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Oxoperoxo molybdenum(VI)- and tungsten(VI) complexes with 1-(2′-hydroxyphenyl) ethanone oxime: Synthesis, structure and catalytic uses in the oxidation of olefins, alcohols, sulfides and amines using H_2O_2 as a terminal oxidant

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ABSTRACT

High yield synthesis of two new oxodiperoxo-molybdate, $PPh_4[MoO(O_2)_2(HPEOH)]$ (**1**), and -tungstate, $PPh_4[WO(O_2)_2(HPEOH)]$ (**2**), complexes with 1-(2′-hydroxyphenyl) ethanone oxime ($HPEOH_2$) as organic ligand has been achieved by adding methanol solution of the ligand to the pale-yellow solution obtained by dissolving molybdic-/tungstic-acid (freshly prepared) in hydrogen peroxide and precipitating the complexes using tetraphenylphosphonium chloride. The orange-yellow complexes have been characterized by elemental analysis, IR, ^1H NMR, UV–Vis spectroscopy and finally by X-ray structure analysis. Both the complexes function as facile olefin epoxidation catalysts with hydrogen peroxide as terminal oxidant and bicarbonate as a co-catalyst at room temperature. Catalytic potentiality of **1** and **2** is also exhibited in the case of oxidation of alcohols, amines and sulfides. The catalysts are very much efficient especially in olefin epoxidation giving high yield, TON (turnover number) and TOF (turnover frequency). The method described is environmentally benign and cost-effective in all the cases.

1. Introduction

A coordinated metal center activates hydrogen peroxide rendering peroxometal complexes, which are important as intermediates in the substrate oxidation catalysis in homogeneous as well as heterogeneous mode [1]. A variety of synthesis of peroxocomplexes of various metals are known [2–4] to catalyze the oxidation of olefins, arenes, phenols, alcohols, phosphines and sulfides [5–9]. The catalytic activity of peroxometal complexes is influenced by the type of metal atom, the number of peroxo ligands attached to the catalyst and the nature of the remaining ligands in the co-ordination sphere [10–20]. In oxoperoxo chemistry of Mo and W, an important structural motif, in which two peroxo groups and a doubly bonded oxo ligand create the median $M(O_2)_2O$ (M = Mo, W) plane, is well known [21]. This core, although recognized as most stable [21] and a common motif in oxoperoxo-molybdenum and -tungsten systems, has in our experience [22], a high formation tendency no doubt, but is also a rather reactive species, which readily performs substrate oxidation, converting itself into a $MO(O_2)^{2+}$ core, which gives more stable compounds than its diperoxo analogue. A group of compounds containing an $MO(O_2)_2$ core with non-deprotonated α-amino acid ligands having the general composition $[MoO(O_2)_2(L–L′H)]$, where L–L′H = glycine, alanine, proline, valine, leucine or serine, were found to be stable at ambient temperature and behaved as stoichiometric reagents for substrate oxidation, themselves being converted to their respective mono peroxo species [23]. However, the catalytic activities of these compounds have not yet been examined [24]. Although recently it has been shown that the $MO(O_2)_2$ cores ligated with bidentate ligands are known to be extremely useful catalysts in the epoxidation of olefins [25–27] and oxidation of alcohols [22,28–31].

Epoxidation of olefins and arenes is an outstanding transformation in organic synthesis since the epoxy compounds are widely used as they are or used for the manufacturing of a wide variety of high demand commodity chemicals such as polyurethanes, unsaturated resins, glycols, surfactants and other products [32]. Out of the many ways to accomplish olefin epoxidation using transition metal compounds as catalysts [1e,33], H_2O_2 is probably the best ecologically sustainable “green” terminal oxidant [34] after dioxygen. Indeed, in certain circumstances it is better than dioxygen insofar as O_2 – organic mixtures sometimes spontaneously ignite [35]. The inaugural report of Na_2WO_4-catalyzed epoxidation of olefins with H_2O_2 as oxidant was made by Payne and Williams [36]. Venturello and coworkers [37] used their catalysts, namely, $(R_4N)_3[PO_4\{W(O)(O_2)_2\}_4]$ for epoxidation of olefins with

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H_2O_2 economy in biphasic system often involving chlorinated solvents. Efficiency of the system is not very high but is higher than the corresponding Mo catalysts, which give lower turnovers and selectivities [38]. BASF patents [39] using Mimoun-type [40] diperoxo-tungsten and -molybdenum complexes further encouraged the studies on the Mo and W catalysts in the area of olefin epoxidation. Noyori and coworkers [41] reported that a ternary system consisting of Na_2WO_4, amino methyl phosphoric acid and n-octylammonium hydrogen sulfate in the presence of H_2O_2 in a solvent-free medium behaved as a much efficient catalyst for alkene epoxidation including 1-dodecene. Kamata et al. [42] recently reported a silicotungstate compound $(Bu_4N)_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)]$ as catalyst with H_2O_2 as oxidant in the CH_3CN medium and claimed that their catalyst showed the highest efficiency among the known epoxidation catalysts [42]. In case of homogeneous molybdenum-catalyzed epoxidations alkyl hydro-peroxide is generally used since many catalysts reportedly failed to activate H_2O_2 [43]. Inspite of the high cost component of the ARCO-Halcon process for using TBHP (*tert*-butyl hydroperoxide) oxidant [44,45], the process is still in use in industries. Besides the cost factor, since alkyl hydroperoxides generate environment pollutants and global warming agents (CO_2) at slightly high temperature, replacement of TBHP by H_2O_2 as oxidant is very much warranted [46].

Reports of metal complexes in the catalytic oxidation of alcohol [47] to aldehyde/ketone and carboxylic acid, sulfide [48] to sulfoxide and sulfones, and amine [49] to nitro, nitroso and hydroxamate have appeared in the literature. Jacobson et al. [50] were one of the first to report the use of Mo and W complexes as catalysts in the oxidation of alcohols. The yields were moderate to poor with poor turnovers. Mo(VI)-peroxo compounds also catalyze the oxidation of alcohols to carbonyl compounds [51] and amides to hydroxamic acids [52,53]. Anionic Mo-peroxo complexes were used as catalysts in the oxidation of alcohols by Trost et al. [54]. The Modena group reported a series of methods in the catalytic oxidations of primary and secondary alcohols [55] and sulfides [56] using Mo-peroxo complexes of picolinic acid and picolinic acid-N-oxide with moderate to good yields. Peroxidic catalytic oxidation [57] of sulfides was also performed using heteropolyacids of Mo and W. Ishii and co workers studied the catalytic oxidation of alcohols and diols [58] as well as aromatic amines [59] using the peroxotungstatophosphate (PCWP) in the presence of 35% H_2O_2 at room temperature. Hetero and isopolytungstato lanthates (III), namely, $[Ln^{III}\{PW_{11}O_{39}\}_2]^{11-}$ and $[LnW_{10}O_{36}]^{9-}$, respectively, and the simple heteropolytungstatophosphates $[PW_{11}O_{39}]^{7-}$ have been used for the oxidation of alcohols, tertiary amines and sulfides by Griffith and co workers [60]. The same group also studied [61] the oxidation of alcohols using the polyoxotungstatothorate (IV) $Na_8[ThW_{10}O_{36}] \cdot 28H_2O$. A molybdenum–copper system [30] has been demonstrated to efficiently catalyze the oxidation of alcohols in aerobic conditions with high selectivity. Recently, bis-quaternary phosphonium salts of peroxo complexes of molybdate and tungstate have been used [62] in the oxidation of alcohols in the presence of 30% H_2O_2. In all previous attempts to oxidize the alcohols, sulfides and amines to their respective oxidation products in the presence of metal complex as catalyst, the turnover numbers were moderate to poor.

