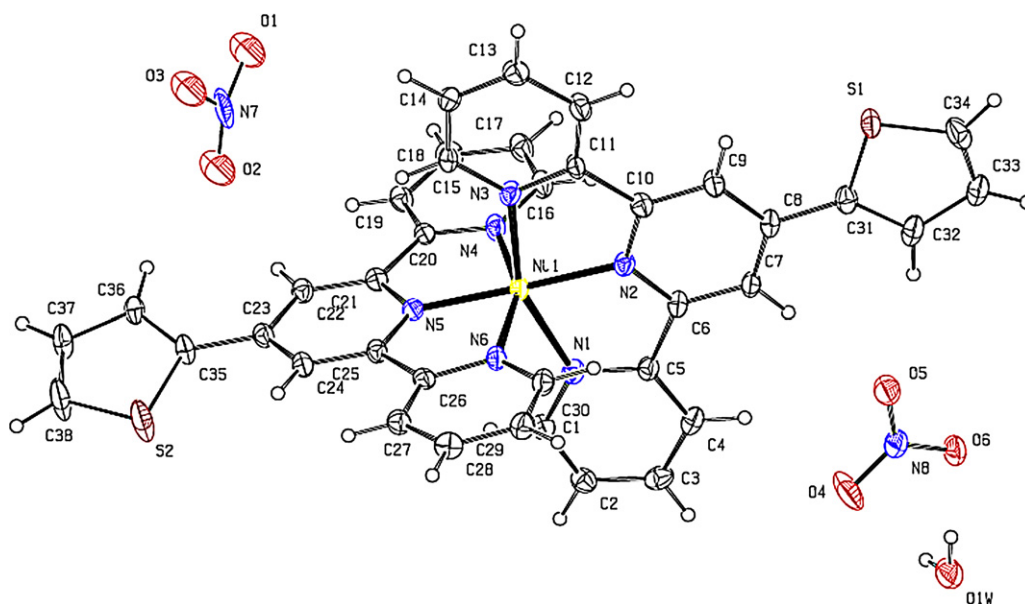


Fig. 3. The labeled diagram of $[\text{Ni}(\text{L})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (**2**). Thermal ellipsoids are at 30% probability level.

179.4°). The Cu1–O4 bond distance is longer than the others, due to hydrogen bonding with nitrate counter ion, making it more labile than the others for substitution.

Complex (**2**) consists of two tridentate chelating 4'-(2-thienyl)-2,2',6',2''-terpyridine ligand. The molecular structure and atom numbering scheme and also the crystal packing are shown in Figs. 3 and 4, respectively. The complex has a distorted octahedral geometry. The two rigid tridentate chelating 4'-(2-thienyl)-2,2',6',2''-terpyridine ligands are the main factors accounting for this distortion. The average Ni–N distance for (**2**) is 2.067(4) Å that is in agreement with the values reported for similar structures [25–27].

There are also different hydrogen bonds in complex (**2**), which are between the nitrate ion and free water molecules, $\text{O1W} \cdots \text{O6} = 2.837(5)$ Å and $\text{O1W}-\text{H1WA}-\text{O6}$ angle of 179.4°, and also $\text{O1W} \cdots \text{O3A}^1 = 2.769(14)$ Å with $\text{O1W}-\text{H1W}-\text{O3A}^1$ angle of 179.0° (symmetry code: (i) $x, y + 1, z - 1$).

