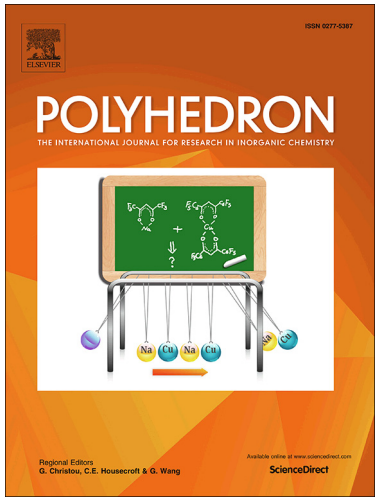

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Synthesis, Crystal Structure and Reactivity of Homobimetallic Vanadium(V) Complexes Derived from Oxaloyldihydrazone Ligands

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Abstract

Treatment of V_2O_5 with dihydrazone ligands (H_4L) (disalicylaldehydeoxaloyldihydrazone (H_4L_1 = H_4slox), bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H_4L_2 = H_4nph) and bis(5-bromosalicylaldehyde)oxaloyldihydrazone (H_4L_3 = H_4sloxBr)) in methanol leads to the formation of homobimetallic vanadium(V) complexes of the composition $[(CH_3)_2NH_2]_2[(VO_2)_2(L)].nH_2O$, where n = 2 (**1**, **2**) and n = 4 (**3**). The reaction of complexes **1-3** with H_2O_2 results in the formation of bis(monooxidoperoxidovanadate(V)) complexes$[\{VO(O_2)\}_2(L)]^{2-}$ and the reaction with HCl leads to the formation of oxidohydroxido species of the composition $[(VO(OH)(L)]^{2-}$. The complexes show great potential for the oxidation of alcohols and the oxidative bromination of some organic substrates.

Introduction

Vanadium occurs as a trace element in biological systems and has been found in enzymes such as haloperoxidases and nitrogenases. Vanadium dependent bromperoxidases have been discovered in some lichens [1], fungi [2] and marine algae [3]. Amavadin is found in amanitae mushrooms [4], farmworms [5] and blood cells of sea squirts (Ascidiceae). The discovery of vanadate(V)-dependent haloperoxidases aroused great interest for their catalytic activity, in which the vanadium(V) ions, in the presence of hydrogen peroxide and a halide anion [6], act as the active centre for the halogenation of organic substrates and are likely involved in the biosynthesis of several compounds with potential medicinal uses [7]. This enzyme was also used for the catalytic oxidation of bromides, which is a key intermediate for the synthesis of organobromo compounds. It has been found that organobromo compounds possess great potential in applications for medicinal purposes, as they have been found to

possess both antimicrobial and anticancer properties [8, 9]. Many marine organisms use natural organobromo compounds for defending themselves from predators [10].

Schiff base hydrazone compounds have been used widely as versatile ligands in coordination chemistry and Schiff base hydrazone vanadium complexes are also attractive models for the elucidation of various biochemical processes, such as antitumoral, antifungal and antiviral activities [11]. Hydrazones that have been derived from the condensation of hydrazides with o-hydroxyaromatic aldehydes or ketones are potentially tridentate ligands and have been reported to give several types of vanadium complexes with the metal in the +4 and +5 oxidation states. Some of these complexes have been found to play an important role as structural as well as functional mimics of vanadium-bromoperoxidase [12] and also as structural models for vanadium(V)-transferrin [13]. Oxaloyldihydrazide can be condensed with 2-hydroxy-arylaldehydes to form hydrazone moieties, which are important O-N-O hexadentate donor ligands. This type of ligand has up to eight coordination sites, which leads to the tendency to stabilize vanadium in its highest oxidation state [14].

From a literature survey [15-18], it has been found that quite a few structural and functional model complexes of bromoperoxidase are known, yet much remains to be learnt about their structural and electronic factors so that a catalytic cycle could be predicted from the stability and activity of the model vanadium complexes. Hence, it is of great importance to synthesize and characterize new vanadium complexes that mimic the enzyme activity and thus help to understand the key structural and electronic features. Accordingly, we report here the synthesis and characterization of new dioxido-vanadium complexes containing hydrazone ligands which have proven to be a promising and attractive in the field of catalysis.

The oxidation of alcohols to aldehydes and ketones is a very important reaction as the products are widely used as reagents in synthetic organic chemistry and also play an important role in the laboratory and as well as in the industries of fine chemicals, medicinally important compounds and in natural products [19-21]. In order to perform this type of transformation, inexpensive and intrinsic waste free oxidants and recyclable catalysts are needed urgently. Molecular oxygen and air are ideal oxidants, and many efficient catalyst systems have been developed for aerobic alcohol oxidation with the use of a transition metal catalyst alone or in combination with stable nitroxyl free radicals. However, on a large scale molecular oxygen cannot be used since its use is constrained by safety concerns, as the combination of O_2, organic solvents and reagents [22, 23] make an explosive mixture. Further, halogenated solvents [22] are undesirable from an environmental point of view.

Another ecofriendly oxidant is hydrogen peroxide (instead of pure oxygen), which can be used safely in oxidation reactions, reducing the safety hazards that occur when an organic solvent is heated under elevated O_2 pressures. Water is the only side product that is expected in H_2O_2 mediated oxidation reactions and so it is easy to work out the reaction mixture. An aqueous solution of H_2O_2 (concentration less than 60%) is quite safe, non-toxic and low-cost. It does not form a homogeneous solution with most organic solvents and it is a moderate inorganic oxidant. Hence, it gives a homo-heterogeneous catalyst system and its separation from the reaction mixture after the completion of the reaction [24] is easy. Although some work has been done on the oxidation of alcohols using homogeneous catalysts with aqueous H_2O_2 as a terminal oxidant [25], heterogeneous systems as a catalyst with H_2O_2 for the oxidation of alcohols still remains a major challenge [26].

Oxidative bromination is a process in which electrophilic bromine is generated using various oxidants. Oxidative bromination of organic molecules represents a fundamental and important procedure for transformations employed in organic and pharmaceutical syntheses [27]. Additionally, a bromination-mimicking reaction of the naturally occurring enzyme vanadium bromoperoxidase found in marine algae has attracted much attention in the past [1-3,7]. Bromination of organic molecules by conventional methods utilized toxic and hazardous elemental bromine, which is health and environmental hazard for large scale syntheses in which half of the bromine ends up as hydrogen bromide waste [28, 29]. However, re-oxidation of HBr using hydrogen peroxide can solve this problem. Although, less harmful and toxic reagents have been developed for oxidative bromination using brominating agents [30], these reagents have limited synthetic utility due to their high cost and generation of organic waste. Hence, efforts are underway to utilise the bromide ion as the bromide source, instead of bromine, [31-36] to develope new and efficient methods for such reactions that are both environmentally and economically favorable.

In view of the above importance of vanadium and its complexes in biological systems, as well as in oxidation catalysis and oxidative bromination catalysis, the present paper describes the synthesis of some vanadium complexes, their characterization them by various conventional methods and their structure determination by X-ray crystallographic techniques. Further, a study on the catalysis of the oxidation of alcohols to aldehydes and ketones and oxidative bromination of some organic compounds is presented.

Experimental

Physical measurements

Hydrazine hydrate, diethyl oxalate, salicylaldehyde, 2-hydroxy-1-naphthaldehyde, 5-bromosalicylaldehyde, V_2O_5, 30% H_2O_2, HCl, KBr, 70% $HClO_4$, alcohols, aniline, aromatic aldehyde and ketones were E-Merck, Himedia or equivalent grades, and solvents were reagent grade, and all were used as received. All operations were performed under aerobic conditions. Vanadium was determined by the standard literature method [37]. A Perkin-Elmer 2400 CHNS/O Analyzer 11 was used to determine C, H, N content. The molar conductance of the complexes at room temperature in DMF solution at 10^{-3} M dilution was measured on a Direct Reading Conductivitymeter-303 with a dip type conductivity cell. Infrared spectra in the region 4000–200 cm^{-1} were recorded using a BX-III/FTIR Perkin Elmer spectrophotometer in KBr discs. The ^1H and ^{13}C NMR spectra were recorded on Bruker Avance II-400 MHz and 100 MHz in DMSO-d_6 or $CDCl_3$ solution using TMS as an internal standard. Electronic spectra were recorded on a Perkin-Elmer Lambda-25 spectrophotometer. Cyclic voltammograms were recorded with a CH Electrochemical Analyzer using a standard three-electrode assembly (glassy-carbon working, Pt wire auxiliary, SCE reference) and 0.1 M tetra-n-butyl ammonium perchlorate (TBAP) as the supporting electrolyte.

X-ray crystallography diffraction

Crystallographic data for complexes **1** and **3** were recorded using an Xcalibur, Eos, Gemini diffractometer equipped with monochromated MoKα radiation (λ = 0.71073 Å) source. CrysAlis PRO and Agilent, 2013 software packages were used for data collection and reduction. For structure solutions and refinements, SHELXT-2014 and SHELX-2014 were used [38]. The structures were solved by direct methods and refined on F^2 by a full matrix least squares [39]. All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atom positions were isotropically refined freely in the final refinement.

Preparation of the ligands

The disalicylaldehydeoxaloyldihydrazone (H_4slox) and bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H_4nph) ligands were synthesized according to our previous literature report [40, 41].

Preparation of bis(5-bromosalicylaldehyde)oxaloyldihydrazone (H_4sloxBr)

Oxaloyldihydrazine was prepared by reacting diethyl oxalate (10 mL) and hydrazine hydrate (7 mL) in a 1:2 M ratio under stirring for 30 min. The product thus isolated was recrystallized from H_2O.

Bis(5-bromosalicylaldehyde)oxaloyldihydrazone (H_4sloxBr) was prepared by reacting oxaloyldihydrazine (3.0 g, 25.42 mmol) in H_2O (100 mL) with 5-bromosalicyaldehyde (10.2 g, 50.84 mmol) in ethanol (20 mL) over a hot plate at 70 °C with constant stirring for 1 h. The yellow precipitate thus obtained was filtered, washed with hot H_2O-ethanol and dried over anhydrous $CaCl_2$.

