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Synthesis and characterization of oxodiperoxo complexes of tungsten(VI) with some Mannich base ligands

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Six oxodiperoxtungsten(VI) complexes, $[\text{WO}(\text{O}_2)_2\text{L-L}]$ (where L-L = morpholinobenzyl benzamide (MBB), piperidinobenzyl benzamide (PBB), piperidinobenzyl urea (PBU), morpholinobenzyl urea (MBU), piperidinobenzyl thiourea (PBTU) and morpholinobenzyl thiourea (MBTU)) have been prepared by stirring $\text{WO}_3 \cdot \text{H}_2\text{O}$ with excess 30% aqueous (w/v) H_2O_2 and then treating with an ethanolic solution of the Mannich base ligand (L-L). These have been characterized by elemental analysis, conductance and magnetic susceptibility measurements, IR spectra, electronic spectra, ^1H NMR, TGA/DTA and cyclic voltammetric studies. These complexes are non-electrolytes and diamagnetic in nature. The ligands are bound to metal in a bidentate mode through carbonyl oxygen/thiocarbonyl sulphur and the ring nitrogen. The complexes also inhibit the growth of pathogen "*Fusarium Spp.*" up to 60%. The cyclic voltammograms of the complexes indicate quasi-reversible redox steps involving complexes.

Keywords: Oxodiperoxtungsten(VI); Mannich base; IR spectra; *Fusarium Spp*; Antifungal activity

1. Introduction

Peroxo complexes of molybdenum(VI) and tungsten(VI) are known for their biological significance and catalytic properties [1–5]. The monooxidiperoxo complexes, $[\text{MO}(\text{O}_2)_2(\text{HMT})]$ and dioxomonoperoxo complexes, $[\text{MO}_2(\text{O}_2)(\text{HMT})]$ (M = Mo or W) (HMT = hexamethylene-tetraamine) have been synthesized and their reactivity has also been investigated [6]. Oxoperoxo and dioxo complexes of molybdenum(VI) and tungsten(VI) with 2-(α -hydroxy alkyl/aryl) – benzimidazole have been characterized for their thermal and spectral properties [7]. Transition metal peroxo species catalyze alkene-epoxidations [8]; peroxo complexes of molybdenum(VI) and tungsten(VI) have been found to catalyze epoxidation of several styrene derivatives enantioselectively in the presence of *t*-BuOOH [9]. A superoxo(oxo)tungsten(VI) complex with 2-(2-hydroxy phenyl) benzimidazole (L), $[\text{WO}(\text{O}_2)\text{L}_2]$ has been reported to readily transfer an oxygen to PPh_3 and yield the peroxo complexes, $[\text{W}^{\text{IV}}(\text{O}_2)\text{L}_2]$ [10].

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Studies on metal complexes of the formaldehyde and benzaldehyde-based Mannich bases have been reported [11]. The synthesis of piperidino benzyl urea and its complexation with Mn^{II} , Co^{II} , Ni^{II} and Cu^{II} has been reported [12]. Another Mannich base, *N*-(morpholino benzyl) benzamide, has been synthesized and its complexes with Cu^{II} , Co^{II} , Ni^{II} and Zn^{II} have been reported [13]. In the present manuscript we describe the synthesis and characterization of oxodiperoxo complexes of tungsten(VI) with some benzaldehyde-based Mannich base ligands.

