A new single pot synthesis of μ-bis(oxido)bis{oxidovanadium(V)} dipicolinato complex with 2-aminopyridinium as counter cation: Spectroscopic, structural, catalytic and theoretical studies

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ABSTRACT

A new dinuclear, μ-bis(oxido)bis{oxidovanadium(V)} dipicolinato complex, [apyH]$_2$[{VOL}$_2$(μ-O)$_2$].2H$_2$O [1], [L = 2,6-dipicolinate; apyH = 2-aminopyridinium] has been synthesized by two different preparative methods using a single pot synthesis involving [VO(acac)$_2$] or VOSO$_4$.3H$_2$O, and 2,6-dicarboxamido-2-pyridylpyridine (H$_2$dcapp). The ligand H$_2$dcapp undergoes vanadium-induced amide hydrolysis to yield the complex **1**. The complex has been characterized by elemental analysis, electronic absorption, IR, ^{1}H NMR, and finally by X-ray crystallography. The electronic absorption bands of **1** have been assigned with the help of TD-DFT calculations. The complex **1** forms a two-dimensional grid along [001] plane, which on combination with one-dimensional polymeric chains along the [100] direction, forms three-dimensional supramolecular framework. Complex **1** exhibited efficient catalytic activity toward selective epoxidation of *cis*-cyclooctene by using *tert*-butylhydroperoxide as an oxidant.

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1. Introduction

Last decades have witnessed a substantial growth in the chemistry of vanadium complexes because of their diverse applications in areas such as catalysis, material science, biological and pharmacological applications as antitumor and antimicrobials and as insulin-mimics [1]. The avid interest in both inorganic and organic vanadium compounds stems from fact that these have been shown to lower plasma glucose and lipid levels, increase peripheral glucose uptake, enhance or mimic the action of insulin, and normalize liver enzyme activities in a variety of animal models of both type I and II diabetes [2]. Therefore, several vanadium compounds have been tested in vitro and in vivo, appear as very promising insulin mimetic active oral drugs [3,4]. The evidence of the biological role of vanadium in vanadate-dependent haloperoxidases and vanadium-nitrogenases is also well documented [5,6].

The use of pyridine carboxamide as a ligand serves as an important construction unit for the coordination chemists [7]. This ligand can be easily prepared by the condensation reaction between pyridyl bearing amines and carboxylic acid precursors promoted by coupling agents [8]. Also, the metal-induced carboxamido bond hydrolysis has been carried out in the presence of various metal ions such as Cu(II) [9], Zn(II) [10], Ni(II) [10], Co(III) [11], Cd(II) [12], La(III) [13], Ce(III) [13], Ce(IV) [14], Pd(II) [15] and Pb (II) [16] ions. However, to the best of our knowledge, any work on V (IV) ion is yet to be reported.

A variety of mononuclear [17] and polynuclear oxido- [18] and dioxidovanadium(V) compounds and complex clusters have been reported [19]. Moreover, only one example of bisoxido-bridged dipicolinate vanadium(V) complex has been reported [20].

With these aspects in mind and in the quest for some interesting supramolecular architecture and catalytic activity we herein, report the synthesis, spectroscopic characterization, crystal structure and catalytic activity of dinuclear bis(μ-oxido)-bridged vanadium complex [apyH]$_2$[{VOL}$_2$(μ-O)$_2$].2H$_2$O [1]. Time dependent density functional theory (TD-DFT) calculations have been deployed to assign the observed electronic absorption spectrum of the complex.