Synthesis of $[(CH_3)_2NH_2]_2[(VO_2)_2(slox)].2H_2O$ (1)

To a suspension of disalicylaldehydeoxaloyldihydrazone (H_4slox) (0.36 g, 1.1 mmol) in a methanol solution (20 ml), obtained by stirring, vanadium pentoxide (V_2O_5) (0.20 g, 1.1 mmol) in methanol (10 mL) was added dropwise and the resulting solution was gently stirred for 30 minutes. The reaction mixture was then refluxed for 1 hour, cooled to room temperature, filtered and dried over $CaCl_2$. Yield: 88%. Color: Yellow. Anal. (%), Calc. for $C_{20}H_{30}N_6O_{10}V_2$ (MW: 616.372 g/mol); C, 38.97; H, 4.91; N, 13.63. Found: C, 38.87; H, 4.92; N, 13.55. IR data (cm^{-1}, KBr): 3367 (s br) ν(OH + NH); 1606 (s) ν(-C=N); 929 (m), 911 (s) ν(V=O); 570 (w) ν(V-O). ^{1}H NMR (400 MHz, DMSO-d_6, Me_4Si) δ (ppm): 6.67-7.44 (m, 8H, Ar-H), 8.83 (s, 2H, C(H)-N). ^{13}C NMR (100 MHz, DMSO-d6, Me_4Si) δ (ppm): 165.67, 164.90, 157.40, 133.66, 132.82, 119.61, 119.55, 116.87, 39.93-38.68. Electronic spectrum in DMF solution, λ_{max} (nm): 330, 418. CV: E_{pc}(V): +0.90, -0.23, -1.71; E_{pa}(V): +1.28, +0.03, -0.59, -1.44.

The complexes $[(CH_3)_2NH_2]_2[(VO_2)_2(nph)].2H_2O$ (**2**) and $[(CH_3)_2NH_2]_2[(VO_2)_2(sloxBr)].4H_2O$ (**3**) were also prepared by following the above procedure using bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H_4nph) (0.47 g, 1.1 mmol) (**2**) and bis(5-bromosalicylaldehyde)oxaloyldihydrazone (H_4sloxBr) (0.53 g, 1.1 mmol) (**3**).

Single crystal of complexes **1** and **3** were obtained within a week by slow evaporation of a complex solution in DMF/water (1:1.5) at room temperature. Complex **2** could not be crystallized despite of our several best efforts.

$[(CH_3)_2NH_2]_2[(VO_2)_2(nph)].2H_2O$ (2)

Yield: 79%. Color: Yellow. Anal. (%), Calc. for $C_{28}H_{34}N_6O_{10}V_2$ (MW: 716.492 g/mol); C, 46.94; H, 4.78; N, 11.73. Found: C, 46.85; H, 4.80; N, 11.86. IR data (cm^{-1}, KBr): 3447 (s br) ν(OH + NH); 1600-1618 (s) ν(-C=N); 954 (w), 918 (s) ν(V=O); 549 (w) ν(V-O). ^{1}H NMR (400 MHz, DMSO-d_6, Me_4Si) δ (ppm): 7.05-8.38 (m, 12H, Ar-H), 9.85 (s, 2H, C(H)-N). ^{13}C

NMR (100 MHz, DMSO-d6, Me_4Si) δ (ppm): 166.42, 165.03, 153.64, 135.11, 133.42, 129.29, 128.30, 127.27, 123.34, 120.52, 110.32, 40.45-39.20. Electronic spectrum in DMF solution, λ_{max} (nm): 333, 453. CV: E_{pc}(V): +0.68, -0.41, -1.05, -1.81; E_{pa}(V): +1.16, +0.35, -0.67. **$[(CH_3)_2NH_2]_2[(VO_2)_2(sloxBr)].4H_2O$ (3)**

Yield: 85%. Color: Yellow. Anal. (%), Calc. for $C_{20}H_{32}Br_2N_6O_{12}V_2$ (MW: 810.194 g/mol); C, 29.65; H, 3.98; N, 10.37. Found: C, 29.54; H, 3.97; N, 10.45. IR data (cm^{-1}, KBr): 3429 (s br) ν(OH + NH); 1610 (s) ν(-C=N); 942 (s), 921 (s) ν(V=O); 572 (w) ν(V-O). ^{1}H NMR (400 MHz, DMSO-d_6, Me_4Si) δ (ppm): 6.73-8.24 (m, 6H, Ar-H), 8.95 (s, 2H, C(H)-N). ^{13}C NMR (100 MHz, DMSO-d6, Me_4Si) δ (ppm): 165.99, 163.94, 162.15, 156.33, 135.53, 134.06, 121.93, 121.35, 107.06, 79.15-78.49, 40.08-30.73. Electronic spectrum in DMF solution, λ_{max} (nm): 309, 328, 428. CV: E_{pc}(V): +1.41, +0.36, -0.32, -0.92; E_{pa}(V): +1.76, +0.62, -0.56.

General experiment for the catalytic oxidation of benzyl alcohol

Benzyl alcohol (0.30 mL, 2.90 mmol), 15 % H_2O_2 (1.31 mL, 5.80 mmol), complexes **1-3** (0.05 mmol) and water (10 mL) were taken in a 50 mL round bottom flask. The reaction mixture was stirred at ambient temperature for 20 min, then the temperature was raised to 70 °C and stirring was continued for 6 h. The reaction mixture containing the crude product was extracted and dried over anhydrous sodium sulfate. To afford the purified product, column chromatography was carried out. The NMR spectra of the oxidation products are given in the supporting information.

General experiment for oxidative bromination

Salicylaldehyde (0.24 g, 2 mmol) was taken in a 50 mL round bottom flask maintained at 0 °C, KBr (0.47 g, 4 mmol) dissolved in 5 mL water was added, followed by the addition of 30% H_2O_2 (1.70 g, 15 mmol). To this reaction mixture, the vanadium(V) complexes **1-3** (0.05 mmol) and 70% $HClO_4$ (0.14 g, 1 mmol) were added and the reaction mixture was stirred at 0 °C. An additional 1 mmol of 70% $HClO_4$ was further added in three equal portions after every 10 minutes, with continuous stirring. A light brown solid product was obtained which was separated using a separating funnel. The crude product thus obtained was then purified by column chromatography to afford the desired product. The NMR spectra of the bromination products are given in the supporting information.

Results and discussion

The complexes were synthesized by the reaction of H_4slox, H_4nph or H_4sloxBr with vanadium pentoxide in a 1:1 molar ratio in methanol under reflux for 1 hour. The complexes were found to have the following compositions: $[(CH_3)_2NH_2]_2[(VO_2)_2(slox)].2H_2O$ (**1**), $[(CH_3)_2NH_2]_2[(VO_2)_2(nph)].2H_2O$ (**2**), $[(CH_3)_2NH_2]_2[(VO_2)_2(sloxBr)].4H_2O$ (**3**), respectively. The complexes are insoluble in common organic solvents, such as dichloromethane, chloroform, benzene, hexane and ether etc., while they are slightly soluble in water, methanol, acetonitrile and acetone, and completely soluble in highly coordinating solvents such as DMSO (dimethyl sulfoxide) and DMF (*N*,*N'*-dimethylformamide). Yellow coloured crystals of complexes **1** and **3** were successfully obtained by recrystallization from DMF/water in a 1:1.5 ratio by volume and isolated by filtration, dried between folds of filter paper and kept under vacuum.

Molar conductance

The molar conductance values for complexes **1-3** are 68.18, 72.11 and 69.34 ohm^{-1} cm^2 mol^{-1}, respectively, at 10^{-3} M dilution in aqueous medium. These values are much less than the molar conductance values for a 2:1 electrolyte. However, they are also slightly less than the molar conductance values for a 1:1 electrolyte [42]. These values show that the complexes either exist as ion pairs in aqueous solution or exhibit very low mobility because of the bigger size of their ions in solution. Therefore, we believe that these complexes, due to their bigger size, have sluggish motion in solution and contribute much less to the molar conductance. Hence, it is suggested that these complexes most probably behave as a 2:1 electrolyte in aqueous medium.

IR spectra

A comparison of the IR spectra of the free ligands H_4slox, H_4nph and H_4sloxBr with those of the complexes suggests that all the ligands are coordinated to the vanadium ions in the enol form in the complexes.

The uncoordinated dihydrazone ligands show a strong band in the region 2998-3622 cm^{-1}. These bands may be assigned due to a joint contribution from the stretching vibrations of secondary -NH groups and -OH bond of phenolic groups. The IR spectra of the complexes show a broad band in the region 3000-3600 cm^{-1}. This band may be assigned to -OH of water molecules present either in the complexes or absorbed by the KBr pellets. On complexation, the characteristic bands due to the -NH groups of the dihydrazone ligands, in the region 2998-3622 cm^{-1}, disappear on complexation, suggesting the enolization of the ligands. The

complexes show a rather strong broad band in the region 3000-3600 cm^{-1} due to water molecules. The νC=O band, observed in the region 1669-1682 cm^{-1} in the free ligands, are also absent in the IR spectra of the complexes. This also supports the fact that enolisation of the dihydrazone ligand occurs on complexation, suggesting the coordination of the dihydrazone ligand to the metal centre in the enol form.

Another important characteristic feature of the IR spectra of the complexes consists of a very strong band in the region 1600-1618 cm^{-1}, these bands are assigned to the stretching vibration of the >C=N group, which shifts to lower frequency, suggesting that the >C=N group is involved in bonding to the metal centre. A new medium to strong band is observed in the region 1454-1523 cm^{-1}, which is characteristic of the NCO- group present in the complexes [43]. The strong new bands observed in the region 911-954 cm^{-1} are assigned to the terminal V=O group stretching vibrations; these stretching vibrations gave us a clear indication about the dioxido nature of the vanadyl group present in the complexes [44]. The weak bands in the low wavenumber region at 570 (**1**), 549 (**2**) and 572 cm^{-1} (**3**) indicate bonding of phenolate/naphtholate oxygen atoms and enolate oxygen atoms to the metal centres and are attributed to V-O stretching vibrations [45].

Nuclear magnetic resonance spectroscopy

^{1}H NMR spectra

The ^{1}H NMR spectra of the dihydrazone ligands H_4slox and H_4nph, as well as complexes **1** and **2**, have been recorded in DMSO-d_6, while the dihydrazone ligand H_4sloxBr and its complex (**3**) have been recorded in a mixture of DMSO-d_6 and $CDCl_3$. The ^{1}H and ^{13}C NMR spectral data for the free dihydrazone ligands and the metal complexes **1-3** are given in Figs. S1-S12.

