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# Synthesis, characterization and catalytic activity of dioxidouranium(VI) complexes of ONNO tetradentate Mannich bases

Mannar R. Maurya<sup>a,\*</sup>, Bekele Mengesha<sup>a</sup>, Shailendra K. Maurya<sup>a</sup>, Fernando Avecilla<sup>b</sup>

<sup>a</sup>Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee–247667, India. E-mail: rkmanfcy@iitr.ac.in; Fax: +91 1332 273560; Tel: +91 1332 285327 <u>https://www.iitr.ac.in/</u>CY/rkmanfcy <sup>b</sup>Grupo Xenomar, Centro de Investigacións Científicas Avanzadas (CICA), Departamento de Química, Facultade de Ciencias, Universidade da Coruña, Campus de A Coruña, 15071 A Coruña, Spain

**Keywords:** Dioxidouranium(VI) complexes; Mannich bases; Crystal structure; Catalytic activity; Oxidative bromination; NMR spectroscopy.

## Abstract

The reaction of dibasic tetradentate ONNO donor Mannich bases, derived from ethylenediamine and 2,4–di–*tert*–butylphenol (H<sub>2</sub>L<sup>1</sup>) (**I**), 2,4–di–methylphenol (H<sub>2</sub>L<sup>2</sup>) (**II**), 2–*tert*–butyl–4– methylphenol (H<sub>2</sub>L<sup>3</sup>) (**III**) and 2,4–di–chlorophenol (H<sub>2</sub>L<sup>4</sup>) (**IV**), with U<sup>VI</sup>O<sub>2</sub>(MeCOO)<sub>2</sub>·2H<sub>2</sub>O in a 1:1 molar ratio in refluxing MeOH gave the corresponding mononuclear *trans*dioxidouranium(VI) complexes of the type *trans*-[U<sup>VI</sup>O<sub>2</sub>L(MeOH)] (H<sub>2</sub>L = H<sub>2</sub>L<sup>1</sup> to H<sub>2</sub>L<sup>4</sup>) (**1–4**) The synthesized complexes are stable in air, reddish-brown in color and soluble in most solvents. There complexes are characterized by elemental analysis, various spectroscopic (FT-IR, UV/Vis, <sup>1</sup>H and <sup>13</sup>C NMR) techniques and single-crystal X-ray analysis of **3** and **4**. The complexes adopt distorted pentagonal bipyramidal geometry around the metal centre. The ligand acts as tetradentate, coordinating through two phenolato oxygen and two imino nitrogen atoms; two oxido groups are *trans* to each other. These complexes are used as catalysts to study the

oxidative bromination of thymol and styrene. The catalytic oxidative bromination of thymol resulted in the formation of three products namely, 2-bromothymol, 4-bromothymol and 2,4-dibromothymol while oxidative bromination of styrene gave two products, 2-bromo-1-phenylethane-1-ol and 1-phenylethane-1,2-diol. In order to find out the optimized reaction conditions for the fixed concentration (10 mmol) of substrate, effects of different amounts of catalyst, KBr, HClO<sub>4</sub>, and oxidant (H<sub>2</sub>O<sub>2</sub>) have been investigated. Under the optimized reaction conditions, all the complexes have shown good catalytic potentials for the oxidative bromination of substrates, establishing the functional similarity to vanadium dependent haloperoxidases. Changes in the UV-visible absorption spectra of dioxidouranium(VI) complexes upon addition of H<sub>2</sub>O<sub>2</sub> suggest the formation of the corresponding oxidoperoxidouranium(VI) complexes.

#### 1. Introduction

Amongst the actinides, uranium can exist in five oxidation states, +2, +3, +4, +5 and +6but only the +4 and +6 states are stable enough to be of practical importance. Uranium complexes are generally dominated by the  $[U^{VI}O_2]^{2+}$  moiety in +6 oxidation state and forms complexes very similar to group 6 transition metal analogues  $[M^{VI}O_2]^{2+}$  (M = Cr, Mo and W) and even similar to  $[VO_2]^+$ . However, the basic difference between  $[MO_2]^{2+}/[VO_2]^+$  and [U<sup>VI</sup>O<sub>2</sub>]<sup>2+</sup> moieties is that former ones generally have *cis*-MO<sub>2</sub> group while dioxido group in uranyl ion in their complexes is essentially *trans*; the angle being close to 180°. Further, depending upon the reaction conditions and ligands used the equatorial plane of uranyl complexes can further extend the coordination number by four, five or six resulting in the formation of complexes of varied geometries [1]. During past one decade, a good number of papers on  $[U^{VI}O_2]^{2+}$ - complexes of polydentate ligands have appeared [1-15] but the catalytically potential of these complexes has been narrowly explored [16]. Such complexes are generally associated with one solvent/neutral donor molecule in equatorial position which is flexible in nature and may play an important role in catalytic reactions like vanadium, molybdenum and tungsten complexes [17-24]. Adam in 2015 has reported dioxidouranium(VI) complexes catalyzed oxidation of various alkenes using H<sub>2</sub>O<sub>2</sub> and TBHP as oxidant [16] and showed that these complexes can act as potential oxidation catalysts but oxidative halogenation of organic substrates has only been reported by us very recently [25]. Such catalytic reaction is generally

observed by model vanadium complexes in the presence of oxidant, halide ion and acid, and considered as a functional mimic of enzymes haloperoxidases [17-20]; a critical review on sustainable bromination of organic compounds has been recently reported by Conte et. al. [26]. Herein we have now prepared and characterized dioxidouranium(VI) {*trans*-[UO<sub>2</sub>]<sup>2+</sup>} complexes of ligands derived from Mannich bases of ethylenediamine and 2,4–substituted phenols (H<sub>2</sub>L<sup>1-4</sup>, Scheme 1), and report our findings on the oxidative bromination of thymol and styrene in the line of functional models of vanadium dependent haloperoxidases. Very recently, we reported dioxidomolybdenum(VI) complexes of these ligands where they act as dibasic tetradentate, coordinating through the two O<sub>phenolate</sub> and two N<sub>amine</sub> atoms. These complexes catalyze oxygen atom transfer (OAT) between benzoin and dimethyl sulfoxide (DMSO) in acetonitrile at 80 °C and result in almost 99 % conversion in only 18 h of reaction time [27].

### 2. Experimental section

#### 2.1. Materials and general methods

 $U^{VI}O_2(MeCOO)_2 \cdot 2H_2O$  (Loba chemie, India), thymol, KBr (S.D. fine chemicals, India), methanol (SRL, India), n-hexane, perchloric acid, 30% H<sub>2</sub>O<sub>2</sub>, and DMSO (Rankem, India) were used as obtained. Other chemicals and solvents were of analytical reagent grade. Ligands I to IV were prepared as reported in our previous paper [27].

Elemental (C, H and N) analysis of the complexes was carried out on an Elementar model Vario–EI–III after drying the samples at 100 °C. IR spectra were recorded as KBr pellets on a Nicolet 1100 FT–IR spectrometer. Electronic spectra of the complexes were recorded in MeCN on a Shimadzu 2600 UV–Vis spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub>/DMSO-d6 on a JEOL ECX 400 MHz spectrometer. The catalytic activity of the metal complexes were studied using Shimadzu 2010 gas chromatogram with an Rtx-1 capillary column (30 m × 0.25 mm × 0.25 µm), and their % conversion and product selectivity were calculated using peak area of substrate and respective products.

## 2.2. Preparation of complexes $[U^{VI}O_2L^{1-4}(MeOH)]$ (1-4)

A representative method for  $[U^{VI}O_2L^1(MeOH)]$  (1) is given here. A solution of  $U^{VI}O_2(MeCOO)_2 \cdot 2H_2O$  (0.424 g, 1 mmol) in 20 mL MeOH was added to a stirred suspension of ligand  $H_2L^1$  (0.496 g, 1 mmol) ) in MeOH (100 mL) (1:1 molar ratio) and the resulting reaction mixture was heated under reflux on a water bath for 10 h. During this period ligands slowly

dissolved and red-brown colored complex precipitated instead. After reducing the solvent volume to ca. 40 mL and cooling to room temperature, the precipitated solid was collected by filtration, washed with MeOH ( $2 \times 5$  mL) and dried under vacuum.

