Catalytic efficacy of an oxido-peroxido tungsten(VI) complex: synthesis, X-ray structure and oxidation of sulfides and olefins

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Catalytic efficacy of an oxido-peroxido tungsten(VI) complex: synthesis, X-ray structure and oxidation of sulfides and olefins

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An oxido-peroxido tungsten(VI) complex [WO(O$_2$)L(CH$_3$OH)] using salicylidene benzoyl hydrazine as a tridentate ONO donor Schiff base (H$_2$L) has been synthesized and characterized by elemental analysis, IR, ^{1}H NMR, molar conductance data, and single-crystal X-ray analysis. The complex was used as a catalyst for epoxidation of olefins and oxidation of sulfides. The results show that epoxides and sulfoxides were produced in high yield, turnover number, and selectivity.

Keywords: Oxido-peroxido complex; Tungsten; Olefin epoxidation; Sulfide oxidation

1. Introduction

Oxido and peroxido transition metal compounds have played an important role in oxidation of organic substrates. A variety of peroxido complexes of various metals are known to catalyze the oxidation of olefins, arenes, phenols, alcohols, phosphines, and sulfides [1–3]. The catalytic activity of peroxido metal complexes is influenced by the type of metal, the number of peroxido ligands attached to the catalyst and the nature of the remaining ligands in the coordination sphere [3–6].

Current interest in tungsten is due to the importance of the metal as an essential trace element that participates in a number of important enzymatic reactions [7]. There are a few reports on preparation and catalytic activity of oxido-peroxide tungsten(VI) complexes in oxidation reactions [8–10].

We recently reported a highly efficient method for oxidation of olefins and sulfides by using an oxido-peroxido Mo(VI) complex [MoO(O$_2$)L(CH$_3$OH)] with salicylidene benzoyl hydrazine (H$_2$L) as ligand [11]. In order to study the effect of metal on catalytic reactivity, herein we report the synthesis, characterization, and comparative catalytic activity of a new oxido-peroxide W(VI) complex [WO(O$_2$)L(CH$_3$OH)] in oxidation of olefins and sulfides under the same condition as given in our previous work (scheme 1).

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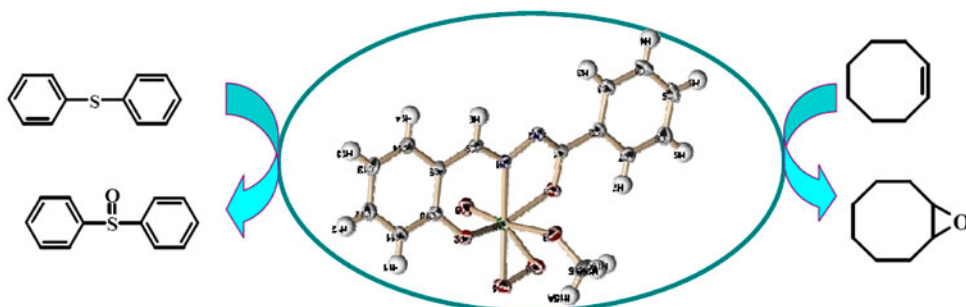
Scheme 1. Epoxidation of olefins and oxidation of sulfides in the presence of [WO(O$_2$)L(CH$_3$OH)].

2. Results and discussion

2.1. *Complex characterization*

[WO(O$_2$)L(CH$_3$OH)] can be synthesized in high yield by treating a H$_2$O$_2$ solution of freshly precipitated tungsten(VI) oxide hydrate, WO$_3$·nH$_2$O, with the Schiff base salicylidene benzoyl hydrazine.

The oxido-peroxido W(VI) complex is yellow, stable to air and light and soluble in methanol, ethanol, acetonitrile, methylene chloride, DMF, and DMSO. The analytical data for the new complex agree very well with the proposed molecular formula.