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2. Results and discussion

2.1. Synthesis

The reaction of [VO(acac)$_2$] or VOSO$_4$.3H$_2$O with H$_2$dcapp in 1:1 stoichiometric ratio in a mixture of water and methanol (1:1v/v) with stirring at RT afforded neutral oxido-bridged dinuclear vanadium complex [apyH]$_2$[{VOL}$_2$(μ-O)$_2$].2H$_2$O (**1**) (L = 2,6-dipicolinate; apyH = 2-aminopyridinium) in good yield. Further, it was observed that, direct reaction of 2,6-dipicolinic acid under analogous reaction conditions with [VO(acac)$_2$] and VOSO$_4$.3H$_2$O in water and methanol mixture (1:1 v/v) gave only mononuclear vanadium(IV) complexes, [VO(κ^3-L)(H$_2$O)$_2$].2H$_2$O and [VO(κ^2-L)(H$_2$O)$_2$].1/2SO$_4$ (L = 2,6-dipicolinate), respectively. This observation is consistent with Xing et al. findings [21]. The crystal structure of **1** reveals that H$_2$dcapp hydrolyzed into 2,6-dipicolinate and 2-aminopyridinium (apyH) in mixed solutions (Scheme 1). The previous reports [16] reveal the fact that the metal cation can induce the cleavage of the carboxamido bond in H$_2$dcapp in the strong polar solvents. Hence, it can be concluded that in this case also the V(IV) ions can induce the same cleavage of the carboxamido bond in the presence of strong polar solvents.

2.2. Characterization

The complex **1** was isolated as air-stable, non-hygroscopic solid. Complex **1** is sparingly soluble in halogenated solvents such as dichloromethane, chloroform and highly soluble in dimethylformamide, dimethylsulphoxide but insoluble in petroleum ether and diethyl ether. Analytical data of **1** corroborated well to their respective formation.

Infrared spectrum of **1** in nujol show a broad and strong C=O stretching vibration at 1676 cm^{-1} due to the out-of-phase vibrations of the monomeric units in the dipicolinato dimer. A strong IR absorption is observed at 1334 cm^{-1} that corresponds to the ν(C−O) vibration [20,22]. Two characteristic frequencies at 3327 and 3159 cm^{-1}, corresponding to the asymmetric and symmetric stretching frequencies of NH$_2$ group of 2-aminopyridine, indicating that this group has not been protonated. Therefore, pyridine nitrogen of 2-aminopyridine has to be protonated. The two sharp IR absorptions at 940 and 873 cm^{-1} corresponding to Davydov split $\nu_{antisym}$(VO$_2$) and ν_{sym}(VO$_2$) vibration modes, respectively.

Solution ^{1}H spectrum of **1** was recorded in DMSO-d_6. The NMR spectrum showed two characteristic sets of resonances indicative of the presence of two different pyridine rings. The first, well-separated set, corresponding to 2-aminopyridinium has been located at δ 6.71 (m, 2H), 7.41 (m, 2H), 7.75 (m, 2H), and 7.88 (d, 2H) ppm while the second set, for dipicolinate resonates at δ 8.17 (d, 4H, J = 7.8 Hz) and 8.53 (t, 2H, J = 7.5 Hz) ppm. A comparison between the two ^{1}H spectra of H$_2$dcapp and 2,6-dipicolinic acid clearly indicates that the two peaks at 8.17 and 8.53 ppm are due to the OC-py-OC pyridine ring.

Electronic absorption spectrum of **1** in DMSO displayed three bands at 254, 272 and at 305 nm. The observed electronic absorption bands have been assigned with the help of time dependent density functional theory (TD-DFT). The first lower energy band observed experimentally at 305 nm while calculated at 303 nm with oscillator strength (f) 0.0162 is attributed to ligand to metal charge transfer (LMCT) from the coordinated oxygen atoms of the ligand to the d-orbital of the metal (Fig. 1). The next band observed at 272 nm and calculated at 270 nm with f = 0.0121 is also assigned to the LMCT charge transfer from the coordinated oxygen atoms to the metal center. While the band calculated at 250 nm with oscillator strength (f = 0.0534) can be assigned to the electron transition from HOMO→LUMO+5. Calculated excitation energies, wavelength, oscillator strength and major contribution are given in the Table 1.

