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Vanadium bromoperoxidase (VBrPO) mimics: synthesis, structure and a comparative account of the catalytic activity of newly synthesized oxidovanadium and oxido-peroxidovanadium complexes†

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The bioinspired catalytic activities of two newly synthesised vanadium(IV)dioxido (complex **1**) and vanadium(V) oxido-peroxido (complex **2**) complexes with the neutral tridentate benzimidazole ligand, 2,6-di-(1*H*-benzo[*d*]imidazol-2-yl)pyridine (Byim) have been established. The bromoperoxidase activities of these complexes have been established through the activation of C–H bonds of substrates like phenol, *o*-cresol and *p*-cresol. The products, characterized by GC analysis shows that good conversions have been achieved. Considering the catalytic efficiency of the complexes, complex **2**, with one in-built peroxido group is found to be more potent than complex **1**. The catalytic cycles of both the complexes have been established from experimental results.

Introduction

The involvement of vanadium in biological processes is well documented.[1] It has been known to be present in plants and various living organisms including humans. It is also known to be present in haloperoxidases, the vanadium-dependent enzymes first isolated from brown algae.[2] A general picture of the active site of haloperoxidases and the mode of action of such enzymes have been established.[2] The active site of haloperoxidases is reported to contain pentacoordinated vanadium(V) as VO_4N motif.[3] The nature of the amino acid of the proteic chain of the enzyme, is well established, as has the presence of the oxido-oxygen and of aqua ligands.[4]

The vanadium complex takes up hydroperoxido (1^-) fragment forming a monoperoxidovanadium complex,[4] and while both mono and diperoxidovanadium complexes could theoretically be formed in acidic aqueous solutions,[4] the former is considered to be more likely as a large excess of hydrogen peroxide around vanadium is not expected in biological systems. Moreover, monoperoxidovanadium complexes are usually more reactive than diperoxido derivatives towards organic and inorganic substrates.[5]

The capability of vanadium and hydrogen peroxide mediated activation of bromide towards bromination of organic substrates has been demonstrated.[6] Vanadium and molybdenum complexes in the presence of molecular oxygen, hydrogen peroxide or organic hydroperoxides, have also been found to accelerate the oxygenation of aromatic and aliphatic hydrocarbons.[7,8]

Structural as well as functional modelling studies of VHPO enzymes using oxidovanadium(V) complexes with VO_4N coordination environments have shown that the five coordinated VO_4N moiety of the active site of VHPO enzymes is converted to the respective monoperoxidovanadium(V) species as an intermediate in the presence of H_2O_2, a reaction which plays the key role in the activity of the enzyme.[9] Although, the propensity of vanadium(V) to coordinate peroxides is known[10] very few peroxidovanadium(V) complexes have been tested for their enzyme mimetic properties.

The development of low molecular mass vanadium complexes with biologically relevant oxidation states of vanadium will help in making further progress in the elucidation of the biological roles of vanadium. The confirmation that in vanadate-dependent haloperoxidase enzymes (VHPO), covalent bonds were formed between vanadium in the active site[11] and the N of imidazole moieties of histidine residues[11] stimulated the design of structural models that contain imidazole, imidazole derivatives, or other N donor ligands coordinated to vanadium.[11]

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† Electronic supplementary information (ESI) available: The figures of GC-MS and gas chromatography. CCDC 1407332 and 914805 for complexes **1** and **2** respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6nj00767h

Such vanadium complexes have also been exploited to mimic other functionally similar systems that model the oxidative halogenation and sulfoxidation of organic substrates.[11] Crans *et al.*[12] and Cornman *et al.*[13] prepared oxidovanadium(IV) {VIVO} and dioxidovanadium(V) {VVO_2} complexes of benzimidazole-derived ligands, providing models for the coordination of histidine in the enzymes. Other structural and functional models of VHPO involving benzimidazole derived ligands have also been reported.[12,13] A scan through the literature reveals that the imidazole based modelling of VHPO is still in its infancy. The development of bio-mimicking VO_4N moieties is highly warranted because of the fact that the vanadium based enzyme mimetic haloperoxidation has considerable relevance concerning the conversion of organic substrates to their valuable brominated analogues. The proposed catalytic cycles of haloperoxidation reactions suggest that the formation of vanadium oxidoperoxido moieties occurs as intermediates, but whether the inbuilt peroxido group or the *in situ* generated peroxido group facilitates the activation of halides is still unclear. Hence, the development of vanadium based complexes having the oxidoperoxido moiety in the core has been thought to be of prime importance in VHPO research to understand the role of peroxido moiety in VHPO modelling chemistry.