With this background we recently reported highly efficient methods for epoxidation of olefins with H_2O_2 as oxidant and $NaHCO_3$ as co-catalyst [27] and the oxidation of alcohols, sulfides, amines with H_2O_2 [22] as oxidant involving Mo and W-based catalysts. Notably, the organic ligand used by us showed almost matchless efficiency of the catalyst with respect to the yield, TON and TOF, compared to all the existing methods of olefin epoxidation was an aldoxime ligand [27a]. So in this paper we report the synthesis, spectroscopic and X-ray crystallographic structure determination of oxodiperoxo-molybdenum and -tungsten complexes with another aldoxime ligand, namely, 1-(2′-hydroxyphenyl) ethanone oxime, $HPEOH_2$, which is introduced by us for the first time as a ligand. In this ligand a steric bulk is imposed by introducing a methyl group by substituting the C–H proton of the aldoxime ligand used earlier [27a] to examine the comparative efficiency of the present complexes as catalysts with that of the former [27a]. The complexes isolated herein are $Ph_4P[MoO(O_2)_2(HPEOH)]$ (**1**) and $Ph_4P[WO(O_2)_2(HPEOH)]$ (**2**). Besides olefin epoxidation we also describe here the catalytic properties of **1** and **2**in the field of oxidation of alcohols, amines and sulfides using H_2O_2 as a terminal oxidant. However, for the olefin epoxidation reaction we have used $NaHCO_3$ as a co-catalyst as in the previous cases. Varieties of substrates of aromatic, carbocyclic and aliphatic origins have been used for the catalytic oxidation mentioned above.

2. Experimental

2.1. Materials

All synthetic works were carried out open to atmosphere. The chemicals, MoO_3, $Na_2WO_4 \cdot 2H_2O$, hydroxylamine hydrochloride were of extra pure quality and obtained from Loba Chemie (India). Hydrogen peroxide (30%, w/v), dichloromethane, *n*-hexane, acetonitrile, diethylether, isopropanol, butanol, 1-octanol, 1-dodecanol, acetone, cyclohexanol, benzaldehyde, cinnamaldehyde, p-phenylene diamine, 1,4-diaminobenzene and methanol were of analytical grade and procured from E. Marck (India). Cyclopentene, cyclohexene, cyclooctene, norbornene, 1-hexene, 2-hexen-1-ol, 1-heptene, 1-octene, 1-decene, *trans*-5-decene and 1-dodecene were the products of Sigma–Aldrich Chemie GmbH, Germany, and were directly used. Styrene, dimethyl sulfide, cinnamyl alcohol and allyl alcohol were obtained from E. Merck (Germany). The epoxides of the corresponding olefins and tetraphenylphosphonium chloride were the products of Aldrich, Germany. Sodium hydrogen carbonate, 1-(2′-hydroxyphenyl) ethanone, benzyl alcohol, phenol and sodium acetate were from Sisco research laboratories (SRL, India). Acetonitille, dichloromethane, acetone and methanol were further purified prior to use following the literature methods [63]. Ethanol (95%) was obtained from Bengal Chemical and pharmaceutical works (Calcutta) and was lime distilled before use. IOLAR II grade dioxygen, dihydrogen, zero air and dinitrogen gas used for chromatographic analysis were obtained from Indian Refrigeration Stores, Calcutta. All the solvents used for chromatographic analysis were either of HPLC-, spectroscopic-, or GR-grade.

2.2. Physical measurements

Infrared spectra were recorded as KBr pellets on Perkin–Elmer FT IR RXI spectrometer and electronic spectra on Hitachi U-3410 UV–Vis NIR spectrophotometer. Elemental analyses were performed using Carlo Erba 1108 Elemental Analyzer. W and Mo were estimated gravimetrically as WO_3 and $[MoO_2(QO)_2]$, respectively, where QOH = 8-hydroxy quinoline. Triply distilled (all glass) water was used throughout whenever necessary. GC measurements were done on an Agilent 6890N gas chromatograph using HP-1 and INNOWAX capillary column in the FID mode with dinitrogen as carrier gas.

2.3. Preparation of the ligand, 1-(2′-hydroxyphenyl) ethanone oxime

Five milliliters of 1-(2′-hydroxyphenyl) ethanone (5.65 g, 41.50 mmol) dissolved in 20 mL of methanol was added to an aqueous solution (15 mL) of hydroxylaminehydrochloride (4.33 g; 62.25 mmol). Sodium acetate (6.81 g; 83 mmol) dissolved in 20 mL of water was then added to the resulting solution and the reaction mixture was refluxed for 2 h. The solution was then cooled to room temperature and poured in a beaker containing ice and stirred vigorously to get a white precipitate. The solid obtained was filtered off and washed with ice-cold water. The same was dissolved in dichloromethane and passed through anhydrous sodium sulfate to remove traces of water. The solid was then crystallized by slow evaporation of its dichloromethane solution. Yield: 4.68 g (80%). *Anal.* Calc. for $C_8H_9O_2N$: C, 63.57; H, 5.96; N, 9.27. Found: C, 63.48; H, 6.00; N, 9.29%. IR (KBr, cm^{-1}): 3686(s), 2246(s), 1640(m), 1591(s), 1441(s), 1405(s), 1293(s), 1237(s), 1159(m), 1127(m), 1009(m), 937(m), 830(m), 742(s), 637(s), 559(w), 507(w), 438(w). ^1H NMR ($CDCl_3$, δ ppm): 2.366 (s, 3H, CH_3); 6.888–7.458 (m, 4H, aromatic protons of $HPEOH_2$); 7.769 (s, 1H from C=N–OH); 11.364 (s, 1H from phenolic OH). UV–Vis (λ_{max}/nm): 305 ($\varepsilon = 4405\ M^{-1}\ cm^{-1}$).

2.4. Preparation of $PPh_4[MoO(O_2)_2(HPEOH)]$ (**1**)

MoO_3 (1.44 g, 10 mmol) was dissolved in 30 mL of H_2O_2 (30%, w/v) by stirring at room temperature (25 °C) to get a pale yellow solution. Addition of 10 mL of a methanolic solution of 1-(2′-hydroxyphenyl) ethanone oxime (1.51 g, 10 mmol) to the above solution on stirring for 1 h produced an orange-red solution. This on treatment with PPh_4Cl (3.75 g, 10 mmol) dissolved in 10 mL of methanol yielded an orange-yellow solid. The solid was filtered off and washed with water under suction and finally washed with diethyl ether, and dried *in vacuo*. Yield: 5.98 g (90%). The compound is soluble in acetonitrile, acetone, dichloromethane, chloroform, methanol and ethanol, but insoluble in water, diethyl ether, benzene and toluene. The crude (1 g, 1.5 mmol) was crystallized from dichloromethane–hexane (1:1) mixture to get **1** (0.95 g) as an orange-yellow crystal (Yield: 95% of the crude). *Anal.* Calc. for $C_{32}H_{28}O_7NPMo$: C, 57.74; H, 4.21; N, 2.11; Mo, 14.43; P, 4.66. Found: C, 57.57; H, 4.41; N, 2.34; Mo, 14.23; P, 4.46%. IR (KBr, cm^{-1}) 3240(b), 1650(w), 1600(m) 1470(m), 1445(s), 1300(m), 1250(m), 1110(s), 1000(s), 945(s), 845(s), 755(m), 720(s), 690(m), 640(m), 570(w), 520(s). UV–Vis (λ_{max}/nm): 310 ($\varepsilon = 4538\ M^{-1}\ cm^{-1}$). ^1H NMR ($CDCl_3$, δ ppm): 2.08 (s, 3H, CH_3); 6.77–7.89 (m, 20H, PPh_4 and 4H, aromatic protons of HPEOH); 9.04 (s, 1H from C=N–OH).

