

## Synthesis, characterization, antibacterial activity and 3D-molecular modeling of some oxoperoxomolybdenum(VI) chelates in mixed (O,O) coordination environment involving 2-hydroxy-1-naphthaldehyde and $\beta$ -diketoenolates

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A new series of four mixed-ligand complexes of oxoperoxomolybdenum(VI) of the general composition,  $[\text{MoO}(\text{O}_2)(2\text{-hnd})(\text{L})]\cdot\text{H}_2\text{O}$ , where 2-hndH = 2-hydroxy-1-naphthaldehyde and LH = o-acetoacetanilide (o-aansH), o-acetoacetotoluidide (o-aatdH), acetylacetone (acacH) or methyl acetoacetate (macacH), has been synthesized by the interaction of  $[\text{MoO}(\text{O}_2)]^{2+}$  (in situ obtained during the interaction of  $\text{MoO}_3$  and 30%  $\text{H}_2\text{O}_2$  on continuous stirring at 50°C for 24 h) and the ligands in aqueous-ethanol medium. The complexes so obtained have been characterized by elemental analyses, molar conductance, decomposition temperature and magnetic measurements, thermogravimetric studies, <sup>1</sup>H-NMR, IR, mass and electronic spectral studies. Antibacterial studies of the ligand and the metal complexes have also been carried out. The complexes have been found to be more potent bactericides than the ligands. The 3D-molecular modeling and analysis for both bond lengths and bond angles have also been carried out for one of the representative compounds,  $[\text{MoO}(\text{O}_2)(2\text{-hnd})(\text{o-aatd})]\cdot\text{H}_2\text{O}$  (**1**), to substantiate the proposed structure. Pseudopentagonal bipyramidal structures have been proposed for these complexes.

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Molybdenum is an essential trace element in the human body, animals and plants<sup>1-3</sup>. The number of known molybdenum containing enzymes exceeds 50. Many enzymes that catalyze redox reactions<sup>4</sup> and many potential catalysts<sup>5-7</sup> contain molybdenum as the metal ion in an active site. Investigation of the structure of molybdenum containing enzymes reveals the presence of a chelated *cis*- $\text{MoO}_2$  unit in the active site of sulfite-oxidase enzymes<sup>8</sup>. This observation has prompted investigations of molybdenum complexes with ligands whose structural features bear a relationship to the active site of molybdenum enzymes<sup>9-12</sup>. A number of Mo(VI) and Mo(IV) complexes were synthesized to model oxomolybdenum enzymes. These complexes range from having four-monodentate ligands<sup>13</sup> to a single tetra dentate ligand<sup>14</sup> attached to the molybdenum center.

The complexes of  $\text{MoO}_2^{2+}$  with tridentate ligands of the general formula  $[\text{MoO}_2(\text{TL})(\text{ML})]$  (TL = tridentate ligand, ML = monodentate ligand) were

synthesized as the model systems of molybdoenzymes catalyzing redox reactions. The model proposed for oxo-transfer reactions considers the direct transfer of an oxygen atom from/to the molybdenum center, and involves terminal O atoms<sup>15-17</sup>. This raises the question of the identification of those structural features of the chelated *cis*- $\text{MoO}_2$  fragment that influence catalytic capacity of the molybdenum compounds<sup>18,19</sup>.

Simple molybdenum compounds<sup>20</sup>, such as  $\text{Na}_2\text{MoO}_4$  and complex compounds such as *cis*- $\text{MoO}_2\text{L}_2$  [L = maltol (3-hydroxy-2-methyl-4-pyrone)] were found to significantly reduce the levels of blood glucose and free fatty acids. Also, Lord *et al.*<sup>21</sup> observed beneficial effects of molybdate treatment on postischaemic cardiac function of diabetic rats<sup>22</sup>.

The polyoxomolybdenum anions have received a lot of interest with their potential applications in catalysis, solid-state technology and medicine, including antitumour and anti-virus (HIV) activity<sup>23,24</sup>. Several molybdenum compounds as model of antineoplastic action were hypothesised<sup>25</sup>.

The chemistry of peroxo complexes of the transition elements has been an interesting subject of investigations since the beginning of 20<sup>th</sup> century, mainly due to their catalytic applications (efficient oxidizing agents for numerous substrates including alkenes, olefins, arenes, alcohols, and sulfides<sup>26</sup>) and due to their ability to generate singlet oxygen<sup>27,28</sup>. Singlet oxygen is a powerful oxidant, which is of interest in chemistry, catalysis, and medicine.

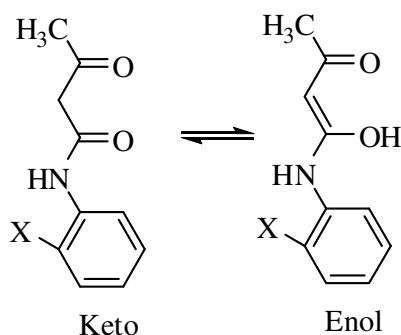
Peroxomolybdates and peroxotungstates are formed in aqueous solutions containing hydrogen peroxide and Mo(VI) or W(VI) over nearly the entire pH range<sup>29</sup>. Few peroxo complexes of molybdenum(VI) and uranium(VI) containing diphenic acid and heterocyclic amines have been synthesized and characterized on the basis of elemental analysis, IR and molar conductance studies. The complexes have the composition  $[M(O_2)(dp)(L_2)]$ , where M = Mo(VI), U(VI), dp = dianion of diphenic acid and L = pyridine, quinoline, *iso*-quinoline, 2-picoline or 4-picoline. The complexes are found to be inert towards oxidation of allyl alcohol, but oxidize triphenylphosphine and triphenylarsine to their respective oxide<sup>30</sup>. Sarkar *et al.*<sup>31</sup> have reported the preparation and characterization of mixed-ligand peroxo compounds of molybdenum(VI) and tungsten(VI) with pyridine. A new series of mixed-ligand peroxo complexes of molybdenum(VI) containing diphenic acid and 2 or 3-pyrazoline-5-one derivatives have recently been synthesized and characterized by Maurya and Thakur<sup>32</sup>.