The ligands H_4slox, H_4nph and H_4sloxBr show signals in the regions δ 12.67-12.90 and 10.99-12.60 ppm. The signal in the region δ 12.67-12.90 ppm is assigned to the -OH proton attached to the phenyl/naphthyl ring, while the peak at δ 10.99-12.60 ppm is due to the secondary -NH proton. This indicates that the free ligands exist in the ketonic form [46-48]. On complexation, these peaks disappear. The absence of these peaks in the ^{1}H NMR spectra of complexes **1-3** suggests that the dihydrazone ligands coordinate to the vanadium centre in the enol form through phenolic/naphtholic oxygen atoms via deprotonation and similarly the carbonyl oxygen atoms via enolization/deprotonation of the –NH proton. The azomethine protons in the ^{1}H NMR spectra of the dihydrazone ligands were observed in the region δ

8.77-9.98 ppm, exhibiting upfield and downfield shifts of about 0.06-0.18 ppm in complexes **1-3**. The upfield and downfield shift of the -CH=N signals is attributed to the drainage of electron density from the nitrogen atoms of azomethine group to the metal centre [49]. The signals due to the phenyl protons appeared at δ 7.00-8.40 (H_4slox), 7.22-8.21 (H_4nph) and 6.87-8.27 ppm in (H_4sloxBr) and in complexes they appeared in the region δ 6.67-7.44 (**1**), 7.05-8.38 (**2**) and 6.73-8.24 ppm (**3**).

^{13}C NMR spectra

The ^{13}C spectra of the complexes **1-3** are very similar to the spectra of the uncoordinated dihydrazones ligands. Comparing the spectra of the ligands to those of the complexes, there are significant shifts in the δ values. The ligands show peaks in the region δ 148.51-150.87 ppm, which are assigned to the azomethine carbon atoms; on complexation the ^{13}C NMR spectra shows downfield shifts to δ 157.40, 153.64 and 156.33 ppm with Δδ = 3.30-7.82 ppm. The free dihydrazone ligands' resonances appear at δ 156.57-158.42 and 155.31-155.90 ppm, which are assigned to the –C-OH and carbonyl carbon atoms, whereas upon complexation these signals are shifted downfield to the regions δ 165.67-166.42 and 163.94-165.03 ppm. The downfield shift of these signals confirms the coordination of the dihydrazones ligands to the metal centres. The aromatic carbon signals of the complexes appear at the expected positions.

Electronic spectra

The electronic spectra of the ligands and complexes were recorded in DMF solutions and the spectra of the complexes are shown in Figs. S13-S15.

The H_4slox and H_4sloxBr free ligands show two strong bands at 304 nm (13130 dm^3 mol^{-1} cm^{-1}), 341 nm (16990 dm^3 mol^{-1} cm^{-1}) and 305 nm (7200 dm^3 mol^{-1} cm^{-1}), 348 nm (8100 dm^3 mol^{-1} cm^{-1}), respectively, in DMF solution, whereas the H_4nph free ligand shows three bands, each of which appear as a couplet in the spectrum overall giving rise to six bands. These bands appear at 318, 330; 375, 391; 433, 486 nm, respectively. The first band at 304, 305, 318 and 330 nm is assigned to the $\pi \rightarrow \pi^*$ transition. The second band at 341, 348, 375 and 391 nm correspond to the $n \rightarrow \pi^*$ transition [50], which is characteristic of the salicylaldimine/naphthaldimine moiety of dihydrazones [51]. The H_4nph ligand shows additional adsorption bands at 433 and 486 nm, while the H_4slox and H_4sloxBr ligands do not show such a band. The weak bands at 433 and 486 nm have their origin in some hidden

transitions present on the ligand molecule. It is imperative to mention that each band in H_4nph splits into two bands which reveals that the dihydrazone ligand exists in the anti-cis conformation in the free state. The complexes show bands at 330 nm (8600 dm^3 mol^{-1} cm^{-1}), 418 nm (5200 dm^3 mol^{-1} cm^{-1}) for **1**, 333 nm (8666 dm^3 mol^{-1} cm^{-1}), 453 nm (6500 dm^3 mol^{-1} cm^{-1}) for **2** and 309 nm (9166 dm^3 mol^{-1} cm^{-1}), 328 nm (9000 dm^3 mol^{-1} cm^{-1}), 428 nm (6333 dm^3 mol^{-1} cm^{-1}) for **3**, respectively. The bands in the region 309-333 nm are assigned to an intra ligand charge transfer band, while the bands at 418 (**1**), 453 (**2**) and 428 nm (**3**) are assigned to a ligand to metal charge transfer (LMCT), which arises from the p-orbital lone pair of the phenolate/naphtholate oxygen atom to an empty d-orbital on the vanadium(V) centre [52].

Electrochemical studies

The cyclic voltammetry of the complexes **1-3** have been recorded in DMF with 2 mM solutions using 0.1 M tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte,e with Ag/AgCl as the reference electrode at a scan rate of 100 mV/s at 25 °C. The cyclic voltammograms of the complexes are shown in Figs. S16-S18.

The cyclic voltammogram of complex **1** shows three reductive waves and four oxidative waves, while the complexes **2** and **3** shows four reductive waves and three oxidative waves. So, complexes **1-3** display three redox-couples in addition to some irreversible reduction and oxidation waves. On the cathodic side, the complexes **2** and **3** show an irreversible reduction wave at -1.81 and -0.32 V, whilst on the anodic side only complex **1** shows an irreversible oxidation wave, at -0.59 V. In the above-mentioned ranges, these reductive and oxidative waves do not have their counter parts in the return scan. Hence, this suggests that the species produced in these reductive and oxidative waves are unstable in DMF solution and return to their original species on the timescale of thecyclic voltammetry. The highly negative charged dihydrazone ligand bonded to the metal centre makes the reduction of the metal centre highly unfavourable, leading to negative Epc values [53]. The cathodic potential in all the complexes are within the range of the values reported for the reduction (V^V/V^{IV}) of the hydrazone vanadium complexes [54]. A comparison of the voltammograms of the complexes with those of the free dihydrazones confirms that the reductive wave in the region (-0.92 V) to (-1.81 V) and the oxidative wave in the region (-0.56) to (-1.44) appear very near to the reductive waves in the region -0.98 V to -1.32 V and the oxidative wave at -0.95 V to -0.97 V in the free ligands, respectively. Similarly, for

complex **3**, the reductive wave at -0.32 V is very close to the reductive wave at -0.49 V (for H_4sloxBr). Hence, these waves in the metal complexes consistently arise due to ligand centred electron transfer reactions. However, the other cathodic and anodic waves in the complexes are quite far from the corresponding ligand waves, hence they are attributed to originate from electron transfer reactions occurring on the vanadium centres.

The first redox couple for complexes **1-3**, with the reductive wave in the region +0.68 to +1.41 V and the oxidative wave in the region +1.16 to +1.76 V, is quasi-reversible with $E_{1/2}$ = +1.09 V (ΔE = 380 mV), +0.92 V (ΔE = 480 mV) and +1.59 V (ΔE = 350 mV)**,** respectively, which most certainly originates from a ligand-based oxidation involving one of the azomethine >C=N- moieties. The second redox couple for complexes **1-3** is either quasi-reversible or irreversible at $E_{1/2}$ = -0.10 V (ΔE = 260 mV), -0.03 V (ΔE = 760 mV) and +0.49 V (ΔE = 260 mV), respectively, which is attributed to reduction of the metal ion ($V^{V}V^{V}/V^{V}V^{IV}$). The third redox couple for complex **2** is quasi-reversible, with $E_{1/2}$ = -0.86 V (ΔE = 380 mV), and is associated to the reduction of the metal ion ($V^{V}V^{IV}/V^{IV}V^{IV}$), as shown below.

$$[V^{V}V^{V}(L)]^{2-} \underset{-e}{\overset{+e}{\rightleftharpoons}} [V^{V}V^{IV}(L)]^{3-} \underset{-e}{\overset{+e}{\rightleftharpoons}} [V^{IV}V^{IV}(L)]^{4-}$$

Complexes **1** and **3** show another redox couple at -1.58 and -0.74 V ($E_{1/2}$) with a peak-to-peak separation equal to 270 and 360 mV, respectively. The values of ΔE of 270 and 360 mV reveal that this wave is certainly quasi-reversible in nature [55]. In view of the facts that this redox couple is close to the reduction peak at -1.32 V (H_4slox) and -1.09 V (H_4sloxBr) in the free ligands and the other complexes show only a reduction wave in the above region, it is suggested that this quasi-reversible process is most likely due to the $V^{V}V^{IV}/V^{IV}V^{IV}$ redox couple along with some contributions from a ligand-based reduction.

Crystal structure

The crystal structures of complexes **1** and **3** have been determined using single crystal X-ray crystallography and a representative ORTEP view of each complex is shown in Figs. 1 and 2. The crystal and structure refinement data for complexes **1** and **3** are presented in Table 1, whilst selected bond lengths and bond angles of the complexes are listed in Table S1. Both complexes crystallized in the monoclinic $P2_1/n$ space group and the asymmetric unit in each complex consists of a vanadium atom and half of the ligand moiety, forming $[(VO_2)_2(L)]^-$.

The ligand coordinates to each metal centre in a tridentate fashion through the -(O-N-O)- donor groups. The positions around the metal centre are occupied by two oxygen atoms, one azomethine nitrogen atom in basal positions and two terminal dioxido groups, forming a pentacoordinated geometry. The vanadium atom adopts a square pyramidal geometry in both complexes. The IR and electronic spectral properties of complex **2** are similar to those of complexes **1** and **3**, hence the arrangement of the ligand atoms around the metal centre for complex **2** are assumed to be similar to those of complexes **1** and **3**, with the vanadium(V) centre also adopting a square pyramidal geometry.

The metal-oxygen bond lengths in complex **1** are 1.8954(16) (V1-O1), 1.9788(14) (V1-O2), 1.6167(17) (V1-O3) and 1.6267(17) Å (V1-O4), whereas the metal nitrogen bond length (V1-N1) is 2.1328(17) Å. The trans angles in the complex, O1-V1-O2 and O4-V1-N1, are 152.40(7) and 136.06(9) °, respectively. Hence, the vanadium atom adopts a distorted square pyramidal geometry with a slight distortion ($\tau = 0.27$).