2.3. Molecular structure determination

Molecular projection for **1** with atom-labels is shown in Fig. 2. Details about the data collection, solution and refinement are enlisted in Table 2 and selected bond lengths and bond angles and hydrogen bond parameters are presented in Tables 3 and 4, respectively. Complex **1** crystallizes in the triclinic crystal system with space group P-1. The vanadium core is in a +5 oxidation state and is coordinated, with three coordination sites occupied with the tridentate dipicolinate ligand in κ^3 manner via one oxygen of each carboxylic group (O3, O5) [V−O distances are 1.996(12) and 2.002(12) Å], one pyridyl nitrogen atom (N1) [V−N1 = 2.096 (14) Å], and two oxido-groups (O1, O2) [V(1)−O(1) 1.621(13); V (1)−O(2) 2.329(12)]. Complex **1** also contains only one of the 2-aminopyridinium as counter cations (apyH) and one water molecules per formula unit in the lattice. The molecular structure can be considered as two identical mononuclear {VO(μ-O)L}$^-$ moieties connected by μ-O atoms. The two {VO(μ-O)L}$^-$ moieties are centrosymmetric via a crystallographic inversion center at the midpoint of the V−V$^{\#1}$ vector. Each vanadium atom in the dinuclear complex exhibits distorted octahedral coordination environment with N1, O3, O5, and O2$^{\#1}$ atoms defining the equatorial plane, and O1, O2 atoms at the apical positions. The metal atom is displaced toward the axial oxido atom [O1] by 0.3420 Å from the equatorial plane. Depending on the orientation of V=O groups with respect to the plane through two vanadium centers and two bridging oxido-groups, the {V$_2$O$_4$}$^{2+}$ core can have five different configurations (syn- and anti-orthogonal, syn- and anti-coplanar, twist) in complexes constructed from two cis-VO$_2^+$ units [23]. Complex **1** may be classified as anti-orthogonal with the two V-(μ-O) distances in the {V$_2$O$_4$} unit markedly asymmetric [V1−O2$^{\#1}$ 1.667(12) Å, V1−O2 2.329(12) Å]. The coordination polyhedra can be best described as two edge-shared vanadium octahedra that are significantly distorted. This distortion arises mainly from the large variation of V−O bond distances and an O1−V1−O2 angle of 177.24(5)°. The terminal V1−O1(oxido) [1.621(13) Å], V1−O2(μ-bridging) [1.667(12) Å], V1−O3(carboxylic) [1.996(12) Å] and V1−O5(carboxylic) [2.002(12) Å] bond distances agree well with the corresponding values reported for related systems [23]. The
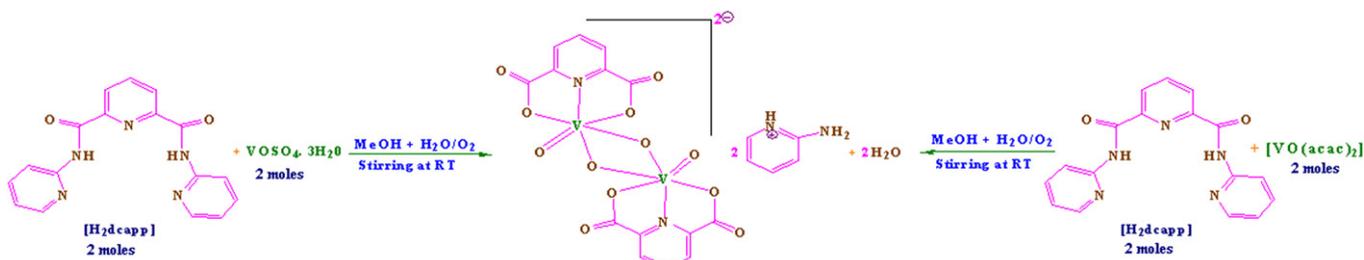
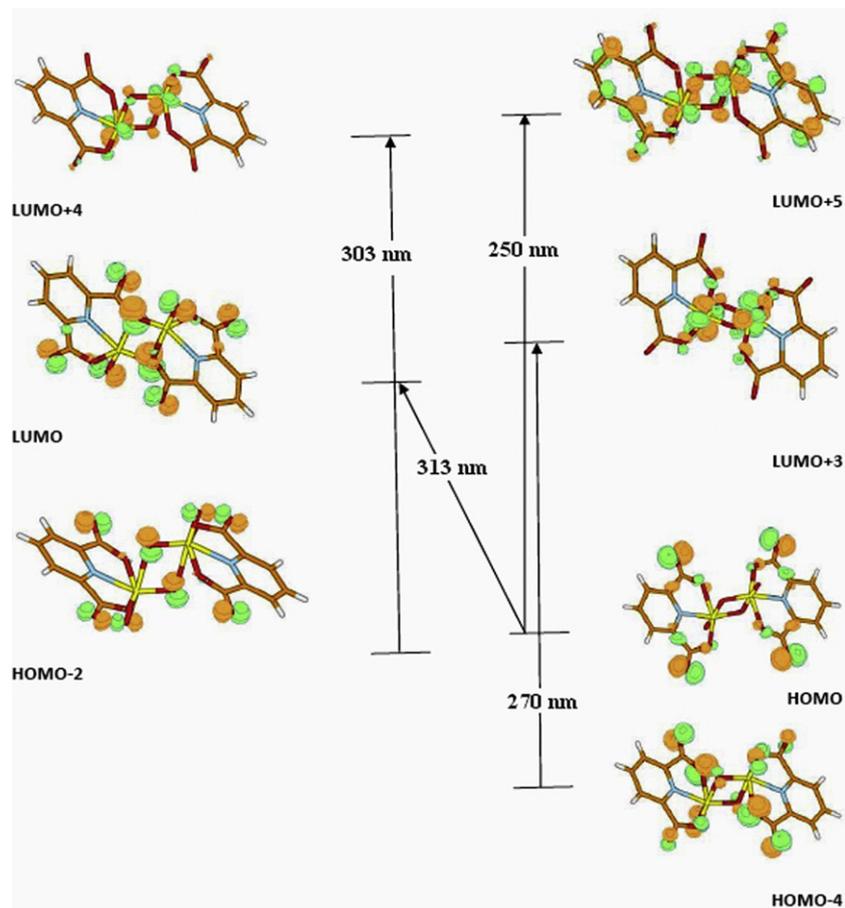**Scheme 1.** Graphical representation for synthesis of **1**.

