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Synthesis, characterization, crystal structure, and reactivity of heterobimetallic dioxovanadium(V) complexes containing multidentate hydrazone ligands

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Two new heterobimetallic complexes of the composition $[(VO_2)_2(\mu_3\text{-slsch})\{Na_2(\mu-H_2O)_2(H_2O)_2\}]_n$ (1) and $[(VO_2)_2(\mu_3\text{-npsch})\{Na_2(\mu-H_2O)_2(H_2O)_2\}(DMF)]_n$ (2) were obtained by reaction of the ligand and vanadium pentoxide in a 1:1 molar ratio in methanol in the presence of Na₂CO₃ (2 equivalents). The complexes obtained were characterized by using various spectroscopic studies. The structures of both the complexes were established by singlecrystal X-ray crystallographic study. We have also explored the catalytic behavior of the complexes in oxidative bromination of phenol red, which is the bio-inspired reaction catalyzed by an enzyme haloperoxidase.

Keywords: Crystal structure; Heterobimetallic; Reactivity; Dioxovanadium(V)

1. Introduction

Oxo-bridged units have been found to be one of the most important structural motifs in the chemistry of first-row transition metals, particularly those complexes containingvanadium [1],manganese [2] and iron [3]. Many metalloproteins and metalloenzymes in which μ -oxo-bridged motifs are incorporated at their active sites have been found to carry out a wide range of functions in biological systems. These enzymes containing homobinuclear (FeII/IV) and

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heterobinuclear (FeII/CuII) active sites are capable of activating dioxygen molecules by a variety of complex mechanisms involving a putative μ -hydroxo species as a key intermediate responsible for the oxidation of a wide range of organic substrates [4-10]. Such compounds with ancillary bridging ligands play a crucial role in biological systems during dioxygen activation by a host of metalloenzymes. The tetra-manganese water oxidase enzyme of the green plant photosystem II is also believed to contain an oxo-bridged active site [11, 12] and the involvement of a V-O-V dimer in the biology of vanadium is suspected on the basis of spectrochemical evidence [13]. Such efficient use of μ -oxido species as catalyst by mother nature in biological systems has made chemists interested in using similar species as an effective catalyst [14, 15].

Homobimetallic compounds dominate this area, even though the potential number of heterometallic pairings significantly outnumbers the former. A synthetic roadblock to expanding heterometallic systems is the inherent challenge of selectively assembling different transition metals together with other metals. This is of particular interest in the field of molecular host guest chemistry, coordination polymers and molecular magnets.

In view of the diverse importance of μ -oxo-bridged heterodinuclear compounds andtheir utility in catalysis and biomimetic studies, we focused our intention develop new methodsforsynthesizingnew heterobimetallic μ -oxo-bridged vanadium complexes by choosing polyfunctional ligand family ofsuccinoyldihydrazones.Further, these ligands possesseight binding sites which can bind to vanadium and other metal centersindifferent coordination modes. The protonation state of these ligands on complexation plays an important role since it offers the opportunity of fine tuning properties such as electrochemical, photophysical and catalytic.

Hence, in this manuscript we report our initial explorations in the coordination chemistry of the ligandsH₄slsch and H₄npsch with vanadium, which can have the tendency to form μ -oxobridged heterobimetallic complexes with other metals. The synthetic and structural studies demonstrate the versatility of H₄slsch and H₄npschto act as a supporting ligand for generating asymmetric dinuclear complexes comprisingof sodium and vanadium ions. This work provides usthe foundation for future reactivity and mechanistic work.

2. Experimental

Solvents were reagent grade and used as received. Other chemicals were E-Merck, Himediaand equivalent grades.

2.1. Physical measurements

Vanadium was determined by a standard literature procedure [16]. C, H and N were determined by microanalytical methods using a Perkin-Elmer 2400 CHNS/O Analyzer 11. Infrared spectra (figures S1 and S2) in the range 4000-450 cm⁻¹ were recorded as KBr discs by using a BX-III/FTIR Perkin Elmer spectrophotometer. The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance II spectrometer at 400 and 100 MHz in DMSO-d₆ solution using TMS as an internal standard. Electronic spectra were recorded on a Perkin-Elmer Lambda-25 spectrophotometer. Cyclic voltammograms were recorded on a CH Electrochemical Analyzer using a standard three-electrode assembly (glassy-carbon working, Pt wire auxiliary, SCE reference) and 0.1 M NBu₄ClO₄ as supporting electrolyte. Mass spectra of the complexes were recorded on a Water ZQ-4000 Micromass Spectrometer. Gas Chromatographic (GC) analysis was performed on a Bruker 430-GC Gas Chromatograph equipped with a 30m × 0.32mm × 0.5 µm HP-Innowax capillary column and flame ionization detector (FID).