$\beta$ -Diketones are well established chelating molecules having two oxygen donor sites forming a very stable six membered chelate ring including central metal ion<sup>33</sup>. Similar to  $\beta$ -diketones, 2-hydroxy-1-naphthaldehyde is also a very good monobasic chelating molecule forming a six membered chelate ring including metal. 2-Hydroxy-1-naphthaldehyde has been proposed previously as a derivatization reagent for hydrazine and isoniazid determination in aqueous solution<sup>34,35</sup> and isoniazid and hydrazine in plasma<sup>36-39</sup>.

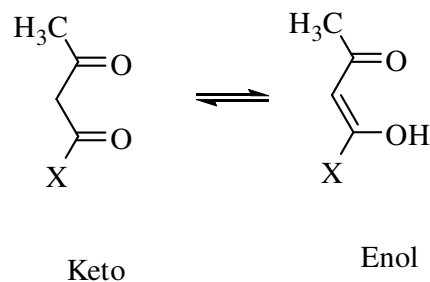
A literature survey on mixed-ligand peroxo complexes of molybdenum(VI) reveals that there is no report on such complexes containing 2-hydroxy-1-naphthaldehyde and  $\beta$ -diketoenolates [(I)]. The present studies have been undertaken in view of the diverse and important applications of molybdenum compounds in general and the peroxomolybdenum compounds in particular.

### Materials and Methods

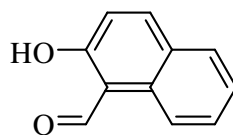
Molybdenum trioxide 99% (Sisco Chem., Bombay), 30% hydrogen peroxide (E. Merck India Ltd. Mumbai), 2-hydroxy-1-naphthaldehyde (Fluka AG Co., Switzerland), *o*-acetoacetanilide, *o*-acetoacetotoluidide (Aldrich Chemical Co. USA), methyl acetoacetate, acetylacetone and DMF (Thomas Baker Chemical Ltd., Mumbai), and ethanol (Bengal Chemical and Pharmaceuticals Ltd., Kolkata) were used as received. All chemicals used were of analytical reagent (A.R.) grade.



= CH<sub>3</sub>, *o*-aatdH  
= OCH<sub>3</sub>, *o*-aansH



X = CH<sub>3</sub>, acacH  
= OCH<sub>3</sub>, macacH



2-Hydroxy-1-naphthaldehyde (2-hndH)

(I)

A suspension of MoO<sub>3</sub> (0.0025 mole, 0.359 g) in 30% H<sub>2</sub>O<sub>2</sub> (35 mL) was stirred for 24 h at 50°C giving a yellow solution. This was filtered and a solution of 2-hydroxy-1-naphthaldehyde (0.0025 mol, 0.430 g) in ethanol (15 mL) was added to the filtrate followed by the addition of 0.0025 mol of β-diketones: *o*-actooactotoluidide (*o*-aatdH) (0.477g), *o*-acetoactanisidide (*o*-aansH) (0.517 g), acetylacetone (acacH) (0.26 mL) or methyl acetoacetate (macacH) (0.27 mL) in (20 mL) ethanol. The resulting mixture was stirred for 2 h. while cooling in an ice-bath. The light brown precipitate appeared was suction filtered with water-ethanol (1:1) solution and dried in a desiccator over anhydrous calcium chloride.

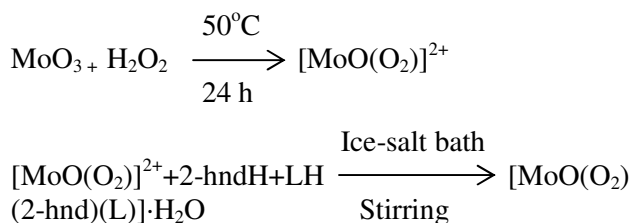
Carbon, hydrogen, nitrogen were determined micro-analytically. The molybdenum content in each chelate was determined<sup>40</sup> as follows. A weighed amount (~200 mg) of the chelate was first decomposed by heating with concentrated nitric acid then strongly heating the residue over 500°C for 45 min until constant weight was obtained. The residue was weighed as MoO<sub>3</sub>.