In view of the above facts, the present project is undertaken to accomplish the synthesis of a dioxidovanadium(IV) complex [VO_2(Byim)] and an oxidoperoxidovanadium(V) complex [$VO(O_2)$(Byim)(MeOH)]ClO_4 with the 2,6-di(1*H*-benzo[*d*]imidazol-2-yl)pyridine ligand to compare their VHPO activities, in order to enrich the chemistry of imidazole based VHPO modelling.

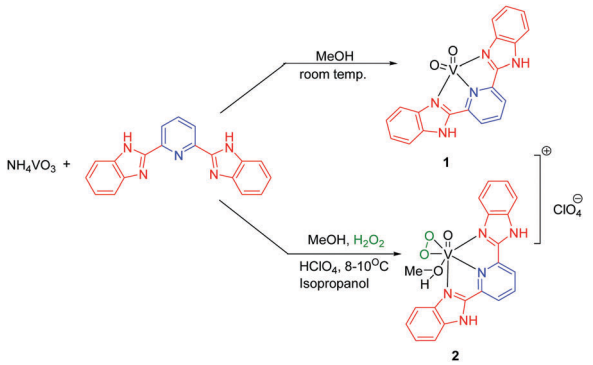
Results and discussion

Synthetic aspects of complexes 1 and 2

The Byim (N, N, N donor) ligand was synthesized following the literature method.[14]

Reaction between equimolar amounts of aqueous VO_4^{3-} solution and Byim ligand (N, N, N donor) in hot aqueous methanol yielded the dioxidovanadium(IV) complex [VO_2(Byim)], (**1**) whereas the treatment of aqueous cold (0–8 °C) VO_4^{3-} solution with H_2O_2 at pH 3 resulted in the formation of red mono oxido-peroxidovanadium(V) species $[VO(O_2)(H_2O)_3]^+$. However, on reaction with the strong tridentate ligand, Byim (N, N, N donor) (MeOH solution) (1 : 1 ratio) generated the red oxidoperoxidovanadium(V), $[VO(O_2)(Byim)(MeOH)]^+$ cation that was isolated as perchlorate salt (**2**). Complexes **1** and **2** (Scheme 1) are soluble in highly polar solvents such as DMF, DMSO and THF and slightly soluble in MeOH, CH_3CN. Complex **1** behaves as a non-electrolyte whereas complex **2** is a 1 : 1 electrolyte (Ω = 109 ohm^{-1} cm^2 mol^{-1} in DMF). Complex **2** is diamagnetic whereas complex **1** has a magnetic moment of 1.74 B.M. at 298 K.

The IR spectra of the oxidovanadium complexes usually show sharp bands in the 942–970 cm^{-1} region due to the ν(V=O) mode; in the present case, the ν(V=O) vibration[15] in complexes **1** and **2** appear at 960 and 955 cm^{-1} respectively.



Scheme 1 Preparation of complexes **1** and **2**.

The characteristic bands of the benzimidazole pyridine group of the ligand appearing at 1585 cm^{-1} and 1261 cm^{-1} are assigned to νC=N and νC–N vibrations respectively.[16]

The bands at 1585 cm^{-1} (νC=N) and 1261 cm^{-1} (νC–N) are shifted to lower wavenumbers at 1575 and 1242 cm^{-1} in complex **1**, whereas in complex **2**, they are shifted to 1569, 1247 cm^{-1} respectively which suggested the coordination of the benzimidazole nitrogen atoms to the metal centre. In complex **1**, there are two sharp bands at 832 and 960 cm^{-1} due to *cis*-[VO_2] structure, which conform with the literature values.[17]

The peroxido complex **2**, shows three IR active vibrational modes associated with the [$V(O_2)$] moiety at 568, 734 and 939 cm^{-1}, which are assigned to the symmetric $V(O_2)$ stretch, the antisymmetric $V(O_2)$ stretch and the O–O intra-stretching mode, respectively.[18]

The presence of these bands confirms the η^2-coordination of the peroxido group. The elemental analysis as well as mass spectral results also support the formulation of the complexes (*vide* synthesis of the complexes).