2. Experimental

2.1. Reagents and reaction condition

Morpholine (Fluka), piperidine (SDS), benzaldehyde (Merck), urea (Merck), thiourea (Ranbaxy), benzamide (Merck), tungstic acid (SDS) and hydrogen peroxide (Merck) were used as supplied. The ligands were prepared by the reported method [12, 13]. The analysis of tungsten was carried out gravimetrically [14]. Carbon, hydrogen, nitrogen and sulphur were analyzed micro-analytically using CHNS analyzer Leco Model-932. Molar conductivity in DMF at room temperature was measured by an Elico conductivity bridge, type CM82T having a conductivity cell with a cell constant of 0.74 using 10^{-3} M solution of complexes. IR spectra of complexes over the region $4000\text{--}400\text{ cm}^{-1}$ were recorded on an FTIR spectrophotometer, Vector -22 using KBr discs. Electronic spectra were run in DMF on a Beckman Du-6 spectrophotometer in the 190–800 nm range using 10^{-3} M solution of the complexes. Magnetic measurements at room temperature were carried out by Gouy's method. Cyclic voltammetric measurements were carried out using a BAS CV 50W electrochemical analyzer in 10^{-3} M DMF solution using 0.01M potassium nitrate solution as supporting electrolyte. TGA/DTG studies have been carried out using a Perkin Elmer (Pyris Diamond) thermal analyzer in N_2 atmosphere in the temperature range 100–1000°C at a heating rate 10° per min.

2.2. Preparation of complexes $[\text{WO}(\text{O}_2)_2\text{L-L}]$

Tungstic acid ($\text{WO}_3 \cdot \text{H}_2\text{O}$) (0.49 g, 2 mmol) was stirred in excess H_2O_2 (30%, 25 cm^3) for 18 h at 45°C . The light yellow solution obtained was filtered. The filtrate was treated with ethanolic solution (10 cm^3) of ligand (2 mmol); MBB (0.59 g), PBB (0.58 g); PBU (0.46 g), PBTU (0.49 g), MBU (0.47 g) and MBTU (0.50 g).

The resulting solution was again stirred for about 6 h at $30\text{--}35^\circ\text{C}$ and then cooled overnight. The precipitates formed in each case were filtered off, washed with aqueous ethanol and dried *in vacuo* at room temperature (yield 56–60%).

3. Results and discussion

The analytical and spectroscopic results (tables 1–3) showed that all complexes have general formula, $[\text{WO}(\text{O}_2)_2\text{L-L}]$ (where L-L = MBB or related ligands). All the complexes are colored, stable in air, insoluble in common organic solvents but fairly

Table 1. Analytical data and some physical properties of the oxodiperoxo tungsten(VI) complexes.

Complex (Empirical formula, mol. wt.)	Color	Dec. (°C) Temp.	Found (Calcd) %					λ_M ($\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)
			C	H	N	S	W	
[WO(O ₂) ₂ MBB]	Light	120	38.50	3.36	4.92	–	32.76	16.92
WC ₁₈ H ₁₉ N ₂ O ₇ (559.19)	Green		(38.58)	(3.42)	(5.00)	–	(32.83)	
[WO(O ₂) ₂ PBB]	Cream	115	40.78	3.86	4.95	–	32.86	17.84
WC ₁₉ H ₂₂ N ₂ O ₆ (558.21)	Yellow		(40.84)	(3.92)	(5.01)	–	(32.93)	
[WO(O ₂) ₂ PBU]	Golden	108	31.30	3.80	8.38	–	36.97	20.16
WC ₁₃ H ₁₉ N ₃ O ₆ (497.15)	Yellow		(31.37)	(3.85)	(8.44)	–	(36.97)	
[WO(O ₂) ₂ PBTU]	Cream	109	30.38	3.66	8.11	6.18	35.76	24.48
WC ₁₃ H ₁₉ N ₃ O ₅ S (513.01)	Yellow		(30.40)	(3.73)	(8.18)	(6.23)	(35.84)	
[WO(O ₂) ₂ MBU]	Light	130	28.81	3.38	8.36	–	35.60	26.84
WC ₁₂ H ₁₇ N ₃ O ₇ (499.12)	Yellow		(28.87)	(3.43)	(8.42)	–	(35.69)	
[WO(O ₂) ₂ MBTU]	Cream	131	31.30	3.80	8.36	6.17	35.77	26.32
WC ₁₂ H ₁₇ N ₃ O ₆ S (515.12)	Yellow		(31.37)	(3.85)	(8.44)	(6.23)	(35.84)	

Table 2. IR spectra (cm⁻¹) of oxodiperoxo tungsten(VI) complexes.