The following physical methods were used to determine the structure of the resulting molybdenum(VI) complexes. Thermogravimetric analysis was done by heating the sample at the rate of 10°C min<sup>-1</sup> up to 1000 °C on a thermal analyzer at Sophisticated Analytical Instrument Facility (Formerly RSIC), Indian Institute of Technology, Bombay. Solid-state infrared spectra were obtained using potassium bromide pellets with a Perkin-Elmer model 1620 FT-IR spectrophotometer at C.D.R.I., Lucknow. Conductance measurements were made in DMF solution using Toshniwal conductivity bridge and dip type cell with a smooth platinum electrode of a cell constant 1.02. Magnetic measurements were performed by Gouy's method using mercury(II) tetrathiocyanatocobaltate(II) as calibrant. The

decomposition temperatures of the complexes were recorded by an electrically operated melting point apparatus (Kumar Industries, Bombay) of heating capacity up to 360°C. Electronic spectra were recorded on Systronics double beam UV-Vis spectrophotometer: 2001. <sup>1</sup>H-NMR spectra in DMSO-d<sub>6</sub>, mass spectra and elemental analysis (micro-analytically) of the complexes were determined at Sophisticated Analytical Instrumentation Facility, C.D.R.I., Lucknow.

## Results and Discussion

The mixed-ligand oxoperoxomolybdenum(VI) complexes of the ligands under study were obtained according to:



where 2-hndH = 2-hydroxy-1-naphthaldehyde, LH = *o*-actooactotoluidide (*o*-aatdH) (1), *o*-acetoactanisidide (*o*-aansH) (2), acetylacetone (acacH) (3) or methyl acetoacetate (macacH) (4).

These complexes (coloured solids) are stable in air. They are thermally stable and their decomposition temperatures are given in Table 1. The analytical data of these complexes are also given in the table. They have been characterized on the basis of infrared spectra, magnetic measurement, <sup>1</sup>H-NMR, mass, electronic spectral and TG studies.

### Infrared spectral studies

The important infrared spectral bands of the complexes and their tentative assignments are given in Table 2. All the complexes display a strong band at

Table 1—Analytical data and some physical properties of the synthesized complexes

Comp. No.	Complexes (empirical formula) (M.W.)	Found/ (Calcd) (%)				Color	Decomp. temp. (°C)	Λ <sub>M</sub> (Ω <sup>-1</sup> cm <sup>2</sup> mole <sup>-1</sup> )	Yield (%)
		C	H	N	Mo				
(1)	[MoO(O <sub>2</sub> )( <i>o</i> -aatd)(2hnd)]·H <sub>2</sub> O (C <sub>22</sub> H <sub>21</sub> NO <sub>8</sub> Mo) (522.94)	50.29 (50.48)	4.14 (4.02)	2.47 (2.68)	18.13 (18.35)	Joy grey	205	11.7	67
(2)	[MoO(O <sub>2</sub> )( <i>o</i> -aans)(2-hnd)]·H <sub>2</sub> O (C <sub>22</sub> H <sub>21</sub> NO <sub>9</sub> Mo) (538.94)	48.48 (48.99)	3.72 (3.90)	2.49 (2.60)	17.58 (17.80)	Golden brown	215	10.9	68
(3)	[MoO(O <sub>2</sub> )(acac)(2-hnd)]·H <sub>2</sub> O (C <sub>16</sub> H <sub>16</sub> O <sub>8</sub> Mo)(431.94)	44.65 (44.45)	3.93 (3.70)	- -	22.49 (22.21)	Light grey	210	11.9	71
(4)	[MoO(O <sub>2</sub> )(macac)(2-hnd)]·H <sub>2</sub> O (C <sub>16</sub> H <sub>16</sub> O <sub>9</sub> Mo) (447.94)	42.16 (42.86)	3.82 (3.57)	- -	21.75 (21.42)	Light grey	218	11.3	74

Table 2—Some important IR spectral bands ( $\text{cm}^{-1}$ ) of the synthesized complexes

Comp. No.	Complexes	$\nu$ (Mo=O)	$\nu(\text{O}_2)$ Peroxo	$\nu$ (Mo-O)	$\nu(\text{C}=\text{O})$ 2-hnd	$\nu(\text{C}-\text{O})$ Phenolic	$\nu(\text{C}=\text{O})$ Acetyl	$\nu(\text{C}=\text{O})$ Amide	$\nu(\text{C}=\text{C})$ Keto-enolate	$\nu(\text{OH})$ Water
(1)	[MoO(O <sub>2</sub> )( <i>o</i> -aatd)(2hnd)]·H <sub>2</sub> O	983	850	712 696	1604	1449	1571	1649	-	3448
(2)	[MoO(O <sub>2</sub> )( <i>o</i> -aans)(2-hnd)]·H <sub>2</sub> O	968	868	716 697	1610	1437	1594	1646	-	3450
(3)	[MoO(O <sub>2</sub> )(acac)(2-hnd)]·H <sub>2</sub> O	960	870	710 650	1620	1465	1645	-	1590	3410
(4)	[MoO(O <sub>2</sub> )(macac)(2-hnd)]·H <sub>2</sub> O	969	865	714 654	*	1465	1643	-	1594	3442

\*Merged with  $\nu(\text{C}=\text{O})$  acetyl

960-983  $\text{cm}^{-1}$ , which has been assigned to  $\nu(\text{Mo}=\text{O})$  mode. The metal peroxo grouping gives rise to three IR active vibrational modes, and these are (O-O) stretching ( $\nu_1$ ), the symmetric (Mo-O) stretching ( $\nu_2$ ) and asymmetric (Mo-O) stretching ( $\nu_3$ ). The characteristic ( $\nu_1$ ) (O-O) mode of the complexes appears at 850-870  $\text{cm}^{-1}$ , while the ( $\nu_2$ ) and ( $\nu_3$ ) modes appear at 650-697  $\text{cm}^{-1}$  and 710-716  $\text{cm}^{-1}$ , respectively. These observations are in agreement with results reported elsewhere<sup>30,41</sup>.