The IR spectrum shows a broad absorption at 3129 cm^{-1} attributed to $\nu_{(O-H)}$ of a methanol coordinated to tungsten and a strong absorption at 1604 cm^{-1} assigned to $\nu_{(C=N)}$ of the imine. The $\nu_{(W=O)}$ and $\nu_{(O-O)}$ bands appear, respectively, at 960 cm^{-1} and 885 cm^{-1} [8, 12].

The ^{1}H NMR spectrum of the complex has been recorded in d$_6$-DMSO. A sharp singlet for OH proton of phenolic group of the ligand at $\delta = 11.54$ ppm is absent in the complex and also a significant downfield shift ($\Delta\delta = 0.94$ ppm) of the signal for the azomethine (−CH=N−) proton in the complex relative to the corresponding ligand demonstrates the coordination through the oxygen of the deprotonated phenol and the azomethine nitrogen [11, 13]. The complex shows multiplets at δ 6.75–8.60 ppm due to the aromatic protons. Coordinated methanol displays two signals at $\delta = 3.17$ and 4.08 ppm in the ^{1}H NMR spectrum of complex [14, 15].

To confirm coordination of the Schiff base, as well as the stereochemistry of the complex, the structure has been determined by X-ray crystallography. An ORTEP view is shown in figure 1. The crystal lattice is stabilized by intermolecular hydrogen O–H…N bonds between hydrogen of coordinated methanol and N2 of Schiff base ligand from neighboring complexes to form an infinite 1-D polymeric array along the α axis (figure 2). The summary of single-crystal X-ray structure refinement is shown in table 1. The complex crystallizes in the monoclinic crystal system and space group $P2_1/c$. The structure is mononuclear, consisting of discrete monomeric units of [WO(O$_2$)(L)(CH$_3$OH)], with a distorted pentagonal-bipyramidal arrangement around tungsten. The structure shows that the ligand is coordinated to tungsten in the expected tridentate O, N, and O in addition to oxido, peroxido, and one methanol. The ligand binds the metal center at O, N, and O forming five-membered and six-membered chelate rings with a bite angle of O(1)–W(1)–N(1) = 72.15(9)° and O(2)–W(1)–N(1) = 81.44(10)° and a bond length of W(1)–O(1) = 2.013 (2) (Å), W(1)–N(1) = 2.172(2) (Å), and W(1)–O(2) = 1.967(2) (Å).
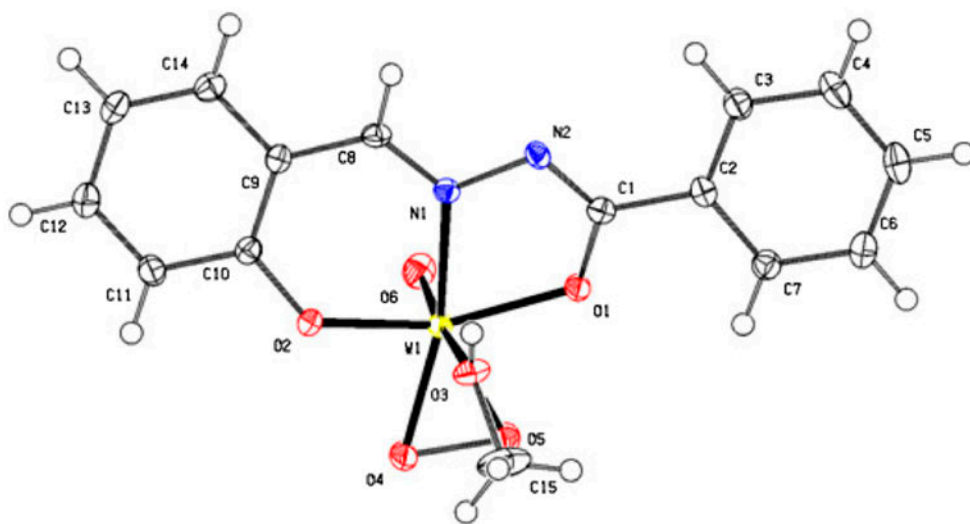
Figure 1.   ORTEP diagram of [WO(O₂)L(CH₃OH)] with thermal ellipsoids drawn at 50% probability.
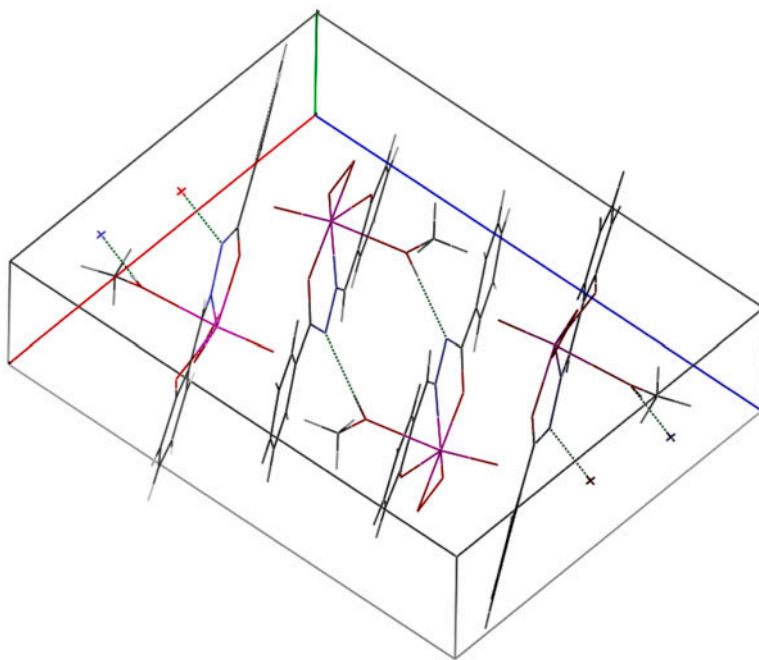