2.5. Preparation of $PPh_4[WO(O_2)_2(HPEOH)]$ (**2**)

$Na_2WO_4.2H_2O$ (3.30 g, 10 mmol), dissolved in 2 mL of water, was acidified with 6(M) HCl until a complete white precipitate of H_2WO_4 was obtained. It was filtered off and washed several times with water. The precipitate was dissolved in 30 mL of H_2O_2 (30%, w/v) by stirring at room temperature (25 °C) until a clear and colourless solution was obtained. 1-(2′-hydroxyphenyl) ethanone oxime (1.51 g; 10 mmol) was added to the above solution and stirred until an orange-red colour developed. PPh_4Cl (3.75 g, 10 mmol) dissolved in 10 mL of methanol was added to the above solution when an orange-yellow solid separated, which was filtered off and washed with water under suction, and finally washed with diethyl ether, and dried in vacuo. Yield: 6.85 g (91%) The solubility of this compound is the same as that of **1**. The crude (1 g, 1.3 mmol) was crystallized from dichloromethane–hexane (1:1) mixture to get orange-yellow crystals. Yield: 0.96 g (96% of the crude). *Anal.* Calc. for $C_{32}H_{28}O_7NPW$: C, 50.90; H, 3.70; N, 1.80; W, 24.42; P, 4.11. Found: C, 51.05; H, 3.79; N, 1.53; W, 24.32; P, 4.10%. IR (KBr, cm^{-1}) 3260(b), 1600(m) 1470(w), 1445(s), 1300(m), 1260(m), 1120(s), 1000(m), 955(s), 830(s), 760(m), 720(s), 670(m), 630(m), 560(w), 520(s). UV–Vis (λ_{max}/nm): 309 ($\varepsilon = 3304\ M^{-1}\ cm^{-1}$). ^1H NMR ($CDCl_3$, δ ppm): 2.22 (s, 3H, CH_3); 6.79–7.86 (m, 20H, PPh_4 and 4H, due to aromatic protons of HPEOH); 9.35 (s, H from C=N–OH).

2.6. X-ray crystallographic data collection and refinement

Single crystals of **1** and **2** suitable for X-ray structure analyses were obtained from dichloromethane and hexane (1:1) solvent mixture. Their diffraction data for **1** and **2** were collected at 295 K on a Bruker SMART-CCD diffractometer (graphite monochromated MoKα-radiation). Relevant crystal data, data collection, and structure refinement parameters are summarized in Table 1. The structures of both complexes were solved by Direct methods with SHELXS-97 [64] and refined using full-matrix least squares on F^2 by SHELXL-97 [64]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed geometrically and treated as riding.

2.7. Experimental procedure of epoxidation and isolation of products

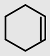
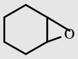
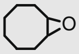
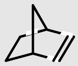
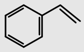
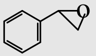
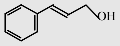
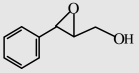
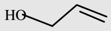
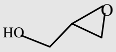
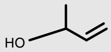
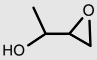
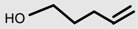
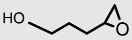
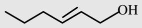
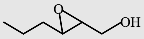
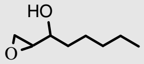
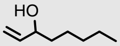
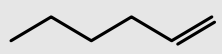
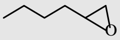
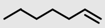
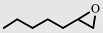
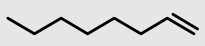
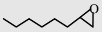
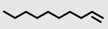
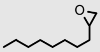
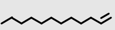
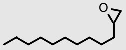
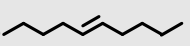
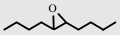
The experimental procedure for the epoxidation of olefins involving a wide variety of substrates is described as follows: an acetonitrile (~10 mL) solution {in some cases, namely, the entries 16–18, a solution of acetonitrile and acetone (3:2 volume ratio) was used} containing a given substrate (ca. 10 mmol), $NaHCO_3$ (2.50 mmol), catalyst **1** or **2** (0.01–0.001 mmol; see Table 2) and 30% H_2O_2 (3.4–6.8 mL; 30–60 mmol) was taken in a flat-bottomed two-neck reaction flask with one neck fitted with a reflux condensor (to check evaporation), the other neck being closed with a septum. The resulting reaction mixture was stirred at 25 °C (in some cases at 40 °C) for a definite period as quoted in Table 2. As and when required an aliquot of the reaction solution was withdrawn from, and H_2O_2 added to, the contents of the flask with the help of a syringe through the septum. Periodically 0.5 mL of the reaction solution was pipetted out (micro pipette) and then subjected to multiple ether extraction, and the extract was also concentrated up to 0.5 mL from which 1 μL solution was withdrawn with the

Table 1
Crystallographic data and structure refinement details for **1** and **2**

Compound	1	2
Empirical formula	$C_{32}H_{28}NO_7PMo$	$C_{32}H_{28}NO_7PW$
Molecular weight (g mol^{-1})	665.46	753.37
Crystal colour	orange–yellow	orange–yellow
Crystal system	Triclinic	Triclinic
T (K)	293(2)	293(2)
Wavelength	0.71073	0.71073
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.010(2)	10.033(2)
b (Å)	10.416(3)	10.416(2)
c (Å)	14.439(5)	14.385(3)
α (°)	83.70(3)	83.55(2)
β (°)	79.83(2)	80.11(2)
γ (°)	82.06(2)	81.99(2)
V (Å^3)	1462(1)	1461(1)
Z	2	2
D_{Calc} (mg m^{-3})	1.512	1.713
$F(000)$	680	744
Scan type	multi-scan	multi-scan
2θ Range (°)	2.88–49.94	2.88–49.98
Reflections collected	5090	5120
Reflections unique	3945	4586
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
hkl Range	$0 \leqslant h \leqslant 11$ $-12 \leqslant k \leqslant 12$ $-16 \leqslant l \leqslant 17$	$0 \leqslant h \leqslant 11$ $-12 \leqslant k \leqslant 12$ $-16 \leqslant l \leqslant 17$
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0448$; $WR_2 = 0.0984$	$R_1 = 0.0307$; $WR_2 = 0.0724$
R indices (all data)	$R_1 = 0.0665$; $WR_2 = 0.1075$	$R_1 = 0.0384$; $WR_2 = 0.0872$
Goodness-of-fit (GOF) on F^2	1.034	1.114
Largest difference peak and hole (e Å^{-3})	1.36 and −0.45	1.43 and −0.85

Table 2
Details of the catalytic epoxidation of olefinic compounds using the Mo- and W-catalysts

$$\text{Olefin} \xrightarrow[\text{3 - 6 eq.} H_2O_2,\ \text{25mol\%}\ NaHCO_3,\ \text{rt}^a]{PPh_4[MO(O_2)_2(EOPH)],\ (M = Mo, W),\ \text{Acetonitrole}} \text{Epoxide}$$

Entry	Substrate	Product[b]	Time	Percentage conversion[c,d]	Percentage yield		Yield percentage[f]	TON[g] (TOF)[h]
					GC[e]	isolated		
1			10 min	91	91		30	4550 (27 300)[i]
			[10 min	91	91		30	4550 (27 300)][i,j]
2			1 h	99	99		27	1980(1980)
			[1 h	96	96		27	1920 (1920)][j]
3			70 min	96	96	88	50	3840 (3291)
			[70 min	95	95	85	50	3800 (3257)][j]
4			30 min	98	98	92	41	9800 (19 600)[i]
			[30 min	96	96	89	41	9600 (19 200)][i,j]
5			5 h	90	90		36	1800 (360)
			[4 h	90	90		29	1800 (450)][j]
6			5 h	70	70	62	40	2800 (560)
			[4.5 h	67	67	57	35	2680 (595)][j]
7			3 h	90	90		70	3600 (1200)
			[2.25 h	90	90		44	3600 (1600)][j]
8			3 h	87	87		55	3480(1160)
			[3 h	80	80		55	3200 (1066)][j]
9			3.25 h	97	97		60	3880(1193)
			[3 h	98	98		50	3920 (1306)][j]
10			90 min	99	99		50	3960 (2640)
			[70 min	98	98		35	3920 (3360)][j]
[a]11			75 min	91	91	85	45	1820(1456)
			[45 min	95	95	88	45	1900 (2533)][i,j]
[a]12			2.25 h	97	97		45	1940 (862)
			[2 h	95	95		36	1900 (950)][j]
13			3 h	96	96		45	1920 (640)
			[3 h	99	99		45	1980 (660)][j]
[a]14	[a]14 		2.5 h	96	96		50	1920 (768)
			[1.75 h	98	98		42	1960(1120)][j]
[a]15	[a]15 		2.5 h	95	95		45	1900 (760)
			[2.25 h	99	99		40	1980 (880)][j]
[a]16	[a]16 		3 h	91	91		40	910(303)
			[2.5 h	99	99		34	990 (396)][j]
[a]17	[a]17 		3 h	90	90	82	20	900 (300)
			[2.5 h	96	96	90	16	960[(384)][j]
[a]18	[a]18 		1.5 h	99	99	86	22	990 (660)
			[80 min	95	95	84	16	950(712)][j]

[a] For entries 11, 12, 14–18, the reaction temperature is 40 °C.