The co-ligand 2-hydroxy-1-naphthaldehyde (2-hndH), used in the present investigation contains two donor sites: (i) the carbonyl oxygen and (ii) the phenolic oxygen. The infrared spectra of 2-hndH shows three spectral bands at 3060, 1630 and 1520  $\text{cm}^{-1}$  assignable to  $\nu(\text{OH})$  (strongly intermolecular hydrogen bonded with carbonyl oxygen),  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}-\text{O})$  (phenolic), respectively. When phenolic oxygen coordinates with the metal center after deprotonation,  $\nu(\text{OH})$  (phenolic) observed at 3060  $\text{cm}^{-1}$  in the free 2-hndH should disappear in the infrared spectra of all these complexes. In fact, this band has been found disappear in all the complexes, suggesting coordination of phenolic oxygen after deprotonation. This is further supported by the low energy shift<sup>42</sup> of  $\nu(\text{C}-\text{O})$  and appearing at 1437-1465  $\text{cm}^{-1}$  in all the complexes compared to  $\nu(\text{C}-\text{O})$  (phenolic) at 1520  $\text{cm}^{-1}$  in the free 2-hndH. The coordination of carbonyl oxygen of this ligand to metal centre was inferred by the appearance of  $\nu(\text{C}=\text{O})$  mode in all the complexes at lower wave numbers, 1604-1620  $\text{cm}^{-1}$  compared to  $\nu(\text{C}=\text{O})$  of the free 2-hndH at 1630  $\text{cm}^{-1}$ .

The two characteristic spectral bands due to coordinated acetoacetylaryl amides (*o*-aatd and *o*-aans) anions are  $\nu(\text{C}=\text{O})$  (acetyl carbonyl) and  $\nu(\text{C}=\text{O})$  (amide carbonyl). These two bands have been observed at 1571-1594 and 1646-1649  $\text{cm}^{-1}$ ,

respectively. These results are in agreement with the data reported elsewhere<sup>42</sup>. The two significant absorption bands on account of the coordinated methyl acetoacetate or acetylacetone anion are  $\nu(\text{C}=\text{O})$  (acetyl) and  $\nu(\text{C}=\text{C})$  modes, and these two have been observed at 1643-1645 and 1590-1594  $\text{cm}^{-1}$ , respectively. These results are in agreement with the reported results<sup>43</sup>.

The IR spectra of all the complexes show a broad band centered at 3410-3450  $\text{cm}^{-1}$ , attributable to  $\nu(\text{OH})$  mode due to the presence of lattice/coordinated water in these complexes.

#### Conductance measurements

The molar conductivities of all the complexes in  $10^{-3} M$  DMF solutions lie in the range 10.9-11.6  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  (Table 1.), as expected for non-electrolytes<sup>44</sup>. Such a non-zero molar conductance value for each of the complexes in the present investigation is most probably due to the strong donor capacity of DMF, which may lead to the displacement of anionic ligand and change of electrolyte type.

#### Magnetic measurements

The observed magnetic moments of these complexes indicate that the complexes are diamagnetic<sup>45</sup>, as expected for molybdenum(VI) complexes.

#### Mass spectral studies

The FAB mass spectrum of a representative complex, [MoO(O<sub>2</sub>)(2-hnd)(macac)]·H<sub>2</sub>O (4) was recorded on a JEOL SX 102/ DA-6000 mass spectrometer/data system using xenon/argon (6KV, 10mA) as the FAB gas in the  $m/z$  range 94.70-507.77. The mass spectral peaks observed at 136, 137, 154, 289 and 307  $m/z$  are matrix (*m*-nitrobenzyl alcohol or NBA) peaks. The spectral peaks observed at 172, 185, 279, 391, 407, 421, 438 and 447  $m/z$  in the complex might be correlated possibly with the following types

Table 3—Electronic spectral data of the synthesized complexes

Comp. No.	Complexes	$\lambda_{\max}$ (nm)	$\nu$ (cm <sup>-1</sup> )	$E$ (L mol <sup>-1</sup> cm <sup>-1</sup> )	Peak assignment
(3)	[MoO(O <sub>2</sub> )(acac)(2-hnd)]·H <sub>2</sub> O	276	36231	2289	Intra ligand transitions
		346	28901	2281	
		375	26666	2217	
(4)	[MoO(O <sub>2</sub> )(macac)(2-hnd)]·H <sub>2</sub> O	279	35842	2290	Intra ligand transitions
		348	28735	2282	
		389	25706	2292	

Table 4—Thermogravimetric data of (4)

S. No.	% Wt. loss (obs.)	% Wt. loss (calcd)	Temp. (°C)	Elimination of
1	4.16	4.10	98	One lattice water molecule
2	11.36	11.16	140	H <sub>2</sub> O + peroxy
3	48.89	49.33	470	H <sub>2</sub> O + peroxy+2-hnd
4	76.77	75.01	980	All ligand moieties