Complexes 2, 3, and 4 were prepared similarly using  $U^{VI}O_2(MeCOO)_2 \cdot 2H_2O$  (0.424 g, 1.0 mmol) in 20 mL MeOH and respective ligands (1 mmol) in 100 mL MeOH. Slow evaporation of methanolic solution of 3 produced single crystals suitable for X-ray study. Crystals of  $[U^{VI}O_2L^4(EtOH)]$  (now numbered 4a) were grown in EtOH by slow evaporation. All analytical measurements were made after drying the metal complexes at 110 °C for 5 h.

*Data for*  $[U^{VI}O_2L^1(MeOH)]$  (1). Yield: 0.605 g (76%). Anal. Calcd for C<sub>33</sub>H<sub>54</sub>N<sub>2</sub>O<sub>5</sub>U (796.83 g mol<sup>-1</sup>): C, 49.74; H, 6.83; N 3.52. Found: C, 49.3; H, 7.0; N, 3.6%.  $\lambda$ [nm] ( $\epsilon$ , litre mole<sup>-1</sup> cm<sup>-1</sup>): 242 (5.63 × 10<sup>3</sup>), 281 (4.45 × 10<sup>3</sup>), 394 (3.62 × 10<sup>3</sup>), 474 (3.41 × 10<sup>3</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.33 (s, 2H), 6.86 (s, 2H) (aromatic), 2.51 (s, 2H, -NH), 3.87 (s, 2H), 2.93 (s, 2H) (-CH<sub>2</sub>-), 1.63 (s, 4H) (-CH<sub>2</sub>CH<sub>2</sub>-), 1.34 (s, 18H), 1.19 (s, 18H) (-CH<sub>3</sub>). <sup>13</sup>C NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 166.65, 138.16, 136.31, 128.97, 125.88, 124.24, 22.57, 122.33, 57.54, 52.84, 35.57, 33.88, 32.57, 31.04.

*Data for*  $[U^{VI}O_2L^2(MeOH)]$  (2). Yield: 0.515 g (82.0%). Anal. Calcd for C<sub>21</sub>H<sub>30</sub>N<sub>2</sub>O<sub>5</sub>U (628.51 g mol<sup>-1</sup>): C, 40.13; H, 4.81; N, 4.46. Found: C, 40.47; H, 4.65; N 4.55%.  $\lambda$ [nm] ( $\epsilon$ , litre mole<sup>-1</sup> cm<sup>-1</sup>): 242 (6.76 × 10<sup>3</sup>), 290 (4.31 × 10<sup>3</sup>), 402 (3.5 × 10<sup>3</sup>), 490 (3.82 × 10<sup>3</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 6.99 (s, 1H), 6.92 (s, 3H) (aromatic), 5.40 (s, 2H, -NH), 4.71-4.69 (dd, 2H), 4.18-4.15 (dd, 2H) (-CH<sub>2</sub>-), 3.90 (t, 2H), 3.70 (t, 2H) (-CH<sub>2</sub>CH<sub>2</sub>-), 3.25 (s, 3H) (CH<sub>3</sub> of MeOH), 2.32 (s, 3H), 2.12 (s, 3H) (CH<sub>3</sub>). <sup>13</sup>C NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 165.88, 130.50, 127.78, 127.29, 126.55, 123.27, 56.30, 52.82, 20.47, 17.24.

*Data for*  $[U^{V1}O_2L^3(MeOH)]$  (3). Yield: 565 g (79%). Anal. Calcd for C<sub>27</sub>H<sub>42</sub>N<sub>2</sub>O<sub>5</sub>U (712.67 g mol<sup>-1</sup>): C, 45.50; H, 5.94; N, 3.93. Found: C, 45.2; H, 5.8; N, 4.0%.  $\lambda$ [nm] ( $\epsilon$ , litre mole<sup>-1</sup> cm<sup>-1</sup>): 242 (broad) (5.4 × 10<sup>3</sup>), 272 (5.95 × 10<sup>3</sup>), 391 (3.08 × 10<sup>3</sup>), 474 (2.3 × 10<sup>3</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 6.85 (s, 2H), 6.64 (s, 2H) (aromatic), 3.81 (s, 2H), 2.94 (s, 2H) (-CH<sub>2</sub>-), 3.25 (s, 3H)(CH<sub>3</sub> of MeOH), 2.51 (s, -NH), 2.12 (s, 4H) (-CH<sub>2</sub>CH<sub>2</sub>-), 1.61s, 9H) 1.32 (s, 9H) (CH<sub>3</sub>). <sup>13</sup>C NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 153.69, 135.49, 127.31, 126.84, 126.54, 122.33, 57.58, 56.82, 34.65, 34.36, 30.86, 29.59, 20.69.

*Data for* [ $U^{VI}O_2L^4(MeOH)$ ] (4). Yield: 0596 g (84%). Anal. Calcd for C<sub>17</sub>H<sub>18</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>5</sub>U (710.17 g mol<sup>-1</sup>): C, 28.75; H, 2.55; N 3.94. (Found: C, 28.6; H, 2.4; N, 4.1%.  $\lambda$ [nm] (ε, litre mole<sup>-1</sup> cm<sup>-1</sup>): 241 (5.53 × 10<sup>3</sup>), 273 (4.22 × 10<sup>3</sup>), 374 (3.4 × 10<sup>3</sup>), 466 (2.6 × 10<sup>3</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.49 (s, 2H), 7.33 (s, 2H) (aromatic), 6.10 (s, 2H, -NH), 4.65 (dd, 2H) (-CH<sub>2</sub>-), 4.36 (dd, 2H) (-CH<sub>2</sub>CH<sub>2</sub>-), 3.30 (s, 3H) (CH<sub>3</sub> of MeOH). <sup>13</sup>C NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 163.14, 130.61, 127.58, 123.55, 117.60, 55.21, 52.55.

#### 2.3. X-Ray crystal structure determination

Three-dimensional X-ray data were collected on a Bruker Kappa Apex CCD diffractometer at room temperature for 3 and at 100(2) K for 4a, by the  $\phi$ - $\omega$  scan method. Reflections were measured from a hemisphere of data collected from frames, each of them covering 0.3° in  $\omega$ . A total of, 81578 for 3 and 87961 for 4a, reflections measured were corrected for Lorentz and polarization effects and for absorption by multi-scan methods based on symmetry-equivalent and repeated reflections. Of the total, 6254 for 3 and 8678 for 4a, independent reflections exceeded the significance level ( $|F|/\sigma |F|$ ) > 4.0. After data collection an empirical absorption correction (SADABS) [28] was applied, and the structures were solved by direct methods and refined by full matrix least-squares on  $F^2$  data using SHELX suite of programs [29] Refinements were done with allowance for thermal anisotropy of all non-hydrogen atoms. In 3, hydrogen atoms were included in calculated position and refined in the riding mode, except for O(1M), O(2M) and N(1), which were located in difference Fourier map and fixed to the atoms. In 4a, hydrogen atoms were included in calculated position and refined in the riding mode, except for O(1M), O(2M), N(1), N(2) and N(4) which were located in difference Fourier map and fixed to the atoms. Due to disorder around EtOH molecule bonded to U(2) atom in compound 4a, two positions for carbon atoms of EtOH molecule were refined with anisotropic atomic displacement parameters. The site occupancy factor was 0.66286 for C(3MA) and C(4MA). A final difference Fourier map showed a high residual density outside: 3.250 and -1.428 e.Å<sup>-3</sup> for **3** and 1.440 and  $-2.417 \text{ e.Å}^{-3}$  for **4a**, next to the uranium atoms. A weighting scheme w =  $1/[\sigma^2(F_0^2) + (0.036900)]$  $P^{2} + 61.142097 P$  for **3**, and  $w = 1/[\sigma^{2}(F_{o}^{2}) + (0.000000 P)^{2} + 34.178295 P]$  for **4a**, where P =  $(|F_0|^2 + 2|F_c|^2)/3$ , were used in the latter stages of refinement. Further details of the crystal structures determination are given in Table 1. CCDC 1876854 (for 3) and 1876855 (for 4a)

contain the supplementary crystallographic data for the structures reported in this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi: \$\$\$\$.