Figure 2.   Depicting intermolecular hydrogen bonded 1-D polymeric array along the *a* axis for [WO(O₂)(L) (CH₃OH)].

Table 1.   Crystal data and structure refinement for [WO(O$_2$)L(CH$_3$OH)].

Empirical formula	C$_{15}$H$_{14}$N$_2$O$_6$W
Formula weight	502.12
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P* 2$_1$/*c*
Unit cell dimensions	*a* = 10.830(8) Å, α = 90°
	b = 9.872(8) Å, β = 105.325(9)°
	c = 14.611(11) Å, γ = 90°
Volume	1507.(2) Å^3
Z	4
Density (Calcd)	2.209 Mg cm^{-3}
Absorption coefficient	7.704 mm^{-1}
F(000)	956
Crystal size	0.12 × 0.24 × 0.24 mm^3
Theta range for data collection	1.95–28.70°
Index ranges	−14 ⩽ *h* ⩽ 14, −13 ⩽ *k* ⩽ 13, −19 ⩽ *l* ⩽ 18
Reflections collected	14,336
Independent reflections	3763 [*R*(int) = 0.0433]
Completeness to θ = 28.70°	96.6%
Absorption correction	Multiscan
Max. and min. transmission	0.4583 and 0.2593
Refinement method	Full-matrix least-squares on *F*^{2}
Data/restraints/parameters	3763/0/218
Goodness-of-fit on *F*^{2}	1.095
Final *R* indices [*I* > 2sigma(*I*)]	*R*1 = 0.0228, *wR*2 = 0.0521
R indices (all data)	*R*1 = 0.0242, *wR*2 = 0.0526
Largest diff. peak and hole	2.111 and −1.653

$R_{\text{int}} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma[F_o^2]$.
$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
$\text{GOOF} = S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.
$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.
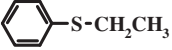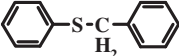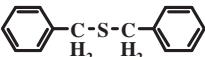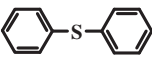$w = 1/[\sigma(F_o^2) + (aP)^2 + bP]$, where P is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$.
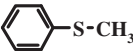
2.2. *Catalytic reactivity*

Selective oxidation of sulfides to the corresponding sulfoxides is a fundamental transformation both in laboratory synthesis and industrial production [16]. In order to compare catalytic reactivity of complex with oxido-peroxido Mo(VI) complex, we used the same optimization condition [11].