In complex **3**, the vanadium-oxygen bond distances are 1.899(4) (V1-O1), 1.998(3) (V1-O2), 1.615(4) (V1-O3) and 1.633(4) Å (V1-O4), whereas the vanadium-nitrogen bond distance is 2.130(4) Å (V1-N1). The trans angles in the complex, O1-V1-O2 and O3-V1-N1, are 156.08(16) and 127.88(19) °, respectively. Hence, the vanadium atom adopts a distorted square pyramidal geometry in this complex as well, with $\tau = 0.47$.

Table 1: Crystal data and structure refinement for complexes **1** and **3**

	Complex 1	**Complex 3**
CCDC	1873709	1873710
Empirical formula	$C_{10}H_{13}N_3O_5V$	$C_{10}H_{12}BrN_3O_6V$
Formula weight	306.17	401.08
Temperature/K	294.08(10)	295.0(3)
Crystal system	monoclinic	monoclinic
Space group	P*21/n*	P*21/n*
a/Å	7.9576(5)	8.2641(10)
b/Å	19.1979(11)	19.540(3)
c/Å	8.5158(5)	9.7305(15)
α/°	90	90
β/°	97.901(6)	101.397(15)
γ/°	90	90
Volume/Å^3	1288.60(13)	1540.3(4)
Z	4	4
Radiation	MoKα (λ = 0.71073 Å)	MoKα (λ = 0.71073 Å)
Data/restraints/parameters	2627/0/177	2293/0/198
Goodness-of-fit on F2	1.111	1.068
Final R indexes [I>=2σ (I)]	R1 = 0.0359, wR2 = 0.0929	R1 = 0.0453, wR2 = 0.1092
Final R indexes [all data]	R1 = 0.0417, wR2 = 0.0960	R1 = 0.0726, wR2 = 0.1243

Molecular packing diagram of the complexes

The molecular packing diagrams along the c-axis, together with hydrogen bond interactions present in the structural unit of the complexes, are shown in Figs. 3 and 4. All the complexes show hydrogen bonding interactions, such as N--H..O and O--H..O bonding interactions

The N--H..O and O--H..O bond lengths are 2.851(3) (N(3)--H(3A)..O(2)) and 2.763(3) Å (O(5)--H(5A)..O(4)) with bond angles of 148 and 173 ° respectively, in complex **1**. In complex **3**, these O bond lengths are 2.954(6) (N(3)--H(3A)..O(2)) and 2.747(7) Å (O(5)--H(5A)..O(4)) with bond angles of 152 and 172° respectively.

Reaction with hydrogen peroxide

In the present study, we examined the oxidation of alcohols and the oxidative bromination of some organic substrates using the vanadium complexes as a catalyst and H_2O_2 as a terminal oxidant. Hence, it was necessary to study the reactivity of the complexes towards H_2O_2 in order to determine the nature of the active complex intermediate catalyst formed in the reaction.

The reaction of complexes **1-3** with an aqueous methanolic solution of 30% H_2O_2 was monitored by UV-visible spectroscopy (Figs. S19-S21). When 30% H_2O_2 in an aqueous methanolic solution was added to a solution of the bis(dioxidovanadate(V)) complexes, the formation of bis(monooxidomonoperoxidovanadate(V)) complexes occurred. The complexes have been tentatively assumed to have the composition $[\{VO(O_2)\}_2(L)]^{2-}$. The bis(monooxidomonoperoxidovanadate(V)) complex can also be isolated by carrying out the reaction of complexes **1-3** with 30% H_2O_2 in methanol in a 1:5 molar ratio at 0 °C. We have also been able to establish the formation of peroxido complexes by iodometric titration. The experimentally determined value of peroxide was 4.55, 4.49 and 4.52% in the peroxido compounds of complexes **1-3**, respectively, which is much less than the values of 9.14, 9.07 and 9.10% calculated on the basis of the formation of the bis(monooxidomonoperoxidovanadate(V)) complexes. This suggests their instability in the solid state, for this contention, sufficient evidences are available in the literature [56]. However, the complexes might be stable in the solution state compared to the solid state. It has been reported that peroxido vanadium complexes containing a hydrazone ligand in the coordination sphere have poor stability in the solid state. Thus, when 20 mL of a 5 x 10^{-5} M solution of complex **1** was treated with 30% aqueous H_2O_2 (a total of 2.440 g, 18.00 mmol)

by adding H_2O_2 solution (10 μL) every 5 mins and spectra were recorded, the absorption bands at 418, 453 and 427 nm showed a decrease in the intensity and a blue shift to 413, 448 and 421 nm for complexes **1-3**, respectively, occurred. However, when a further amount of H_2O_2 was added to the vanadium complexes in methanol, an increase in the intensity of the band at 330 and 309 nm for complexes **1** and **3**, accompanied by a red shift to 333 nm for complex **1** and a blue shift to 305 nm for complex **3** occurred, while further addition of H_2O_2 to a solution of complex **2** resulted in a decrease in the intensity of the band at 333 nm, with the blue shift to 329 nm. Similarly, the band at 331 nm for complex **3** showed an increase in intensity with a red shift to 338 nm. The continuous addition of 30% H_2O_2 also showed the presence of one isosbestic point at 362 nm for complex **1** and 372 nm in complex **3**, while two isosbestic points were observed at 357 and 384 nm for complex **2**. This result indicates the formation of V^VO-(O_2) species [57, 58] and that both metal-centred oxidations take place.

Reactions in acidic and basic solutions

The reactivity of complex **1** with HCl was monitored by electronic absorption spectroscopy. The electronic absorption spectral changes observed on the addition of 1 drop portions of methanol saturated with HCl gas to a methanolic solution of complex **1** (20 mL of 7.02 x 10^{-5} M) resulted in the features shown in Fig. S22. The addition of 1 drop portions of an HCl methanolic solution to the solution of the complex led to a progressive decrease in the intensity of the 419 nm band accompanied by a red shift (bathochromic shift) to 422 nm, while the band at 331 nm showed an increase in its intensity with a marginal red shift (bathochromic shift) to 333 nm. The methanolic solution of the complex, upon addition of the HCl solution, darkens in colour. Complexes **2** and **3** (Figs. S23 and S24) also show similar behaviour on addition of a saturated solution of HCl gas in methanol. The continuous addition of an HCl solution to the complex solution shows the presence of two isosbestic points at 375 and 458 nm for complex **1**, 405 and 493 nm for complex **2** and 383 and 466 nm for complex **3**. These results reflect the formation of oxidohydroxido complexes of the composition $[(VO(OH)(L)]^{2-}$ [59]. The spectral patterns retain to their original features on the addition of a methanolic solution of KOH (10^{-4} M) (Figs. S25-S27), hence, the reaction is reversible. This reversibility is an important observation for the catalytic activity of vanadate-dependent haloperoxidases and the structure active site [60].

Catalytic oxidation of alcohols

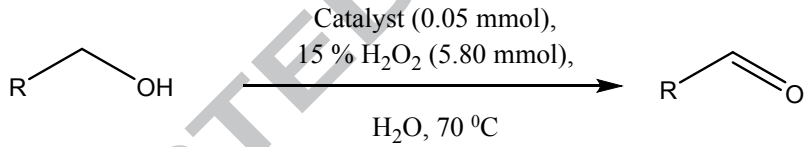
The catalytic activity was initially tested using benzyl alcohol as a standard substrate, (5.80 mmol) 15% H_2O_2 and (0.005 mmol) complex **1** were used as an oxidant and catalyst,

respectively. This reaction gave benzaldehyde as the sole product. The effect of other parameters, such as temperature, solvent, concentration of catalyst and effect of additives (Table S2) were also investigated. Firstly, the reaction was carried out at different temperatures and the best conversion was at 70 °C (Table S2, entry 5, Fig. 5). The solvent effect was also studied, using both polar and non-polar solvents. In non-polar solvents, such as hexane, CH_2Cl_2, toluene, xylene and benzene, a lower yield of benzaldehyde (in the range 3.4-14.0%) was found, while in polar solvents, the yield of benzaldehyde increased to the range 19.2-38.3%. This may be due to the higher dielectric constant of the polar solvents. It was found that H_2O (15% H_2O_2) as a medium gave the best yield of the product (38.3%) **(**Fig. 6). Hence, water became the solvent of choice for the reaction. Different amounts of the complex catalyst were examined and it was found that 0.05 mmol of the catalyst led to the highest yield (83.8%) (Table S2, entry 22, Fig. 7). Using the standard amount of catalyst (0.05 mmol), a temperature of 70 °C and H_2O (10 mL) as a solvent, the effect of additives was also studied. The oxidation of benzyl alcohol was also performed using different sources of vanadium, such as vanadyl acetylacetonate, $VOSO_4$, V_2O_5 and $NaVO_3$, but it was found that the complex gave the best yield. The present vanadium complex is formed from a multidentate ligand in which some bonding sites remain uncoordinated. These uncoordinated bonding sites offer more stability to the complex, which enable the complex to afford the best yield of benzaldehyde compared to vanadyl acetylacetonate, V_2O_5, $VOSO_4$ and $NaVO_3$. The reaction was also tested in the absence of the catalyst at 70 °C in H_2O, but no conversion of benzyl alcohol to benzaldehyde occurred, hence the catalyst is the active species in the reaction. The recyclability of complex **1** was investigated for the oxidation of benzyl alcohol (Fig. S28). The catalytic activity of complexes **2** and **3** were also tested using the same reaction conditions. Following the above standardized protocol, the catalytic oxidation of several alcohols has been studied (Table 2).