Crystal structure of complexes 1 and 2

Single crystal X-ray diffraction analysis (Table 1) reveals that complexes **1** and **2** crystallize in the triclinic $P\bar{1}$ space group. ORTEP views of asymmetric units of complexes **1** and **2** are shown in Fig. 2 and 3 respectively. The phase purity of the complexes was confirmed by comparing the powder X-ray diffraction (PXRD) patterns (Fig. 4 and 5) of the powdery sample with those generated by simulation based on the single-crystal structures. It is found that the bulk powder samples give patterns all of which do not match exactly with those obtained theoretically from the single crystal structure ascribing to the fact that the crystals were grown immersed in solvents which have entered the crystal lattice and thus changed the cell dimensions, leading to such minor difference. The crystal structure of complex **1** consists of a discrete monomeric unit, [$V(O)_2$(Byim)] and a DMF solvent molecule while complex **2** consists of the discrete monomeric cationic unit, $[VO(O_2)(Byim)(MeOH)]^+$ together with a discrete disordered perchlorate ion and a methanol solvent molecule. In both complexes the vanadium atom is coordinated by one neutral tridentate ligand, Byim (N, N, N donors) in the *mer* configuration. The N_3O_2

Table 1 X-ray diffraction analysis data of complexes **1** and **2**

Parameters	Complex **1**	Complex **2**
Empirical formula	$C_{22}H_{20}N_6O_3V$	$C_{21}H_{21}ClN_5O_9V$
M	467.38	573.82
T/K	298	298
λ/Å	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Unit cell dimensions		
a/Å	9.3945(2)	7.1370(4)
b/Å	9.7730(3)	12.7274(7)
c/Å	11.4652(3)	14.9056(9)
α/°	95.855(2)	68.085(4)
β/°	92.247(2)	79.864(4)
γ/°	98.309(2)	88.108(4)
V/Å^3	1034.61(5)	1235.72(13)
Z, D/g cm^{-3}	2, 1.500	2, 1.542
F(000)	482	588
Crystal size/mm	0.07 × 0.09 × 0.18	0.06 × 0.08 × 0.16
θ range for data collection (°)	1.79, 27.53	1.50, 27.49
Reflection	17 396	20 358
Independent reflections (R_{int})	4730, 0.033	5597 (0.050)
Completeness to $\theta = \theta_{max}$ (%)	99.1	99.4
Refinement method	Full-matrix-least-squares on F^2	
Data/restraints/parameters	4730/0/295	4333/0/367
Goodness-of-fit on F^2	1.033	1.033
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0455	R_1 = 0.0536
	wR_2 = 0.1054	wR_2 = 0.1556
R indices (all data)	R_1 = 0.0677	R_1 = 0.0753
	wR_2 = 0.1154	wR_2 = 0.1419
Largest diff. peak, hole/Å^3	−0.58, 0.27	−0.46, 0.66

coordination sphere around the vanadium atom in complex **1** is defined by the Byim ligand and by two cisoid oxido-groups. The V═O distances of 1.609(2) and 1.610(2) Å are typical of non-hydrogen bonded V═O groups. Other bond lengths, *e.g.* (V1–N1), (V1–N2) and (V1–N3) at 2.175(2), 2.075(2), 2.032(2) Å are in accord with reported values for comparable complexes.[19] The ligand forms two five membered rings with bite angles of 72.71(7)° (N1–V1–N2) and 73.42(7)° (N2–V1–N3). The geometry of the coordination sphere can be assessed from the τ value of 0.195 which indicates that it is closer to square pyramidal than the trigonal biprismatic-ideal geometry, O1 as the axial atom.

The three ring nitrogens of the neutral tridentate Byim ligand occupy the tetragonal plane together with the terminal oxygen O2. The vanadium atom is displaced from the tetragonal plane toward the apex by 0.071(2) Å. The V–N1 bond length is comparatively long as a consequence of the trans effect[20] caused by the equatorial oxido group. The oxido-peroxidovanadium complex (complex **2**) contains a mononuclear cation, with the metal bonded to one tridentate neutral ligand Byim, one peroxido group, one oxido atom and one coordinated methanol molecule. The coordination environment around vanadium can be described

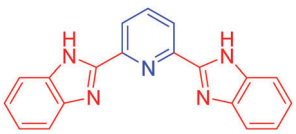


Fig. 1 Structure of the ligand.

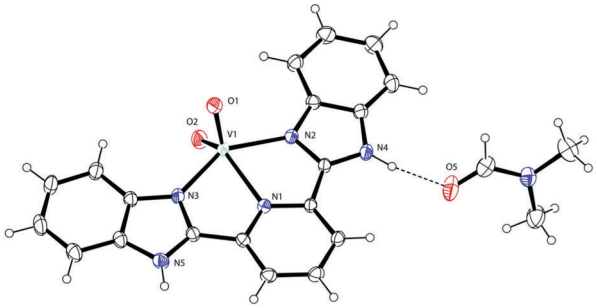


Fig. 2 The structure of **1** with ellipsoids at 30% probability. Hydrogen bonds shown as dotted lines as dotted lines.