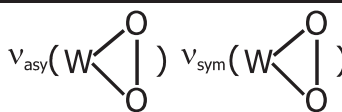
Complex	$\nu(\text{W=O})$	$\nu(\text{C=Z})$	Z=O or S	$\nu(\text{C-N-C})$	$\nu(\text{N-H})$	$\nu(\text{O-O})$		
							$\nu_{\text{asy}}(\text{W-O-O})$	$\nu_{\text{sym}}(\text{W-O-O})$
[WO(O ₂) ₂ MBB]	920	1585	1080	3420	865	755	585	
[WO(O ₂) ₂ PBB]	930	1590	1085	3380	876	750	620	
[WO(O ₂) ₂ PBU]	935	1640	1120	3438	870	762	582	
[WO(O ₂) ₂ PBTU]	925	1285	1115	3440	864	765	588	
[WO(O ₂) ₂ MBU]	952	1624	1101	3440	868	763	612	
[WO(O ₂) ₂ MBTU]	945	1270	1102	3435	866	754	625	

Table 3. Electronic spectra (nm) of oxodiperoxo tungsten(VI) complexes.

Complex	λ_{max} (nm)
[WO(O ₂) ₂ MBB]	279, 280, 282
[WO(O ₂) ₂ PBB]	280, 292, 293
[WO(O ₂) ₂ PBU]	290, 292, 294
[WO(O ₂) ₂ PBTU]	289, 293, 294
[WO(O ₂) ₂ MBU]	282, 295, 298
[WO(O ₂) ₂ MBTU]	283, 293, 294

soluble in DMSO and DMF. The complexes do not have sharp melting points and decompose above 100°C.

3.1. Conductance and magnetic measurements

The molar conductivity of these complexes in DMF are in the range 16–27 $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, indicating the non-electrolytic nature of the complexes (table 1). All the complexes are diamagnetic as expected for oxoperoxo tungsten(VI) complexes.

3.2. IR spectra

The IR spectra of all the complexes (table 2) exhibit bands characteristic of the coordinated oxo, peroxy groups and the ligand with three vibrational modes at 865–876, 750–765 and 582–625 cm^{-1} , assigned to O–O intrastretching (ν_1), asymmetric O–W–O stretching (ν_3) and symmetric O–W–O stretching (ν_2) modes respectively. These bands confirm the η^2 -coordination of the peroxy group [15]. An additional sharp band at 920–952 cm^{-1} is assigned to $\nu(\text{W}=\text{O})$ [16, 17]. Thus, IR spectra confirm the presence of $[\text{WO}(\text{O}_2)_2]$ in these complexes.

In order to determine the mode of bonding of the Mannich base ligands with tungsten, the IR spectra of ligands was compared with those of corresponding complexes. In MBB and PBB ligands, a sharp band at 1620 and 1610 cm^{-1} appeared due to $\nu(\text{C}=\text{O})$ of amide group and another band assigned to $\nu(\text{C}-\text{N}-\text{C})$ of morpholine and piperidine rings appeared at 1100 and 1105 cm^{-1} , respectively. In the corresponding complexes $[\text{WO}(\text{O}_2)_2\text{MBB}]$ and $[\text{WO}(\text{O}_2)_2\text{PBB}]$, these bands appear at lower frequencies indicating bonding of ligands through carbonyl oxygen and ring nitrogen of morpholine/piperidine (table 2).

In PBU and MBU, a sharp band due to $\nu(\text{C}=\text{O})$ of amide group appeared at 1650 and 1640 cm^{-1} and another band due to $\nu(\text{C}-\text{N}-\text{C})$ of morpholine and piperidine rings appeared at 1130 and 1120 cm^{-1} , respectively. In $[\text{WO}(\text{O}_2)_2\text{PBU}]$ and $[\text{WO}(\text{O}_2)_2\text{MBU}]$, the $\nu(\text{C}=\text{O})$ band appeared at 1640 and 1624 cm^{-1} while $\nu(\text{C}-\text{N}-\text{C})$ of piperidine and morpholine rings appeared at 1120 and 1101 cm^{-1} , respectively. Both bands exhibit negative shifts relative to their corresponding positions in free ligands indicating the coordination through carbonyl oxygen and ring nitrogen.