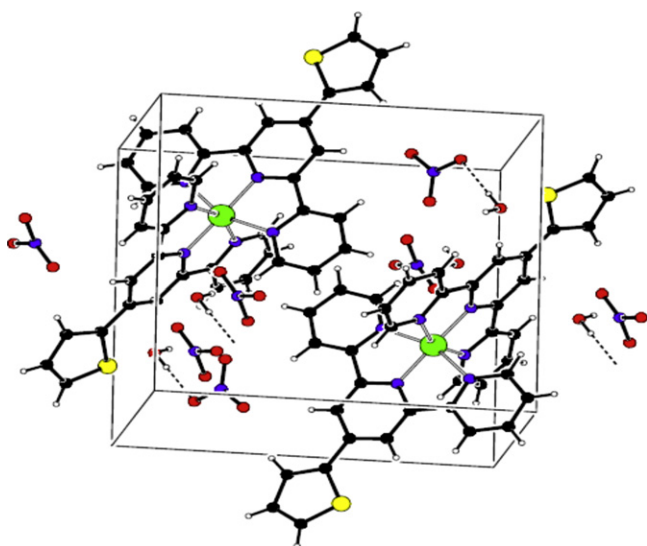


Fig. 4. Crystal packing diagram for $[\text{Ni}(\text{L})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (**2**). Hydrogen bonds are shown as dashed lines.

3.3. Catalytic sulfoxidation and effect of TMAO

In order to find the optimum conditions for oxidation reactions, an attempt was made to investigate the effects of solvent and TMAO as promoter on the oxidation of organosulfides. At first, oxidation of methylphenylsulfide as a model substrate was carried out in various solvents such as acetone, methanol, ethanol, dichloromethane, chloroform, dichloroethane and acetonitrile. The reactions were run with molar ratio of 1:25:50 for catalyst:substrate:oxidant that was found as optimum conditions. The polar solvents, i.e. methanol, ethanol and acetonitrile were more effective than less polar solvents (see Table 2). Since H_2O_2 is not completely soluble in less polar organic solvents such as dichloromethane, dichloroethane and chloroform, the oxidation yields are low in these solvents.

Furthermore, to investigate the effect of oxidant in the catalytic systems, oxidation of methylphenylsulfide was carried out using various molar ratios of oxidant to sulfide (see Fig. 5). The oxidation reactions with 2 equiv. H_2O_2 afforded 88% and 80% conversions for $[\text{Cu}(\text{MeOH})(\text{O}-\text{NO}_2)(\text{L})](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and $[\text{Ni}(\text{L})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, respectively. Higher amounts of H_2O_2 up to 3 and 4 equiv. led to growth in the conversions, but decreased the selectivity to sulfoxide in both catalytic systems. The decrease in selectivity is faster in $[\text{Cu}(\text{MeOH})(\text{O}-\text{NO}_2)(\text{L})](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ compared to $[\text{Ni}(\text{L})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, so the highest selectivity to sulfoxide as well as reasonably high conversions were obtained with 2 equiv. of H_2O_2 (see Fig. 5).

Table 2
Effect of solvent on the oxidation of methylphenylsulfide catalyzed by (**1**) and (**2**).^a

Solvent	Conversion (%) ^b	Conversion (%) ^c
Acetone	16	10
Methanol	44	49
Ethanol	59	56
Dichloromethane	11	9
Chloroform	9	5
Dichloroethane	15	13
Acetonitrile	73	70

^a Condition of reaction: the molar ratio for catalyst:substrate:oxidant are 1:25:50. The reactions were run for 60 min at room temperature.

^b GC yields based on the starting sulfides with catalyst (**1**).

^c GC yields based on the starting sulfides with catalyst (**2**).