[b] Selectivity = 100%.

[c] A control experiments (omission of catalysts **1** and **2** as well as HCO_3^-) does not show any conversion to epoxide or other probable products.

[d] Omission of only the bicarbonate shows a gross conversion of the 60–70% in each case in the same condition.

[e] The detailed calculation of GC yield is given as Supplementary material.

[f] This is the yield of control experiment, excluding the catalysts, but not $NaHCO_3$ which remains in the reaction solution at the same 25 mol% concentration. When the control experiment uses $NaHCO_3$ at a catalytic concentration the conversion and yield percentage become negligible.

[g] TON = ratio of moles of product (here epoxide) obtained to the moles of catalyst used.

[h] The corresponding TOFs (TON h^{-1}) are shown in parentheses.

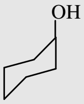
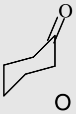
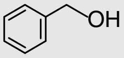
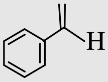
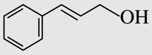
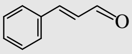
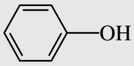
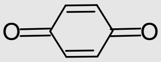
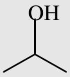
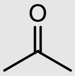
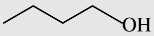
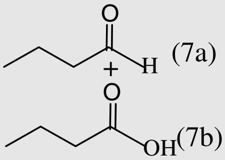
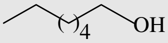
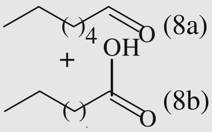
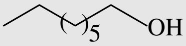
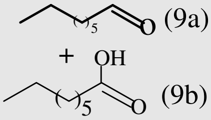
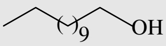
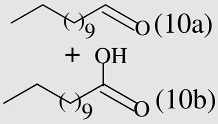
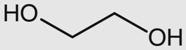
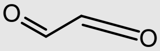
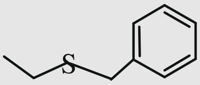
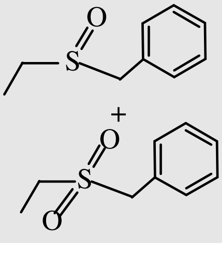
[i] Values extrapolated.

[j] The results for M = W are included within [ ]. The mole ratio of catalyst: substrate = 1:10000 (for entry 4), 5000 (for entry 1), 4000 (for entries 3 and 6–10), 2000 (for entries 2, 5, 11–15), 1000 (for entries 16–18). For entries 16, 17 and 18, acetonitrile and acetone solvent mixtures were used in 2:1 volume ratio.

help of a gas syringe and injected into the GC port. The retention times of the peaks were compared with those of commercial standards and for GC yield calculation nitrobenzene was used as an internal standard. For few cases, especially for olefinic alcohols, the identity of the product was confirmed by GC–MS analysis. The isolated yield for selected substrates (Table 2) was obtained by multiple ether extraction of the reaction solution after the reaction was over (known from GC results) and then evaporating the ether and acetonitrile by distilling at a mildly reduced pressure (using water aspirator) and kept over P_2O_5 in a desiccator and weighed in a micro-balance. The identity of the products was confirmed by IR and NMR probing. This method is applicable only when the yield of the product is 98–100%, but for lower yield percentage the reaction solution was subjected to preparative TLC and the highly intense spot was cut out and plunged in CH_2Cl_2 which serves as an eluant, and then the resulting solution was dried over $MgSO_4$, filtered through a short silica gel pad and finally evaporated to dryness to yield only the epoxide as residue. The residue was kept over P_2O_5 for 15 min and weighed. In cases where the epoxide separated as solid during concentration, the same

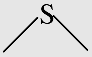
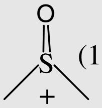
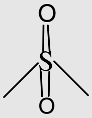
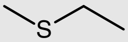
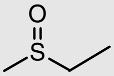
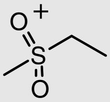
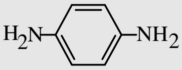
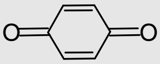
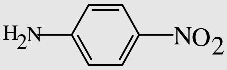
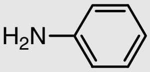
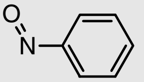
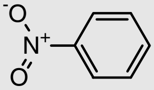
Table 3
Catalytic oxidation of various alcohols, sulfides and amines in refluxing acetonitrile (78 °C) using **1** and **2** as catalysts and H_2O_2 as oxidant

$$\text{Alcohols/Sulphides/amines} \xrightarrow[\text{CH}_3\text{CN, H}_2\text{O}_2\text{ (4 - 6 eqv.), at refluxing condition}]{\text{PPh}_4[\text{MO(O}_2)_2\text{(EOPH)], M = Mo \& W (0.1\%)}} \text{Products}$$

Entry	Substrate	Time (h)	Product	Percentage yield[a]		TON[b]	
				1	**2**	**1**	2
1		24		81	85	810	850
2		24		63	65	630	650
3		24		89	92	890	920
4		5		98	99	980	990
5	CH_3OH	16	HCHO (5a) + HCOOH (5b)	44 + 35	46 + 33	440 + 350	460 + 330
6		20		93	97	930	970
7		15		60 + 20	67 + 24	600 + 200	570 + 240
8		22		46 + 25	48 + 28	460 + 250	480 + 280
9		22		62 + 15	64 + 16	620 + 150	640 + 160
10		30		80 + 2	83 + 3	800 + 20	830 + 30
11		11		88	91	880	910
12		1		4 + 96	5 + 95	40 + 960	50 + 950

(continued on next page)

Table 3 (*continued*)

Entry	Substrate	Time (h)	Product	Percentage yield[a]		TON[b]	
				1	**2**	**1**	2
13		1	 (13a) +  (13b)	4 + 96	3 + 97	40 +960	30 + 970
14		1	 (14a) +  (14b)	96 + 4	94 + 6	960 + 40	940 + 60
15		6	 (15a) +  (15b)	54 + 30	60 + 32	540 + 300	600 + 320
16		7	 (16a) +  (16b)	78 + 18	79 + 19	780 + 180	790 + 190

[a] Based on substrate concentration.

[b] Turnover number (TON) is defined as a ratio of the moles of product obtained to the moles of catalyst used.

was filtered off, washed, vacuum dried and weighed in a microbalance.

2.8. Experimental procedure for the oxidation of alcohols, amines and sulfides

Alcohols, amines and sulfides (25.0 mmol) were separately weighed and put in a 50 mL two-neck flask and dissolved in 10 mL CH_3CN and catalyst **1** or **2** (0.025 mmol, 0.1 mol%) was added separately to each and every substrate. The resulting solutions were then separately treated with 30% H_2O_2 (in total 11.3 mL; 100 mmol; 400 mol%; 4 equiv. with respect to substrates) portion-wise throughout the entire time span and the reaction mixtures were separately refluxed for a period given in Table 3. The refluxing solutions were periodically cooled and an aliquot was taken out and treated as in the case of olefin substrates for gas chromatographic analysis at regular intervals.

For the isolated yield, the solvent (CH_3CN) was distilled out and the residual liquid (water from H_2O_2) was shaken with CH_2Cl_2 (5 mL) in a separatory funnel when the aqueous and organic layers separated and the latter was taken out with the help of a dropper and the aqueous layer was repeatedly (3–4 times) washed with CH_2Cl_2. The washings were mixed with the organic extract and the solution mixture (organic) was distilled out and the left residue was extracted with ether. From the ether extract the respective oxidized products were isolated and characterized as described below.