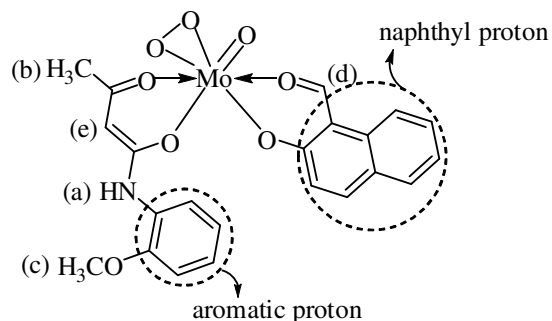
of ion associations<sup>46</sup>: [MoO(O<sub>2</sub>)(2-hnd)(macac)]<sup>+</sup> (429) - 8[H]<sup>+</sup> (421); [MoO(O<sub>2</sub>)(2-hnd)]<sup>+</sup> (314) + [matrix]<sup>+</sup> (136) - 3[H]<sup>+</sup> (447); [MoO(O<sub>2</sub>)(macac)]<sup>+</sup> (259) + [matrix]<sup>+</sup> (136) - 4[H]<sup>+</sup> (391); [MoO(O<sub>2</sub>)(2-hnd)]<sup>+</sup> (314) - [O-O]<sup>+</sup>(32) - 4[H]<sup>+</sup> (279); [MoO(2-hnd)]<sup>+</sup> (283) + [matrix]<sup>+</sup> (154) + [H]<sup>+</sup> (438); [macac]<sup>+</sup>(115) + [matrix]<sup>+</sup> (289) + 3 [H]<sup>+</sup> (407); [O-O]<sup>+</sup> (32) + [matrix]<sup>+</sup> (154) - [H]<sup>+</sup> (185); [2-hnd]<sup>+</sup> (172). These results are consistent with the proposed molecular composition of the complex (4).

#### Electronic spectral studies

Electronic spectra of two complexes (3) and (4) were recorded in 10<sup>-3</sup> M DMF solutions. The electronic spectral peaks observed in each of the complexes along with the molar extinction coefficients are given in the Table 3. The high intensity peak(s) (in UV-region) in each of the complexes are due to intra-ligand<sup>24</sup> n → π\* / π → π\* transitions.

#### Thermogravimetric studies

The thermograms of two representative compounds namely, [MoO(O<sub>2</sub>)(2-hnd)(acac)]·H<sub>2</sub>O (3) and [MoO(O<sub>2</sub>)(2-hnd)(macac)]·H<sub>2</sub>O (4) were recorded in the temperature rang 50-1000 °C at the heating rate of 15°C/min. The first weight loss in the complex (3) was observed at 95°C, which corresponds to 3.88% against a theoretical weight loss of 4.16% for the removal of one water molecule. This suggests the presence of one lattice water molecule in this complex. A second weight of 11.66%, in this compound, was observed at 160°C against calculated weight loss of 11.57% for the removal of one peroxy (O-O) group from the complex. A third weight loss of



Indexing of various protons

#### (II)

51.11% was observed at 430°C (calcd. loss for one 2-hnd moiety = 51.16%). This suggests the elimination of one 2-hnd moiety from the complex. The final weight loss of 76.77% around 980°C was noticed in this compound. This corresponds to the removal of all the ligand moieties (except oxo group) from the complex (calcd. weight loss to all ligand moieties 74.08%). The final residue roughly corresponds to MoO<sub>3</sub> (obs. = 23.23%, calcd. = 33.32%). (4) shows the three weight losses as reported in the Table 4. The final residue roughly corresponds to MoO<sub>3</sub> (obs. residual mass = 23.23%, calcd. = 32.11%).

#### <sup>1</sup>HMR spectral studies

The proton NMR spectrum of one representative compounds namely [MoO(O<sub>2</sub>)(2-hnd)(*o*-aans)]·H<sub>2</sub>O (2) was recorded in DMSO-*d*<sub>6</sub> using TMS as a reference. (2) displays a multiplet of proton signals due to aromatic protons of phenyl/naphthyl group at δ 7.23-8.95 ppm and a singlet at δ 10.87 ppm due to -NH (a) proton of *o*-aans moiety. The proton signals at δ 3.3, 2.20, 2.02 and 1.23 ppm are most probably due to proton groups, such as, -CH<sub>3</sub> (c), -CH (d), -CH (e) -CH<sub>3</sub> (b), respectively, present in this compound. The proton signal at 2.50 ppm is most probably due to solvent (DMSO-*d*<sub>6</sub>) taken. The absence of enolic/hydroxyl proton signal at ~ 12 ppm in the complex indicates the coordination of enolic

oxygen to the metal ion after deprotonation<sup>47</sup>. The indexing of various protons is given in (II)

#### Antibacterial studies

The antibacterial activity of the ligand 2-hndH and the mixed-ligand complexes,  $[\text{MoO}(\text{O}_2)(2\text{-hnd})(\text{acac})]\cdot\text{H}_2\text{O}$  (2) and  $[\text{MoO}(\text{O}_2)(2\text{-hnd})(\text{macac})]\cdot\text{H}_2\text{O}$  (3) were tested against *E. coli* and *V. cholera* using Streptomycin as the standard antibacterial agent. The diffusion agar technique<sup>48,49</sup> (at a concentration of  $300 \mu\text{g cm}^{-3}$  in DMSO) was used to evaluate the antibacterial activity of the synthesized mixed-ligand complexes.