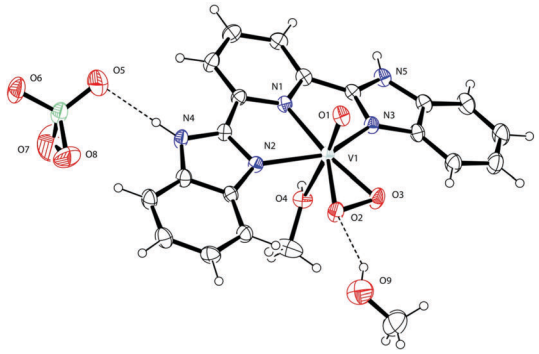


Fig. 3 The structure of **2** with ellipsoids at 30% probability. Hydrogen bonds shown as dotted lines. The perchlorate anion is disordered – only one orientation is shown.

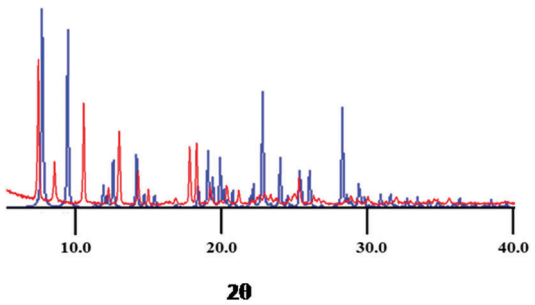


Fig. 4 Comparison of powder X-ray diffraction pattern and the simulated PXRD pattern obtained from single crystal X-ray diffraction of complex **1**.

as distorted seven co-ordinate pentagonal-bipyramid. The axial positions of the coordination polyhedron are occupied by the oxido group O1 and the oxygen atom O4 of the coordinated methanol molecule. The structural parameters are consistent with other vanadium(v) oxido-peroxido complexes which generally feature the vanadium atom coordinated to an oxido atom in an axial position and the peroxide bound in the equatorial positions.[21] The five atoms in the equatorial plane show an r.m.s deviation of 0.007 Å with the V atom 0.251(2) Å from the plane in the direction of the terminal oxygen O1. The length of the oxido V–O1 double bond is 1.602(3) Å which is consistent with values found in typical oxidovanadium(v) complexes.[22] The trans effect can be observed in the elongation of the apical coordinated methanol (V–O4) bond [2.262(3) Å], compared with the equatorial

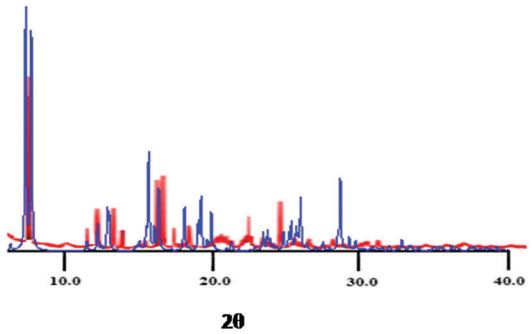


Fig. 5 Comparison of powder X-ray diffraction pattern and the simulated PXRD pattern obtained from single crystal X-ray diffraction of complex **2**.

V–N3 distance [2.129(3) Å]. Again, the V–N1 bond distance [2.146(3) Å], is longer than the V–N2 bond distance [2.132(3) Å] due to the trans oxygen atoms of the η^2-peroxido ligand. The equatorial V–O (peroxido) bonds have comparable lengths (1.855(3) and 1.862(3) Å), with an O–O bond distance of 1.420(4) Å while the O2–V1–O3 angle is 44.94(11)°, and the O1–V1–O3–O2 torsion angle is 96.4(2)°. The tridentate neutral Byim ligand binds the metal forming two five-membered chelate rings at the vanadium centre with the corresponding bite angles of 73.72(11)° (N1–V–N2) and 73.29(11)° (N1–V–N3). The relevant bond lengths and bond angles are presented in Table 2.

A comparison of the dimensions in the coordination spheres shows some interesting variations in the V–N bond lengths, thus while V1–N1 is longer in **1** by 0.030 Å, V1–N2 and V1–N3 are longer in **2** by 0.061, 0.099 Å. There are clearly conflicting influences here. The increase in coordination number going from 5 in **1** to 7 in **2** would tend to increase all bond lengths while the inclusion of the peroxido group in **2** is likely to have an electronic effect. Indeed it has previously been reported[13] that in such complexes the presence of the peroxide decreases the bond lengths of other ligands and this may account for the decrease in V1–N1 in **2** compared to **1**.