In PBTU and MBTU ligands, $\nu(\text{C}=\text{S})$ appeared at 1295 and 1290 cm^{-1} and $\nu(\text{C}-\text{N}-\text{C})$ of the heterocyclic rings appeared at 1130 and 1122 cm^{-1} , respectively, whereas in $[\text{WO}(\text{O}_2)_2\text{PBTU}]$ and $[\text{WO}(\text{O}_2)_2\text{MBTU}]$ complexes, the $\nu(\text{C}=\text{S})$ band appeared at 1285 and 1270 cm^{-1} while $\nu(\text{C}-\text{N}-\text{C})$ of piperidine and morpholine rings appeared at 1115 and 1102 cm^{-1} , respectively. As compared to free ligands both bands show negative shifts indicating coordination through thiocarbonyl sulphur and ring nitrogen to tungsten.

Thus, IR spectra confirm that ligands are coordinated to tungsten in a bidentate chelating mode.

3.3. Electronic spectra

The electronic spectra in DMF (table 3) of the complexes show three high energy absorption bands in the region 279–298 nm. The bands are close in energy and cannot be assigned precisely. However, two may be assigned to peroxy \rightarrow tungsten [18] and oxygen (π and σ) \rightarrow tungsten charge transfer (LMCT) bands [18]. The third band can be assigned to intraligand transitions. The molar extinction coefficient of all three bands are in the range 25,000–35,000 $\text{L cm}^{-1} \text{mol}^{-1}$. There is no evidence of a d–d transition, consistent with W(VI).

3.4. ^1H NMR spectra

The ^1H NMR spectrum of a representative ligand, morpholinobenzyl benzamide (MBB), was recorded in deuterated methanol. The spectrum shows a triplet at

Table 4. Thermogravimetric analysis of oxodiperoxo tungsten(VI) complexes.

Complex	(% Weight loss)		Residue compound WO ₂	(% Weight left)		E (kJ mol ⁻¹)	Z (s ⁻¹)	-ΔS* (JK ⁻¹ mol ⁻¹)
	Found	Calcd.		Found	Calcd.			
[WO(O ₂) ₂ MBB]	61.05	61.40	WO ₂	38.95	38.60	8.81	109.64	15.05
[WO(O ₂) ₂ PBB]	61.00	61.33	WO ₂	39.00	38.67	8.95	173.78	51.81
[WO(O ₂) ₂ PBU]	56.02	56.58	WO ₂	43.98	43.42	9.54	114.81	13.69
[WO(O ₂) ₂ PBTU]	57.32	57.92	WO ₂	42.68	42.08	10.59	130.01	25.29
[WO(O ₂) ₂ MBU]	56.34	56.75	WO ₂	43.66	43.25	12.46	153.29	40.36
[WO(O ₂) ₂ MBTU]	57.80	58.09	WO ₂	42.20	41.91	15.64	192.41	61.15

The decomposition of all the complexes follow first order kinetics, as evident from the linear plot of $-\log[-\log(1-\alpha)/T^2]$ versus $1/T$. From the value of intercept and slope of the plots, the value of frequency factor (Z), entropy of activation (ΔS*) and energy of activation (E) were obtained. The value of frequency factor (Z) and entropy of activation (ΔS*) were calculated from the equations:

$$\text{Intercept} = \log\left(\frac{ZR}{\beta E}\right)$$

$$\Delta S^* = 2.303 \log\left(\frac{Zh}{kT}\right)$$

where k is Boltzmann’s constant, h Planck’s constant, T the peak temperature and β the heating rate. The thermoanalytical data of the complexes is given in table 4.