(1) Carbonyl compounds were isolated as their respective yellow-orange 2,4-dinitrophenyl hydrazone derivatives and the respective carbonyl compounds were generated from the derivatives by acid hydrolysis. The purity of the DNP derivatives was checked by the integration of the respective ^{1}H NMR spectrum in each case. (2) The reaction solutions supposed to contain carboxylic acid were treated with aqueous $NaHCO_3$, and the aqueous layer was concentrated and allowed to stand for 30 min. when the corresponding acids were isolated as their colourless Na-salts. (3) The sulfones were crystallized out as solids on concentrating the aqueous layer while the unreacted sulfides and sulfoxides remained in the CH_2Cl_2 layer. The materials in the CH_2Cl_2 layer were separated by fractional distillation. (4) 1,4-Benzoquinone (from phenol) (see Table 3) was extracted out from the reaction solution by diethylether and evaporation of ether deposits the off-white material. (5) The mixture of products, 1,4-benzoquinone and 4-nitroaniline obtained from 1,4-diaminobenzene, was separated by steam distillation since the quinone is steam volatile. (6) Other amines and their oxidized products were separated by column chromatography and their identities were checked by NMR spectroscopy. It may be mentioned that for all the above procedures the amount of products

separated corresponds with the GC results (see also Table 3), but with slightly lower yield.

2.9. Recovery of catalyst

The residue left after distilling ether and acetonitrile at mildly reduced pressure was thoroughly shaken with diethyl ether repeatedly in which each of the substrates and the products was almost quantitatively extracted. The orange-yellow solid residue left was the catalyst as verified by IR spectroscopy.

3. Results and discussion

3.1. Synthetic aspect and general characterization

Complexes **1** and **2** were synthesized by dissolving MoO_3 or H_2WO_4 (freshly precipitated) in H_2O_2 and treating the resulting solution with 1-(2′-hydroxyphenyl) ethanone oxime dissolved in methanol, followed by addition of methanol solution of tetraphenylphosphonium chloride. The complexes are air stable. The molar conductance of complexes **1** and **2** are 123 and 125 Ohm^{-1} cm^2 mol^{-1} indicating that the complexes behave as 1:1 electrolyte [65]. The vibration arising at 3686 cm^{-1} is due to the presence of the OH function in –C═N–OH moiety, in the case of free ligand. In the case of **1** and **2**, the said vibration undergoes a downward shift to 3240 of **1** and to 3260 of **2** after complexation. The peak arising at 2246 cm^{-1}, due to the presence of phenolic OH, in $HPEOH_2$ disappears in **1** and **2** due to deprotonation of phenolic OH before the O → M bond formation. The peak arising at 1600 cm^{-1} in both **1** and **2** is due to the coordinated C═N vibration, arising from downshifting of the 1640 cm^{-1} vibration in the free ligand. The ν (M═O) vibration appears as a strong bond at 945 and 955 cm^{-1} in **1** and **2**, respectively. The ν (O–O) vibration appears as an intense band at 845 (**1**) and 830 cm^{-1} (**2**). A medium to weak intensity band in the region of 640 and 570 cm^{-1} in case of **1** and 630 and 560 cm^{-1} in case of **2** are assignable to asymmetric and symmetric vibrations, respectively of the MO_2 triangle formed from terminally coordinated $O_2{}^{2-}$ ligand [66]. The vibration appearing at 1445, 1110, 1000, 755, 720, 690 and 520 cm^{-1} in case

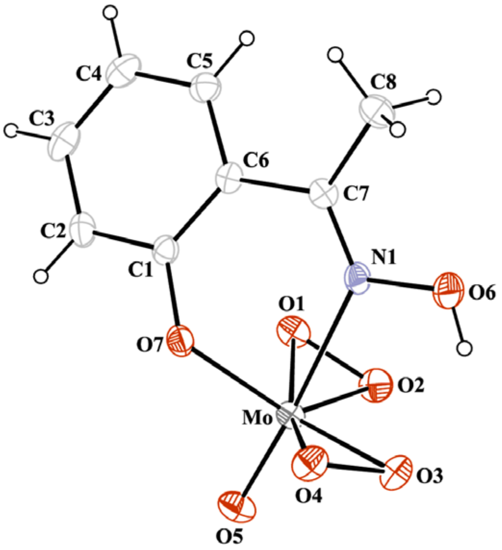


Fig. 1. An ORTEP view of anionic part of complex **1**.

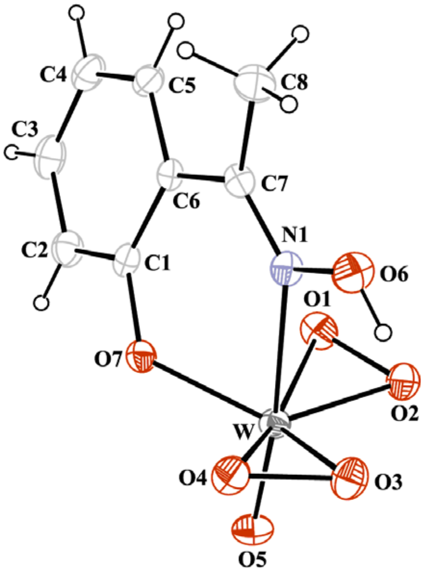


Fig. 2. An ORTEP view of anionic part of complex **2**.

Table 4
Selected bond lengths (Å) and angles (°) for **1** and **2**

Bond lengths	**1** (**M = Mo**)	**2** (**M=W**)
M–O7	1.979 (3)	1.968(4)
M–O4	1.967 (3)	1.962(4)
M–O3	1.941 (3)	1.937(5)
M–O2	1.916 (3)	1.907(4)
M–O1	1.944 (3)	1.941(5)
M–O5	1.673 (3)	1.694(4)
M–N1	2.396 (3)	2.377 (5)
Bond angles	**1**	**2**
O7–M–O4	89.2 (1)	89.1 (2)
O7–M–O3	130.7 (1)	131.4 (2)
O7–M–O2	128.5 (1)	129.0 (2)
O7–M–O1	85.5 (1)	85.5 (2)
O7–M–O5	100.1 (1)	99.8 (2)
O7–M–N1	74.8 (1)	75.1 (2)
O4–M–O3	44.4 (1)	45.0 (2)
O4–M–O2	131.0 (1)	131.4 (2)
O4–M–O1	158.0 (1)	158.4 (2)
O4–M–O5	98.8 (1)	98.7 (2)
O4–M–N1	77.1 (1)	77.0 (2)
O3–M–O2	87.8 (1)	87.6 (2)
O3–M–O1	129.7 (1)	129.9 (2)
O3–M–O5	102.6 (1)	102.0 (2)
O3–M–N1	78.3 (1)	78.7 (2)
O2–M–O1	44.5 (1)	44.9 (2)
O2–M–O5	102.7 (1)	102.2 (2)
O2–M–N1	83.9 (1)	84.6 (2)
O1–M–O5	103.2 (1)	102.8 (2)
O1–M–N1	80.9 (1)	81.5 (2)
O5–M–N1	173.3 (1)	173.2 (2)

Table 5
Hydrogen bonding geometry (Å, °) in **1**

D–H· · ·A	D–H	H· · ·A	D· · ·A	D–H· · ·A
O6–H6A· · ·O3	0.82	2.06	2.709(5)	135.2(3)
C5–H5· · ·O1^{i}	0.93	2.53	3.438(6)	163.4(3)
C3–H3· · ·O3^{ii}	0.93	2.49	3.416(7)	171.9(3)
C12–H12· · ·O7^{iii}	0.93	2.63	3.235(5)	123.4(3)
C19–H19· · ·O4^{iv}	0.93	2.53	3.346(6)	147.1(3)
C23–H23· · ·O5^{v}	0.93	2.60	3.236(7)	126.1(3)
C25–H25· · ·O4^{vi}	0.93	2.67	3.387(7)	134.2(3)
C29–H29· · ·O2^{vii}	0.93	2.55	3.408(6)	154.0(3)

Symmetry codes: (i) $-x+1, -y, -z$; (ii) $x+1, +y, +z$; (iii) $-x, -y, -z+1$; (iv) $x-1, +y+1, +z$; (v) $-x, -y+1, -z+1$; (vi) $x, +y+1, +z$; (vii) $-x, -y+1, -z$.