Table 2 Selected bond lengths (Å) and bond angles (°) of complexes **1** and **2**

Bond lengths (Å)					
Complex **1**					
V1–O1	1.609(2)	V1–O2	1.610(2)	V1–N1	2.175(2)
V1–N2	2.074(2)	V1–N3	2.032(2)	O5–C21	1.217(5)
Complex **2**					
V1–O1	1.605(3)	V1–O2	1.854(3)	V1–O3	1.865(3)
V1–O4	2.262(3)	V1–N1	2.145(3)	V1–N2	2.135(3)
V1–N3	2.131(3)	O2–O3	1.420(4)	O4–C20	1.434(7)

Bond angles			
Complex **1**			
O1–V1–O2	109.05(9)	O1–V1–N3	101.00(8)
O2–V1–N3	100.64(8)	O1–V1–N2	98.97(8)
O2–V1–N2	98.79(8)	N3–V1–N2	145.69(7)
O1–V1–N1	116.94(8)	O2–V1–N1	133.95(8)
N3–V1–N1	73.42(7)	N2–V1–N1	72.71(7)
Complex **2**			
O1–V1–O2	102.67(14)	O1–V1–O3	101.61(14)
O2–V1–O3	44.94(11)	O1–V1–N3	94.73(12)
O2–V1–N3	127.22(12)	O3–V1–N3	83.02(12)
O1–V1–N2	95.96(12)	O2–V1–N2	81.79(11)
O3–V1–N2	126.23(12)	N3–V1–N2	145.61(12)
O1–V1–N1	92.19(12)	O2–V1–N1	152.55(12)
O3–V1–N1	153.49(12)	N3–V1–N1	73.29(11)
N2–V1–N1	73.72(11)	O1–V1–O4	170.91(12)
O2–V1–O4	86.25(12)	O3–V1–O4	85.91(12)
N3–V1–O4	81.01(11)	N2–V1–O4	83.44(11)
N1–V1–O4	78.92(10)		

Both structures show hydrogen bonds involving the complexes and the solvent molecules. Thus in **1** there is a strong hydrogen bond between N4–H and solvent DMF oxygen atom O5 $(1-x, -y, -z)$ with dimensions N···O 2.717, H···O 1.95 Å, N–H···O 147°. In both N4 and N5 from donor hydrogen bonds, N4 to O5 with dimensions 3.057, 2.22 Å, 164° and N5 to O1 $(1+x, y, z)$ with dimensions 3.085, 2.29, 154°. The solvent methanol is involved in two hydrogen bonds; as a donor to a peroxide oxygen O2 $(1+x, -1+y, z)$ with dimensions 2.888, 2.14 Å, 151° and as an acceptor from O4 $(-1+x, y, z)$ with dimensions 2.678, 2.04 Å, 124°.

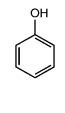
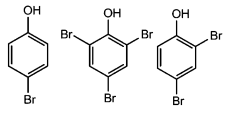
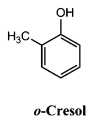
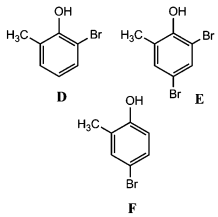
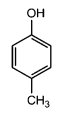
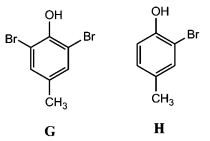
Peroxidative bromination of phenols by complexes 1 and 2

Among the vanadium haloperoxidases, vanadium bromoperoxidase contains 1 mol of vanadium(v) per mol of subunit.[23] The halide assisted oxidative bromination of organic substrates catalysed by vanadium complexes under physiological conditions has been considered as model reactions for VHPOs.[24] It has been proposed[25] that VHPO, in the active state, contains peroxido moiety, but it is not clear whether an in-built peroxido group or an *in situ* generated peroxido group is responsible for the activation of halides. In order to understand the active unit around the vanadium in VHPO, we have designed and synthesized one oxidovanadium and other peroxidovanadium complexes with the same ligand and employed them in catalysing the oxidation of bromides to form different aromatic bromo compounds. Phenol, *o*-cresol and *p*-cresol were used as substrates for this purpose. To obtain optimum results,[26] the pH of the reaction medium was kept ~3. Control experiments of the bromination reactions performed by maintaining all other additives and parameters fixed without the catalyst, show that the yield of the brominated products are negligibly small after a long period of reaction, while in the presence of the catalyst, the percentage yields of the brominated products are appreciably high (Table 3).

The yields of the brominated products from *p*-cresol, *o*-cresol and phenol substrates with catalyst **1** are 19%, 35% and 15% respectively whereas for catalyst **2** the corresponding percentage yields are 79%, 66% and 58% respectively. The results suggest that, for catalyst **2** the highest percentage of brominated products is found for *p*-cresol, while for catalyst **1**, the maximum is obtained for *o*-cresol. During the course of catalytic bromination reactions, although other possible brominated products are obtained depending upon the substrates, the dibrominated products are the major ones for phenol and *p*-cresol while in the case of *o*-cresol, the mono brominated one is the major product (for catalyst **2**).

