

Research paper

Supramolecular bimetallic vanadium(V) complex driven by hydrogen bonding and O...O chalcogen bonding interaction: Oxidation of cyclohexane and its application toward C–H bond activation

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ABSTRACT

Vanadium(V) complex was synthesized in good yield and characterized by FT-IR, UV-Visible and NMR spectroscopy. The structure of the complex was confirmed by single X-ray crystallography. X-ray structural analysis the complex featuring O...O chalcogen bonding interaction and other short interaction. The O...O intermolecular interactions distance is 2.794 Å. Clearly, the O...O intermolecular distance in the O-linked complex is less than the sum of van der Waals atomic radii of oxygen 3.00 Å ($r_{vdw}(O) = 1.50 \text{ \AA}$). Oxidations of cyclohexane to cyclohexanol were also carried out, using the synthetic complex as a catalyst. The catalytic studies were carried out successfully using m-chloroperbenzoic acid as oxidant at 100 °C, under solvents free conditions. The catalytic protocols are very simple and the catalyst can be recovered without any lost in products formation in the next consecutive cycle.

1. Introduction

Hydrocarbons, especially those containing saturated hydrocarbons are the main constituents of natural gas and oil, which are the main feedstock for chemical industry [1–4]. Hence, chemical transformations of these materials to more valuable oxygenated products such as alcohols, ketones, acids, and peroxides is a demanding goal both in catalysis, industries as well as in the field of research in contemporary chemistry [5–8]. Activating C–H bonds of cyclohexane by oxidation to produce cyclohexanol, and cyclohexanone that are important industrial raw materials for the production of adipic acid, and caprolactam which in turn can be used in manufacturing of nylon-6,6 and nylon-6 [9–13]. In view of economic and environmental important, and the need to search for more active, efficient and selective catalysts for such oxidation reactions that can operate under sustainable conditions is challenging.

In many cases, the used of noble metal catalysts such as zirconium, ruthenium, rhodium, and iridium complexes were usually used as catalysts for C–H bond activation [14–23]. However, the used of these novel metals find many drawbacks and limited services because of their expensive, environmental pollution and catalyst life. Hence, in order to reduce their usage, some non-noble transitional metals are required. In particular, vanadium complexes are well known as an attractive class of catalysts for oxidation of cyclohexane [7,8,24–26]. However, many

vanadium complexes catalyzed the oxidation of cyclohexane in presence of hydrogen peroxide and acid promoter. Hanson and co-workers reported, vanadium complex of the composition (HQ)₂VO(OiPr) (HQ = 8-quinolinate) catalyzed the oxidation of cyclohexane to cyclohexanol using nitric acid as promoter in presence of hydrogen peroxide [27]. Pombeiro and co-workers, synthesis three alkali heterobimetallic vanadium(V) coordination polymers (V^v/M (M = Na, K, Cs) bearing bis(salicylaldehyde)-oxaloyldihydrazone ligand and applying them in oxidation catalysis, for oxidation of cyclohexane [28]. Therefore, few reports are known to exist for aerobic oxidation of cyclohexane under mild conditions using vanadium catalyst.

In this article, we report the synthesis, full characterization, structural features and aerobic oxidations of cyclohexane using newly synthesized vanadium complexes. The reactions were carried out under simple conditions using mCPBA as an oxidant. Moreover, the catalyst can be prepared in air using commercially available reagents, making the overall process inexpensive, simple, and accessible without using any dry box or Schlenk techniques. Hence, in this work we aim to develop a simple catalytic system which can be used for green oxidation processes in organic chemistry.