[WO(O$_2$)(L)(CH$_3$OH)] was a catalyst for the oxidation of various sulfides and olefins. A series of structurally diverse sulfides were subjected to the oxidation using the complex as catalyst and UHP as oxidant. Aliphatic and aromatic sulfides underwent clean and selective oxidation to the corresponding sulfoxide under air, in impressive yields and turnover number (TON). The results are summarized in table 2. Aromatic sulfides undergo oxidation more easily than aliphatic substrates. Significantly, the maximum selectivity of 88–100% was achieved at 81–100% of conversion for the substrates (table 2).

To gain insight into the catalytic mechanism, reaction progress was monitored using UV–vis spectrometry (figure 3). Monitoring the UV–vis spectra of the catalytic reaction mixture shows no evident changes in absorption peaks, which suggests that the oxidation state of the W(VI) moiety remains unchanged in the reaction. According to this study and also by comparison with the literature, a mechanism for oxidation of various sulfides to sulfoxides using [WO(O$_2$)L(CH$_3$OH)] was proposed (scheme 2). The reaction proceeds with nucleophilic attack of the uncoordinated sulfide on one oxygen of the peroxido,

Table 2. Oxidation of sulfides catalyzed by $[WO(O_2)L(CH_3OH)]^a$.

Substrate	Conversion (%)[b] (TON)[c]	Selectivity (%)[d]
⬡–S-CH$_3$	100 (93)	94
⬡–S-CH$_2$CH$_3$	100 (93)	92
⬡–S-C$_{H_2}$⬡	100 (93)	90
⬡–C$_{H_2}$-S-C$_{H_2}$⬡	100 (93)	88
⬡–S–⬡	100 (93)	95
CH_3CH_2–S–CH_2CH_3	81 (76)	100
$CH_3(CH_2)_2$–S–$(CH_2)_2CH_3$	83 (77)	100
$CH_3(CH_2)_7$–S–$(CH_2)_7CH_3$	83 (77)	100

[a]The molar ratios for catalyst: substrate: UHP are $1:93:167$. The reactions were performed in $70:30$ mixture of CH_3OH /CH_2Cl_2 (1.2 mL) under air at room temperature.
[b]The GC conversion (%) are measured relative to the starting sulfide after 35.25 min.
[c]TON = (mM of sulfoxide + mM of sulfone)/mM of catalyst.
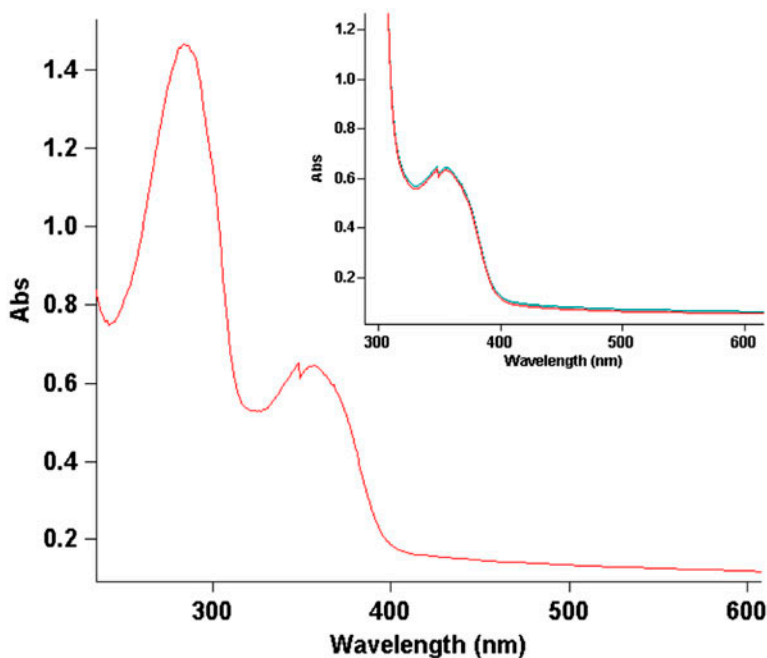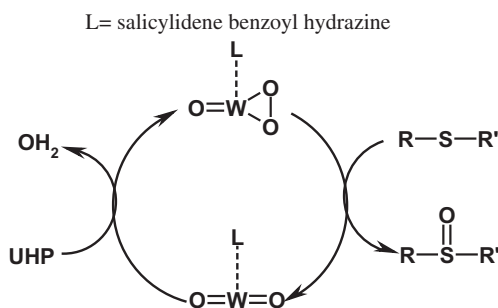[d]Selectivity to sulfoxide = (sulfoxide %/(sulfoxide % + sulfone %)) × 100.