2.2. X-ray crystallography diffraction

Single crystals of **1** and **2** were obtained by slow evaporation from water/DMF solutions after a few days. Intensity data for the compounds were measured using an Xcalibur Eos Gemini diffractometer equipped with monochromated MoK_a radiation (($\lambda = 0.71073 \text{ Å}$) source. The CrysAlis PRO, Agilent, 2013 software packages were used for data collection and reduction [17a]. In all cases, absorption corrections based on multiscans were applied [17b]. The structure was solved by direct methods and refined on F² by a full matrix least squares [17c] procedure based on all data minimizing R = $\Sigma \parallel F_0 \mid - |F_c|| \Sigma \mid F_0 \mid$, wR = [$\Sigma [w (F_0^2 - F_c^2)^2] / \Sigma (F_0^2)^2$]^{1/2} and S = [$\Sigma [(F_0^2 - F_c^2)^2 / (n-p)]^{1/2}$. SHELXT-2014 and SHELX-2014 were used for structure solutions and refinements [17d]. All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atom positions were placedat a calculated distance and refined freely in the final refinement. Crystal data and structure refinement parameters of **1** and **2** are in table 1.

2.3. Synthetic procedures

2.3.1. General procedure for synthesis of ligandsH₄**slsch and H**₄**npsch.**Ligand preparation involves two steps. In the first step it involved condensation of diethyl succinate with hydrazine hydrate in 1:2.5 molar ratio in ethanol to give succinoyldihydrazide. In the second step, condensation of succinoyldihydrazide (2 g, 13.70 mmol) with 2-hydroxy-1-benzaldehyde (3.68 g, 30.16 mmol) and 2-hydroxy-1-naphthaldehyde (5.19 g, 30.16 mmol) gave the desired ligands H₄slsch and H₄npsch in moderate yield.

2.3.2. Bis(2-hydroxy-1-benzaldehyde)succinoyldihydrazone, H₄slsch. Yield: 5.281 g (47%). M.p: 225-227 °C (lit [17. (c)]: 300°C),Color: white. Anal (%), Calcd for C₁₈H₁₈N₄O₄ (MW: 354.37): C, 61.01; H, 5.12; N, 15.81; Found: C, 60.68; H, 5.15; N, 15.65,

2.3.3. Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone, H₄**npsch.** Yield: 5.281g (47%). M.p: 245-247 °C (lit [17. (d)] 254°C, Color: yellow.Anal (%), Calcd for C₂₆H₂₂N₄O₄(MW: 454.49): C, 68.71; H, 4.88; N, 12.33; Found: C, 68.71; H, 4.88; N, 12.33.

2.4. General procedure for synthesis of complexes 1 and 2

A suspension of vanadium pentoxide (0.2 g, 1 mmol) in methanol solution was added dropwise to a solution containing H₄slsch (0.35 g, 1 mmol; for 1) and H₄npsch (0.39 g, 1 mmol; for 2) in 1:1 molar ratio at room temperature. The reaction mixture was refluxed for 40 min, then cooled to room temperature, followed by addition of sodium carbonate (0.22 g, 2 mmol) and stirred well until the brown solution turned yellow. The yellow solution was allowed to stand at room temperature for 1 h, until the precipitate settled. The mixture was filtered, washed three times with warm methanol(5 mL each time), collected and dried over CaCl₂ to obtain the desired complexes 1 and 2. Single crystal of 1 and 2 were obtained by slow evaporation of DMF solutions at ambient temperature within a fortnight.

2.4.1. [Disodium (di (μ-aquo) (μ₃-bis-(2-hydroxybenzylidene) succinohydrazide)
(bis(dioxidovanadate(V)]:[(VO₂)₂(μ₃-slsch)(Na₂(μ-H₂O)₂]_n·4H₂O (1). Yield: 0.57 g (75%).
M.p: >300 °C;Color: Yellow. Anal (%), Calcd for C₁₈H₄₀N₄NaO₂₀V₂ (MW 757.4 g/mol): C,
28.54; H, 5.32; N, 7.40; Found: C, 28.73; H, 5.30; N, 7.49. IR data (cm⁻¹, KBr): 3426 (vs br)