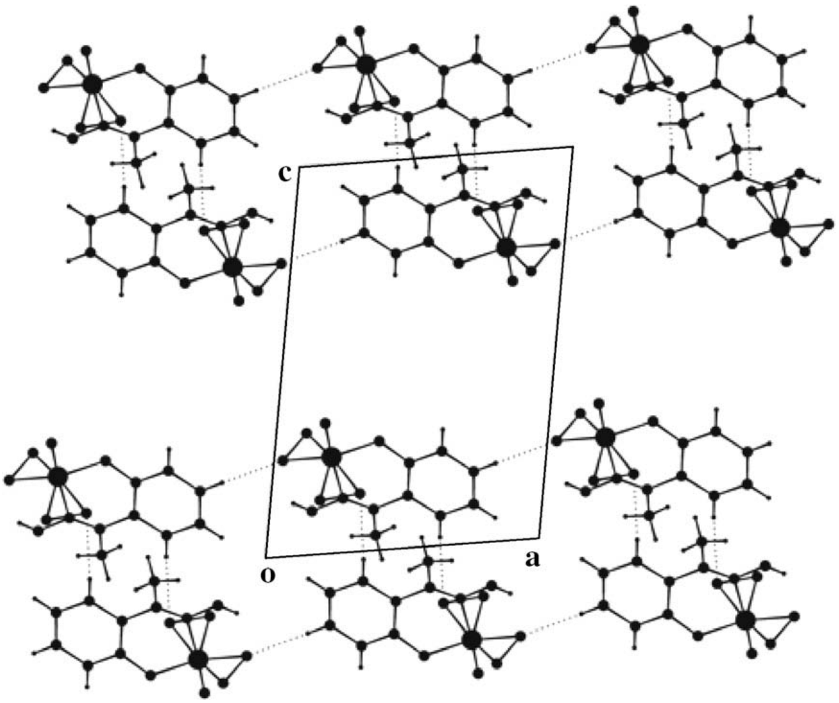


Fig. 3. Packing diagram of complex (**1**) showing the formation of two-dimensional network.

Table 6
Hydrogen bonding geometry (Å, °) in **2**

D–H···A	D···H	H···A	D···A	D–H···A
O6–H6A···O3	0.82	2.07	2.700(5)	134.4(4)
C3–H3···O3^{i}	0.93	2.48	3.409(5)	175.0(5)
C5–H5···O1^{ii}	0.93	2.50	3.406(4)	163.6(4)
C19–H19···O4^{iii}	0.93	2.52	3.339(6)	146.3(5)
C29–H29···O2^{iv}	0.93	2.53	3.393(5)	153.9(5)
C23–H23···O5^{v}	0.93	2.58	3.237(5)	128.3(5)
C25–H25···O4^{vi}	0.93	2.62	3.363(4)	136.6(5)

Symmetry codes: (i) $x+1, +y, +z$; (ii) $-x+1, -y, -z$; (iii) $-x+1, -y-1, -z+1$; (iv) $x, y-1, z+1$; (v) $x, y-1, z$; (vi) $-x, -y-1, -z+1$.

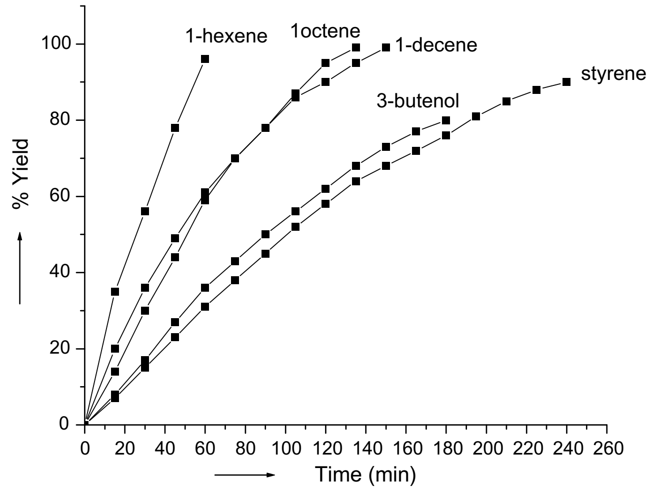


Fig. 4. Plot of percentage yield vs. time using **2** as catalyst keeping all other parameters same as in Table 2 for the oxidation of styrene, 3- butenol, 1-octene, 1- decene and 1-hexene.

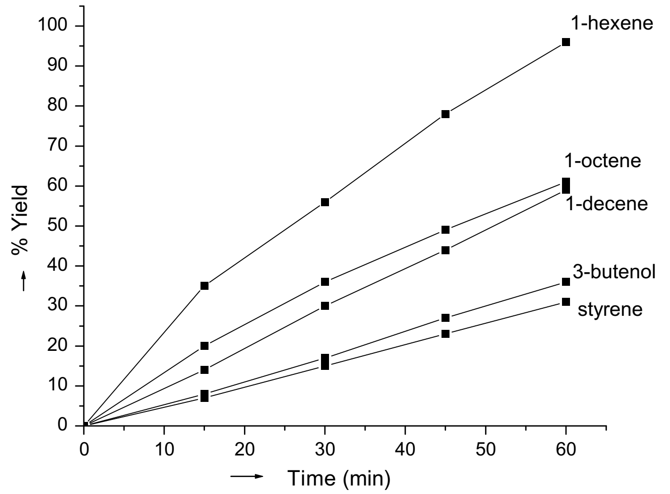


Fig. 5. Plot of percentage yield vs. time selecting the linear portions of each of the corresponding curve shown in Fig. 4.

of **1** and 1445, 1120, 1000, 760, 720, 690 and 520 cm^{-1} in case of **2** are due to the Ph_4P^+ ion. The HPEOH$^-$ → M (VI) LMCT transition in **1** (310 nm) as well as in **2** (309 nm) occurs almost at the same wavelength. No other peak appears in the UV–Vis spectrum in both the complexes. The ^{1}H NMR signals arising at 9.04 and 9.35 ppm in **1** and **2**, respectively, is assignable to the N-coordinated C=N–OH proton. In the case of free ligand this peak arises at 7.76 ppm. This large positional shift of the OH protons of the C=N–OH moiety on coordination is due to the high order of deshielding of the proton owing to the combined effect of metal complexation and hydrogen binding between the OH proton and peroxo moiety present in the metal complexes. The peak at 11.36 ppm is observed in the free ligands, but disappears in both **1** and **2**. This is due to the deproto-

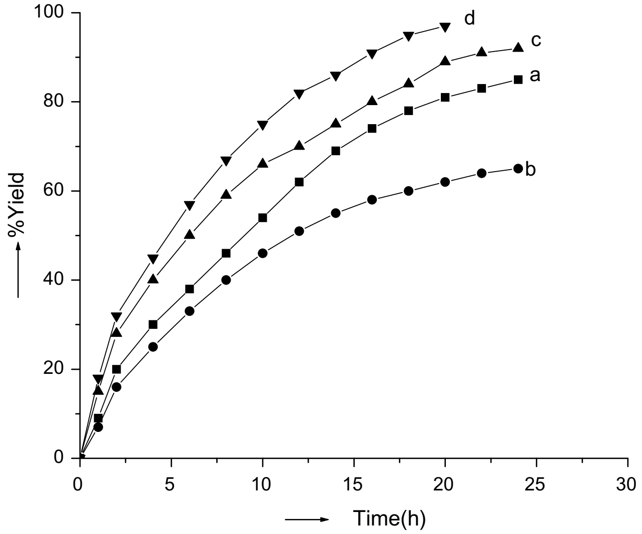


Fig. 6. Plot of yield (based on amount of substrate) versus time for the conversion of (a) cyclohexanol to cyclohexanone, (b) benzyl alcohol to benzaldehyde, (c) cinnamyl alcohol to cinnamaldehyde, (d) isopropanol to isopropanone using **2** as catalyst.

nation of the phenolic OH group on coordination. (All the three UV–Vis and NMR spectra are included as Fig. S1 as supplementary material.)