It can be argued that as catalyst **2** containing bound peroxido group from the beginning, proposed to be an obligatory state

Table 3 Details of catalytic bromination of aromatic alcohols using complex **1** and **2** as catalyst[a,b] in presence of H_2O_2 as terminal oxidant and KBr in acidic medium at room temperature

Entry	Substrate	Brominated products	% yield of brominated products: Catalyst **1**	Catalyst **2**
1	 Phenol	 A B C	15	58 A (5) B (2) C (51)
2	 *o*-Cresol	 D E F	35	66 D (2) E (3) F (61)
3	 *p*-Cresol	 G H	19	79 G (45) H (34)

[a] Blank experiments were performed *i.e.* without adding the catalyst only while other additives and parameters remaining the same. For entry 1 *ca.* 12%, entry 2 *ca.* 23%, and entry 3 *ca.* 15% conversions took place. [b] The mole ratio of catalyst/substrate = 1 : 100 (entries 1–3 using catalyst **1** and **2**).

during VHPO mediated haloperoxidation, acts as a better VHPO mimic than complex **1**. So, it is clear that catalyst **2** is more potent than catalyst **1** because of the in-built peroxido group.

The catalytic cycles for both **1** and **2** have been established (Fig. 6 and 7) by experimental findings, where reaction intermediates were collected at different time intervals and characterised by ESI-MS analysis (Fig. 6 and 7). During the catalytic process, catalyst **1** (MS *m*/*z*: 394 [M^+]) first accepts one proton (MS *m*/*z*: 395 [M^+]) intermediate II, which subsequently is converted to a bound peroxido intermediate IV in the presence of peroxide.

The bromonium ion is generated from bromide ion by peroxide mediated oxidation, and subsequent attack of a bromonium ion on one of the oxygen atoms of the peroxido group (intermediate IV) generates intermediate V (MS *m*/*z*: 513 [M^+ + 23]) (Fig. 6). The uptake of a proton from a surrounding water molecule leads to the liberation of hypobromous acid (HOBr) followed by the restoration of the native state (I).

During the catalytic process, catalyst **2** is converted to intermediate II (MS *m*/*z*: 542.5 [M^+]) (Fig. 7) which is subsequently attacked by a bromide ion at one of the oxygen atoms of the peroxido group forming an intermediate III (MS *m*/*z*: 622.4 [M^+]) (Fig. 7).

The intermediate III further reacts with one mole of hydrogen peroxide leading to the generation of hypobromous acid (HOBr) thereby forming an intermediate IV (MS *m*/*z*: 559.5 [M^+])

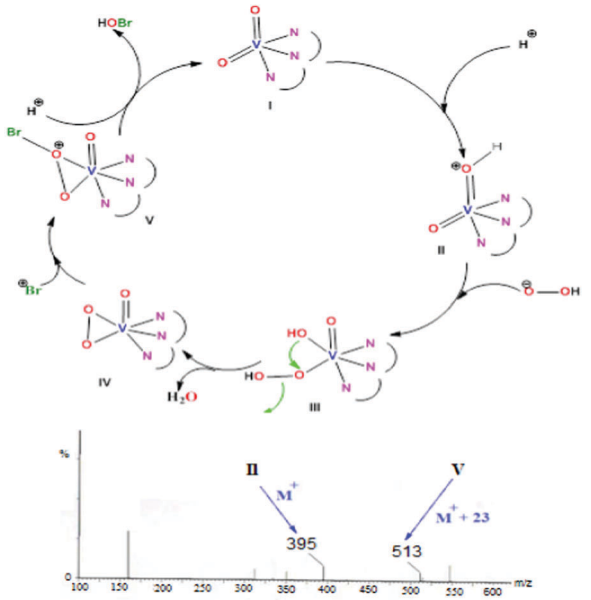


Fig. 6 Proposed catalytic cycle and corresponding mass spectra complex **1**.

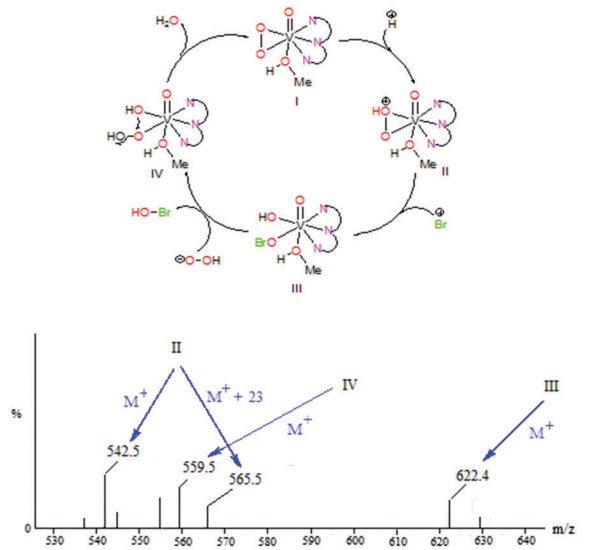


Fig. 7 Proposed catalytic cycle and corresponding mass spectra for complex **2**.