v(OH), 1571, 1550, 1478, 1450, 1356, 1290, 1216, 1154, 1031, 954, 900, 761, 725, 626, 579, 484, 469. ¹H NMR (400 MHz, DMSO-d₆,Me₄Si): δ (ppm): 7.02-7.86 (m, 8H, Ar-H), 8.3 (s, 2H, C(H)=N), 2.5 (s, 4H, (-CH₂). ¹³C NMR (100 MHz, DMSO-d₆,Me₄Si): 174.27, 163.15, 153.56, 131.76, 131.28, 118.59, 118.21, 115.52, 40.72 ppm. Electronic spectrum, [λ_{max} , nm]: CH₃CN solution, λ_{max} (nm): 323 nm, 417 nm.

2.4.2. [Disodium (di (μ-aquo)(μ₃-bis-(2-hydroxynaphthalen-1-yl)methylene) succinohydrazide (bis(dioxidovanadate(V)]:[(VO₂)₂(μ₃-npsch)(Na₂(μ-H₂O)₂(H₂O)₂)(DMF)]_n (2). Yield: 0.65 g (72%). M.p: >300 °C; Color: Light brown. Anal (%), Calcd for C₃₂H₄₄N₆Na₂O₁₅V₂ (MW 900.59 g/mol): C, 42.68; H, 4.92; N, 9.33; Found: C, 42.68; H, 4.92; N, 9.33. IR data (cm⁻¹, KBr): 3461 (vs br) v(OH), 1604, 1558, 1455, 1399, 1352, 1335, 1196, 942, 921, 822, 746, 588, 538, 510. ¹H NMR (400 MHz, DMSO-d₆,Me₄Si): δ (ppm): 7.02-7.86 (m, 12H, Ar-H), 8.3 (s, 2H, C(H)=N), 2.5 (s, 4H, (-CH₂). (100 MHz, DMSO-d₆,Me₄Si): 174.35, 164.93, 150.55, 133.64, 132.89, 128.62, 127.45, 126.72, 122.74, 122.61, 120.10, 109.77, 40.05 ppm. Electronic spectrum, [λ_{max}, nm]: CH₃CN solution, λ_{max} (nm): 371 nm, 421 nm.

2.4.3. Oxidative bromination of phenol red. Oxidative bromination was carried out using 1 and 2 at room temperature. In a typical experiment, vanadium(V) complexes were dissolved in CH_3CN/H_2O in a 3:7 ratioand added to a solution containing KBr (0.24g, 2 mmol), phenol red (0.35g, 1 mmol) and 30% H_2O_2 (10 ml). After 4 minutes the solution turned red,following the addition of 70% $HClO_4$ (0.5 mmol) it was stirred for 1 h. An additional 0.5 mmol was added to the reaction mixture at every 30 minute interval. The reaction mixture was then extracted, dried over anhydrous Na₂SO₄ and purified by column chromatography to get the product.

3. Results and discussion

3.1. Synthesis and spectral characteristics

The ligands (hydrazone = H₄slsch, H₄npsch) under study (figure 1) were prepared according to a literature report [18]and were characterized by melting point, IR, ¹H NMR and ¹³C NMR spectroscopies; characterization details are presented in the Experimental section. Complexes **1** and **2**of the composition $[(VO_2)_2(\mu_3-slsch)(Na_2(\mu-H_2O)_2)(H_2O)_2]_n \cdot 4H_2O$ (**1**) and $[(VO_2)_2(\mu_3-npsch){Na_2(\mu-H_2O)_2(H_2O)_2}(DMF)]_n$ (**2**)were synthesized in good yield (scheme 1).

$$V_2O_5 + H_4 \text{slsch} \xrightarrow{\text{Methanol}} [(VO_2)_2(\mu_3 - \text{slsch})\{Na_2(\mu - H_2O)_2(H_2O)_2\}]_{II}$$

 $V_2O_5 + H_4npsch \xrightarrow{Methanol} [(VO_2)_2(\mu_3-npsch)\{Na_2(\mu-H_2O)_2(H_2O)_2\}(DMF)]_n$

Scheme 1. Schematic diagram showing preparation of complexes.

The complexes are insoluble in common organic solvents such as MeOH, EtOH, CH₂Cl₂, CHCl₃, CCl₄, ether, acetone and benzene,sparingly soluble in acetonitrile and readily soluble in DMF/DMSO. The analytical data obtained for both the complexes are in agreement with the proposed structural formula.