<<Table 1>>

## 2.4. Catalytic activity study

*Note:*  $HClO_4$  is explosive in nature, though we did not face any problem in handling it at lower scale. However, a due precaution must be taken in its handling.

## 2.4.1. Oxidative bromination of thymol

Thymol (1.50 g, 10 mmol), 30% aqueous  $H_2O_2$  (2.27 g, 20 mmol) and KBr (2.38 g, 20 mmol), were mixed in a flask containing 20 mL water and stirred at room temperature. The catalyst (0.001 g,  $1.6 \times 10^{-3}$  mmol) and 70% HClO<sub>4</sub> (10 mmol, 1.43 g) was then added to it and the reaction mixture was stirred at room temperature for 2 h. A small aliquot at every 30 min was withdrawn, extracted with n-hexane, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and analyzed quantitatively by gas chromatograph on the basis of their relative peak area of the respective product. The confirmation of products was carried out by GC-MS after their separations.

## 2.4.2. Oxidative bromination of styrene

Styrene (1.04 g, 10 mmol), 30% aqueous  $H_2O_2$  (2.27 g, 20 mmol) and KBr (2.38 g, 20 mmol), were mixed in a flask containing 20 mL water and stirred at room temperature. The catalyst (0.001 g,  $1.6 \times 10^{-3}$  mmol) and 70% HClO<sub>4</sub> (20 mmol, 2.86 g in 2 equal portions, one at t = 0 min and other at t = 30 min) was then added to it and the reaction mixture was stirred at room temperature for 2 h. A small aliquot at every 30 min was withdrawn, extracted with n-hexane, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and analyzed quantitatively by gas chromatograph as mentioned above. The confirmation of products was carried out by GC-MS after their separations.

#### 3. Results and Discussion

Ligands I - IV (H<sub>2</sub>L<sup>1-4</sup>) were prepared by the condensation of ethylenediamine, formaldehyde and 2,4–substituted phenols (1 : 2 : 2 molar ratio) in MeOH (Scheme 1, above)

(Yields: 1, 76%; II, 74%; III, 50% and IV, 62%) [27]. Reaction of these ligands with  $U^{VI}O_2(MeCOO)_2 \cdot 2H_2O$  in 1:1 molar ratio in MeOH (Scheme 1, bottom), results in the formation of the corresponding dioxidouranium(VI) complexes,  $[U^{VI}O_2(L^{1-4})(MeOH)]$  (1–4) in good yields. All complexes are air stable red-brown solids and soluble in common organic solvents such as MeOH, CHCl<sub>3</sub>, MeCN, DMSO, DMF etc.

#### <<Scheme 1>>

#### 3.1. Solid state characterization

ORTEP diagram for the complexes  $[UO_2L^3(MeOH)]$  (3) and  $[UO_2L^4(EtOH)]$  (4a) are shown in Figs. 1 and 2, respectively and their crystal packing are presented in Figs. 3 and 4, respectively. Selected bond distances and angles are given in Table 2. Both compounds are mononuclear complexes, which crystallize in a monoclinic space group  $P2_1/n$  and present two complexes in the asymmetric unit. The structures adopt a distorted pentagonal bipyramidal geometry around of metal centre. The ligands act as tetradentate, coordinating through two phenoxido oxygen and two amine nitrogen atoms. The amine nitrogen atoms present a distorted sp<sup>3</sup> hybridized bonding network. U centres complete the coordination sphere by bonding to two O<sub>oxido</sub> terminal oxygen atoms and one oxygen atom from solvent molecules (MeOH or EtOH). The U<sup>VI</sup>=O bond lengths [1.769(8)-1.766(4) Å in compound 3 and 1.766(4)-1.796(4) in compound 4a] are similar to other in the literature [15, 30] The two distances U<sup>VI</sup>–O<sub>phenoxido</sub> [2.215(8)-2.235(9) Å in compound **3** and 2.304(4)-2.205(4) Å in compound **4a**] are shorter than the U<sup>VI</sup>–O<sub>solvent</sub> [2,585(8) Å in compound **3** and 2.455(4) Å in compound **4a**]. The equatorial plane is occupied by the O<sub>phenoxido</sub> atoms, O(3) and O(4), by the N<sub>amine</sub> atoms, N(1) and N(2) and by the oxygen atom (O1M) of MeOH or ETOH molecules. They are distorted respect to the planarity, [mean deviation from the plane 0.0856(60) Å in compound 3 and 0.0956(29) Å in compound 4a]. In an ideal pentagonal bipyramidal polyhedron the angle between adjacent atoms of equatorial plane is 72°. The angles between adjacent atoms are in the range 68.9(4)°-77.1(3)° in compound **3** and between 67.32(15)°-78.58(14)° in compound **4a** (see Table 2). The terminal oxido atoms occupy the axial sites. The angle between the plane containing the two terminal oxido atoms and U(1) atoms with the equatorial planes are 89.97(31)° in 3 and 89.49(1.02)° in 4a. The crystal packing present hydrogen bonds between the electronegative atoms (see Table S1

of SI and Figs 3 and 4), which determine dimeric aggregates in antiparallel form.  $\pi$ - $\pi$  Interactions are not present in the structures.

<<Figures 1-4>> <<Table 2>>

### 3.2. Spectral studies

IR spectroscopic analyses of all the ligands and the uranium complexes were carried to confirm the coordination modes of ligands. The IR spectra of all complexes exhibit one sharp band around 850-868 cm<sup>-1</sup> (Table S2 of SI), due to the asymmetric ( $v_3$ ) stretching of *trans*-[UO<sub>2</sub>] core [13, 31]. Coordination of phenolate oxygen and nitrogen functionalities could not be ascertained unequivocally by IR spectral study because the spectra of the ligands as well as complexes both exhibit v(OH) and v(NH) bands around 3400 and 3100 cm<sup>-1</sup>, respectively. The former band may be only due to the coordinated MeOH. However, coordination of these functionalities are well supported by single crystal X-ray study (vide supra). The characteristic band due to methylene group appears in the spectra of the ligands as well as the complexes around 2800–3000 cm<sup>-1</sup>.

Experimental section collects UV/Vis spectral data of *trans*–[UO<sub>2</sub>]<sup>2+</sup> complexes recorded in MeCN and Figs. S1 and S2 of SI) give detail of the spectral profiles of ligands and complexes, respectively. The detail interpretation of spectral data of ligands is reported earlier [27]. UV-Vis region of the spectra of complexes essentially show two bands which seem like split bands of  $\pi \rightarrow \pi^*$  transition. A medium intensity band at ca. 390 nm is assigned due to  $n \rightarrow \pi^*$  transition while a low intensity band at ca. 470 nm is assigned due to the ligand to metal charge transfer transition[14, 32].

<sup>1</sup>H NMR spectra of ligands and complexes recorded in CDCl<sub>3</sub>, presented in the experimental section also supplement the coordinating modes of ligand to the metal complex. Thus, the absence of the signal in complexes, that appears at  $\delta = 10.25-10.73$  ppm due to two equivalent nature of phenolic –OH protons in ligands, indicates the coordination of the phenolic oxygen after its deprotonation [27]. Signals due to methylene groups (connecting to –N and aromatic ring) and –NH protons have no systematic trend but are observed in ligands as well as in complexes. Protons of methyl group of MeOH appear at ca. 3.3 ppm. Aromatic protons of all ligands and complexes and methyl protons of ligands I, II and III and their corresponding complexes appear in the expected region with slight variations.

The <sup>13</sup>C NMR data recorded in DMSO-d<sub>6</sub> are listed in the experimental section; a <sup>13</sup>C NMR spectrum of complex **4** is presented here as a representative (Fig. S3 of SI). The coordination–induced <sup>13</sup>C NMR chemical shifts due to coordination of phenolic oxygens and imino nitrogens further supplement the binding mode of the ligands. A significant shifts,  $\Delta \delta = [\delta(\text{complex}) - \delta(\text{ligand})]$  was observed for the signals of the carbon atoms in the vicinity of the coordinating atoms (Table 3). Thus, the carbons bearing the phenolic oxygens (C<sub>1</sub>/C<sub>1</sub>') with a  $\Delta \delta$  value of -0.52 to 15.82 ppm, ethylene carbons (connecting to –NH and aromatic, C<sub>7</sub>/C<sub>7</sub>') with a  $\Delta \delta$  value of -2.06 to 6.19 ppm and ethylene carbons (-CH<sub>2</sub>CH<sub>2</sub>-, C8/C8') with a  $\Delta \delta$  value of 1.05 to 6.83 ppm confirm the coordination of the corresponding accompanying functionalities to uranium. Other signals in the spectra of complexes appear well within the expected region.