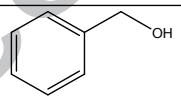
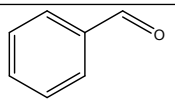
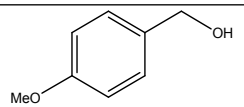
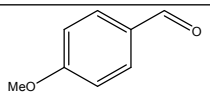
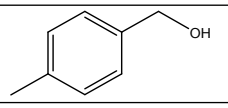
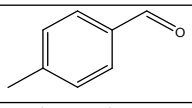
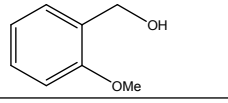
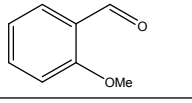
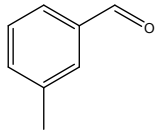
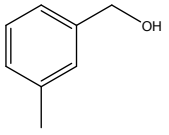
Both types of primary benzyl alcohols, containing electron donating and electron withdrawing substituents, (Table 2, entries 1-11, 14) were oxidized in good to excellent yield to the corresponding aldehyde. From the results in Table 2, we conclude that primary benzyl alcohols containing electron donating groups gave a higher yield than benzyl alcohols containing electron withdrawing groups. Primary benzyl alcohols containing substituents at their meta and ortho positions, with both electron donating and electron withdrawing groups, were also oxidized, but their yield was less compared to primary benzyl alcohols with substituents at the para position. Benzyl alcohol containing double bond functional groups,

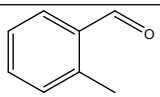
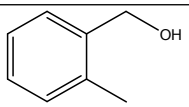
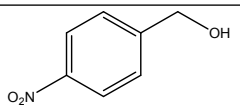
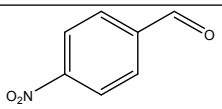
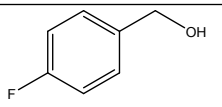
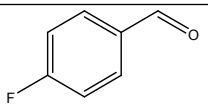
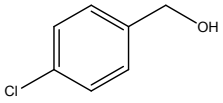
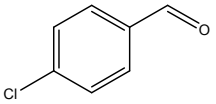
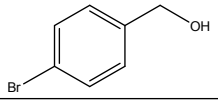
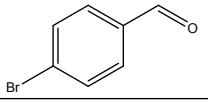
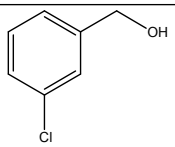
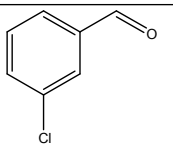
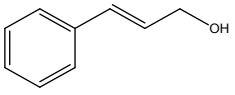
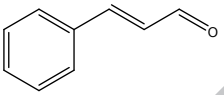
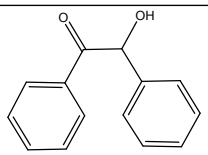
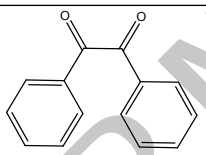
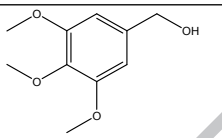
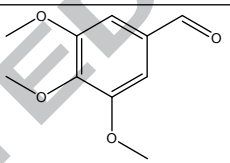
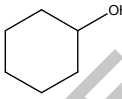
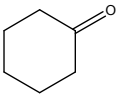
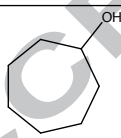
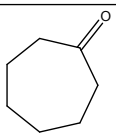
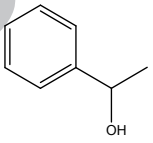
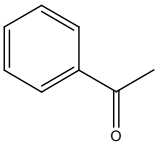
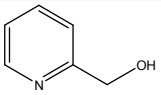
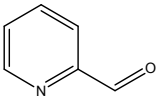
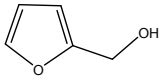
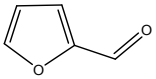
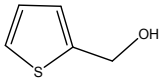
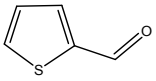
such as cinnamyl alcohol (Table 2, entry 12), was selectively oxidized; the double bond remaining unaffected. Benzoin was also oxidized to benzil (Table 2, entry 13) with a good yield. Secondary alcohols, such as cyclohexanol, cycloheptanol and phenyl ethanol (Table 2, entries 15-17) were also oxidized, but the yield was less than 2%. Hence, this system cannot oxidize secondary alcohols and secondary benzyl alcohols. It is worth noting that hetero-aryl alcohols, such as 2-thiophene methanol (Table 2, entry 20), are interesting substrates, since they resist oxidation under most aerobic conditions involving transition metals. This is due to their strong coordinating ability to transition metals. Surprisingly, 2-thiophene methanol was oxidized in good conversion to the corresponding aldehyde. 2-Furan methanol and 2-pyridine methanol (Table 2, entries 19, 18) were also oxidized, but the low conversion of 2-pyridine methanol was attributed to the electron-withdrawing effect of ring nitrogen substitution. The propargylic alcohol 2-hexyne-1-ol was also oxidized to 2-hexyne-1-al when stirred for 50 h with a low yield (< 20%), without oxidizing the triple bond functional group (Table 2, entry 21). Aliphatic alcohols such as n-butanol and n-octanol (Table 2, entries 22, 23) were also oxidized in a time period of 50 h.

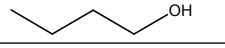
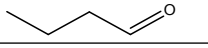
Table 2: Catalytic oxidation of different alcohols using complexes **1-3**



R = aryl, alkyl, heteroaryl

Entry	Substrate	Product	Time (h)	Yield (%)		
				Complex 1	Complex 2	Complex 3
1			6	82(83.8)[a]	82(84)[a]	81(83)[a]
2			7.2	88(90)[a]	86(87)[a]	88(89)[a]
3			7.2	85(87)[a]	81(84)[a]	83(86)[a]
4			7.2	86(89)[a]	84(88)[a]	86(87)[a]
5			7.2	84(85)[a]	80(82)[a]	82(84)[a]

6			7.2	81(84)[a]	78(81)[a]	82(83)[a]
7			7.2	74(75)[a]	70(73)[a]	72(74)[a]
8			7.2	77(79)[a]	74(77)[a]	76(78)[a]
9			7.2	78(79)[a]	76(77)[a]	77(80)[a]
10			7.2	76(78)[a]	73(74)[a]	75(77)[a]
11			7.2	72(74)[a]	70(72)[a]	72(73)[a]
12			12	78(80)[a]	71(74)[a]	75(78)[a]
13			7.1	85(88)[a]	80(83)[a]	82(84)[a]
14			6.5	91(93)[a]	87(89)[a]	89(90)[a]
15			6.5	(1.1)[a]	(0.8)[a]	(0.9)[a]
16			6.5	(1.6)[a]	(0.9)[a]	(1.3)[a]
17			9	(1.0)[a]	(0.4)[a]	(0.8)[a]
18			7	76(80)[a]	72(75)[a]	73(77)[a]
19			6.2	85(89)[a]	83(88)[a]	85(88)[a]
20			5.4	83(87)[a]	81(84)[a]	82(85)[a]
21			50	16(18)[a]	17(19)[a]	17(19)[a]

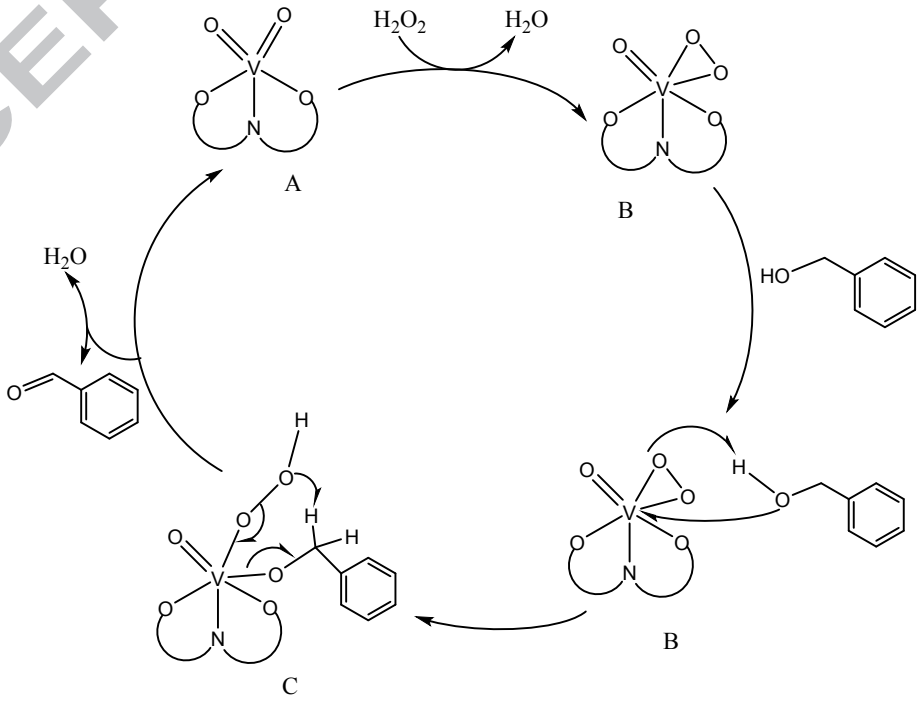
22			50	70(75)[a]	64(71)[a]	68(72)[a]
23			50	27(30)[a]	25(27)[a]	26(29)[a]

Reaction conditions: Catalyst (0.05 mmol), 15 % H_2O_2 (5.80 mmol), H_2O, Temperature (70 °C)
[a]GC Yield

The oxidation products obtained by oxidizing alcohols using complexes **2** and **3** are in good agreement with the products obtained using complex **1**, the only difference is in the yield. Complex **1** shows a slightly higher catalytic activity, giving a yield of > 5% greater than complexes **2** and **3**. Based on the differences of the ring substituent on complexes **2** and **3**, we can suggest that this plays a small role in the catalytic behaviour of these complexes, i.e. the presence of the naphthyl group in complex **2** and the electron withdrawing group of complex **3** result in a slightly lower catalytic performance compared to that of complex **1**.

Plausible mechanism for the oxidation

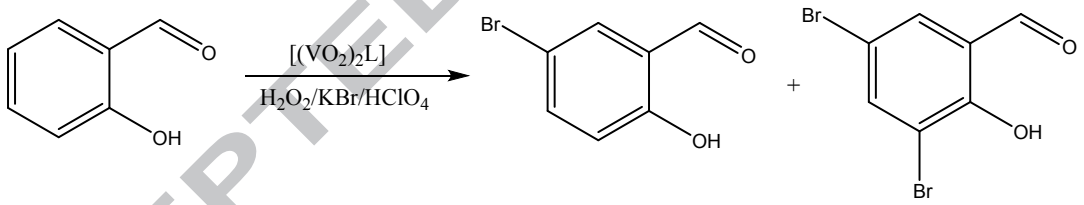
Regarding the oxidation mechanism, a catalytic cycle is proposed for the oxidation of alcohols to aldehydes and ketones in Scheme 1. First, the vanadium(V) complex (A) reacts with hydrogen peroxide forming oxidoperoxido-vanadium(V) species (B). This species (B) then reacts with benzyl alcohol via hydrogen abstraction on the α-hydroxyl group to afford a vanadium alcohol adduct (C). Next the benzaldehyde product is formed via β-hydrogen elimination from species (C), accompanied by dehydration [61].