3.2. UV-Vis spectra

The UV-vis spectra of **1** and **2** were recorded in acetonitrile solutions with concentration of 10^{-5} mol L⁻¹. The electronic spectra show two absorption bands at 323 nm and 388 nm (for **1**) (figure S3) and 326 nm and 413 nm (for **2**) (figure S4). The strong absorption bands at 323 nm and 321 nm are due to an intra-ligand transition, most probably, π - π * whereas the bands at 388 nm and 392 nm are assigned to LMCT arising from transfer of charge from the p-orbital of a phenolate-oxygen to an empty d-orbital of the vanadium(V) center [20].

3.3.¹H NMR and ¹³C NMRspectra

In order to confirm the coordination modes of the ligand to the metal center,¹H and ¹³C NMR spectroscopieswere employed. The¹H NMR and ¹³C NMRspectra of the free ligands and complexes were recorded in DMSO-d₆ (figures S5-S8) using TMS as an internal standard reference, and the details of the data given in the Experimental section. The free ligands exhibit a resonance at δ =11.72 ppm, δ =11.30 ppm, δ = 10.18 ppm and 10.15 ppm which are assigned to –OH and -NH groups. These signals disappeared confirming deprotonation of both the -OH and –NH protonsupon complexation (figures S5 and S6). The coordination mode of the ligand to the metal ion was also studied by coordination-induced ¹³C NMR chemical shifts.

The azomethine carbons in both ligands appear at 167.55 ppm and 168.28 ppm, whereas,upon complexation,¹³C NMR spectra show upfield shifts to 163.15 and 164.93 ppm with $\Delta \delta = 2$ -3 ppm (figures S7 and S8) in both the complexes. The coordination of enol oxygencarbons C8 and C12 were indicated by downfield shifts with $\Delta \delta = 1$ -2 ppm.The signals of aromatic carbon atoms appeared tthe expected positions both the ligands and complexes with slight shifts in their positions.

3.4. Electrochemical studies

The electrochemical studies were carried out for both the heterobimetallic complexes in DMF solution using TBAP (0.1 M) as supporting electrolyte at a scan rate of 100 mV. Complex 1(figure S9) shows four quasi-reversible redox couples with peak potential differences>50 mV. Towards the positive scan, redox couples with $E_{1/2} = \pm 0.23$ V and $E_{1/2} = \pm 1.42$ V were observed. The first redox couple at $E_{1/2} = +0.23$ V (process at potential E = +0.34 V) is attributed to the metal oxidation (M^{2+/3+}), while the second redox process at $E_{1/2} = +1.42$ V is assigned to the oxidation of the ligand. The negative scan also shows two quasi-reversible redox couples, the first redox couple at $E_{1/2} = -0.52$ V and the other one at $E_{1/2} = -1.02$ V. The second redox couple with $E_{1/2} = -1.02$ V is attributed to the metal reduction (M^{+5/+4}) which is in agreement to the literature report [21]. The first couple at $E_{1/2} = -0.52$ V is assigned to the reduction of the ligand.Similarly,2 (figure S10) shows three quasi-reversible redox couples with peak potentials> 90 mV. In the positive scan, the redox couples with $E_{1/2} = \pm 0.31$ V and $E_{1/2} = \pm 1.2$ V are attributed to metal oxidation $(M^{2+/3+})$ and ligand oxidation, respectively. In the negative potential scan, the quasi-reversible redox couple at $E_{1/2} = -1.01$ V is assigned to metal reduction $(M^{+5/+4})$, and a peak at $E_{1/2} = -0.47$ V is due to ligand oxidation. Electrochemical studies of both complexes show similar results; these similarities arise due to the presence of $[(VO_2)_2]^+$ in the structural units of both the complexes, which is also confirmed by other spectroscopies studies.

3.5. Crystal structure description

The asymmetric unit of **1** (figure 2) and **2** (figure 3) is composed of one vanadium(V) ion, one sodium ion, half of the ligand moiety, one oxido atom and three aqua ligands, whereas in **2**, one additional solvent molecule (dimethylformamide) is present. Both of the complexes are arranged into $[(VO_2)_2(L)]_2$ units that are interconnected through the differently bound oxido-

sodiummoieties, $[Na_2(\mu-O)]$ in **1** and $[Na_2(\mu-H_2O)_3]$ in **2**, resulting in the formation of distinct one-dimensional heterobimetallic networks.