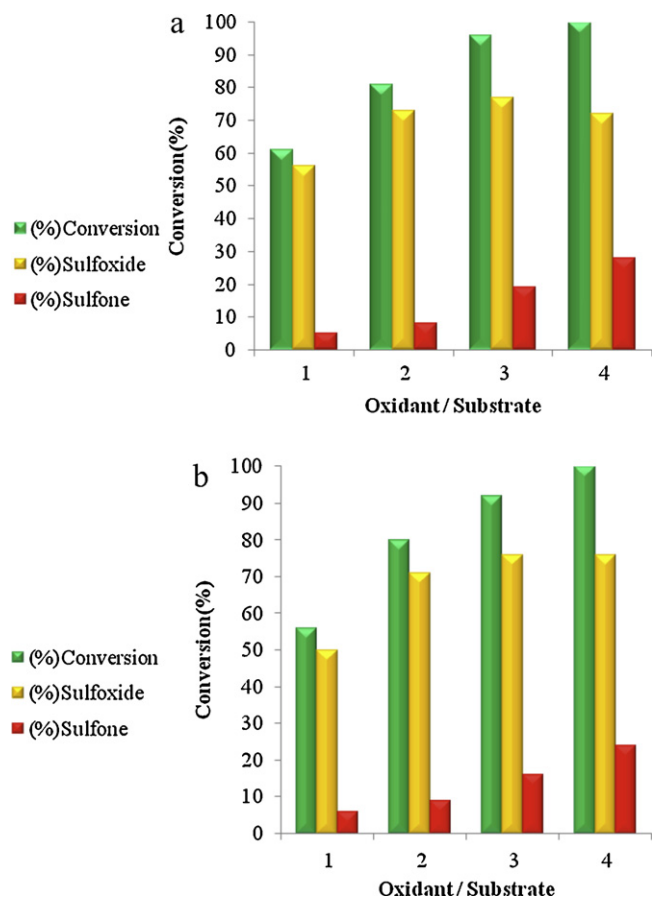


Fig. 5. The effect of amount oxidant on the oxidation of methylphenylsulfide by (a) complex (1) and (b) complex (2).

We found that under experimental conditions in this work, the oxidation occurred to a 3:1 mixture of sulfoxide and sulfone in 73% conversion in the presence of 4 mol% of the complex (1) in acetonitrile. Addition of 3 mol% TMAO to the reaction mixture led the oxidation to a 15:1 mixture of sulfoxide and sulfone (94% sulfoxide)

in 99% conversion. The selectivity and conversion of the sulfoxide were further increased to >99% when the amount of TMAO was increased to 5 mol% for catalyst. A control experiment without complex (1) provided the sulfoxide in only 5% yields and no sulfone was observed. These studies suggest that complex (1) together with TMAO catalyzed the oxidation of sulfide to the sulfoxide in the presence of 30% hydrogen peroxide. Also, the same procedures were performed with complex (2), as it shown in Fig. 6 and the results were presented in Table 3.

To study the applicability of this catalyst for oxidation of other sulfides, a series of aryl alkyl, aryl allyl, diaryl and dialkyl sulfides, were oxidized to the corresponding sulfoxides (see Table 4). The reactivity and conversions were dependent on the nature of the substituents. In the case of allyl sulfides, no oxidation was observed at the carbon–carbon double bond. Similarly, benzylic sulfides could be oxidized to the corresponding sulfoxides without affecting the benzylic C–H bond [14]. Dialkyl sulfides were moderately reactive providing the corresponding sulfoxide. These oxidations could usually be stopped at the sulfoxide stage without over oxidation to the sulfone.

The higher activity of complex (1) can be explained by the presence of labile methanol ligand. The presence of this weak and labile ligand, have a key role in the formation of active “metal-oxo” species. This was confirmed by the longer Cu–O bond distance than normal condition. Also the vacant site in complex (1) affect the formation of “metal-oxo” species than the other eight coordinated complex (2). Moreover, the conversion average of oxidation reactions catalyzed by complex (1) and (2), increased from 76.75% and 74.1% to 91.6% and 88%, respectively. These figures show that the catalytic amount of TMAO enhance the conversion and selectivity of the oxidation of organosulfides. This happened because TMAO facilitated the formation of “metal-oxo” species in metal complexes especially in copper complex. Based on our knowledge; it is the first report for catalytic oxidation of organosulfides co-catalyzed by TMAO. Finally, we think that TMAO facilitate the reaction by changing the oxygen source from hydrogen peroxide to TMAO and the latter is more controllable than H_2O_2 . It means that the TMAO oxidize the organosulfides to corresponding sulfoxides and then is recycled by hydrogen peroxide. The oxidation was stopped at sulfoxide step for the selectivity of TMAO for formation of sulfoxide.