Scheme 1: Plausible mechanism for the catalytic oxidation of alcohols (only one unit of the complex is shown)

Oxidative bromination

To optimize the reaction conditions for the oxidative bromination of some organic molecules, we used salicylaldehyde as a model substrate (Table S3). The reactions were studied in detail using complex **1** as the pre-catalyst. We varied different parameters, such as amount of catalyst/substrate ratios, effect of the amount of KBr, effect of H_2O_2 and volume of $HClO_4$. The maximum conversion of salicylaldehyde was achieved with 4 mmol of $HClO_4$, 2 mmol of substrate, 15 mmol of H_2O_2, 0.05 mmol of catalyst and 0.476 g (4 mmol) of KBr. It is known that in the presence of H_2O_2 and bromide, the bromination of organic substrates is catalyzed. Further, it has been demonstrated that vanadate-dependent bromoperoxidases and vanadium compounds have the ability to mimic this reaction. The bromination of trimethoxybenzene by the VO_2^+ ion [62] and also that of phenol red by $[VO(O_2)(H_2O)]^+$ [62] and related species [62] are typical examples. Here, we show that the present complex catalyzes the oxidative bromination of salicylaldehyde and other organic substrates using aqueous H_2O_2/KBr in the presence of $HClO_4$.

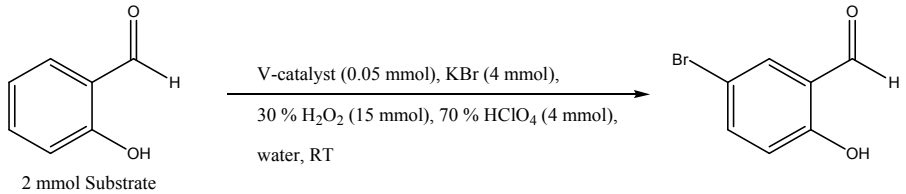


It has been shown that during oxidative bromination with H_2O_2/KBr catalyzed by V_2O_5 and oxovanadium(V) complexes [63], vanadium, with one or two equivalents of H_2O_2, forms monoperoxo $\{VO(O_2)^+\}$ or bis(peroxo) $\{VO(O_2)_2^-\}$ species. These peroxo species ultimately cause oxidation of bromide, most probably via an hydroperoxide intermediate. The subsequent bromination of the substrate [15a, 64] takes place by the oxidized bromine species (Br_2, Br_3^- and/or HOBr). No brominated product was obtained when the catalyst was not added to the reaction mixture. This demonstrates the active role of the dioxidovanadium complex in the catalytic bromination; the acid $HClO_4$ was also found to be essential. During the course of the reaction, the complexes decompose slowly when larger amounts of $HClO_4$ (6 mmol or more) were used. The decomposition of the complex catalyst can be reduced when $HClO_4$ is added to the reaction mixture successively in about 4-5 equal portions.

When complex **1** was used as a pre-catalyst, the reactions were studied by varying parameters such as the amount of catalyst/substrate ratios, the effect of the amount of KBr, effect of H_2O_2 and volume of $HClO_4$. The reaction was first examined with different amounts of catalyst/substrate and it was found that the reaction proceeded well with a 1:40 molar ratios. First, the reaction was carried out at low temperature (0 °C) and then it was raised to room temperature. The effect of the amount of KBr was also tested by using a complex/substrate 1:40 molar ratio and it was found that complex/substrate/KBr in 1:40:80 molar ratio gave a good yield. The effect of hydrogen peroxide was also tested and it was found that a 1:40:80:300 molar ratio of complex/substrate/KBr/hydrogen peroxide gave the best conversion. An investigation of the effects of thte acid were also carried out and it was found that 4 mmol of $HClO_4$ gave a good yield (Table S4). The effect of solvent was also examined by using different solvents and it was found that water gave the maximum yield. The oxidative bromination reactions were also performed using different sources of vanadium, such as $NaVO_4$, V_2O_5, $VOSO_4$ and vanadylacetylacetonate, but it was found that complex **1** gave the best catalytic performance. This is most probably due to the greater stability of the complex as some bonding sites remain uncoordinated in the dihydrazone complex. In this connection, it is imperative to mention that Rehder and Pessoa have carried out original works on the oxidative bromination of some organic substrates by vanadium complexes derived from dihydrazones [65, 66].

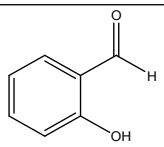
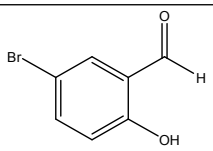
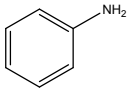
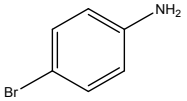
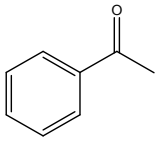
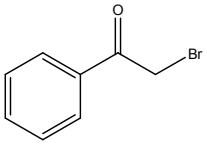
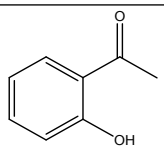
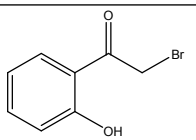
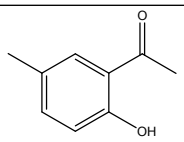
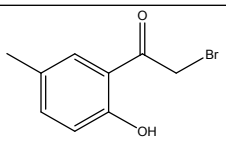
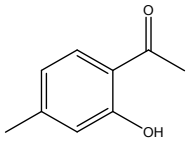
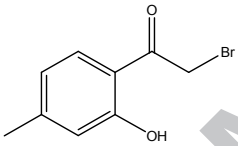
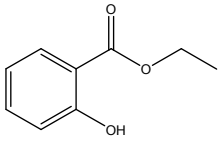
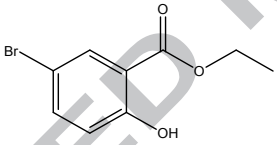
In order to explore the validity of this method, other organic substrates were also investigated. Some selected results are listed in Table 3. With the optimized conditions for the oxidative bromination, the reaction was carried out using 4 mmol of $HClO_4$, 2 mmol of substrate, 15 mmol of H_2O_2, 0.05 mmol of catalyst and 4 mmol of KBr, respectively.

Table 3: Oxidative bromination reaction of some organic substrate catalyzed by complexes **1-3**



2 mmol Substrate

Entry	Substrate	Product	Time (min)	Yield (%) (isolated)			Melting point (°C)
				Complex 1	Complex 2	Complex 3	

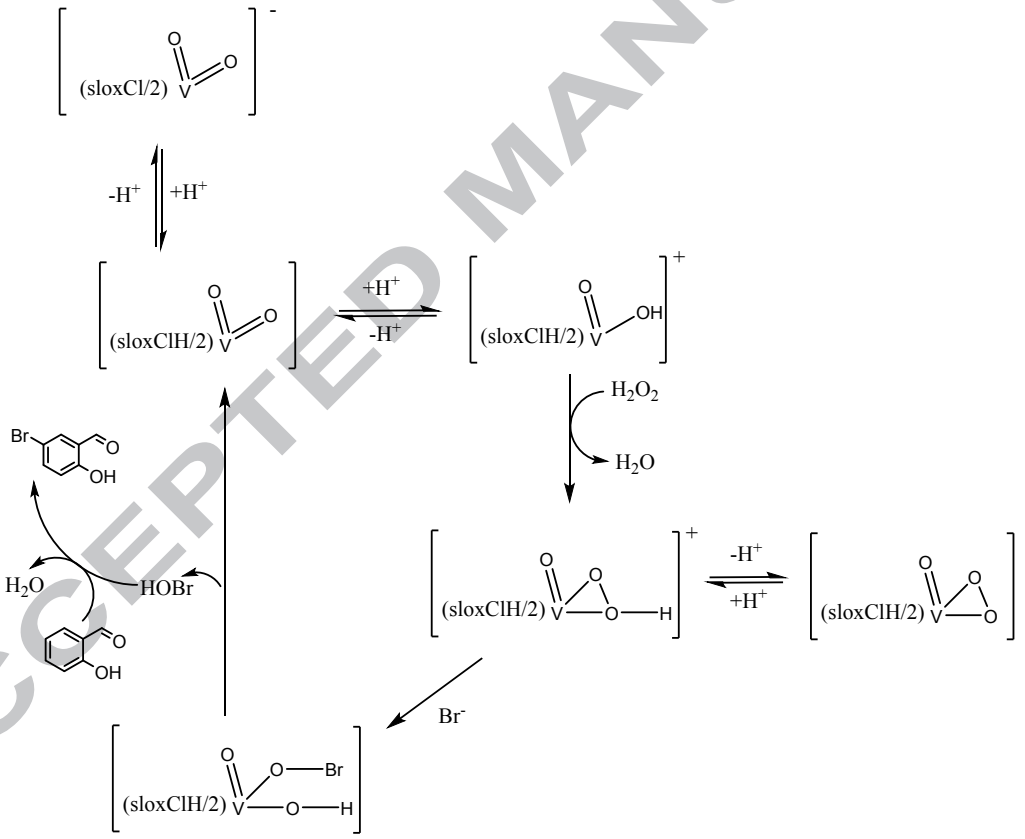
1			35	91	87	90	104
2			30	86	82	84	62
3			33	87	83	86	51
4			30	84	80	83	46
5			45	90	85	88	65
6			45	92	89	90	67
7			30	86	85	85	52

[a]Reaction conditions: salicylaldehyde (0.24 g, 2 mmol), H_2O_2 (1.70 g, 15 mmol), catalyst (0.02 g, 0.05 mmol), KBr (0.47 g, 4 mmol), HClO4 (0.57 g, 4 mmol) and water (5 mL).

The bromination reaction of salicylaldehyde gave a good yield of 5-bromo salicylaldehyde in 35 min (Table 3, entry 1). Aniline was also brominated giving p-bromoaniline as the product within a time period of 30 min (Table 3, entry 2). Bromination of acetophenone gave α-bromoacetophenone as the only product with a good yield within the time period of 33 min (Table 3, entry 3). The bromination reaction of 2-hydroxy acetophenone was also performed, which generated the product α-bromo-2-hydroxy acetophenone within 30 min (Table 3, entry 4) the yield was lower than that of unsubstituted acetophenone. Other substituted ketones, such as 5-methyl-2-hydroxy-acetophenone and 4-methyl-2-hydroxy-acetophenone, were also smoothly monobrominated to give the corresponding α-bromoketone in high yields (Table 3, entries 5 and 6). The bromination reaction of ethyl salicylate gave the product 5-bromoethyl salicylate with 86% yield (Table 3, entry 7).