Complex 1 crystallizes in the triclinic space group P-1. The asymmetric unit of the complex $[(VO_2)_2(\mu_3-slsch)]_2$ consists of one vanadium ion, one terminal oxido ion (O3), one bridging oxido ion (O4) and one-half tetra-deprotonated ligand in the transoid conformation, shown in figure 2. The bridging oxygen (O4) forms a linker to the sodium ion forming a M-O-M core, in which the sodium ionis bonded by four water molecules. The ligand coordinates to the metal centers in tridentate fashion through the azomethine nitrogen (N1), phenolic oxygen (O1) and carbonyl oxygen atom, the fourth and fifth positionsare occupied by oxido (O3) and bridging oxido $(\mu$ -O4) in both the arm of the ligand. The transoid basal position of the complexes consists of two oxygens and one azomethine nitrogen, whereas the apical position consists of the bridging V-O. The V-O bond lengths (table S1) range from 1.617(3) Å [V-O4], 1.652(3) Å [V=O3], 1.907(3) Å [V-O1] to 1.972(2) Å [V-O2] whereas the V-N bond length of the azomethine is 2.131(3) Å, larger than that of the average V-O bond length by 0.344Å. The trans angles in the complex are O1-V1-O2 (152.29(12) and O3-V1-N1 (140.27(13), with $\tau = 0.2$ (table S1). Hence, the geometry around the vanadium center can be described as distorted square pyramidal. The values of bond lengths and angles around the vanadium ion found in the present study are in agreement with those reported in the literature [22]. Another interesting property of the complex is the presence of sodium ions together with one μ -O4 group and two water molecules. The sodium center consists of two µ-O4 at the axial positions [Na1-O4, 2.377(3)] and four water molecules at the equatorial sites [Na1-O5, 2.405(3), Na1-O6¹, 2.450(4) Å], resulting in the formation of a six-coordinate [Na-O₆] octahedral geometry around the sodium ion.Na-O bond lengths are similar to those found in other hetero-metallic Na-V compounds [22]. Therefore, the ligand in the complex acts in a μ_3 [O-N-O] bridging mode [N₂O₄] which binds to two vanadium ions forming $[(VO_2)_2L]$, together with two bridging sodium ions from oxygen (O4) ions $[\mu$ -O4] forming a tetra-metallic [V₂Na₂(μ_3 -slsch)] fragment with metal separation of 8.972 Å [V1...V1¹], 14.291 Å [Na1...Na1¹] and 3.747 Å [Na1...V1]. Therefore, the synthesized complex consists of two different metal ions [V₂Na₂] with different geometrical arrangements, in which two vanadium ions adopt five-coordinate distorted square pyramidal geometry whereas for the sodium ions, a regular octahedral geometry has been observed. In addition, four water molecules are present in the complex; these water molecules can be best described as lattice water forming

inter- and intra-molecular hydrogen bonding with the complex, which together construct a $[(VO_2)_2(\mu_3-L)Na_2(\mu-O4)_2(H_2O)_4\}]\cdot 4H_2O$ unit. The presence of two μ -O4 bridging oxido ions generates a more complex structure which is interconnected to another part of the fragment molecules, resulting in the formation of an infinite one dimensional ladder like metal-organic chain (figure 4). Further extension of the 1D coordination network results in a 3D supramolecular assembly (figure 5).

In 2 (figure 3), the asymmetric unit bears similar $[(VO_2)_2(\mu_3-L)]$ blocks which are structurally identical to 1, but different through one coordinated solvent molecule (dimethylformamide) which coordinates to sodium ions and two bridging water molecules (μ -H-₂O) compared to 1. The ligand coordinates to the metal center and participates in complex formation through O, N, O donor atoms with oxygen and nitrogen of the azomethine at the basal position, whereas the fourth equatorial position is occupied by oxygen atom (O3) and the axial position by one bridging oxido O4 [μ -O4]. The bridging oxido [μ -O4] provide a linkage to sodium ions, together with one terminal water and three bridging water molecules resulting in the formation of six-coordinate, distorted octahedral sodium ions.