Figure 3. UV–vis spectra of $[WO(O_2)L(CH_3OH)]$ solution (5×10^{-4} M) in $70:30$ mixture of CH_3OH/CH_2Cl_2 (1/1 v/v), Inset shows the electronic spectrum of reaction mixture (catalyst : UHP : SMe$_2$; $1:100:200$) in the same solvent which does not show any changes during the time.

L= salicylidene benzoyl hydrazine

Scheme 2. Plausible mechanism for catalytic oxidation of sulfides to sulfoxides with UHP as an oxidant.

Table 3. Catalytic oxidation of olefins catalyzed by $[WO(O_2)L(CH_3OH)]^a$.

Substrate	Product	Conversion (%)[b] (TON)[c]	Selectivity (%)[d]
		93 (277)	100
		100 (298)	100
		85 (253)	100
OH	OH	97 (289)	100
CH₃	CH₃	93 (277)	100
		100 (298)	100
		91 (271)	100
		98 (292)	100

[a]The molar ratios for catalyst: substrate: NaHCO₃ : H₂O₂ are 1 : 298 : 117 : 1170. The reactions were performed in (70 : 30) mixture of CH₃OH/CH₂Cl₂ (1.2 mL) under air at room temperature.
[b]The GC conversion (%) are measured relative to the starting olefin after 74.5 min.
[c]TON = (mM of product)/mM of catalyst.
[d]Selectivity to epoxide = (epoxide %/(epoxide % + aldehyde %)) × 100.

yielding sulfoxide and generating the related molybdenum(VI) dioxido complex. The primary catalyst is then regenerated with reaction of dioxido complex and UHP oxidant, which reenters the cycle.

The epoxidation of olefins to epoxides is a valuable transformation for organic synthesis since epoxides are highly important intermediates in the preparation of various chemically and biologically active compounds [17–19]. High-valent metal oxido-peroxido species have demonstrated the ability to catalyze the epoxidation of alkenes, via homogeneous as well as heterogeneous routes [10, 20]. Therefore, this study was further extended to the epoxidation of several different linear and cyclic olefins using the complex (table 3). The complex showed high potential and selectivity as catalyst in the epoxidation of olefins at room temperature in the presence of $NaHCO_3$ as a promoter and H_2O_2 as a terminal oxidant. Indene and cyclooctene could be almost quantitatively converted into the corresponding epoxides after a reaction time of 74.5 min. The result of catalytic studies using oxido–peroxido W(VI) catalyst reveals that the efficiency of $[WO(O_2)L(CH_3OH)]$ toward all substrates is almost the same with maximum conversion (85–100%), TON, and selectivity (100%).