From the physico-chemical and spectral evidence discussed above, we propose that the oxodiperoxo tungsten(VI) complexes are seven coordinate with pentagonal bipyramidal geometry (figure 4).

3.6. Antifungal activity

The *in vitro* biological screening effects of the investigated compounds were tested against the pathogen “*Fusarium* spp.” by the poisoned food method using Potato Dextrose Agar (PDA) nutrient as the medium [20]. The screening effects of the corresponding ligands against the same bacteria were also tested and results were compared with those obtained with complexes. The test solutions were prepared by dissolving the compounds in DMF. PDA mixed with test solution was poured into sterilized petri-plates. After solidification, the plates were inoculated with seven day old culture of pathogen by placing 2 mm bit in the centre of plates. The inoculated plates were incubated at 27°C for 4 days. The linear growth of fungus in control and treatment were recorded at different concentrations of the complexes. The growth inhibition of “*Fusarium* spp.” over control was calculated as per Vincent [20].

$$\% \text{ Inhibition}(I) = \left[\frac{C - T}{C} \right] \times 100$$

where I = percent inhibition, C = growth of fungus in (mm) in control, and T = growth of fungus in (mm) in treatment.

Table 5. *In vitro* efficacy of ligands and complexes against *Fusarium* Spp. Colony diameter of control $C = 33$ mm.

Complexes	Colony diameter (in mm) at 100 ppm	% Inhibition $I = [(C-T)/C] \times 100$ at 100 ppm	Colony diameter (in mm) at 200 ppm	% Inhibition I at 200 ppm
MBB	30.00	9.00	26.60	19.39
PBB	31.60	4.24	27.10	17.87
PBU	30.50	7.57	25.40	23.03
PBTU	30.50	8.50	26.50	24.50
MBU	30.00	8.70	27.40	25.60
MBTU	32.30	8.50	25.60	23.40
[WO(O ₂) ₂ MBB]	25	24.24	18	45.45
[WO(O ₂) ₂ PBB]	24	27.27	16	51.51
[WO(O ₂) ₂ PBU]	22	33.33	14	57.7
[WO(O ₂) ₂ PBTU]	21	36.66	12	63.3
[WO(O ₂) ₂ MBU]	20	39.40	16	51.5
[WO(O ₂) ₂ MBTU]	21	36.36	13	60.6

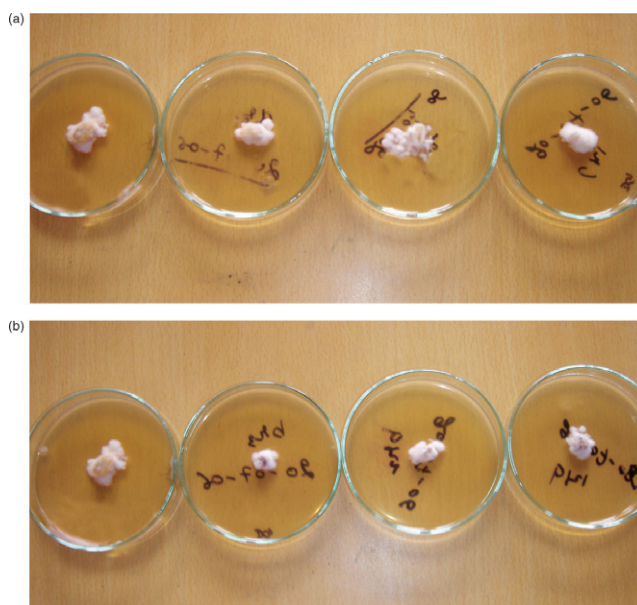
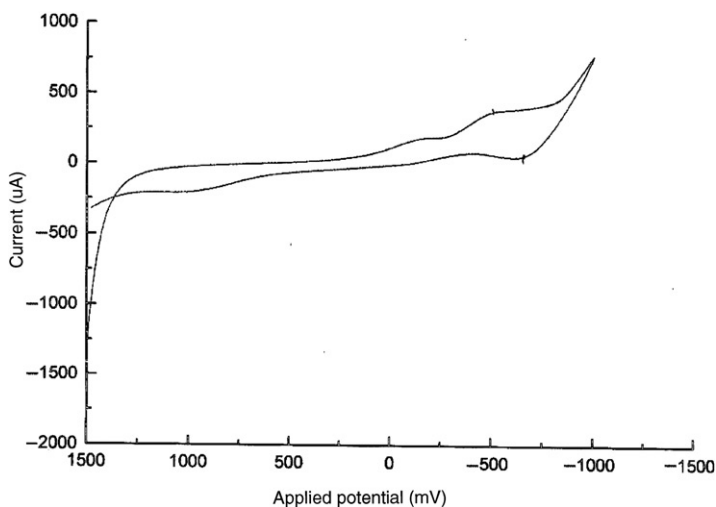
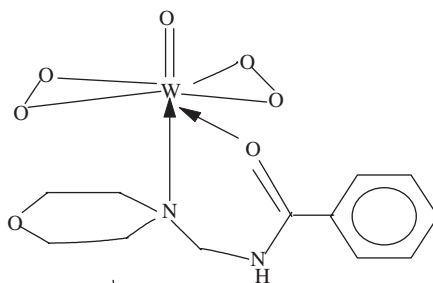
Figure 2. (a) Anti-fungal activity of [WO(O₂)₂(MBB)]. (b) Anti-fungal activity of [WO(O₂)₂(PBU)].