The vanadium-oxygen (V-O) bond lengths are 1.912(15) Å [V1-O1], 1.957(14) Å [V1-O2] and V=O bond lengths are 1.609(15) Å [V=O4], 1.645(15) Å [V=O3], whereas the V-N bond length is 2.108(17) Å, closer to that of the average V-O, V=O and V-N bond length of 1 (table S1). The *trans* angles in 2 are O1-V1-O2, 148.67(6) and O3-V1-N1, 142.56(7) with $\tau =$ 0.1(table S1). However, the main distinct features of 2 consist of sodium ions bonded to three bridging aqua ligands along with one H₂O and DMF together forming a more complex structure $[[Na_2(\mu-H_2O)_3(H_2O)_2]]$. The coordination geometry around the vanadium(V) center can be described as slightly distorted square pyramidal. Hence, the ligand in the complex acts in a μ_3 [O-N-O] bridging mode [N₂O₄] which binds to two vanadium ions forming [(VO₂)₂npsch], together with two bridging sodium ions from oxygen atom [µ-O4] forming tetra-metallic [V₂Na₂(µ₃-npsch)] fragments with metal-metal separation of 9.457 Å [V1...V1¹], 3.368 Å [Na1...Na1¹], and 3.748 Å [Na1...V1]. Complex 2 consists of two different metal ions [V₂Na₂] with different geometrical arrangement, in which two vanadium ions adopt five-coordinate distorted square pyramidal geometry whereas in the case of two sodium ions, a distorted octahedral geometry has been observed; together both vanadium and sodium ions construct $[(VO_2)_2(\mu_3-L) Na_2(\mu-O4)_2(H_2O)_4]$ · 4H₂O unit. The Na-O, V-O, V-N bond lengths and bond

angles around the two metal ions match the values reported in the literature [22]. The presence of bridging aqua $[\mu$ -H₂O] ligands generates a more complex structure which is interconnected to another sodium ion, resulting in the formation of an infinite one-dimensional coordination network (figure 5). The 3D supramolecular assembly (figure 4) of **2** is constructed considering together the presence of inter- and intra-molecular hydrogen bonding.

3.6. Crystal packing diagram

Crystal packing diagrams of **1** and **2** areshown in figure 4.Complex **1** crystallized in triclinic (space group P-1) with Z = 1 and **2**crystallized in monoclinic (space group I2/n) with Z = 4. The unit cell volume and density at ambient temperature (291.93-295.7°) are d = 1.603 g/cm³, V = 782.30(15) Å³ for **1** and d = 1.513 g/cm³, V = 3945.0(5) Å³ for **2**. The unit cell length and cell angles in **1** are a = 7.258(9) Å, b = 10.381(12) Å, c = 10.831(9) Å, a = 95.321(8)°, $\beta = 100.093(9)^\circ$, $\gamma = 100.885(10)^\circ$ and for **2**, a = 24.162(2) Å, b = 6.164(3) Å, c = 27.158(17) Å, a = 90°, $\beta = 102.757(7)^\circ$, $\gamma = 90^\circ$. Complexes **1** and **2** have different packing arrangements. The complete fragment of the ligand along with vanadium and sodium ions results ina 1D arrangement in **1**. In **2**, the complex packing results into three parallel 1D arrangements. The packing efficiency of complexes are 68.09% for **1** and 67.51% for **2**; the packing index of **2** is slightly lower compared to **1**.



Scheme 2. Schematic diagram showing reaction of 1 and 2 with H_2O_2 .

The reaction of $[(VO_2)_2(\mu_3\text{-slsch})\{Na_2(\mu\text{-H}_2\text{O})_2(\text{H}_2\text{O})_2\}]_n$ (1) and $[(VO_2)_2(\mu_3\text{-}npsch)\{Na_2(\mu\text{-H}_2\text{O})_2(\text{H}_2\text{O})_2\}]_n$ (2) with H₂O₂ in actonitrile solution was studied using UV/Vis spectroscopy. In 1, initially we observed a decrease in absorbance at 385 nm upon addition of H₂O₂ and the changes observed result in the presence of one isosbestic point at 340 nm, whereas the band at 312 nm shows a bathochromic shift to 320 nm (figure 6A). The absorbance decreases with increase in H₂O₂concentration. Similarly, in 2 upon addition of H₂O₂, the solution showed a similar trend and the changes observed resulted in the presence of two isosbestic points at 373 nm and 438 nm. Further, after addition of the H₂O₂ solution, the series of spectra (figure 6B) show a gradual decrease at 413 nm and the appearance of a more intense band at 326 nm. These changes in the electronic spectra in both the complexes were attributed to the formation of corresponding V^VO-(O₂) species and hence the results obtained are consistent with the reported literature [23].

3.8. Mimetic activity of dioxovanadium(V) complexes with 3,5-di-tert-butylcatechol



Scheme 3. Schematic diagram showing catalytic oxidation of 3,5-di-tert-butylcatecholto 3,5-di-tert-butylquinone by **1** and **2**.