Fig. 1. Selected orbital transitions for the complex **1** (orbital contour value 0.07).

bonding arrangement around vanadium(V) agrees well with other dinuclear dioxidovanadium(V) complexes of tridentate ligands reported in the literature [19,20,24]. The trans influence of the oxido [O1] group in one apical position of the vanadium octahedron manifests itself by elongation of the bond distance for the apically bonded bridging oxygen atom [V1−O2$^{\#}$ = 2.329(12) Å] when compared to the distance for the other oxygen atom [V1−O2 = 1.667(12) Å]. To rationalize the changes in the bonding structure of {VO(μ-O)L}$^{-}$ upon dimerization, we can compare with those other reported bis(μ-oxido)-bridged vanadium(V) complexes [19] in which V=O bond distances are comparable within experimental error [1.610(6) and 1.615(6) Å], while in our case the V−O2 bond involving the bridging oxygen atom is 0.044 (12) Å longer than the terminal V−O1 distance. This slight bonding asymmetry within the dioxidovanadium(V) ion is because of the formation of the weak intermolecular V−O bond bridging the halves of the dinuclear complex. As expected, significant bond

localization is also observed in the carboxylic groups of the dipicolinate ligand. In fact, the terminal C−O bond lengths are approximately 0.07 Å shorter than the C−O distances involving the coordinated-to-vanadium oxygen atoms. The intramolecular V−V separation in the complex is 3.145 Å and falls within the range of known V−V distances in doubly bridged vanadium polynuclear systems [23c,25].