Plausible mechanism of the oxidative bromination

A plausible mechanism of the oxidative bromination is shown in Scheme 2, in which an electrophilic mechanism is preferably predicted, with bromination at either para or ortho positions. When $HClO_4$ is added into the reaction mixture, the complex species [VOL/2] is, most likely, transformed into $[VO(OH)(HL/2)]^+$ and when H_2O_2 is added, the corresponding oxidoperoxido/oxidohydroperoxido species $[VO(O_2)L/2]^-$/$[VO(HO_2)L/2]$ may, most likely, be formed in acidic methanol. Thus, the active species essential for the catalytic reaction is generated. The coordination of peroxide to vanadium activates peroxide. This allows nucleophilic attack of the bromide ion [67] which then releases hypobromous acid, which causes bromination of organic substrates. Electron spray ionization mass spectra on model systems has shown that a hypobromite intermediate may also be involved in the reaction [68].



Scheme 2: Plausible mechanism of bromide oxidation by complex **1** in presence of H_2O_2, KBr and $HClO_4$.

Conclusion

In conclusion, in this paper we have reported the synthesis of the bimetallic dioxidovanadium(V) complexes $[(CH_3)_2NH_2]_2[(VO_2)_2(L)].nH_2O$ (where n = 2 (**1** and **2**); n = 4 (**3**)), which have been characterized by various physico-chemical studies. The structures of

the complexes have been established unequivocally by X-ray crystallography. Further, we have carried out the catalytic oxidation of benzyl alcohols, hetero-aryl alcohols, propargylic alcohol and aliphatic alcohols and the oxidative bromination of some organic substrates using the homobimetallic complexes. The catalytic processes for the oxidation and bromination are appreciable due to their simplicity and the availability and cheapness of the vanadium(V) complexes as catalysts. Moreover, the catalysts can be recovered without any loss of product formation in the subsequent cycles.

Supplementary data

The crystallographic data of complexes **1** and **3** can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Data can be obtained free of charge on quoting the depository numbers CCDC 1873709 and 1873710. via https://www.ccdc.cam.ac.uk/conts/retrieving.html.

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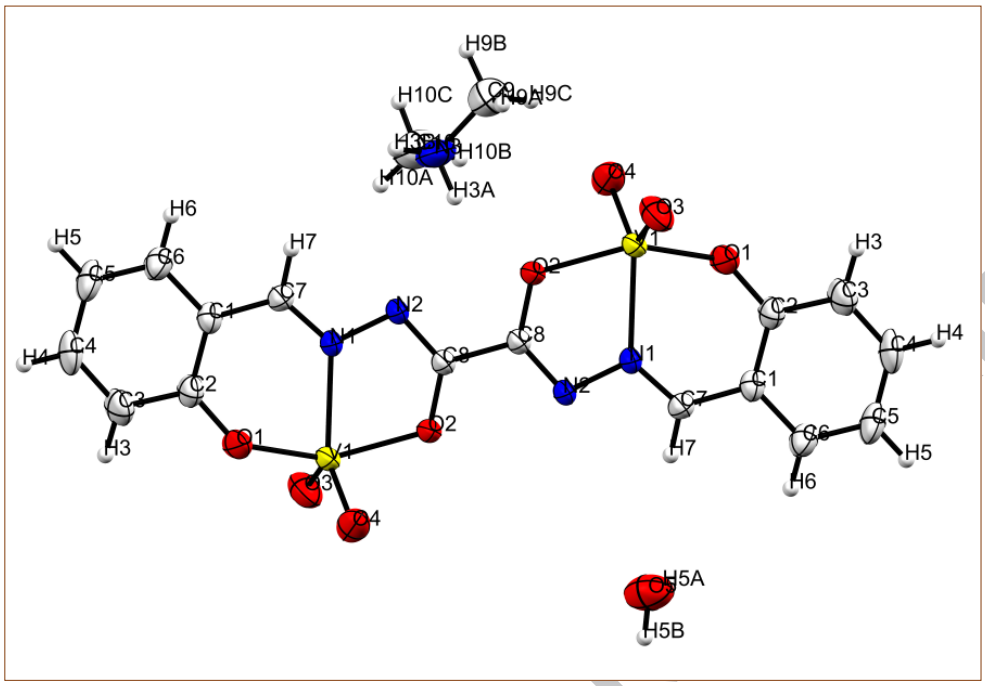

Fig. 1: Crystal structure of the complex $[(CH_3)_2NH_2]_2[(VO_2)_2(slox)].2H_2O$ (**1**)

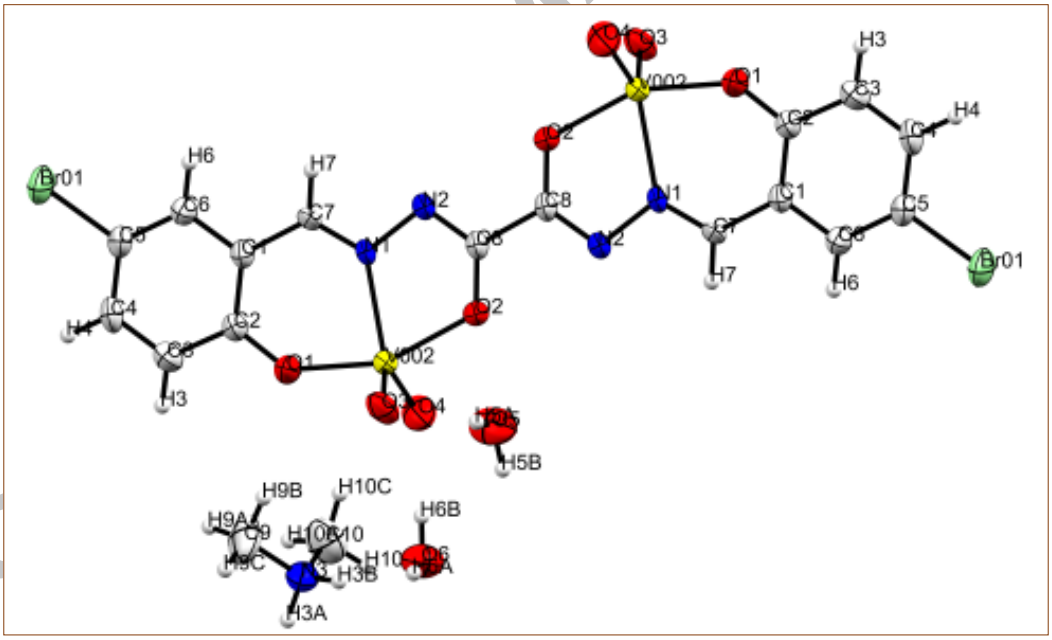

Fig. 2: Crystal structure of the complex $[(CH_3)_2NH_2]_2[(VO_2)_2(sloxBr)].4H_2O$ (**3**)

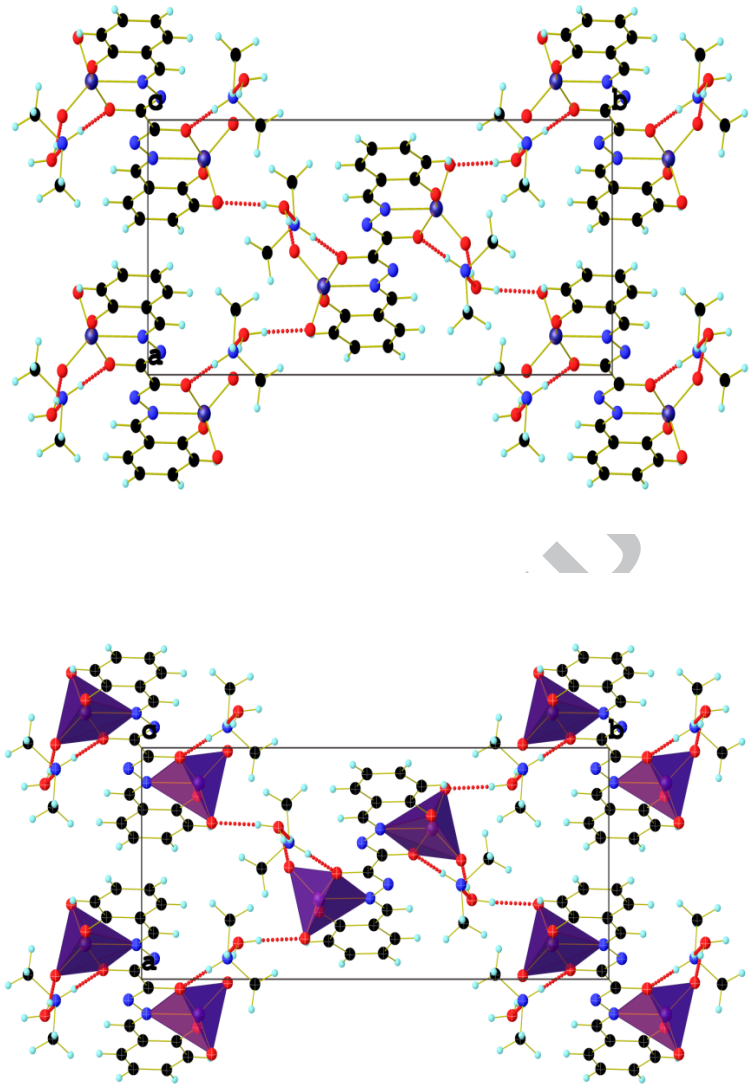

Fig. 3: Packing diagram of the complex $[(CH_3)_2NH_2]_2[(VO_2)_2(slox)].2H_2O$ (**1**) with a polyhedral plot around the vanadium ion