The oxidation of catechol to quinones catalyzed by binuclear copper complexes in the presence of O₂ is one of the most important biochemical transformations [24]. In our study, catalytic oxidation of 3,5-di-tert-butylcatechol to 3,5-di-tert-butylcyclohex-4-ene-1,2-dione using our newly synthesized complex $[(VO_2)_2(\mu_3-slsch) \{Na_2(\mu-H_2O)_2(H_2O)_2\}]_n$ (1) in acetonitrile solution was monitored by employingUV/Vis spectroscopy. In a typical experiment, 100 µL of the complex in acetonitrile solution $(1 \times 10^{-4} \text{ M})$ was transferred to a 1 cm path-lengthcell. The reaction was initiated by the addition of 3,5-di-tert-butylcatechol (1×10-2 M) solution. Absorbance vs wavelength plots were generated from each experiment, which were recorded every 5 minutes in the region of 300-700 nm of the electronic spectrum (figure 7). The reaction mixture changed color after 2 minutesupon addition of 3,5-di-tert-butylcatechol. This change indicates the coordination of the substrate to the vanadium center. This is also evident from the strong intense absorption bands appearing at 554 nm, which is characteristic of charge transfer bands in vanadium complexes containing catecholate ligands [25]. These bands also increase in intensity on subsequent addition of 3,5-di-tert-butylcatechol, indicating the formation of noninnocent complexes with vanadium(V), during the course of the reduction of the vanadium center from $V(V) \rightarrow V(IV)$. Many vanadium-catechol containing compounds have been reported and often they are not stable towards internal redox reactions, indicating the formation of o-benzoquinones from these systems. The completion of the reactions was determined spectrophotometrically by monitoring the increase in absorbance at 400 nm ($e = 1600 \text{ M}^{-1} \text{ cm}^{-1}$) as a function of time, which is the characteristic absorption band of 3,5-di-tert-butylcyclohex-4ene-1,2-dione. The product was purified by column chromatography and the yield of 3,5-di-tertbutylcyclohex-4-ene-1,2-dionewas 62% with a turnover frequency of 20.66 h⁻¹, which are comparable to the literature reported values for other model systems[26]. The productwas also confirmed by ¹H and ¹³C NMR spectroscopy. Yield: 62%. ¹H NMR (400 MHz, CDCl₃): 6.93 (d, 1H, J = 2.28 Hz), 6.21(d, 1H, J = 1.52Hz), 1.26 (s, 9H), 1.22 (s, 9H) ppm; ¹³C NMR (100 MHz, CDCl₃): d 181.26, 180.17, 163.46, 150.07, 133.60, 122.22, 36.16, 35.61, 29.34, 28.01 ppm,

3.9. Oxidative bromination activity of complexes 1 and 2



Scheme 4. Schematic diagram showing oxidative bromination of phenol red to bromo-phenol blue catalyzed by **1** and **2**.

Dioxovanadium complexes containing VO_2^+ moiety have been found to be promising candidates for catalyzing oxidative bromination of organic substrates, such as trimethoxybenzene, salicylaldehyde and phenol [27]. The reactions, in which vanadium haloperoxidases act as catalyst take place in the presence of H₂O₂and bromide. In our study, taking into an account the importance of vanadium haloperoxidase enzymes, we investigated the oxidative bromination of phenol red usingour newly synthesized complexes [(VO₂)₂(μ_3 slsch){Na₂(μ -H₂O)₂(H₂O)₂}]_n (1) and[(VO₂)₂(μ_3 -npsch){Na₂(μ -H₂O)₂(H₂O)₂}]_n (2),as catalyst precursor in the presence of H₂O₂, HClO₄ and KBr.During this process, 1 and 2 react with two equivalents of H₂O₂, forming bis-(peroxo) [(VO₂)₂⁻] species(which readily oxidize bromide)resulting in the formation of a hydroperoxo intermediate. The oxidized bromine species Br₂⁻, Br₃⁻ or, most likely, HOBrwere then trapped by the organic substrate (phenol red) which resulted in a color change of the solution from yellow to blue, which indicated formation of the brominated product phenol blue [28].The crude product was extracted, dried over anhydrous sodium sulfate, the solution filtered and the solvent evaporated under reduced pressure to obtaina red powder. The product was purified using column chromatography. The brominated product obtained was also confirmed by¹H NMR spectroscopy. Color: light red powder; yield: 57%.¹H NMR (400 MHz, CDCl₃): 7.87-8.09 (m, 4H), 9.10 (s, 2H), 7.55 (s, 4H).