Table 5 shows that on increasing the concentration of the complexes, the colony diameter of the fungus decreases and hence percent inhibition increases. On doubling the concentration of the complexes the percent inhibition also doubles, which shows linear relationship between concentration and percent inhibition. The increase in antimicrobial activity is due to faster diffusion of metal complexes as a whole through the cell membrane or due to combined activity effect of the metal and the ligand. Such increased activity of the metal complexes can be explained on the basis of Overtone's concept [21] and Tweedy's chelation theory [22]. The lipid membrane that surrounds the cell favors passage of only lipid soluble materials due to lipophilicity being an important factor which controls the antimicrobial activity. On chelation, the polarity of the metal ion will be reduced to a greater extent due to overlap of the ligand orbital and

Figure 3. Cyclic voltammogram of $[\text{WO}(\text{O}_2)_2(\text{MBB})]$.Figure 4. Probable structure of $[\text{WO}(\text{O}_2)_2(\text{MBB})]$.

partial sharing of the positive charge of the metal ion with donor group. Antifungal activities of $[\text{WO}(\text{O}_2)_2\text{MBB}]$ and $[\text{WO}(\text{O}_2)_2\text{PBU}]$ are shown in figure 2.

3.7. Cyclic voltammetry

Cyclic voltammetry of a representative complex, $[\text{WO}(\text{O}_2)_2\text{MBB}]$, was carried out using a BAS CV 50 W electrochemical analyzer in DMF solution using 0.01 M potassium nitrate as supporting electrolyte. The cyclic voltammogram (figure 3) shows a cathodic peak with peak potential $E_{\text{pc}} = -0.575 \text{ V}$ and peak current $i_{\text{c}} = 14 \mu\text{A}$. In the reverse scan, the anodic peak appears with peak potential $E_{\text{pa}} = -0.750 \text{ V}$ and peak current $i_{\text{a}} = 9 \mu\text{A}$. The $\Delta E_{\text{p-p}}$ is 0.175 V and $i_{\text{c}}/i_{\text{a}} = 1.61$. Higher values of $\Delta E_{\text{p-p}}$ and $i_{\text{c}}/i_{\text{a}}$ indicate that redox processes are quasi-reversible and oxidation of reduced product W(IV) in the reverse step takes place slowly, probably either due to adsorption of reduced product on electrode surface or slower rate of oxidation. The $E_{1/2}$ of the

complex is -0.662 V, indicating that the complex can be a catalyst in redox reactions. Complexes of this type have been reported recently [23].

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