(Fig. 7) which thereafter regenerates catalyst **2** (I) by losing water molecule. Thus, the catalytic cycle is completed. The proposed cycles confirm the mechanism of catalytic activities of two newly synthesized vanadium complexes. These proposed cycles are consistent with other VHPO model systems.[27]

Conclusions

The design, synthesis and biomimicking activity of two vanadium complexes have been presented in this communication. Complexes **1** and **2** contain the VN_3O_2, VN_3O_4 coordination spheres respectively. The complexes were tested for bromoperoxidase activity.

It is found that both the complexes are capable of inducing the oxidative bromination of phenol, *o*-cresol and *p*-cresol, thereby mimicking the role of the vanadium based bromoperoxidase enzyme. So, the two dioxidovanadium(IV) and oxido-peroxido vanadium(V) complexes can catalyse the peroxidative bromination of organic substrates in general, and phenol and phenol derivatives in particular. The reactivity of the oxido-peroxidovanadium(V) complex (**2**) is greater than that of the dioxidovanadium(IV) complex (**1**) analogue which is likely to be due to the presence of the oxidoperoxido moiety in complex **2** which has a structure similar to that found for the active site of VHPO enzyme. Hence, the present work suggests that the in-built peroxido group in the VHPO model complex facilitates the oxidation of bromide ion while mimicking the VHPO activity.

Experimental

Materials

Ammonium metavanadate ($NH_4VO_3{\cdot}2H_2O$), pyridine 2,6-dicaroxylic acid and orthophenylenediamine were obtained from S.D. Fine-Chem. Ltd (India). Extra pure variety of *ortho*-phosphoric acid. Potassium hydroxide pellets and methanol (G.R.) were the products of E. Merck (India) and were used directly. All other reagents used were of analytical grade. The analytical grade solvents used for physico-chemical studies were further purified before use wherever necessary, by literature methods.[28]

Physical measurements for the characterization of the complexes

UV-vis spectra were recorded on a Schimadzu U-1700 spectrophotometer; IR spectra (KBr disk) were recorded on Perkin-Elmer IR spectrophotometer. Electrical conductivities of 10^{-3} M dm^{-3} DMF solution of the complexes were measured with a Systronics 304 digital conductivity meter. Magnetic susceptibility measurements were made with a vibrating sample magnetometer PAR 155 model. Microanalytical (C, H, N) data were collected on a Perkin-Elmer 2400C elemental analyzer. All pH measurements were made with an Elico (India) digital pH meter. The mass spectral analyses were done using mass spectrometer (model: XEVO-G2QTOF#YCA351).

Syntheses of the ligand and metal complexes

2,6-Di-(1*H*-benzo[*d*]imidazol-2-yl)pyridine (Byim). To a mixture of orthophenylenediammine (2.17 g, 2 equiv., 20.0 mmol) and pyridine-2,6-dicarboxylic acid (1.67 g, 1 equiv., 10.0 mmol) about 95 mL of orthophosphoric acid was added and the mixture was refluxed at about 240 °C for 6–7 hours. Once the reaction was complete, the mixture was allowed to cool and then the mixture was added dropwise to the crushed ice. A light blue suspension appeared which was filtered and washed several times with $NaHCO_3$ solution. The product was air dried and then recrystallized from ethanol as white solid, the structure of the ligand is presented in Fig. 1; yield 65%. ^{1}H NMR (300 MHz, [D_6]DMSO) δ (ppm) 13.00 (s, 2H, N–H), 8.31–8.38 (d, 2H, Py–H), 8.19–8.21 (t, 1H), 7.78–7.82 (m, 4H, Ph–H), 7.32–7.36 (m, 4H, Ph–H). IR (KBr, pellet, cm^{-1}): 3089s (νN–H), 1735m (νC–C), 1585 (νC═N), 1261s (νC–N), 1225m, 852m, 764vs (dPh(C–H)). UV-vis (MeOH): λ = 305, 325 nm.