<<Table 3>>

### 3.3. Catalytic activity study

#### 3.3.1. Oxidative bromination of thymol

The synthesized complexes **1**, **2**, **3** and **4** have been used as catalyst to study catalytic oxidative bromination of thymol (a monoterpene) in the presence of KBr, 70% aqueous HClO<sub>4</sub> and 30% H<sub>2</sub>O<sub>2</sub> in aqueous solution under appropriate reaction conditions. All reactions were run in triplicate and carried out in a 100 mL reaction flask in aqueous medium at room temperature. The bromination reaction takes place on the most activated site as a result of electrophilic aromatic substitution in the phenolic ring. Thus, the oxidative bromination of thymol led to the formation of 2-bromothymol and 4- bromothymol while further bromination of these also gave 2,4- dibromothymol (Scheme 2). In fact, these products are usual and reported in the literature [24, 33]. As observed in *cis*-[MO<sub>2</sub>]- complexes (M = V, Mo and W) [23,24,32,33], the reaction of complexes with KBr in the presence of H<sub>2</sub>O<sub>2</sub> and HClO<sub>4</sub>, catalytically generate HOBr and/or Br<sup>+</sup>, Br<sub>2</sub>, Br<sup>3-</sup> which brominate thymol. A similar reaction may also be presumed by *trans*-[UO<sub>2</sub>]<sup>2+</sup>- complexes.

<<Scheme 2>>

In order to obtain the best suited reaction conditions for the maximum oxidative brominated products, reaction conditions were optimized considering 2 as a representative

catalyst. Thus, for 10 mmol of thymol (1.50 g), four different amounts of catalyst (0.0005, 0.001, 0.002, 0.003 g), three different amounts of 30% aqueous  $H_2O_2$  (10, 20 and 30 mmol), three different amounts of KBr (10, 20 and 30 mmol) and three different amounts of 70% aqueous  $HClO_4$  (10, 20 and 30 mmol, added in three equal portions to the reaction mixture, first portion at t = 0 and other two portions after every 30 min intervals) were taken in 20 mL water and the reaction was carried out at room temperature for 2h. The pH noted just before adding  $HClO_4$  was ca. 5.9 while after addition of first portion i.e. 10 mmol of  $HClO_4$ , it was ca. 1.0. The pH slowly increases to ca. 1.5 during the course of reaction but again it comes down to ca. 1.0 after addition of next 10 mmol of  $HClO_4$ . Thus, the slow decomposition of complex is very likely during the course of reaction at such a low pH.

Details of all reaction conditions and the corresponding conversions of thymol are summarized in Figs. S4-S7 and Table S3 (See SI). It may be concluded from the data presented in Table S3 that the optimized reaction conditions (entry no. 10) for the best conversion of 10 mmol (1.50 g) of thymol with the catalyst **2** are those using 0.002 g catalyst, 30 mmol 30%  $H_2O_2$ , 30 mmol KBr, and 30 mmol 70% HClO<sub>4</sub>. Under these conditions the obtained conversion is 99% where the selectivity of different major products follows the order: 4-bromothymol (91%) > 2,4-dibromothymol (5%) > 2-bromothymol (4%). However, reducing the amount of HClO<sub>4</sub> to 10 mmol under above reaction conditions results in the reduction of conversion of thymol to 82% but the selectivity of the 2,4-dibromothymol improves to 31% and that of 4-bromothymol shrinks to 60%. Thus, depends upon the requirement of the desired product(s), reaction conditions may be tuned. Leaving the reaction for ca. 10h under the conditions of entry 10 of Table S3, a quantitative conversion of thymol was observed with not much change in the selectivity of products.

Other three catalysts i.e. **1**, **3** and **4** were also tested under the above optimized reaction conditions and the results are presented in Table 4. All the four complexes show comparable catalytic activity between 97-99% (also see Fig. 5) along with high turnover frequency. Again 4-bromothymol is highest in selectivity (ca. 90%). Blank reaction under above reaction conditions gave only 32 % conversion (Table 4).

<<Table 4>> <<Figure 5>>

We have also studied the catalytic potential of complex 2 towards the oxidative bromination of thymol in different biphasic solvent systems and their effect on the selectivity of different products. The catalytic potential of 2 is almost the same in most mixed solvent systems studied here (Table 5) but the selectivity of products slightly varies. The selectivity of 4bromothymol is as highest (95%) in CHCl<sub>3</sub>-H<sub>2</sub>O followed by 93% in hexane-H<sub>2</sub>O and 91% in water. Thus, it seems that 4-bromothymol is the preferred product over 2,4-dibromothymol possibly due to steric hindrance which does not favour further bromination of monobromothymol in aprotic solvents (Table 4). The biphasic (H<sub>2</sub>O-CH<sub>3</sub>OH) blank reaction under above reaction conditions gave almost similar conversion as obtained in single phasic system.

#### <<Table 5>>

These complexes show almost similar conversion as reported for  $[V^{V}O(acac)(L)]$  [Hacac = acetyl acetone, H<sub>2</sub>L = 6,6'-(2-(pyridin-2-yl)ethylazanediyl)bis(methylene)bis(2,4-di-*tert*-butylphenol)] (ca. 99%) [20], Cs(H<sub>2</sub>O)[V<sup>V</sup>O<sub>2</sub>{3,5-bis(2-hydroxyphenyl)-1-phenyl-1,2,4-triazole}] (99%) [5b], [K(H<sub>2</sub>O)<sub>2</sub>][VO<sub>2</sub>L] (H<sub>2</sub>L = ligands derived from 4,6-diacetyl resorcinol and isonicotinoyl hydrazide, nicotinoyl hydrazide, benzoyl hydrazide or 2-furoyl hydrazide (90-98%) [5c] and  $[Mo^{VI}O_2L]^{2+}$  (H<sub>2</sub>L = Schiff base ligands derived from 8-formyl-7-hydroxy-4-methylcoumarin and hydrazides (94-99%) [23], and little better than reported for  $[W^{VI}O_2]^{2+}$  complexes (91-96%) [24]. However, the selectivity of 4-bromothymol is relatively high (more than 90%) for uranium complexes over other catalysts. In case of  $[U^{VI}O_2]^{2+}$  complexes, under optimized reaction conditions higher amounts of KBr, H<sub>2</sub>O<sub>2</sub> and HClO<sub>4</sub> (3 equivalent each for 10 mmol of substrate) versus lower amounts of these reagents for vanadium, molybdenum and tungsten complexes used and this might be responsible for higher amount of 4-bromothymol.

#### 3.3.2. Oxidative bromination of Styrene

The synthesized complexes 1, 2, 3 and 4 have also been used as catalysts to study the oxidative bromination of styrene. We have considered complex 2 again as a representative catalyst and the oxidative bromination of styrene was carried out at room temperature in the presence of KBr, 70% aqueous HClO<sub>4</sub> and 30% aqueous H<sub>2</sub>O<sub>2</sub> in water. This led to the formation of (a) 2-bromo-1-phenylethane-1-ol and (b) 1-phenylethane-1,2-diol along with some minor

oxidized products (totaling ca. 1%), though literature reports the formation of one more product i.e. 1,2-dibromo-1-phenylethane (Scheme 3) [21,33,34].