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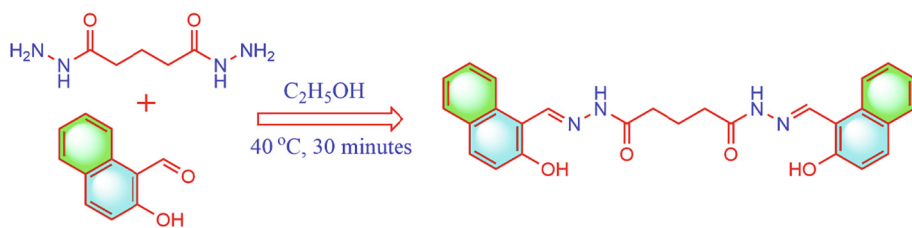
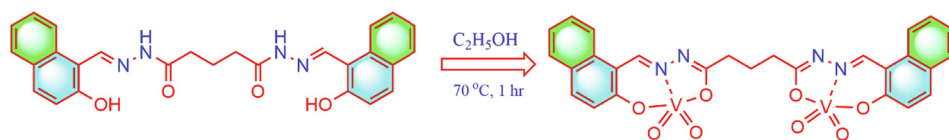
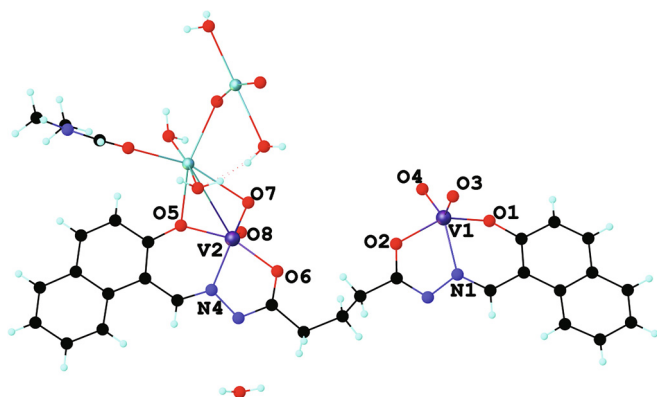
Scheme 1. Schematic diagram showing the preparation of ligand (H_4LG).Scheme 2. Schematic diagram showing the preparation of vanadium(V) complex (VO_2LG).Fig. 1. Crystal structure of vanadium(V) complex (VO_2LG).

Table 1

Crystal data and structure refinement for VO_2LG .

Empirical formula	$C_{30}H_{37}N_5Na_2O_{16}V_2$
Formula weight	871.50
Temperature/K	296.08(11)
Crystal system	triclinic
Space group	$P-1$
$a/\text{\AA}$	8.3309(6)
$b/\text{\AA}$	11.9489(19)
$c/\text{\AA}$	19.6741(15)
$\alpha/^\circ$	98.623(9)
$\beta/^\circ$	91.246(6)
$\gamma/^\circ$	104.582(10)
Volume/ \AA^3	1870.3(4)
Z	2
Radiation	MoK α ($\lambda = 0.71073$)
Data/restraints/parameters	6537/0/505
Goodness-of-fit on F^2	1.512
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.1357$, $wR_2 = 0.3849$
Final R indexes [all data]	$R_1 = 0.1559$, $wR_2 = 0.4016$

Table 2

Bond Lengths for VO_2LG .

Atom	Atom	Length/ \AA
V1	O1	1.867(5)
V1	O3	1.611(6)
V1	O2	1.959(5)
V1	N1	2.126(7)
V1	O4	1.653(6)
V2	O7	1.630(6)
V2	O8	1.614(6)
V2	O6	1.999(6)
V2	N4	2.115(7)
V2	O5	1.897(6)

Table 3

Bond Angles for VO_2LG .

Atom	Atom	Atom	Angle/ $^\circ$
O1	V1	O2	144.3(3)
O1	V1	N1	80.9(2)
O3	V1	O1	105.3(3)
O3	V1	O2	104.3(3)
O3	V1	N1	102.8(3)
O3	V1	O4	110.6(4)
O2	V1	N1	73.3(2)
O4	V1	O1	97.3(3)
O4	V1	O2	90.7(3)
O4	V1	N1	145.7(3)
O7	V2	O6	95.8(3)
O7	V2	N4	128.2(3)
O7	V2	O5	95.9(3)
O8	V2	O7	108.6(3)
O8	V2	O6	94.8(3)
O8	V2	N4	122.6(3)
O8	V2	O5	102.7(3)
O6	V2	N4	73.9(2)
O5	V2	O6	154.6(3)
O5	V2	N4	81.1(3)

2. Experimental section

2.1. Materials and methods

Solvents were reagent grade and used as received. Bis(2-hydroxy-1-naphthaldehyde)-glutaryldihydrazide (H_4LG) was prepared in good yield as shown in Scheme 1. Other chemicals such as vanadium pentoxide, hydrazine hydrate, m-chloroperbenzoic acid, salicylaldehyde, sodium carbonate, diethyl glutarate, were E-Merck, Himedia, and equivalent grades. C, H and N were determined by microanalytical method using a Perkin-Elmer 2400 CHNS/O Analyzer 11. Infrared spectra were recorded as KBr discs using Perkin Elmer BX-III/FTIR Spectrophotometer ($4000\text{--}200\text{ cm}^{-1}$). The ^1H NMR and ^{13}C NMR spectra were recorded on AMX-400 MHz and 100 MHz in $\text{DMSO-}d_6$ solution using TMS as internal standard. Solution electronic spectra were recorded on a Perkin-Elmer Lambda-25 spectrophotometer.