[$V(O)_2$(Byim)]·DMF (complex 1)

Ammonium metavanadate (0.06 g, 1 equiv., 0.50 mmol) was dissolved in hot water. The ligand H_2Byim (0.31 g, 1.00 mmol) was dissolved in hot MeOH and was added to above metal salt solution at room temperature. The colour of the resulting solution changed to yellow after 15 min of stirring at room temperature, but the yellow precipitate started appearing after further 1 h of stirring, which was continued for about 3 hours for complete precipitation. The yellow solid was filtered off, washed with MeOH and collected; yield 70%. The DMF solution of this dioxidovanadium complex was kept in freeze from which yellow crystals of the desired compound appeared after seven days. Anal. calcd for $C_{19}H_{13}N_5O_2V$: C, 57.72; H, 3.27; N, 17.67; V, 12.93; found C, 58.67; H, 3.35; N, 18.92; V, 12.97; IR (KBr, pellet, cm^{-1}): 3067s (νN–H), 1715m (νC–C), 1575 (νC═N), 1242s (νC–N), 1205m, 1008(m), 960(s) 832m [V═O], 744vs (dPh(C–H)). UV-vis (DMF): λ = 222, 321, 368 and 448 nm. ES mass (*m*/*z*): 394.38.

[$VO(O_2)$(Byim)(MeOH)] ClO_4 (complex 2)

Ammonium metavanadate (0.06 g, 1 equiv., 0.50 mmol) was dissolved in 1.0 mL of hydrogen peroxide at 8–10 °C in a beaker, and the pH of the resulting solution was made 3 by adding dilute HNO_3. In a separate beaker, the ligand (0.15 g, 1 equiv., 0.50 mmol) was dissolved in hot methanol and the solution was cooled to about 8–10 °C. Thereafter, to the methanolic solution of the ligand, ammonium metavanadate solution in hydrogen peroxide was added drop wise with constant stirring. After the addition was completed, 3 mL of $HClO_4$ was added and the resulting orange-red mixture was stirred for about 5–6 hours, then a little amount of isopropanol was added as precipitant and the resulting solution was again stirred for about half an hour and the precipitate was filtered. The filtrate was kept in freeze. Orange red crystals of the desired peroxidocomplex appeared in three days; yield 30%. Anal. calcd for $C_{20}H_{17}ClN_5O_8V$: C, 44.42; H, 2.98; N, 12.95; V, 9.42; found. C, 45.37; H, 3.02; N, 12.98; V, 9.67; IR (KBr, pellet, cm^{-1}): 3089s (νN–H), 1730m (νC–C), 1569 (νC═N), 1247s (νC–N), 1215m, 1002(m), 955(s) [V═O], 939(s) [O–O], 842m, 734vs, 568m, 514 (dPh(C–H)). UV-vis (DMF): λ = 220, 247, 318, 372 and 465 nm. ES mass (*m*/*z*): 541.3.

Safety note! Perchloric acid and perchlorate salts with organic ligands are potentially explosive and must be handled with care.

X-ray crystal structure analysis for complexes 1 and 2

X-ray diffraction data for the crystals of the complexes **1** and **2** were collected at 298 K on a Bruker AXS SMART APEX II diffractometer equipped with a CCD detector[29] with a fine focus of 1.75 kW sealed tube using Mo Kα radiation (λ = 0.71073 Å). Crystallographic data and details of the structure determinations are summarized in Table 1. The data were processed using

SAINT and absorption corrections were made using SADABS.[30] The structures were solved by direct methods and refined by full-matrix-least-squares on F^2 using the SHELX program[31] within the WINGX software. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were placed with fixed thermal parameters at idealized positions. The perchlorate anion in 2 was disordered. Perspective views of the molecules are given in Fig. 2 and 3.

Experimental set up for the catalytic bromination of aromatic alcohols

A mixture of complex **1** (the catalyst) (3.63 mg, *i.e.* 9.23×10^{-3} mmol), and a representative substrate, namely phenol (90.0 mg, *i.e.* 0.92 mmol; for other cases *vide* Table 3), was dissolved in a 5.000 mL CH_3CN solvent and the solution was taken in a 100 mL stoppered conical flask. To the above solution, 1.0 mL aqueous solution of KBr (0.22 g, 1.84 mmol) and 1.0 mL (9.80 mmol) of 30% H_2O_2 were added under stirring conditions. The pH of the resulting solution was adjusted to 3 by adding 2 N hydrochloric acid. The resulting yellow solution was stirred continuously at room temperature for 20 h for the completion of the reaction. Thereafter, the products were quantitatively extracted with diethyl ether (2.0 mL) so that practically the entire reaction product was transferred to the ether layer. Then the ether extract was concentrated to $\sim$1.0 mL by slow evaporation and from the extract, 1.0 μL of the solution was taken in a gas syringe and injected through a GC port. The products were characterized by gas chromatography (Agilent 6890N GC System). The same method was followed in case of complex **2** (the catalyst) except that complex **2** was used instead of complex **1**.

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