The results have shown that $[MoO(O_2)(L)(CH_3OH)]$ and $[WO(O_2)(L)(CH_3OH)]$ are almost equally effective in catalysis of sulfide oxidation and epoxidation of olefins.

3. Experimental

Chemicals and solvents were purchased from Fluka and Merck Chemical companies. Salicylidene benzoyl hydrazine (H_2L) has been synthesized according to published procedure [21].

Elemental analysis (carbon, hydrogen, and nitrogen) was obtained from a Carlo ERBA Model EA 1108 analyzer. FT-IR spectrum was obtained using a Unicam Matson 1000 FT–IR spectrophotometer using KBr disks at room temperature. Molar conductance was determined in methanol (ca. 10^{-3} M) at room temperature using a Toa CM 405 conductivity meter. The ^1H NMR spectra of the complex in d_6-DMSO were obtained using a Bruker FT–NMR 500 MHZ spectrometer. The products of oxidation reactions were determined and analyzed by HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m…320 lm…0.25 lm) and flame-ionization detector.

3.1. *Preparation of [WO(O₂)L(CH₃OH)]*

An aqueous solution (10 cm^3) of $Na_2WO_4 \cdot 2H_2O$ (0.825 g, 2.5 mM) was acidified with HCl solution (6 M), and a white precipitate of $WO_3 \cdot nH_2O$ was obtained. It was filtered off and washed several times with water and ethanol. The precipitate was transferred quantitatively into a beaker and dissolved in H_2O_2 (30%, 5 cm^3) by stirring at room temperature (25 °C) to get a clear and colorless solution. Salicylidene benzoyl hydrazine (H_2L, 2.5 mM) dissolved in a minimum volume of methanol (ca. 15 cm^3) was added to the above solution with stirring (5 min), and a light-yellow solid separated out. The solid was filtered off, washed thoroughly with water, methanol, and diethyl ether, and dried in vacuo. The compound crystallized from CH_3OH to give yellow crystals. Yield 0.93 g (74%). $C_{15}H_{14}N_2O_6W$ (Mw = 502.12): Calcd C 35.05, H 2.79, N 5.62; found C 35.1, H 2.76, N 5.62.

3.2. *General procedures for epoxidation of olefins*

To a solution of olefins (0.28 mM), $NaHCO_3$ (0.11 mM), and catalyst (9.4×10^{-4} mM) in MeCN (0.5 mL) was added H_2O_2 (1.1 mM, 30% H_2O solution) as oxidant. After the

reaction was over, for products analysis, the solution was subjected to multiple ether extraction and the extract was concentrated to $0.5 \, cm^3$ by distillation in a rotary evaporator at room temperature, and then, a sample (2 μL) was taken from the solution and analyzed by GC. The retention times of the peaks were compared with those of commercial standards, and chlorobenzene was used as an internal standard for GC yield calculation.

3.3. *General procedures for oxidation of sulfides*

To a solution of sulfide (0.28 mM) and catalyst (0.003 mM) in 70 : 30 mixture of CH_3OH/CH_2Cl_2 (1.2 mL) was added urea hydrogen peroxide (UHP) (0.5 mM) as oxidant. The mixture was stirred at room temperature, and the progress of the reaction was monitored by GC by removing small samples of the reaction mixture. To establish the identity of the products unequivocally, the retention times and spectral data were compared to those of commercially available compounds using chlorobenzene as an internal standard.

4. Conclusion

We have synthesized and characterized an oxido-peroxide W(VI) complex and have used it as catalysts in olefin and sulfide oxidation. The complex is catalytically active in the oxidation of sulfides and epoxidation of olefins to their respective oxidation products under homogeneous conditions. This study affords new impetus to designing new oxido-peroxido W(VI) complexes as homogeneous oxidation catalysts.

Supplementary material

The CIF file of crystal structure of complex has been deposited with the CCDC, No. 794733. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223–336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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