2.2. X-ray crystallography diffraction

Crystallographic data for the complex were recorded using Xcalibur, Eos, Gemini diffractometer equipped with a monochromated Mo K radiation ($\lambda = 0.71073\text{ \AA}$) source. For data collection and reduction CrysAlis PRO; Agilent, 2013 software packages were used. Semi empirical absorption based on multiscan was used with the help of SADABS software [29]. SHELXT-2014 and SHELXL-2014 was used for structure solutions and refinements [30]. Refinement based on F^2 procedure minimizing $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$, $wR = \frac{[\sum [w(F_o - F_c)^2]]^{1/2}}{[\sum wF_o^2]^{1/2}}$

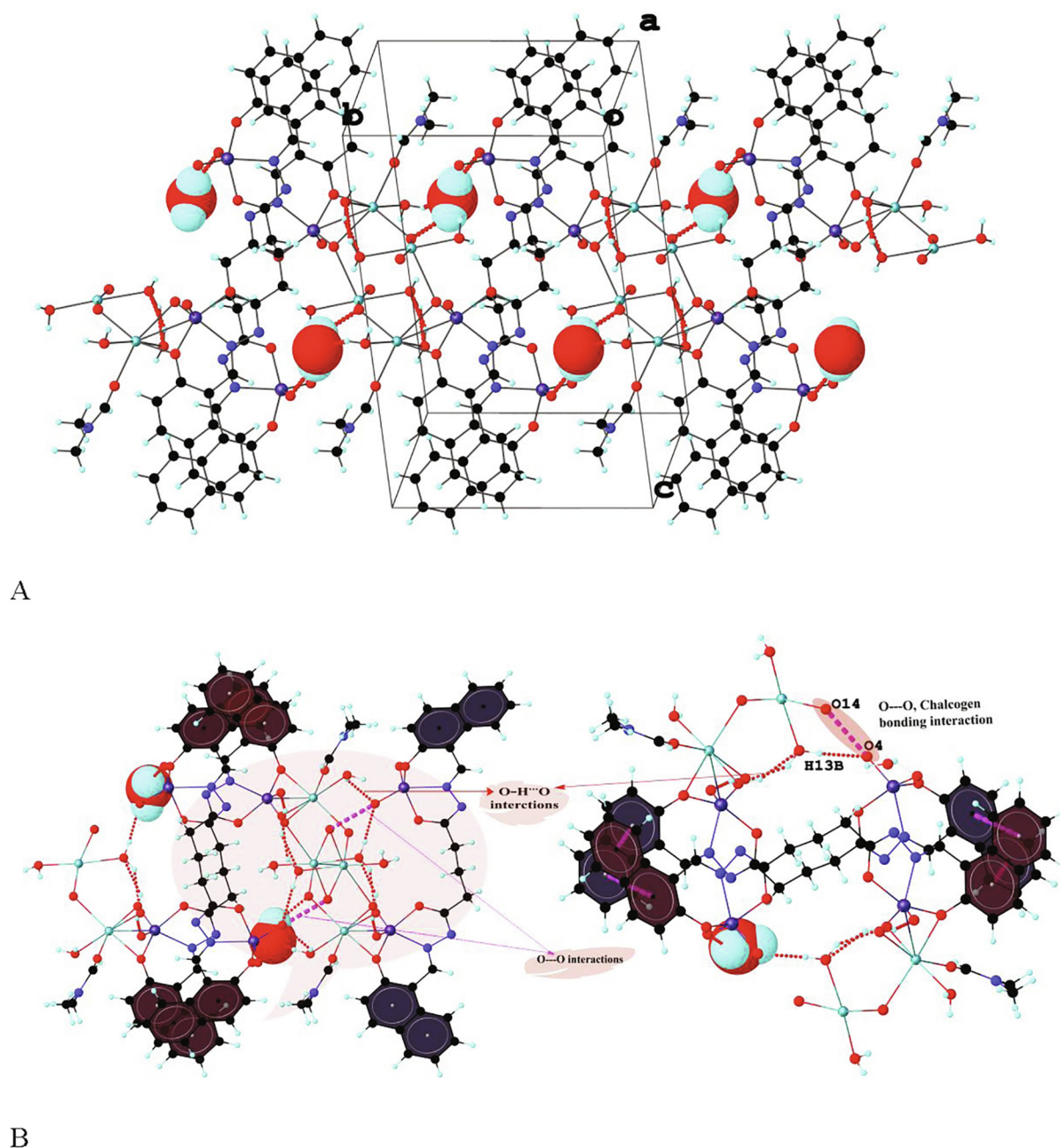


Fig. 2. (A) Perspective view packing diagram of VO₂LG showing O – H...O interactions and (B) Pi-pi staging and O...O interactions.

$(F_o^2 - F_c^2)^2 / \Sigma (F_o^2)^{1/2}$ and $S = [\Sigma [(F_o^2 - F_c^2) / (n - p)]]^{1/2}$ were applied. All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atom positions were isotropically refined in the final refinement.