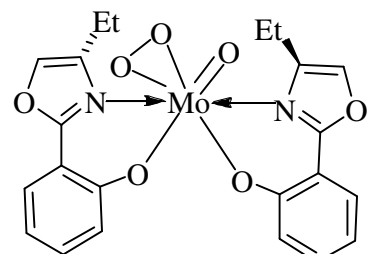
Table 5—Antibacterial study of the ligand and metal complexes

S. No.	Compound	Zone of inhibition in (mm)	
		<i>E. coli</i>	<i>V. cholera</i>
1.	2-Hydroxy-1-naphthaldehyde	31	33
2.	$[\text{MoO}(\text{O}_2)(2\text{-hnd})(\text{acac})]\cdot\text{H}_2\text{O}$ (2)	36	38
3.	$[\text{MoO}(\text{O}_2)(2\text{-hnd})(\text{macac})]\cdot\text{H}_2\text{O}$ (3)	35	37

The results of the bactericidal screening of the ligand and complexes are recorded in Table 5. The metal complexes are found to be more potent bactericides than the ligand. The enhancement in the activity of complexes can be explained on the basis of chelation theory<sup>50,51</sup>.

#### 3D Molecular modeling and analyses

In view of the hepta-coordination of the present complexes (vide infra), and also taking into account of



Structure of bis(phenolato-oxazoline) monoperoxomolybdenum(VI)

(III)

Table 6—Various bond lengths of compound  $[\text{MoO}(\text{O}_2)(2\text{-hnd})(o\text{-aatd})]\cdot\text{H}_2\text{O}$  (1)

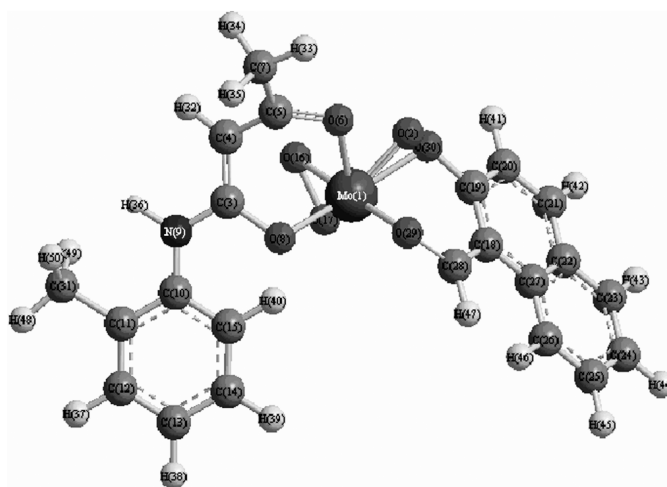
S. No.	Atoms	Actual bond length	Optimal bond length	S. No.	Atoms	Actual bond length	Optimal bond length
1	C(31)-H(50)	1.113	1.113	29	C(13)-H(38)	1.1	1.1
2	C(31)-H(49)	1.113	1.113	30	C(13)-C(14)	1.337	1.42
3	C(31)-H(48)	1.113	1.113	31	C(12)-H(37)	1.1	1.1
4	C(28)-H(47)	1.1	1.1	32	C(12)-C(13)	1.337	1.42
5	C(28)-O(29)	1.355	1.355	33	C(11)-C(31)	1.497	1.497
6	C(26)-H(46)	1.1	1.1	34	C(11)-C(12)	1.337	1.42
7	C(26)-C(27)	1.337	1.42	35	C(10)-C(15)	1.337	1.42
8	C(25)-H(45)	1.1	1.1	36	C(10)-C(11)	1.337	1.42
9	C(25)-C(26)	1.337	1.42	37	N(9)-H(36)	1.05	1.05
10	C(24)-H(44)	1.1	1.1	38	N(9)-C(10)	1.266	1.462
11	C(24)-C(25)	1.3372	1.42	39	C(7)-H(35)	1.113	1.113
12	C(23)-H(43)	1.1	1.1	40	C(7)-H(34)	1.113	1.113
13	C(23)-C(24)	1.337	1.42	41	C(7)-H(33)	1.113	1.113
14	C(22)-C(27)	1.337	1.42	42	C(5)-C(7)	1.497	1.497
15	C(22)-C(23)	1.337	1.42	43	C(5)-O(6)	1.355	1.355
16	C(21)-H(42)	1.1	1.1	44	C(4)-H(32)	1.1	1.1
17	C(21)-C(22)	1.337	1.42	45	C(4)-C(5)	1.3371	1.503
18	C(20)-H(41)	1.1	1.1	46	C(3)-N(9)	1.266	1.462
19	C(20)-C(21)	1.337	1.42	47	C(3)-O(8)	1.355	1.355
20	C(19)-O(30)	1.355	1.355	48	C(3)-C(4)	1.337	1.337
21	C(19)-C(20)	1.337	1.42	49	O(6)-Mo(1)	1.94	-
22	C(18)-C(28)	1.337	1.503	50	O(29)-Mo(1)	1.944	-
23	C(18)-C(27)	1.337	1.42	51	Mo(1)-O(30)	1.94	-
24	C(18)-C(19)	1.337	1.42	52	O(8)-Mo(1)	1.94	-
25	O(16)-O(17)	1.428	1.428	53	O(17)-Mo(1)	1.7414	-
26	C(15)-H(40)	1.1	1.1	54	O(16)-Mo(1)	1.94	-
27	C(14)-H(39)	1.1	1.1	55	Mo(1)-O(2)	1.7543	-
28	C(14)-C(15)	1.337	1.42				

the well established hepta-coordinate pseudopentagonal bipyramidal structure<sup>28</sup> of bis(phenolato-oxazoline) monoperoxomolybdenum(VI) [(III)] [having a monobasic bidentate (O,N-donor) phenolato-oxazoline ligand similar to monobasic (O,O-donor) 2-hndH and