<<Scheme 3>>

Consequently, the reaction was investigated by changing different parameters that may affect the rate of styrene bromination and the selectivity of different products. Thus, for 10 mmol of styrene (1.04 g, 10 mmol), four different amounts of catalyst (0.0005, 0.001, 0.002, 0.003 g), three different amounts of 30% aqueous H<sub>2</sub>O<sub>2</sub> (10, 20 and 30 mmol), three different amounts of KBr (10, 20 and 30 mmol) and three different amounts of 70% aqueous HClO<sub>4</sub> (10, 20 and 30 mmol, added in three equal portions to the reaction mixture as mentioned above). Details of all reaction conditions and the corresponding conversion of styrene are summarized in Table S4 and Figs. S8-S11 of SI. From the data presented in table, it is clear that the optimized reaction conditions (entry no. 9) for the maximum conversion of 10 mmol (1.04 g) of styrene are those using 0.001 g ( $1.6 \times 10^{-3}$  mmol) of catalyst, 2.26 g (20 mmol) of 30% H<sub>2</sub>O<sub>2</sub>, 3.57 g (30 mmol) of KBr, and 2.86 g (20 mmol) of 70% HClO<sub>4</sub>. Under these conditions the obtained conversion is 99% where the selectivity of the two products follows the order: 1-phenylethane-1,2-diol (69%) > 2-bromo-1-phenylethane-1-ol (31%). While the selectivity of products varies with the change of reaction conditions, their order is maintained for all reaction conditions (Table S4). Again, leaving the reaction for ca. 10h under the conditions of entry 9 of Table S4, a quantitative conversion of styrene was observed.

Other three catalysts, i.e. **1**, **3** and **4** were also tested under the above optimized reaction conditions for the maximum conversion of styrene. The results are accessible in Fig. 6 and Table 6. It is clear from the data that all the four complexes show comparable catalytic activity (99%) along with high turnover frequency showing no effect of the substituents on the benzene ring on the catalytic activity and within the two products, the selectivity of 1-phenylethane-1,2-diol is always higher (62-69%) than that of 2-bromo-1-phenylethane-1-ol (31-38%). Blank reaction gave only 38% conversion

<<Figure 6>> <<Table 6>>

We have also studied the catalytic potential of complex 2 towards the oxidative bromination of styrene in different biphasic solvent systems and their effect on the selectivity of

different products. Thus, catalytic potential of **2** is almost the same in all solvent systems (Table S5 of SI), except in DCM-H<sub>2</sub>O where it is slightly lower. However, the selectivity of products varies. The selectivity 1-phenylethane-1,2-diol follows the order:  $CH_3CN-H_2O \approx Hexane-H_2O$  (80 %) >  $CHCl_3-H_2O$  (79%) >  $DCM-H_2O$  (78%) >  $MeOH-H_2O \approx H_2O$  (67%). Thus, it seems that the expected product, 1,2-dibromo-1-phenylethane completely hydrolyses with water to 2-bromo-1-phenylethane-1-ol which in turn further hydrolyses to some extent to 1-phenylethane-1,2-diol.

Catalytic activity of these complexes towards oxidative bromination of styrene also compares well with  $[V^VO(OEt)(EtOH)(L)]$  (H<sub>2</sub>L = Schiff bases derived from 2-hydroxy-1acetonaphthone or 2-hydroxy-1-napthaldehyde and salicylhydrazide, benzoylhydrazide and anthranylhydrazide) (96-97% conversion with 63-69% selectivity towards diol) and  $[Mo^{VI}O_2(X-$ Hsal-dahp)(H<sub>2</sub>O)] [(X-sal = salicylaldehyde and its derivatives, dahp = 1,3-diamino-2hydroxypropane) (97-99% conversion with 61% selectivity towards diol) [21, 34]. Their catalytic activities are even better than recently reported for  $[U^{VI}O_2(pip-2,4-dmp)(MeOH)]$ (92%) [25].

#### 3.4. Reactivity

It was observed recently by <sup>51</sup>V NMR study by some of us that the  $[VO(O_2)(L)]$ -type species is an active intermediate during catalytic study of oxidative bromination of thymol in the presence of oxidant H<sub>2</sub>O<sub>2</sub> [20]. Conte *et al.* have written in their review articles that an oxidomonoperoxidovanadium(V) complex oxidizes the Br<sup>-</sup> ion to HOBr/Br<sub>2</sub> in the presence of acid [27,35,36]. The formations of similar monoperoxido species have also been suggested as an active intermediate by molybdenum and tungsten complexes [23, 24]. In order to generate information for such an intermediate in *trans*-[UO<sub>2</sub>]-complexes, we have also treated these complexes with H<sub>2</sub>O<sub>2</sub> and monitored the changes by UV–Vis spectroscopy. Thus, the sequential addition of a 30% H<sub>2</sub>O<sub>2</sub> solution (0.108 g, 0.95 mmol) dissolved in 5 mL of MeCN to a 25 mL of 9.97 × 10<sup>-2</sup> M solution of [U<sup>VI</sup>O<sub>2</sub>L<sup>2</sup>(MeOH)] (**2**) in MeCN resulted in the spectral changes as presented in Fig. 7. The band at 490 nm slowly disappears with a decrease in intensity while 402 nm band slowly becomes shoulder along with marginal increasing in intensity and shifting to 350

nm. The UV-band appearing at 290 nm shifts to 286 nm along with only marginally decrease in intensity. These changes also generate two isosbestic points at 305 and 379 nm which suggest the transformation of dioxidouranium(VI) complex to its oxidoperoxido form, based on the knowledge gathered from vanadium, molybdenum and tungsten complexes treated with H<sub>2</sub>O<sub>2</sub> under similar conditions [23, 24, 35]. Other complexes show almost similar spectral changes upon treatment with H<sub>2</sub>O<sub>2</sub> (Figs. S12-S14 of SI). These spectral changes are similar to oxidoperoxido- vanadium, molybdenum- and tungsten complexes. However, the mechanism responsible for the catalytic conversion of Br<sup>-</sup> ion to HOBr/Br<sub>2</sub> may differ as proposed for haloperoxidases [36, 37]. To gather information, we have recorded MALDI-TOF mass spectrum of an in-situ generated intermediate after performing catalytic reaction for thymol under the optimized reaction, as concluded in entry no. 10 of Table S3 i.e. complex 2 (0.002 g), thymol (10 mmol), 30% H<sub>2</sub>O<sub>2</sub> (30 mmol), KBr (30 mmol) and 70% HClO<sub>4</sub> (30 mmol), and extracting reaction mixture in chloroform. An intense peak observed at m/z 954.38 corresponding to the formula  $[U^{VI}O(O_2)_2(L)(diBrth)]$  (cal. Mass = 954.5) (Fig. S15) possibly suggests the formation of peroxido species along with the interaction of brominated thymol to uranium. However, considering the overall coordination number and oxidation 6 of uranium in the above intermediate, it is likely that tetradentate ligand is coordinated to uranium only though nitrogens of the four coordinating atoms. <<Figure 7>>

#### 4. Conclusions

Four *trans*-dioxidouraniumnum(VI) complexes, *trans*-[U<sup>VI</sup>O<sub>2</sub>L<sup>1-4</sup>(MeOH)] (1–4) have been prepared from potential dibasic tetradentate ONNO type Manisch base ligands derived from ethylenediamine and 2,4–di–*tert*–butylphenol(H<sub>2</sub>L<sup>1</sup>) (I) and 2,4–di–methylphenol (H<sub>2</sub>L<sup>2</sup>) (II), , 2–*tert*–butyl–4–methylphenol (H<sub>2</sub>L<sup>3</sup>) (III), and 2,4–di–chlorophenol (H<sub>2</sub>L<sup>4</sup>) (IV). These complexes have been characterized by various spectroscopic techniques. Single crystal X-ray study of complexes **3** and **4** confirms a distorted pentagonal bipyramidal geometry around uranium where ligands act as tetradentate, coordinating through two phenoxido oxygen and two amine nitrogen atoms. Oxidative bromination of thymol and styrene has successfully been carried out using these complexes as catalyst, signifying them useful functional model of

vanadium dependent haloperoxidases. Under the optimized reaction conditions, all complexes show comparable catalytic activity (97-99%) towards the oxidative bromination of thymol where 4-bromothymol has highest (89-91%) selectivity among the three products, 2-bromothymol, 4-bromothymol and 2,4-dibromothymol formed. Similarly, a comparable catalytic conversion (99%) of styrene with two products, 1-phenylethane-1,2-diol and 2-bromo-1-phenylethane-1-ol were obtained using these complexes as catalyst where the selectivity of former one is always higher (62-69%) than that of later one. In the presence of  $H_2O_2$ , the formation of corresponding oxidoperoxidouranium(VI) complexes, similar to oxidoperoxido- vanadium, molybdenum- and tungsten complexes, have also been demonstrated in solution but the mechanism possibly follows the different pathway(s) for the catalytic conversion of Br<sup>-</sup> ion to HOBr/Br<sub>2</sub> than that proposed for haloperoxidases.