Crystal packing in **1** is stabilized by intra- and intermolecular C−H−O hydrogen bond interactions. An interesting feature of the crystal packing in **1** is the infinite 1D chains (Fig. 3) resulting from C−H−O interactions between adjacent dimer molecules running parallel to the [100] direction. These distances for C−H−O interactions are 1.956−2.615 Å and are within the range reported by other workers [26]. The successive dimeric units between adjacent one-dimensional chains along the [100] direction are separated by 8.141(1)−8.208(3) Å. The C(3)−H(3)−O(3), C(2)−H(2)−O(2) and C (4)−H(4)−O(1) hydrogen bonds [C(3)−H(3)−O(3) (1 + x, y, z) 2.615 (2) Å, C(3)−H(3)−O(3) 150.98(11) Å, C(2)−H(2)−O(2)(1−x, 1−y, −z) 2.291(2) Å, C(2)−H(2)−O(2) 137.78(11) Å, C(4)−H(4)−O(1)(1−x, 1−y, 1−z) 2.632(12) Å, C(4)−H(4)−O(1) 115.91(5)] connect the dimeric molecules related by the c-glide and translation into a 2D grid in the (001) plane (Fig. 4). The combination of the 2D grid in the (001) plane and a 1D chain along the [100] direction results in a 3D supramolecular architecture. Interestingly, only a few dinuclear vanadium complexes with a multidimensional framework have been structurally characterized using single-crystal X-ray analysis, where a 2D or 3D molecular assembly is established via hydrogen bonds involving either the solvent atoms or the cation [18d,19a,20,23c].

Table 1
Selected excitation energies (eV), wavelength (nm), oscillator strengths (*f*) and transition type for **1**.

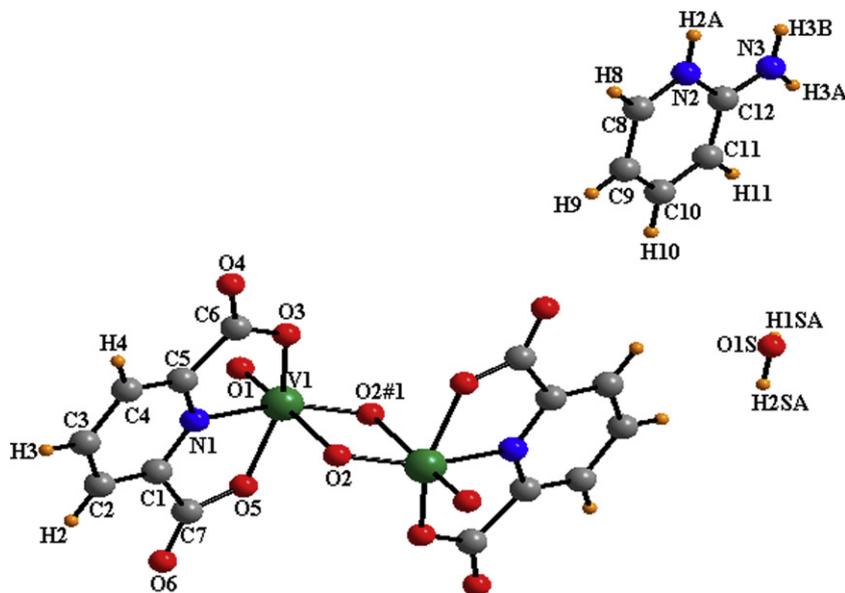| Excitation Energy (eV)	Wavelength (nm)	Oscillator Strength (*f*)	Major Contribution
3.9575	313	0.0022	n→π^{*}
4.0907	303	0.0162	n→ M
4.1026	302	0.0373	n→M
4.1868	270	0.0121	n→M
4.9695	250	0.0534	n→π^{*}

Fig. 2. Projection view of **1** with only one of the counter cations and water molecules per formula unit (ellipsoids with 50% probability).

2.4. Catalytic application of complex

To evaluate the selectivity and efficiency of the complex **1** as catalyst toward epoxidation of alkene, *cis*-cyclooctene was used as a model substrate. This complex was found to catalyze the epoxidation of *cis*-cyclooctene with *tert*-BuOOH as the oxidizing agent in heterogeneous condition and converted 95% of cyclooctene to cyclooctene oxide with 100% selectivity and 313 turnover number. The higher product yield of cyclooctene oxide may be due to the synergic effect of vanadium and lattice. Many vanadium schiff base catalysts have been reported for alkene epoxidation. Studies on relative comparison of this catalytic system with previously reported systems show that conversion and selectivity are higher than other systems [27] but similar to system reported by Rayati et al. [19f].