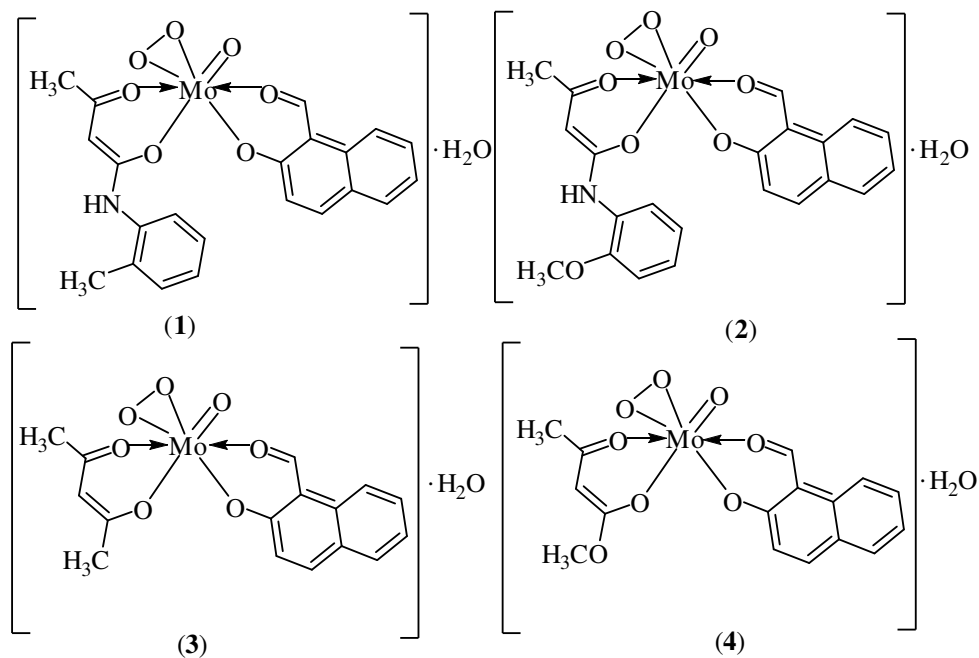
LH ligands in the present investigation], the molecular modeling of a representative compound, [MoO(O<sub>2</sub>)(2-hnd)(*o*-aatd)]·H<sub>2</sub>O (I), is based on its pseudopentagonal pseudopentagonal bipyramidal structure. The details of bond lengths and bond angles as per the 3D structure

Table 7—Various bond angles of compound [MoO(O<sub>2</sub>)(2-hnd)(*o*-aatd)]·H<sub>2</sub>O (I)