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## Schemes



**Scheme 1.** Synthetic routes for the preparations of ligands and corresponding dioxidouranium(VI) complexes along with their structures.



**Scheme 2.** Products of the oxidative bromination of thymol. 2-Brth = 2-bromothymol, 4-Brth = 4-bromothymol and 2,4-dibrth = 2,4-dibromothymol.



**Scheme 3.** Expected products upon oxidative bromination of styrene: (a) 1,2–dibromo-1-phenylethane, (b) 2-bromo-1-phenylethane-1-ol and (c) 1-phenylethane-1,2-diol. Only two products (b and c) were obtained here under optimized reaction conditions.

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## Tables

## Table 1

Crystal Data and Structure Refinement for [UC	$D_2L^3(MeOH)$ ] (3) and $[UO_2L^4(EtOH)]$ (4a).
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	3	<b>4</b> a
Formula	$C_{27}H_{42}N_2O_5U$	$C_{18}H_{20}Cl_4N_2O_5U$
Formula weight	712.66	724.19
Г, К	296(2)	100(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	14.3077(12)	10.6553(6)
b/Å	16.2307(13)	24.9128(15)
c/Å	24.925(2)	16.9982(10)
3/0	92.714(4)	97.998(2)
V/Å <sup>3</sup>	5781.7(8)	4468.3(5)
	8	8
7000	2800	2736
$D_{calo}/g \text{ cm}^{-3}$	1.637	2.153
µ/mm <sup>−1</sup>	5.651	7.776
ℋ(°)	1.50 to 28.62	1.46 to 27.86
R <sub>int</sub>	0.1152	0.0715
Crystal size/ mm <sup>3</sup>	$0.21\times0.16\times0.05$	$0.38 \times 0.28 \times 0.23$
Goodness-of-fit on F <sup>2</sup>	1.062	1.119
$R_1[I \ge 2\sigma(I)]^a$	0.0674	0.0374
$R_2$ (all data) <sup>b</sup>	0.1721	0.0805
Largest differences peak and hole ( $e^{A^{-3}}$ )	3.250 and -1.428	1.440 and -2.417

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}| \cdot {}^{b}wR_{2} = \{\Sigma[w(||F_{o}|^{2} - |F_{c}|^{2}|)^{2}] / \Sigma[w(F_{o}^{2})^{2}]\}^{1/2}$ 

## Table 2

Bond lengths [Å] and angles [°] for the compounds for  $[UO_2L^3(MeOH)]$  (3) and  $[UO_2L^4(EtOH)]$  (4a).

Bond lengths	3	4a
U(1)-O(1)	1.769(8)	1.766(4)
U(1)-O(2)	1.765(9)	1.796(4)
U(1)-O(3)	2.215(8)	2.304(4)
U(1)-O(4)	2.235(9)	2.205(4)
U(1)-O(1M)	2.585(8)	2.455(4)
U(1)-N(1)	2.526(12)	2.623(5)
U(1)-N(2)	2.579(10)	2.605(5)
Angles	3	4a
O(2)-U(1)-O(1)	173.8(4)	173.48(19)
O(2)-U(1)-O(3)	94.2(3)	89.41(17)
O(1)-U(1)-O(3)	87.1(3)	90.12(17)
O(2)-U(1)-O(4)	89.7(4)	89.82(17)
O(1)-U(1)-O(4)	92.0(4)	93.50(17)
O(3)-U(1)-O(4)	151.8(3)	153.53(14)
O(2)-U(1)-O(1M)	92.8(3)	95.29(16)
O(1)-U(1)-O(1M)	93.4(4)	90.88(16)
O(3)-U(1)-O(1M)	77.1(3)	75.15(14)
O(4)-U(1)-O(1M)	74.8(3)	78.58(14)
O(2)-U(1)-N(2)	88.2(3)	91.51(16)
O(1)-U(1)-N(2)	86.7(3)	84.42(16)
O(3)-U(1)-N(2)	137.3(4)	137.21(14)
O(4)-U(1)-N(2)	70.7(4)	69.26(15)
O(1M)-U(1)-N(2)	145.4(4)	147.09(15)
O(2)-U(1)-N(1)	89.7(4)	84.46(17)
O(1)-U(1)-N(1)	90.6(4)	89.26(17)
O(3)-U(1)-N(1)	69.0(3)	70.21(14)

O(4)-U(1)-N(1)	139.2(3)	135.99(15)	
O(1M)-U(1)-N(1)	145.6(3)	145.36(14)	
N(2)-U(1)-N(1)	68.9(4)	67.32(15)	
23			3
MR spectral data (δ in ppm	) of ligands and comp	exes.	
$\begin{array}{c c} Cl & O \\ 3 \\ 2 \\ 1 \\ -5 \\ 6 \\ 7 \\ -8 \\ 8 \\ 8 \\ -7 \\ 6 \end{array}$	Cl 1/2' 3' 4' 5' Cl	NS	

## Table 3

 $^{13}C$  NMR spectral data ( $\delta$  in ppm) of ligands and complexes.



Compound <sup>a</sup>	C <sub>1</sub> /C <sub>1</sub> ′	C <sub>7</sub> /C <sub>7</sub> ′	C8/C8′
$H_2L^1(\mathbf{I})$	150.83	51.35	49.69
$\left[\mathrm{U}^{\mathrm{VI}}\mathrm{O}_{2}\mathrm{L}^{1}(\mathrm{MeOH})\right](1)$	166.65	57.54	52.84
$(\Delta\delta)$	(15.82)	(6.19)	(3.15)
$H_2L^2$ (II)	153.13	58.36	51.77
$[U^{VI}O_2L^2(MeOH)]$ (2)	165.88	56.30,	52.82
(Δδ)	(12.75)	(-2.06)	(1.05)
$H_2L^3$ (III)	154.21	58.05	50.89
$[U^{VI}O_2L^3(MeOH)]$ (3)	153.69	57.58	56.82
(Δδ)	(-0.52)	(-0.47)	(5.93)
$H_2L^4$ (IV)	154.43	52.31	45.72
$[U^{VI}O_2L^4(MeOH)]$ (4)	163.14	55.21	52.55
(Δδ)	(9.11)	(2.90)	(6.83)

<sup>a</sup>  $\Delta \delta = [\delta \text{ (complex)} - \delta \text{ (free ligand)}].$ 

## Table 4

Conversion, turn over frequency and selectivity parameters for various catalysts for the oxidative bromination of thymol. 

Catalyst	TOF [h <sup>-1</sup> ] <sup>a</sup>	Conv. [%]	Selectivity	r <b>[%]</b>			
			2- Brth	4-Brth	2,4-diBrth		
$[U^{VI}O_2L^1(MeOH)]$ (1)	1515	97	5	90	5		
$[U^{VI}O_2L^2(MeOH)]$ (2)	1547	99	4	91	5		
$[U^{VI}O_2L^3(MeOH)] (3)$	1515	97	4	90	6		
$[U^{VI}O_2L^4(MeOH)]$ (4)	1531	98	6	89	5		
Without catalyst		32	4	90	6		
<sup>a</sup> TOF values calculated at 2 h reaction time.							
Table 5							

## Table 5

Solvent effect on the oxidative bromination of thymol and selectivity of products catalysed by complex **2**.

Entry	Solvents	Conv. (%)	Selectivity (%)		
			2- Brth	4-Brth	2,4-diBrth
1	H <sub>2</sub> O	99	4	91	5
2	MeOH-H <sub>2</sub> O	95	3	90	7
3	DCM-H <sub>2</sub> O	99	5	88	7
4	MeCN-H <sub>2</sub> O	99	5	90	5
5	CHCl <sub>3</sub> -H <sub>2</sub> O	93	2	95	3
6	$C_6H_{14}$ - $H_2O$	98	3	93	4

## Table 6

Conversion, turn over frequency and selectivity parameters for various catalysts for the oxidative bromination of styrene.