3. Conclusion

In conclusion, in this work we have presented new one-pot synthesis of dinuclear, μ-bis(oxido)bis{oxidovanadium(V)} dipicolinato complex [apyH]$_2$[{VOL}$_2$(μ-O)$_2$].2H$_2$O [**1**] by two preparative methods through vanadium-induced hydrolysis of H$_2$dcapp ligand. The crystal structure of the dimeric complex reveals two edge-sharing vanadium octahedra with N$_2$O$_4$ chromophores. The C−H−O interactions link the molecules into infinite polymeric chains along the [100] direction. The molecular assemblies generated by C−H−O hydrogen bonds exhibit 3D supramolecular architecture. Furthermore, it has been shown that complex **1** effectively catalyze the epoxidation of *cis*-cyclooctene to cyclooctene oxide with 100% selectivity.

Table 2
Crystallographic data for **1** at 100(2) K.

	1
Empirical formula	C$_{24}$H$_{24}$N$_6$O$_{14}$V$_2$
Formula weight	722.37
Color and habit	Yellow, irregular
Crystal size/mm	0.25 × 0.23 × 0.22 mm
Crystal system, space group	Triclinic, *P*−1
a/Å	8.1409(6)
b/Å	8.9534(6)
c/Å	10.4459(8)
β/°	84.978(3)
γ/°	68.298(2)
V/Å^3	704.65(9)
Z, *D$_c$*/mg m^{-3}	1, 1.702
μ/mm^{-1}	0.747
T/K	100(2)
λ(Mo-K*α*)/Å	0.71073
No. of reflections/Unique	11 612/4254
No. of refined parameter	181
R factor [*I* > 2*σ*(*I*)]	0.0375
*wR*2 [*I* > 2*σ*(*I*)]	0.1620
R factor (all data)	0.0400
*wR*2 (all data)	0.1645
GoF	1.429

Table 3
Selected bond lengths [Å] and bond angles [°] for **1** at 100(2) K.

	1
V(1)−O(1)	1.621(13)
V(1)−O(2)#1	1.667(12)
V(1)−O(3)	1.996(12)
V(1)−O(5)	2.002(12)
V(1)−N(1)	2.096(14)
V(1)−O(2)	2.329(12)
O(2)−V(1)#1	1.667(12)
O(3)−C(6)	1.301(13)
O(4)−C(6)	1.224(14)
O(5)−C(7)	1.313(14)
O(6)−C(7)	1.213(14)
O(1)−V(1)−O(2)#1	105.25(6)
O(1)−V(1)−O(5)	96.41(6)
O(2)#1−V(1)−O(5)	97.17(5)
O(1)−V(1)−O(3)	96.91(6)
O(3)−V(1)−O(5)	149.07(5)
O(1)−V(1)−N(1)	102.93(6)
O(2)#1−V(1)−N(1)	151.36(6)
O(5)−V(1)−N(1)	74.59(5)
O(3)−V(1)−N(1)	75.28(5)
N(1)−V(1)−O(2)	74.33(5)
O(2)#1−V(1)−O(2)	77.44(5)
O(3)−V(1)−O(2)	82.84(5)
O(5)−V(1)−O(2)	82.54(5)
O(1)−V(1)−O(2)	177.24(5)

Table 4
Hydrogen bond parameters for **1** at 100(2) K.

D–H–A–X	d H–A Å	D D–A Å	θ D-H–A°
Complex **1**			
O(1S)–H(1SA)–O(1)[a]	1.96	2.810(17)	173
O(1S)–H(2SA)–O(4)[b]	1.96	2.796(17)	163
N(3)–H(3A)–O(6)[c]	2.16	3.023(17)	167
N(3)–H(3B)–O(1S)[d]	2.01	2.843(12)	158
C(2)–H(2)–O(2)[e]	2.29	3.065(2)	138
C(4)–H(4)–O(1)[f]	2.55	3.088(15)	116
C(8)–H(8)–O(4)[g]	2.42	3.359(15)	169
C(11)–H(11)–O(5)[h]	1.85	2.791(15)	169

[a] Symmetry equivalent: 2 − x,1 − y,−z.
[b] Symmetry equivalent: x,−1 + y,z.
[c] Symmetry equivalent: −1 + x,y,1 + z.
[d] Symmetry equivalent: −1 + x,y,z.
[e] Symmetry equivalent: 1 − x,1 − y,−z.
[f] Symmetry equivalent: 1 − x,2 − y,−z.
[g] Symmetry equivalent: x,−1 + y,z.
[h] Symmetry equivalent: −1 + x,y,1 + z.