S. No.	Atoms	Actual bond angles	Optimal bond angles	S. No.	Atoms	Actual bond angles	Optimal bond angles
1	H(45)-C(25)-C(26)	120.003	120	52	C(31)-C(11)-C(12)	120	121.4
2	H(45)-C(25)-C(24)	120.003	120	53	C(31)-C(11)-C(10)	120	121.4
3	C(26)-C(25)-C(24)	119.994	-	54	C(12)-C(11)-C(10)	120	120
4	H(44)-C(24)-C(25)	120.004	120	55	C(15)-C(10)-C(11)	120	120
5	H(44)-C(24)-C(23)	120.002	120	56	C(15)-C(10)-N(9)	120	120
6	C(25)-C(24)-C(23)	119.994	-	57	C(11)-C(10)-N(9)	120	120
7	H(47)-C(28)-O(29)	117.85	116.4	58	C(19)-O(30)-Mo(1)	109.5	-
8	H(47)-C(28)-C(18)	117.85	120	59	C(28)-O(29)-Mo(1)	110.163	-
9	O(29)-C(28)-C(18)	124.3	-	60	O(16)-O(17)-Mo(1)	74.7514	-
10	H(46)-C(26)-C(27)	120.001	120	61	O(17)-O(16)-Mo(1)	59.9999	-
11	H(46)-C(26)-C(25)	120	120	62	H(36)-N(9)-C(10)	120	118
12	C(27)-C(26)-C(25)	120	-	63	H(36)-N(9)-C(3)	120	118
13	C(26)-C(27)-C(22)	119.999	120	64	C(10)-N(9)-C(3)	120	124
14	C(26)-C(27)-C(18)	119.999	120	65	C(3)-O(8)-Mo(1)	109.5	-
15	C(22)-C(27)-C(18)	120	120	66	N(9)-C(3)-O(8)	117.85	-
16	H(43)-C(23)-C(24)	120	120	67	N(9)-C(3)-C(4)	117.85	120
17	H(43)-C(23)-C(22)	120	120	68	O(8)-C(3)-C(4)	124.3	124.3
18	C(24)-C(23)-C(22)	120	-	69	H(35)-C(7)-H(34)	109.52	109
19	C(27)-C(22)-C(23)	119.999	120	70	H(35)-C(7)-H(33)	109.462	109
20	C(27)-C(22)-C(21)	120	120	71	H(35)-C(7)-C(5)	109.462	110
21	C(23)-C(22)-C(21)	119.998	120	72	H(34)-C(7)-H(33)	109.442	109
22	H(42)-C(21)-C(22)	120.001	120	73	H(34)-C(7)-C(5)	109.442	110
23	H(42)-C(21)-C(20)	120	120	74	H(33)-C(7)-C(5)	109.5	110
24	C(22)-C(21)-C(20)	120	-	75	H(32)-C(4)-C(5)	123.404	120
25	H(41)-C(20)-C(21)	120	120	76	H(32)-C(4)-C(3)	123.404	120
26	H(41)-C(20)-C(19)	119.999	120	77	C(5)-C(4)-C(3)	113.191	-
27	C(21)-C(20)-C(19)	120	-	78	C(7)-C(5)-O(6)	114.702	120
28	C(28)-C(18)-C(27)	119.999	120	79	C(7)-C(5)-C(4)	114.702	121.4
29	C(28)-C(18)-C(19)	119.999	120	80	O(6)-C(5)-C(4)	130.596	124.3
30	C(27)-C(18)-C(19)	120	120	81	C(5)-O(6)-Mo(1)	109.5	-
31	O(30)-C(19)-C(20)	115.699	124.3	82	O(6)-Mo(1)-O(29)	90	-
32	O(30)-C(19)-C(18)	124.299	124.3	83	O(6)-Mo(1)-O(30)	80.0001	-
33	C(20)-C(19)-C(18)	120	120	84	O(6)-Mo(1)-O(8)	89.9999	-
34	H(39)-C(14)-C(15)	120	120	85	O(6)-Mo(1)-O(17)	135.249	-
35	H(39)-C(14)-C(13)	120	120	86	O(6)-Mo(1)-O(16)	89.9999	-
36	C(15)-C(14)-C(13)	119.999	-	87	O(6)-Mo(1)-O(2)	64.4926	-
37	H(38)-C(13)-C(14)	120	120	88	O(29)-Mo(1)-O(30)	80.8698	-
38	H(38)-C(13)-C(12)	120	120	89	O(29)-Mo(1)-O(8)	90	-
39	C(14)-C(13)-C(12)	120.001	-	90	O(29)-Mo(1)-O(17)	134.751	-
40	H(50)-C(31)-H(49)	109.52	109	91	O(29)-Mo(1)-O(16)	180	-
41	H(50)-C(31)-H(48)	109.462	109	92	O(29)-Mo(1)-O(2)	85.973	-
42	H(50)-C(31)-C(11)	109.462	110	93	O(30)-Mo(1)-O(8)	166.395	-
43	H(49)-C(31)-H(48)	109.442	109	94	O(30)-Mo(1)-O(17)	103.594	-
44	H(49)-C(31)-C(11)	109.442	110	95	O(30)-Mo(1)-O(16)	99.1301	-
45	H(48)-C(31)-C(11)	109.5	110	96	O(30)-Mo(1)-O(2)	16.1646	-
46	H(37)-C(12)-C(13)	120	120	97	O(8)-Mo(1)-O(17)	89.9999	-
47	H(37)-C(12)-C(11)	120	120	98	O(8)-Mo(1)-O(16)	90	-
48	C(13)-C(12)-C(11)	120	-	99	O(8)-Mo(1)-O(2)	154.131	-
49	H(40)-C(15)-C(14)	120	120	100	O(17)-Mo(1)-O(16)	45.2487	-
50	H(40)-C(15)-C(10)	120	120	101	O(17)-Mo(1)-O(2)	110.81	-
51	C(14)-C(15)-C(10)	120	-	102	O(16)-Mo(1)-O(2)	94.0269	-



(IV)



Proposed pseudopentagonal bipyramidal structures of complexes

(V)

[(IV)] are given in Tables 6 and 7, respectively. For convenience of looking over the different bond lengths and bond angles, the various atoms in the compound in question are numbered in Arabic numerals. In all, 157 measurements of the bond lengths (55 in numbers), plus the bond angles (102 in numbers) are listed. Except few cases, optimal values of both the bond lengths and the bond angles are given in the Tables along with the actual ones. The actual bond lengths/bond angles given in the tables are calculated values as a result of energy

optimization in CHEM 3D Ultra<sup>52</sup>, while the optimal bond length/optimal bond angle values are the most desirable/ favorable (standard) bond lengths/bond angles established by the builder unit of the CHEM 3D. The missing of some values of standard bond lengths/bond angles may be due to the limitations of the software, which we had already noticed in modeling of other systems<sup>53</sup>. In most of the cases, the actual bond lengths and bond angles are close to the optimal values, and thus, the proposed structures of the compound (1) as well as of the others are acceptable.



## Conclusions

The satisfactory analytical data and all the studies given above suggest that the present complexes may be formulated as  $[\text{MoO}(\text{O}_2)(2\text{-hnd})(\text{L})]\cdot\text{H}_2\text{O}$ , where 2-hnd = 2-hydroxy-1-naphthaldehyde, and LH = *o*-acetoacetanilide (*o*-aans), *o*-acetoaceto-toluidide (*o*-aatd), acetylacetone (acacH) or methyl actoacetate (macac). Keeping in view the monomeric hepta-coordination of all the complexes, and the well established hepta-coordinate pseudopentagonal bipyramidal structure of bis(phenolato-oxazoline)monoperoxomolybdenum(VI) (**III**) [having a monobasic bidentate (O, N-donor) phenolato-oxazoline ligand similar to monobasic (O, O-donor) 2-hndH and LH ligands in the present investigation], a pseudopentagonal bipyramidal structure (**V**) has been proposed for these complexes. X-ray crystallographic studies, which might confirm the proposed structures, could not be carried out, as suitable crystals were not obtained.

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