Entry	Catalyst	Conv.	TOF	Selectivity (%)	
		(%)	$(h^{-1})^{a}$	2-bromo-1-	1-phenylethane-1,2-diol
				phenylethane-1-ol	
1	$[U^{VI}O_2L^1(MeOH)](1)$	99	3094	33	67
2	$[U^{VI}O_2L^2(MeOH)]$ (2)	99	3094	31	69
3	$[U^{VI}O_2L^3(MeOH)] (3)$	99	3094	37	63
4	$[U^{VI}O_2L^4(MeOH)]$ (4)	99	3094	38	62
5	Without catalyst	38		20	80

<sup>*a*</sup> TOF values calculated at 2 h of reaction time.



**Fig. 1.** ORTEP for the compound [UO(L<sup>3</sup>(MeOH)] (**3**). All the non-hydrogen atoms are presented by their 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.



**Fig. 2.** ORTEP for the compound  $[UO_2(L^4)(EtOH)]$  (4a). All the non-hydrogen atoms are presented by their 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.



**Fig. 3.** Crystal packing in the compound  $[UO_2L^3(MeOH)]$  (3). Drawing was done in ball and sticks with mercury 3.7 program.



**Fig. 4.** Crystal packing in the compound  $[UO_2L^4(EtOH)]$  (**4a**). Drawing was done in ball and sticks with mercury 3.7 program.



Fig. 5. Plot presenting conversion of thymol in the presence of different  $[UO_2]^{2+}$  complexes and without catalyst.



**Fig.6.** Plot presenting conversion of styrene in the presence of different  $[UO_2]^{2+}$  complexes.



Fig. 7. Plots presenting the spectral changes during titration of  $[U^{VI}O_2L^2(MeOH)]$  (2) with  $H_2O_2$ . Spectra were obtained after successive addition of one drop portions of 30%  $H_2O_2$  (0.108 g, 0.95 mmol) dissolved in 5 mL of MeCN to 25 mL of 9.97 × 10<sup>-2</sup> M solution of 2 in MeCN.

## **Supporting Information**

# Synthesis, characterization and catalytic activity of dioxidouranium(VI) complexes of ONNO tetradentate Mannich bases

M. R. Maurya, B. Mengesha, S. K. Maurya, F. Avecilla

## Table S1

Hydrogen bonds in the compounds  $[UO_2(L^3)(MeOH)]$  (3) and  $[UO_2(L^4)(EtOH)]$  (4a).

D-HA c	compound	d(D-H) Á	d(HA) Á	d(DA) Å	<(DHA) °	
N(2)-H(2)O(9)	(3)	0.91	2.49	3.290(13)	147.4	
O(1M)-H(1M)O	<b>(3) (3)</b>	0.85	2.16	3.006(13)	179.5	
N(2)-H(2)O(9)	(3)	0.91	2.49	3.290(13)	147.4	
O(2M)-H(2M)O	<b>(6)</b> ( <b>3</b> )	0.85	2.10	2.950(12)	179.6	
O(1M)-H(1M)O	<b>(8)</b> (4a)	0.85	2.00	2.760(6)	148.8	
N(2)-H(2N)O(5)	)#1 ( <b>4a</b> )	0.93	2.21	3.049(6)	151.0	
O(2M)-H(2M)O	(3) (4a)	0.91	1.80	2.645(6)	152.7	
N(3)-H(3N)O(2)	)#2 ( <b>4</b> a)	1.11	1.99	2.935(6)	140.1	

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 x+1,y,z

## Table S2

Selected IR data (in cm<sup>-1</sup>) for the ligands and complexes with tentative assignments.

Entry	Compounds	v(OH)	ν(N-H)	v <sub>asym</sub> (O=U=O)
1	$H_2L^1(\mathbf{I})$	3440 (b)	3130	
2	$[U^{VI}O_2L^1(MeOH)]$ (1)	3450 (b)	2834, 3099	850
3	$H_2L^2$ (II)	3270 (b)	3000	-
4	$[U^{VI}O_2L^2(MeOH)]$ (2)	3430 (b)	2960, 3015	868
5	$H_2L^3$ (III)	3425 (b)	3050	-
6	$[U^{VI}O_2L^3(MeOH)]$ (3)	3450 (b)	2865, 2953	868
7	$H_2L^4$ (IV)	3440 (b)	2990, 3128	6
8	$[U^{VI}O_2L^4(MeOH)]$ (4)	3470 (b)	2899, 3066	863

## Table S3

Conversion of thymol (1.5 g, 0.010 mol) using  $[U^{VI}O_2(eda-2,4-dmp)(MeOH)]$  (2) as a catalyst, turn over frequency, and selectivity of different products for 2 h of reaction time under different reaction conditions.

Entry	KBr	H <sub>2</sub> O <sub>2</sub>	HClO <sub>4</sub>	Catalyst	Conv.	TOF	Selectiv	ity [%]	
	[g (mmol)]	[g (mmol)]	[g (mmol)]	[mg (mmol)]	[%]	[h <sup>-1</sup> ]	2-Brth	4-Brth	2,4-diBrth
1	1.19 (10)	1.13 (10)	1.43 (10)	0.5 (8.0 × 10 <sup>-4</sup> )	46	2875	11	68	21
2	1.19 (10)	1.13 (10)	1.43 (10)	1 (1.6 × 10 <sup>-3</sup> )	60	1875	13	78	9
3	1.19 (10)	1.13 (10)	1.43 (10)	2 $(3.2 \times 10^{-3})$	64	1000	12	76	12
4	1.19 (10)	1.13 (10)	1.43 (10)	3 (4.8 × 10 <sup>-3</sup> )	43	448	12	81	7
5	1.19 (10)	2.26 (20)	1.43 (10)	2 (3.2 × 10 <sup>-3</sup> )	66	1031	13	70	17
6	1.19 (10)	3.39 (30)	1.43 (10)	2 (3.2 × 10 <sup>-3</sup> )	67	1046	12	67	21
7	2.38 (20)	3.39 (30)	1.43 (10)	2 (3.2 × 10 <sup>-3</sup> )	75	1172	12	66	22
8	3.57 (30)	3.39 (30)	1.43 (10)	2 (3.2 ×10 <sup>-3</sup> )	82	1281	9	60	31
9	3.57 (30)	3.39 (30)	2.86 (20)	2 (3.2 × 10 <sup>-3</sup> )	91	1422	3	85	12
$10^a$	3.57 (30)	3.39 (30)	4.29 (30)	2 (3.2 × 10 <sup>-3</sup> )	99	1547	4	91	5
11	3.57 (30)	3.39 (30)	4.29 (30)	blank	32		4	90	6
9 10 <sup>a</sup> 11	3.57 (30)         3.57 (30)         3.57 (30)         3.57 (30)	3.39 (30)         3.39 (30)         3.39 (30)         3.39 (30)	2.86 (20) 4.29 (30) 4.29 (30)	$2 (3.2 \times 10^{-3}) 2 (3.2 \times 10^{-3}) 2 (3.2 \times 10^{-3}) blank$	91 99 32	1422 1547	3 4 4	85 91 90	12 5 6

<sup>a</sup> The optimized conditions mentioned here are the best among the different sets of reactions carried out.