4. Experimental

4.1. Materials and Physical measurements

Analar grade chemicals were used through out. All the synthetic manipulations were performed under oxygen atmosphere. Solvents were dried and distilled before use following the standard literature procedures. 2,6-pyridinedicarboxlic acid (Aldrich), $VOSO_4.3H_2O$ (Aldrich), $[VO(acac)_2]$ (Aldrich), 2-aminopyridine (S.D. Fine), *cis*-cyclooctene (Aldrich), *t*-butyl hydroperoxide (Fluka) were procured and used as received. 2,6-dicarboxamido-2-pyridylpyridine (H_2dcapp) was prepared and purified following the literature procedure [28].

Elemental analyses were performed by the Sophisticated Analytical Instrumental Facility, Central Drug Research Institute, Lucknow. Infrared spectra and Electronic spectra were obtained on a Perkin–Elmer-577 and Perkin–Elmer Lambda-35 spectrometer, respectively. ^{1}H NMR spectra were recorded on a JEOL AL-300 FTNMR instrument. GCMS studies were done with the Shimadzu-2010 instrument containing an Rtx-5MS-30Mt column of 0.25 mm internal diameter.

4.2. Synthesis of complex

4.2.1. $[apyH]_2[\{VOL\}_2(\mu\text{-}O)_2].2H_2O$ (1)

This complex was prepared by the following two methods:

(a) To the stirring aqueous solution (15 mL) of the ligand, H_2dcapp (0.640 g, 2 mmol) was added into methanol solution (15 mL) of $[VO(acac)_2]$ (0.530 g, 2 mmol) in dropwise manner. The resulting solution was stirred at room temperature for 12 h until the color of the solution changes from dark green to yellow. The resulting solution was filtered and left at room

temperature for slow evaporation crystallization. After two weeks, light yellow color crystals were separated, and air dried. Yield: (0.648 g, 90%). Anal. Calc. for $C_{24}H_{24}N_6O_{14}V_2$: C, 39.88; H, 3.32; N, 11.63. Found: C, 39.88; H, 3.35; N, 11.48. IR (cm^{-1}, nujol):$\nu = $ 3479, 3327, 3159, 3088, 2925, 1676, 1477, 1431, 1334, 1168, 1073, 940, 873, 757, 679, 591, 516, 450. ^{1}H NMR (δ ppm, 300 MHz, DMSO-d_6, 298 K): 8.53 (t, 2H, J = 7.5 Hz), 8.17 (d, 4H, J = 7.8 Hz), 7.88 (d, 2H), 7.75 (m, 2H), 7.41 (m, 2H), 6.71(m, 2H). UV–VIS {DMSO, λ_{max} nm (ϵ/M^{-1} cm^{-1})}: 254(21 639), 272 (24 839), 305(25 924).

(b) It was also prepared by the same method as described above except that $VOSO_4.3H_2O$ (0.434 g, 2 mmol) was added in place of $[VO(acac)_2]$. The complex separated as green color crystals and air dried. Yield: (0.576 g, 80%).

4.3. X-ray crystallographic study

X-ray data for **1** was collected on Bruker APEX II and Bruker AXS SMART APEX CCD area detector diffractometers using graphite monochromatized Mo-Kα radiation at 100(2) and 293(2) K. SAINT and SMART software packages [29] were used for data collection and data integration for **1**. Structure solution and refinement were carried out using the SHELXTL-PLUS software package [29]. The non-hydrogen atoms were refined with anisotropy thermal parameters. All the hydrogen atoms were treated using appropriate riding models. The computer programme PLATON was used for analyzing the interaction and stacking distances [30].

4.4. Computational Details

Geometrical characterization of the complex was performed at the level of density functional theory (DFT) using B3LYP functional [31]. For the atoms C, H, N, O and V 6-311G** basis set was used. The energies and intensities of the 40 lowest-energy spin allowed electronic excitations for the complex were calculated using time dependent-DFT (TD-DFT) at the same level of theory. All calculations were performed using the Gaussian 03 programme [32]. Molecular orbital diagrams were constructed using the MOLDEN programme [33].