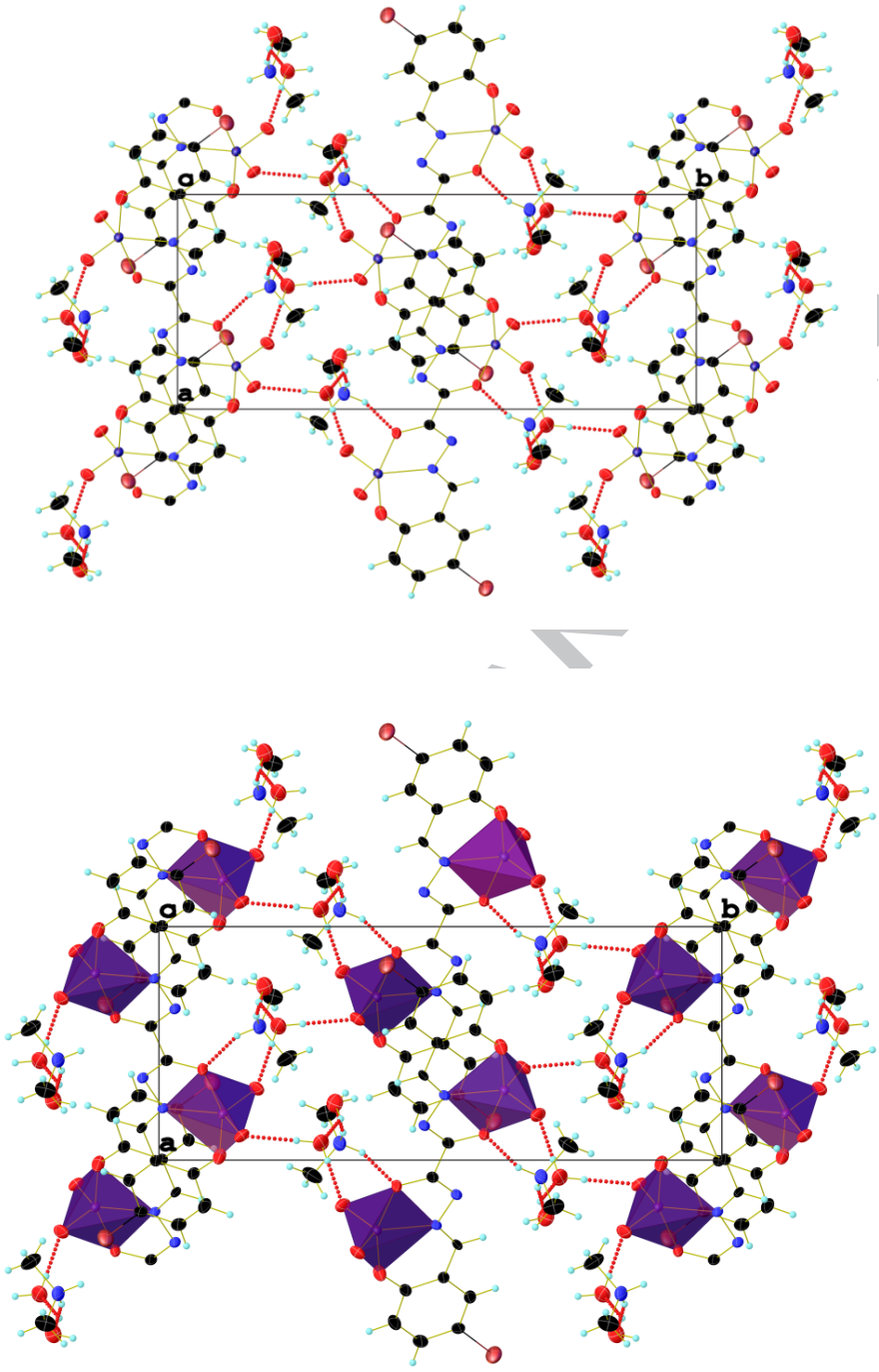

Fig. 4: Packing diagram of the complex $[(CH_3)_2NH_2]_2[(VO_2)_2(sloxBr)].4H_2O$ (**3**) with a polyhedral plot around the vanadium ion

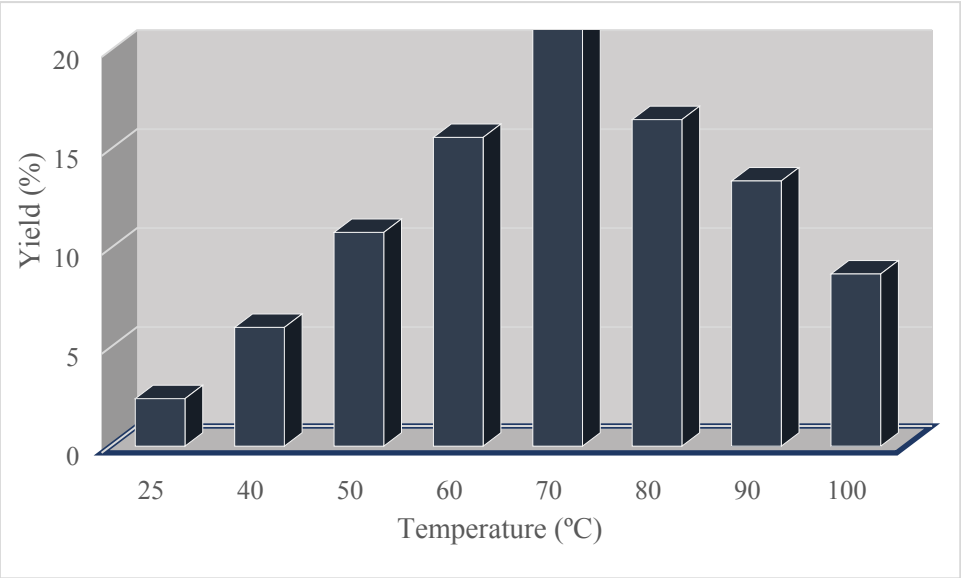

Fig. 5: Effect of temperature on the oxidation of benzyl alcohol ((benzyl alcohol (0.3 mL, 2.90 mmol), 15% H_2O_2 (1.31 mL, 5.80 mmol), catalyst (0.003 g, 0.005 mmol))

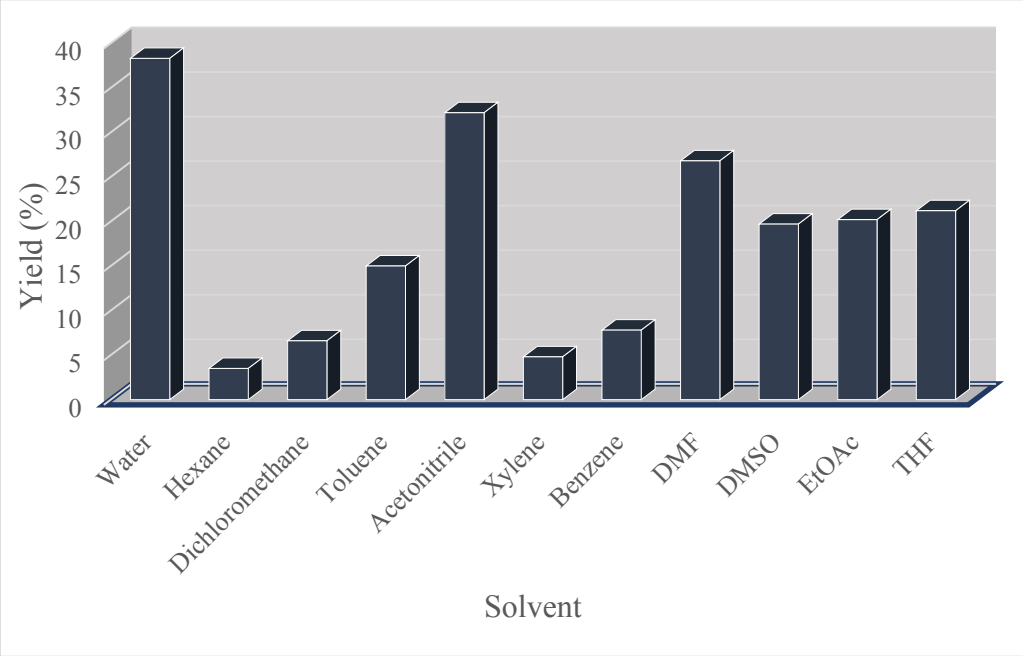

Fig. 6: Effect of solvent on the oxidation of benzyl alcohol

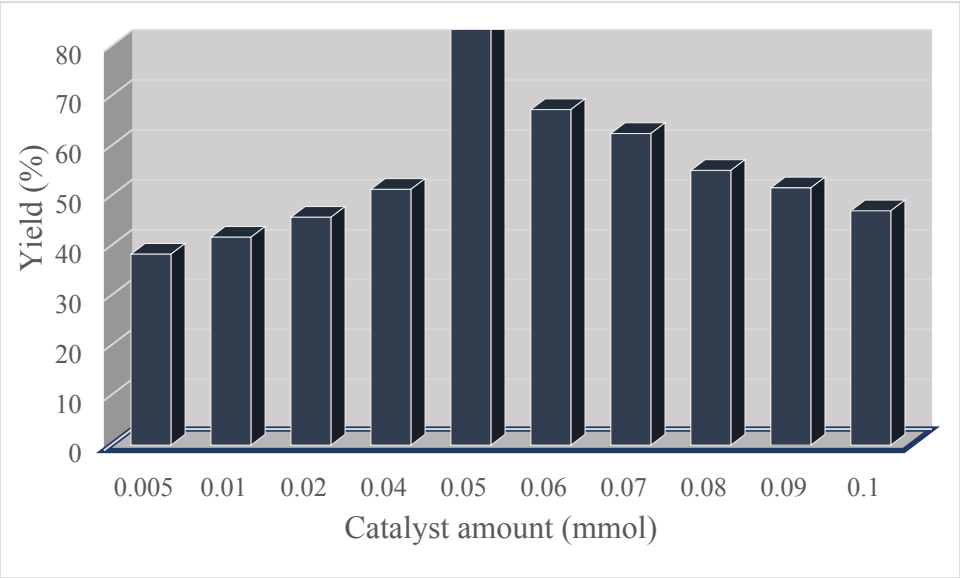

Fig. 7: Effect of concentration of the catalyst on oxidation of benzyl alcohol

The reaction of disalicyaldehydeoxaloyldihydrazone with vanadium pentoxide in methanol yields the vanadium(V) complex $[(CH_3)_2NH_2]_2[(VO_2)_2(slox)].2H_2O$, which oxidizes alcohols to aldehydes and ketones with H_2O_2 as the terminal oxidant.