*3.2. Description of the molecular structure of complex **1** and complex **2***

Crystal structures of complexes **1** and **2** consist of discrete monomeric anions, $[MO(O_2)_2(HPEOH)]^-$, (M = Mo in **1** and W in **2**, HPEOH = 1-(2′-hydroxyphenyl) ethanone oximate), and tetraphenylphosphonium, $[PPh_4]^+$ cations (see Figs. 1 and 2 for the ORTEP [67] view). The close similarity between the crystallographic parameters, e.g., unit cell dimensions, space group, atomic coordinates, crystal packing of **1** and **2** indicates that the complexes are isostructural and subsequent discussions relating to complex **1** are also applicable to complex **2**. The coordination geometry around the metal atom can be best described as pentagonal bipyramidal with the axial sites being occupied by the nitrogen (N1) and the oxo (O5) ligands. The phenolate oxygen (O7) and the peroxo moieties (O1, O2 and O3, O4) define the equatorial plane with the Mo atom displaced by −0.374(1) Å [−0.369(1) Å for the W atom in **2**] from the equatorial plane towards the oxo-oxygen (O5). This is consistent with the observations in oxodiperoxo molybdenum(VI)- and tungsten(VI) complexes which generally feature the metal atom coordinated to the oxo-group in the axial position and the two peroxide ligands bound in the equatorial positions [3]. The chelated 1-(2′-hydroxyphenyl) ethanone oxime ligand fragment (C1–C7, N1, O6, O7), excluding the methyl group (C8), is essentially planar (r. m. s. deviation 0.110 Å for complex **1** and 0.106 Å for complex **2**) and is approximately orthogonal to the equatorial plane (O1–O4, O7); the dihedral angle between the two planes is 86.6(1)° in **1** [87.3(1)° in **2**]. Selected bond distances and angles for **1** and **2** (Table 4) correspond well to those of other seven coordinate Mo and W oxoperoxo complexes [31]. The lengthening of the Mo–N1 [2.397(3) Å] and W–N1 [2.377(5) Å] distances in **1** and **2** compared to the Mo–N [2.194(3)–2.269(3) Å] and W–N [2.264(6)–2.273(6) Å] bond lengths in complexes [68] where the ligand nitrogen atoms coordinate the metal center equatorially reflects the strong trans influence of the oxo ligand [69].

Similarity of the crystallographic parameters, i.e. unit cell, space group, and closely related crystal packing of **1** and **2** indicates possible isostructurality between them. Three isostructural parameters i.e. π (cell parameters isostructurality index), $I_i(n)$ (coordinates isostructurality index) and I_v (volume isostructurality index) were calculated for the structures 1 and 2 following the procedure described by Fábián et al. [70]. The obtained parameters [$\pi = 0.003$; $I_i = 85.5\%$, $I_v = 97.6$] reveal a high degree of isostructurality between the complexes.

The crystal packing arrangements in the structures exhibit several intermolecular C–H···O hydrogen bonds between the anions, and the cations and the anions (Table 5). The 1-(2′-hydroxyphenyl) ethanone oxime carbon atom C3 at (*x*, *y*, *z*) is hydrogen bonded to peroxo O3 atom at (1 + *x*, *y*, *z*) producing infinite one-dimensional parallel chains propagating along [1 0 0] direction. Adjacent anionic chains are further linked, where C5 atom at (*x*, *y*, *z*) is hydrogen bonded to peroxo O1 atom (1 − *x*, −*y*, −*z*) generating a two-dimensional network in the (1 0 1) plane (Fig. 3). Additional intermolecular C–H···O hydrogen bonds involving the carbon atoms of the tetraphenylphosphonium cations and oxygen atoms of the anions stabilize the molecular structures for both complexes (Table 6).

*3.3. Summary of the results of catalytic oxidation by **1** and **2***

The complexes show good catalytic activities in peroxidic oxidation of various olefins, alcohols, sulfides to their corresponding epoxides (Table 2), aldehydes or ketones, sulfoxides and sulfones (Table 3). Table 3 also shows the mixture of oxidized products obtained by amine oxidation.

Using **2** as a representative catalyst, $NaHCO_3$ (0.25 equiv.) as cocatalyst and H_2O_2 as terminal oxidant, a plot of percentage yield versus time for the oxidation of some representative substrates, namely, 1-hexene (entry 13), 1-octene (entry 15), styrene (entry 5), 3-buten-2-ol (entry 8), 1-decene (entry 16) is presented in Fig. 4, where each curve maintains a gross linearity up to 1 h time span but thereafter deviate from linearity showing a slow reaction rate. Plot of percentage yield versus time selecting the linear portions of the corresponding curves is presented in Fig. 5, which shows that the initial rate of the reaction (up to 1 h) follows a first-order kinetics and hence the TOF rightly has the unit, h^{-1}, in the case of olefin epoxidation. However, the selectivity in olefin oxidation is not shown for alcohol oxidation especially in the cases of aliphatic alcohols. Lack of selectivity in the case of aliphatic alcohols is due to the fact that only in the aromatic case resonance stabilization of C═O bond makes it reasonably immune against attack by necleophiles [71,72] (here O_2^{2-}). Actually, so long as there is a remarkable concentration of H_2O_2, the aromatic aldehydes formed are not oxidized to their corresponding acids. It is observed that with increase in chain length of the aliphatic alcohols the rate of catalytic oxidation decreases and the aldehyde is exclusively obtained from *n*-dodecanol (entry 10). The conversion of $CH_3OH \rightarrow HCHO$ is very much important for the industrial and pharmacological use of formaldehyde.

Notably, oxidation of 1,4-diaminobenzene (entry 15) to quinone is industrially important, though the simultaneous production of *p*-nitroaniline is interesting from reactivity standpoint. A reduction in the time of reflux increases the proportion of *p*-nitroaniline produced. The same was found to occur in case of aniline (entry 16) where also a reduction in the time of reflux increases the proportion of nitroso benzene. The oxidation of dimethyl sulfide (entry 13) to dimethyl sulfone goes via a dimethyl sulfoxide intermediate. If the time of reflux and amount of peroxide are reduced, it is possible to get a selective and quantitative yield of DMSO and the same observations were noticed for the other two sulfides (entries 12 and 14). Among the three sulfides, dimethyl sulfide and methyl benzyl sulfide rapidly convert to sulfone. So in these two cases if time and peroxide concentration are reduced, it is possible to get their sulfoxide products with high yield.

As shown in Table 4 it is apparent that tungsten complex **2** is more efficient catalyst than that of the analogous molybdenum complex **1**. A plot of percentage yield versus time for the oxidation of some representative substrates, namely, cyclohexanol (entry 1), benzyl alcohol (entry 2), cinnamyl alcohol (entry 3) and isopropanol (entry 6) is shown in Fig. 6 using **2** as a representative catalyst and H_2O_2 as oxidant.

3.4. Comparison of the catalytic properties of the complexes

The result of catalytic studies using these two catalysts reveals that the proactive olefins such as cyclic olefins (reported in Table 2) show similar behaviour towards epoxidation. On the other hand, the tungsten compound shows higher reactivity toward the less reactive substrates like alcohol-functionalized olefins than that achieved from the molybdenum compound. The entries in which time requirement for obtaining higher yield is long and the entries where high temperature is required to get the optimum yield, H_2O_2 should be added intermittently because with decreasing concentration of H_2O_2, the produced epoxides start to decompose to diols. Considering yields of the oxidation products of alcohols, sulfides and amines reported in Table 3 it can be stated that tungsten complex **2** is a more efficient catalyst than that of the corresponding molybdenum complex **1.**

4. Rationalization of stoichiometric and catalytic reactivity of *1* and *2*

The complexes are capable of furnishing the stoichiometric oxidation by transferring one of the peroxo oxygens to the substrates. The stoichiometric oxidation can be represented by the equations shown below, where $[MO(O_2)_2(HPEOH)]^-$, (M = Mo or W) represents the complex anions of **1** and **2**. Also in each case a representative substrate is taken into account.