4.5. Catalytic reactions

Oxidation of *cis*-cyclooctene was carried out using $[apyH]_2[\{VOL\}_2(\mu\text{-}O)_2].2H_2O$ [**1**] as catalyst. In a typical reaction, *cis*-cyclooctene (1.10 g, 10 mmol) and *tert*-butylhydroperoxide (3.36 g, 30 mmol) were mixed in 10 mL of chloroform and the reaction mixture was heated with stirring at 61°C for 4 h. The catalyst (23 mg, 0.032 mmol) was added to the reaction mixture and progress of the reaction was monitored by TLC. After complete consumption of the *cis*-cyclooctene, the volume of the reaction mixture was concentrated under reduced pressure and the residue was triturated with diethyl ether. The catalyst thus separated was filtered and dried. The filtrate was concentrated to give the crude
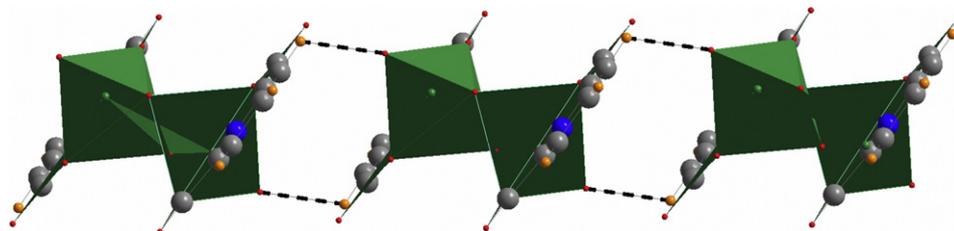
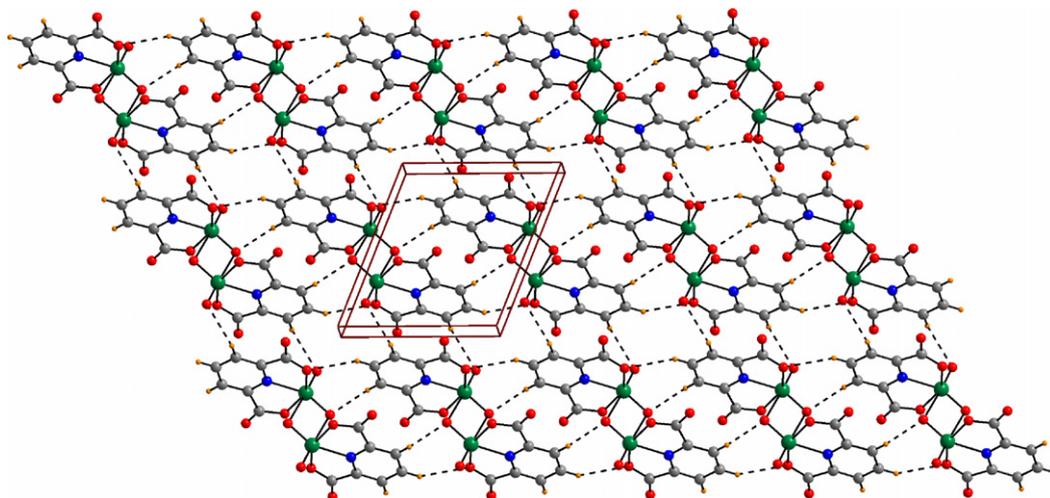**Fig. 3.** 1D polymeric chain along the [100] direction through C–H–O hydrogen bonding in **1**.

Fig. 4. 2D grid in the (001) plane, viewed along the *c* axis through C−H−O hydrogen bonding in complex **1**.

product, which was purified by gradient column chromatography using 60−120 mesh silica and EtOAc/hexane as the eluent. The recovered catalyst was reusable without purification.

Appendix 1. Supplementary material

The crystallographic data in CIF format has been deposited with CCDC (CCDC deposition number are 727 642 (at 100(2) K) and 727 643 (at 293(2) K)). This data can be obtained free of charge at www.ccdc. cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internet.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

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