4. Conclusion

We have synthesized two new heterobimetallic complexes of the following compositions, $[(VO_2)_2(\mu_3-slsch) \{Na_2(\mu-H_2O)_2(H_2O)_2\}]_n$ (1) and $[(VO_2)_2(\mu_3-npsch) \{Na_2(\mu-H_2O)_2(H_2O)_2\}]_n$ (2), using V₂O₅ as the starting material and polyfunctional hydrazone ligand. For testing the feasibility of the complexes as catalyst precursors for oxidative bromination reaction that are catalyzed by haloperoxidase enzyme, we performed experiments using phenol red as a substrate for bromination. The oxidative bromination results obtained are similar compared to literature reports, producing phenol blue in moderate yield as a brominated product. In addition, we have also extended our work for the catalytic oxidation of 3,5-di-tert-butylcatechol to 3,5-ditert-butylcyclohex-4-ene-1,2-dione using 1 as catalyst. The results obtained are in agreement with the literature report; the catalyst is efficient for accelerating the reaction in good yield. We will continue to explore the efficiency of vanadium complex as a catalyst for further application.

Appendix A. Supplementary data

The cif files of $[(VO_2)_2(\mu_3-slsch) \{Na_2(\mu-H_2O)_2(H_2O)_2\}]_n$ (1) and $[(VO_2)_2(\mu_3-npsch) \{Na_2(\mu-H_2O)_2(H_2O)_2\}]_n$ (2) were deposited with the Cambridge Crystallographic Data Centre (1497273 and 1497295). These data can be obtained via https://summary.ccdc.cam.ac.uk/structure-summary-form, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk. Supplementary data related to this article can be found in the online version.

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Graphical abstract





B.Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone (H4npsch)

Figure 1. Structural formula of the ligands used in this study and their numbering scheme.









Figure 3. Crystal structure of 2 showing the asymmetric unit (A) and complete fragment (B).



Figure 4. ORTEP drawing and polyhedral representation of an infinite one-dimensional structure of $[(VO_2)_2(\mu_3-slsch)\{Na_2(\mu-H_2O)_2(H_2O)_2\}]_n(1)$ and $[(VO_2)_2(\mu_3-npsch)\{Na_2(\mu-H_2O)_2(H_2O)_2\}]_n(2)$, V by dark blue polyhedral, Na by light blue polyhedral.





Figure 6. Spectral changes observed during the reaction of H_2O_2 with $[(VO_2)_2(\mu_3-slsch) \{Na_2(\mu-H_2O)_2(H_2O)_2\}]_n(1)$ A and $[(VO_2)_2(\mu_3-npsch) \{Na_2(\mu-H_2O)_2(H_2O)_2\}]_n(2)$ B. The spectra were recorded upon the dropwise addition of a 2×10^{-2} M H_2O_2 solution to a 1.32×10^{-5} M solution of 1 and 2 in CH₃CN (10 mL).





Figure 7. (a) Change in spectral pattern for the reaction of **1** with 3,5-DTBC in CH₃CN after observing the reaction for 6 h. (b) A plot of absorbance *vs* time.



Table 1. Crystal data and structure refinement parameters of 1 and 2.			
	1	2	
CCDC No.	1497295	1497273	
Empirical formula	$C_{18}H_{40}N_4O_{20}NaV_2$	C ₁₆ H ₂₁ N ₃ O _{7.5} VNa	
Formula weight	757.41	450.29	
Temperature/K	291.93(10)	295.7(2)	
Crystal system	Triclinic	Monoclinic	
Space group	P-1	12/a	
a/Å	7.2582(9)	24.162(2)	
b/Å	10.3808(12)	6.1642(3)	
c/Å	10.8313(9)	27.1577(17)	
α/°	95.321(8)	90	
β/°	100.093(9)	102.757(7)	
$\gamma/^{\circ}$	100.885(10)	90	
Volume/Å ³	782.30(15)	3945.0(5)	
Z	1 · ·	8	
μ/mm ⁻¹	0.700	0.571	
Reflections collected	5653	7229	
Independent reflections	3487/0/247	3010/0/282	
Data/restraints/parameters	1.060	1.084	
Final R indexes $[I \ge 2\sigma(I)]$	R1 = 0.0622, wR2 = 0.1783	R1 = 0.0312, wR2 = 0.0760	
Final R indexes [all data]	R1 = 0.0713, $wR2 = 0.1897$	R1 = 0.0366, wR2 = 0.0789	

Table 1. Crystal data and structure refinement parameters of 1 and 2.