## Table S4

Entry	KBr	$H_2O_2$	HClO <sub>4</sub>	Catalyst	Conv.	Selectivity [	%] <sup>a</sup>
	[g (mmol)]	[g (mmol)]	[g (mmol)]	[mg (mmol)]	[%]	b	
						U	C
1	1.19 (10)	1.13 (10)	1.43 (10)	0.5 (8 × 10 <sup>-4</sup> )	43	12	88
2	1.19 (10)	1.13 (10)	1.43 (10)	1 (1.6 × 10 <sup>-3</sup> )	56	19	81
3	1.19 (10)	1.13 (10)	1.43 (10)	2 (3.2 × 10 <sup>-3</sup> )	32	13	87
4	1.19 (10)	1.13 (10)	1.43 (10)	3 (4.8 × 10 <sup>-3</sup> )	52	13	87
5	1.19 (10)	2.26 (20)	1.43 (10)	1 (1.6 × 10 <sup>-3</sup> )	75	17	83
6	1.19 (10)	3.39 (30)	1.43 (10)	1 (1.6 × 10 <sup>-3</sup> )	47	12	88
7	2.38 (20)	2.26 (20)	1.43 (10)	1 (1.6 × 10 <sup>-3</sup> )	88	25	75
8	3.57 (30)	2.26 (20)	1.43 (10)	1 (1.6 × 10 <sup>-3</sup> )	92	4	96
9	3.57 (30)	2.26 (20)	2.86 (20)	1 (1.6 × 10 <sup>-3</sup> )	99	31	69
10	3.57 (30)	2.26 (20)	4.29 (30)	1(1.6 × 10 <sup>-3</sup> )	99	32	68
11	3.57 (30)	2.26 (20)	4.29 (30)	blank	38	20	80

Conversion of styrene (1.04 g, 10 mmol), using complex **2** as a catalyst, turn over frequency, and product selectivity for 2 h of reaction time under different reaction conditions.

<sup>*a*</sup> b = 2-bromo-1-phenylethane-1-ol and c = 1-phenylethane-1,2-diol.

## Table S5

Solvent effect on the selectivity of products catalysed by complex  $\mathbf{2}$ 

Entry	Solvents	Conv. [%]	Selectivity [%]	
			2-bromo-1-phenylethane-1-ol	1- phenylethane-1,2-diol
1	H <sub>2</sub> O	99	33	67
2	MeOH-H <sub>2</sub> O	98	33	67
3	DCM-H <sub>2</sub> O	92	22	78
4	CH <sub>3</sub> CN-H <sub>2</sub> O	99	20	80
5	CHCl <sub>3</sub> - H <sub>2</sub> O	99	21	79
6	$C_6H_{14}$ - $H_2O$	98	20	80



Fig. S1. UV-Visible spectra of ligands I - IV recorded in MeCN.

MP 



Fig. S2. UV-Visible spectra of dioxidouranium(VI) complexes (1 - 4) recorded in MeCN. (a) Recorded in the region 250-550 nm and (b) Expanded region of 300-600 nm with more concentrated solution.



**Fig. S3.** <sup>13</sup>C NMR spectrum of  $[UO_2L^4(EtOH)]$  (4). Spectrum below 50 ppm is not shown as this region has only solvent and water signals.

R



**Fig. S4.** Effect of variation of amount of catalyst on the oxidative bromination of thymol. Reaction conditions: thymol (1.5 g, 10 mmol), 30% aqueous  $H_2O_2$  (10 mmol, 1.13 g), KBr (10 mmol, 1.19 g), and HClO<sub>4</sub> (10 mmol, 1.43 g) at room temperature.

-



**Fig. S5.** Effect of variation of amount of oxidant on the oxidative bromination of thymol. Reaction conditions: thymol (1.5 g, 10 mmol), catalyst  $[U^{VI}O_2L^2(MeOH)]$  (2) (0.002 g,  $3.2 \times 10^{-3}$  mmol), KBr (10 mmol, 1.19 g), and HClO<sub>4</sub> (10 mmol, 1.43 g) at room temperature.



Fig. S6. Effect of varying amount of additive (KBr) on the oxidative bromination of thymol. Reaction conditions: thymol (1.5 g, 10 mmol), catalyst [ $U^{VI}O_2L^2(MeOH)$ ] 2 (0.002 g,  $3.2 \times 10^{-3}$  mmol), 30% aqueous H<sub>2</sub>O<sub>2</sub> (30 mmol, 3.39 g), and HClO<sub>4</sub> (10 mmol, 1.43 g) at room temperature.

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Fig. S7. Effect of varying amount of  $HClO_4$  on oxidative bromination of thymol. Reaction conditions: thymol (1.5 g, 10 mmol), catalyst  $[U^{Vl}O_2L^2(MeOH)]$  (2) (0.002 g,  $3.2 \times 10^{-3}$  mmol), 30% aqueous  $H_2O_2$  (30 mmol, 3.39 g), and KBr (30 mmol, 3.57 g), at room temperature.



**Fig. S8.** Effect of variation of amount of catalyst on the oxidative bromination of styrene. Reaction conditions: styrene (1.04 g, 10 mmol), 30% aqueous  $H_2O_2$  (10 mmol, 1.13 g), KBr (10 mmol, 1.19 g), and HClO<sub>4</sub> (10 mmol, 1.43 g) at room temperature.



**Fig. S9.** Effect of variation of amount of oxidant on the oxidative bromination of styrene. Reaction conditions: styrene (1.04g, 10 mmol), catalyst  $[U^{VI}O_2L^2(MeOH)]$  (2) (0.001g,  $1.6 \times 10^{-3}$  mmol), KBr (10 mmol, 1.19 g), and HClO<sub>4</sub> (10 mmol, 1.43 g) at room temperature.



Fig. S10. Effect of varying amount of additive (KBr) on the oxidative bromination of styrene. Reaction conditions: styrene (1.04 g, 10 mmol), catalyst  $[U^{v_1}O_2L^2(MeOH)]$  (2) (0.001 g,  $1.6 \times 10^{-3}$  mmol), 30% aqueous H<sub>2</sub>O<sub>2</sub> (20 mmol, 2.26 g), and HClO<sub>4</sub> (10 mmol, 1.43 g) at room temperature.



**Fig. S11.** Effect of varying amount of  $HClO_4$  on oxidative bromination of styrene. Reaction conditions: styrene (1.04 g, 10 mmol), catalyst [U<sup>VI</sup>O<sub>2</sub>L<sup>2</sup>(MeOH)] (**2**) (0.001g,  $1.6 \times 10^{-3}$  mmol), 30% aqueous H<sub>2</sub>O<sub>2</sub> (2.26 g, 20 mmol), and KBr (3.57 g, 30 mmol), at room temperature.



Fig. S12. Plots representing the Spectral changes during titration of  $[U^{VI}O_2L^1(MeOH)]$  (1) with  $H_2O_2$ . Spectra were obtained after successive addition of one drop portion 30%  $H_2O_2$  (0.108 g, 0.95 mmol) dissolved in 5 mL of MeCN to 25 mL of  $8.75 \times 10^{-2}$  M solution of 1 in MeCN.

CRIF



**Fig. S13.** Plots representing the Spectral changes during titration of  $[U^{VI}O_2L^3(MeOH)]$  (3) with  $H_2O_2$ . Spectra were obtained after successive addition of one drop portion 30%  $H_2O_2$  (0.108 g, 0.95 mmol) dissolved in 5 mL of MeCN to 25 mL of  $7.7 \times 10^{-2}$  M solution of 3 in MeCN.



**Fig. S14.** Plots representing the Spectral changes during titration of  $[U^{VI}O_2L^4(MeOH)]$  (4) with  $H_2O_2$ . Spectra were obtained after successive addition of one drop portion 30%  $H_2O_2$  (0.108 g, 0.95 mmol) dissolved in 5 mL of MeCN to 25 mL of  $6.48 \times 10^{-2}$  M solution of 4 in MeCN.

CRI



**Fig. S15.** MALDI–MS spectrum for the reaction mixture extracted from chloroform after carrying our catalytic reaction for the oxidative bromination of thymol.

## **Graphical abstract**

# Synthesis, characterization and catalytic activity of dioxidouranium(VI) complexes of ONNO tetradentate Mannich bases

M. R. Maurya, B. Mengesha, S.K. Maurya, F. Avecilla,

Synthesis and characterization of *trans*-dioxidouranium(VI) complexes with dibasic tetradentate ONNO donor ligands are reported. These complexes are used as catalysts for the oxidative bromination of thymol and styrene.





## Highlights

# Synthesis, characterization and catalytic activity of dioxidouranium(VI) complexes of ONNO tetradentate Mannich bases

Mannar R. Maurya, Bekele Mengesha, Shailendra K. Maurya, Fernando Avecilla

## Highlights

- 1. Four dioxidouranium(VI) complexes of tetradentate dipodal ligands are reported.
- 2. All complexes are well characterised.
- 3. X-ray single crystal structures of two dioxidouranium(VI) complex are reported.

Accepting

4. These complexes are good catalysts for the oxidative bromination of thymol and styrene.