Stoichiometric:

A. Olefin epoxidation

$$[MO(O_2)_2(HPEOH)]^- + 2e^- \rightarrow [M(O)_2(O_2)(HPEOH)]^- + O^{2-} \qquad (1)$$

$$R^1CH{=}CHR^2 + O^{2-} \rightarrow R^1CH(O)CHR^2 + 2e^- \qquad (2)$$

Adding (1) and (2) we get Eq. (3)

$$[MO(O_2)_2(HPEOH)]^- + R^1CH{=}\,CHR^2 \rightarrow [M(O)_2(O_2)(HPEOH)]^- + R^1CH(O)CHR^2 \qquad (3)$$

B. Alcohol oxidation

$$C_6H_5CH_2OH + O^{2-} \rightarrow C_6H_5CHO + H_2O + 2e^- \qquad (4)$$

Adding (1) and (4) we get Eq. (5)

$$[MO(O_2)_2(HPEOH)]^- + C_6H_5CH_2OH \rightarrow [M(O)_2(O_2)(HPEOH)]^- + C_6H_5CHO + H_2O \qquad (5)$$

C. Sulfide oxidation
(i) Sulfoxide

$$R^1SR^2 + O^{2-} \rightarrow R^1S(O)R^2 + 2e^- \qquad (6)$$

Adding (1) and (6) we get Eq. (7)

$$[MO(O_2)_2(HPEOH)]^- + R^1SR^2 \rightarrow [M(O)_2(O_2)(HPEOH)]^- + R^1S(O)R^2 \qquad (7)$$

(ii) Sulfone

$$R^1S(O)R^2 + O^{2-} \rightarrow R^1S(O)_2R^2 + 2e^- \qquad (8)$$

Adding (1) and (8) we get Eq. (9)

$$[MO(O_2)_2(HPEOH)]^- + R^1S(O)R^2 \rightarrow [M(O)_2(O_2)(HPEOH)]^- + R^1S(O)_2R^2 \qquad (9)$$

D. Amine oxidation

$$C_6H_5NH_2 + 2O^{2-} \rightarrow C_6H_5NO + H_2O + 4e^- \qquad (10)$$

Multiplying Eq. (1) by (2) we get Eq. (11)

$$2[MO(O_2)_2(HPEOH)]^- + 4e^- \rightarrow 2[M(O)_2(O_2)(HPEOH)]^- + 2O^{2-} \qquad (11)$$

Adding Eqs. (10) and (11) we get Eq. (12)

$$C_6H_5NH_2 + 2[MO(O_2)_2(HPEOH)]^- \rightarrow 2[M(O)_2(O_2)(HPEOH)]^- + C_6H_5NO + H_2O \qquad (12)$$

Catalytic:

A. Olefin epoxidation – Role of bicarbonate

When H_2O_2 is used as a sole oxidant the catalytic efficiency is rather poor, but when $NaHCO_3$ is added as an additive (a co-catalyst) the efficiency of the catalysis system increases many fold. The key aspect [73,74] of such reaction is that H_2O_2 and bicarbonate react in an equilibrium process to produce peroxymonocarbonate ($HCO_4{}^-$), which is a more reactive nucleophile than H_2O_2 and speeds up the reaction. Eq. (13) shows the conversion of bicarbonate to peroxymonocarbonate

$$HCO_3{}^- + H_2O_2 \rightarrow HCO_4{}^- + H_2O \qquad (13)$$

The basic principle of the catalytic reaction is the conversion of diperoxo-complexes to monoperoxo-complexes transferring oxo species to the substrates and the conversion of monoperoxo complexes to the diperoxo complexes reacting with $HCO_4{}^-$ to regain the catalytic activity. This principle is explained by Eqs. (14)–(17)

$$[MO(O_2)_2(HPEOH)]^- + R^1CH{=}CHR^2 \rightarrow [M(O)_2(O_2)(HPEOH)]^- + R^1CH(O)CHR^2 \qquad (14)$$

$$[MO_2(O_2)(HPEOH)]^- + HCO_4{}^- \rightarrow [MO(O_2)_2(HPEOH)]^- + HCO_3{}^- \qquad (15)$$

$$HCO_3{}^- + H_2O_2 \rightarrow HCO_4{}^- + H_2O \qquad (16)$$

Adding Eqs. (14)–(16) we have Eq. (17)

$$R^1CH{=}CHR^2 + H_2O_2 + \{[MO(O_2)_2(HPEOH)]^-\} \rightarrow R^1CH(O)CHR^2 + H_2O + \{[MO(O_2)_2(HPEOH)]^-\} \qquad (17)$$

B. Alcohol oxidation

$$[MO(O_2)_2(HPEOH)]^- + C_6H_5CH_2OH \rightarrow [M(O)_2(O_2)(HPEOH)]^- + C_6H_5CHO + H_2O. \qquad (18)$$

$$[M(O)_2(O_2)(HPEOH)]^- + H_2\,O_2 \rightarrow [MO(O_2)_2(HPEOH)]^- + H_2O \qquad (19)$$

Adding Eqs. (18) and (19) we get,

$$C_6H_5CH_2OH + H_2O_2 + \{[MO(O_2)_2(HPEOH)]^-\} \rightarrow C_6H_5CHO + 2H_2O + \{[MO(O_2)_2(HPEOH)]^-\} \qquad (20)$$

C. Sulfide oxidation
(i) Sulfoxide

$$R^1SR^2 + [MO(O_2)_2(HPEOH)]^- \rightarrow R^1S(O)R^2 + [M(O)_2(O_2)(HPEOH)]^- \qquad (21)$$

Adding Eqs. (19) and (21) we get,

$$R^1SR^2 + H_2O_2 + \{[MO(O_2)_2(HPEOH)]^-\} \rightarrow R^1S(O)R^2 + H_2O + \{[MO(O_2)_2(HPEOH)]^-\} \qquad (22)$$

(ii) Sulfone

$$R^1S(O)R^2 + [MO(O_2)_2(HPEOH)]^- \rightarrow R^1S(O)_2R^2 + [M(O)_2(O_2)(HPEOH)]^- \qquad (23)$$

Adding Eqs. (19) and (23) we get,

$$R^1S(O)R^2 + H_2O_2 + \{[MO(O_2)_2(HPEOH)]^-\} \rightarrow R^1S(O)_2R^2 + H_2O + \{[MO(O_2)_2(HPEOH)]^-\} \qquad (24)$$

D. Amine oxidation
Multiplying Eq. (19) by 2 we get

$$2[M(O)_2(O_2)(HPEOH)]^- + 2H_2O_2 \rightarrow 2[MO(O_2)_2(HPEOH)]^- + 2H_2O \qquad (25)$$

$$2[MO(O_2)_2(HPEOH)]^- + C_6H_5NH_2 \rightarrow 2[M(O)_2(O_2)(HPEOH)]^- + C_6H_5NO + H_2O \qquad (26)$$

Adding Eq. (25) and (26) we get,

$$C_6H_5NH_2 + 2H_2O_2 + 2\{[MO(O_2)_2(HPEOH)]^-\} \rightarrow C_6H_5NO + 3H_2O + 2\{[MO(O_2)_2(HPEOH)]^-\} \qquad (27)$$

5. Concluding remarks

In this work we have arrived at a situation that both Mo and W complexes are almost equally effective olefin epoxidation catalysts where H_2O_2 is the oxidant. In the cases of alcohol, sulfide and amine oxidation, however, the tungsten catalysts are slightly more potent than that of the analogous molybdenum containing catalysts under homogeneous mode. A comparison of epoxidation efficiency between the two-oximate ligands, namely, salicylaldoxime [27a] or 1-(2′-hydroxyphenyl) ethanone oxime, bound to $MoO(O_2)_2$ moiety indicates that the former is a bit superior than the sterically hindered latter one in majority of cases. However, reverse is the case in the difficulty epoxidisable long-chain alkenes such as 1-octene, 1-decene, 1-dodecene and *trans*-5-decene. Also in the case of cyclopentene, TOF in this case is higher than that of the earlier case [27a].

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Supplementary material

CCDC 661870 and 661869 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.05.017.

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