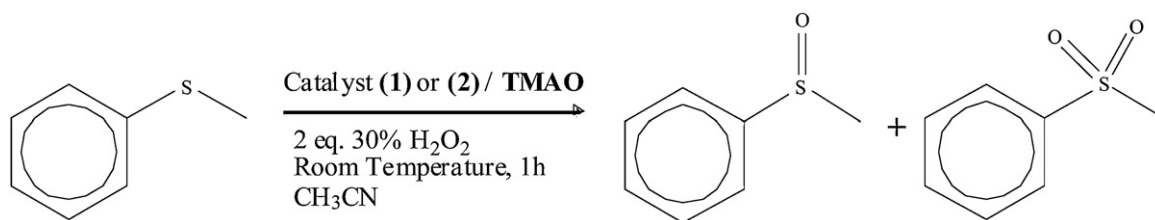


Fig. 6. Catalytic sulfoxidation of methylphenylsulfide by complex (1) or complex (2) in the presence of TMAO.

Table 3
Oxidation of methylphenylsulfide using complex (1) and (2) as catalyst and effect of TMAO as promoter.^a

Entry	Complex (1)	Complex (2)	TMAO	Conversion (%) ^b	Sulfoxide(%)	Sulfone (%)	Selectivity (%) ^c
1	4 mol%	–	None	81	73	8	90
2	–	–	5 mol%	5	~5	–	100
3	4 mol%	–	3 mol%	99	93.5	5.5	94
4	4 mol%	–	5 mol%	>99	~99	1	99
5	–	4 mol%	None	80	71	9	89
6	–	–	5 mol%	5	~5	–	100
7	–	4 mol%	3 mol%	95	89	6	94
8	–	4 mol%	5 mol%	95	92	3	97

^a Substrate (1 mmol), complex (1) or (2) (4 mol%), TMAO (5 mol%) and 30% H_2O_2 (2 mmol) were stirred for 1 h at RT in CH_3CN (2 mL).

^b Analyzed by GC.

^c Selectivity(%) = $\frac{\text{sulfoxide}(\%)}{[\text{sulfoxide}(\%) + \text{sulfone}(\%)]}$.

Table 4Oxidation of organosulfides using complex (1) and (2) as catalyst in the presence and absence of TMAO as promoter.^a

Entry	Substrate	Complex (1), conv.(/select.%) ^{b,d}	Complex (1), without TMAO conv.(/select.%) ^{c,d}	Complex (2), conv.(/select.%) ^{b,d}	Complex (2), without TMAO conv.(/select.%) ^{c,d}
1	Dimethylsulfide	89/97	73/92	82/97	71/89
2	Dipropylsulfide	93/97	78/90	89/94	76/88
3	Diphenylsulfide	95/97	76/92	90/95	71/85
4	Benzylphenylsulfide	89/96	74/93	87/97	70/86
5	Dibenzylsulfide	91/97	79/90	86/96	76/88
6	Methylphenylsulfide	99/94	81/90	95/94	80/89
7	Ethylphenylsulfide	94/96	80/92	89/96	78/92
8	Diallylsulfide	83/97	73/86	86/97	71/81

^a Substrate (1 mmol), complex (1) or (2) (4 mol%), TMAO (5 mol%) and 30% H₂O₂ (2 mmol) were stirred in acetonitrile (2 mL) at room temperature.^b Yields and conversions in the presence of TMAO. The yield was calculated based on starting substrate, by using GC and with comparison of authentic samples.^c Yields and conversions in the absence of TMAO. The yield was calculated based on starting substrate, by using GC and with comparison of authentic samples.^d Selectivity(%) = sulfoxide(%) / [sulfoxide(%) + sulfone(%)].

The more experimental and theoretical studies can help us to find out how the TMAO stop the reaction at sulfoxide step.

4. Conclusion

The oxidation of sulfides to sulfoxides is described using complex (1), (2) and TMAO in the presence of 30% aqueous H₂O₂ at ambient temperature. The addition of TMAO enhances the sulfoxide selectivity and conversion. From an environmental and economic standpoint, this procedure provides a simple method for the formation of sulfoxides from sulfides.

Supplementary

Full crystallographic details are deposited with Cambridge Structural Database (CCDC No. 778308 for complex (1) and 778309 for complex (2)). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK.

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