2.3. Synthesis of hydrazone ligand (H₄LG)

A solution of 2-hydroxy-1-naphthaldehyde (0.34 g, 2 mmol) in ethanol (5 mL) was added to a stirred solution of glutaroyldihydrazide (0.16 g, 1 mmol) in ethanol (2 mL) at room temperature, resulting in an immediate color change from white to light yellow. The solvent volume was reduced to approximately 5 mL and the sample stirred at 40 °C for 30 min, resulting in formation of a yellow crystalline solid that was collected by filtration, washed with aqueous ethanol (2 mL), and dried under vacuum. Yield: 74%. Anal. found %: C, 69.18; H, 5.14; N, 11.91. Calculated % for C₂₇H₂₄N₄O₄: C, 69.22; H, 5.16; N, 11.96. ¹H NMR

(DMSO-*d*₆, 400 MHz): δ_H 10.77 (s, 2H, OH), 9.78 (s, 2H, NH), 7.96–7.06 (m, 12H, aromatic), 2.05–3.35 (m, 6H, CH₂).

2.4. Synthesis of VO₂LG

A solution of hydrazone ligand (0.47 g, 1 mmol) in methanol (5 mL) was added to a stirred solution of aqueous vanadium pentoxide (0.2 g, 1 mmol) at room temperature, the resulting mixtures were heated to 70 °C for 1 hr. The reaction mixtures were cooled to room temperature and followed by addition of sodium carbonate (0.11 g, 1 mmol) under stirring condition for 30 min, filtered, washed with methanol and dried to obtain a brown colour solid. Single crystal was obtained successfully by slow evaporation of the solvents at room temperature. Anal. found %: C, 51.39; H, 3.17; N, 8.84. Calculated %: C, 51.45; H, 3.20; N, 8.89. FT-IR bands (KBr pellets, cm⁻¹): 3454, 3190, 3050, 1613, 1560, 1467, 1416, 1326, 1185, 950, 750. ¹H NMR (DMSO-*d*₆, 400 MHz): δ_H

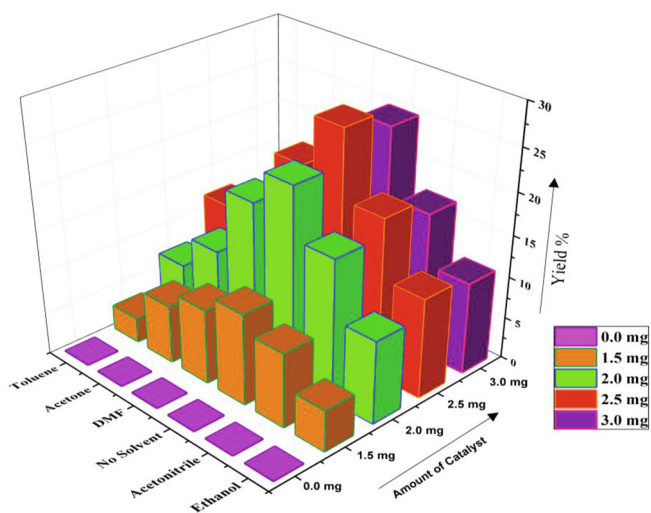


Fig. 3. Effect of solvent and the amount of catalyst on oxidation of cyclohexane.

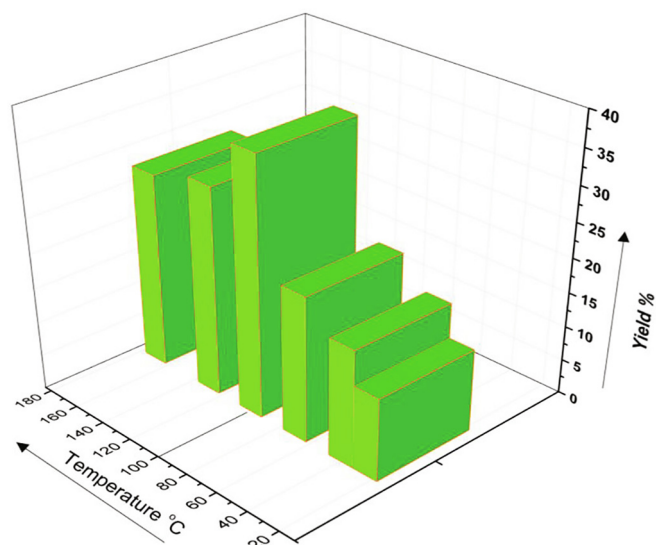


Fig. 4. Effect of temperature for catalytic oxidation of cyclohexane.

7.95–6.73 (m, 12H, aromatic), 8.85 (s, 2H, H-C=N) 2.99–2.34 (m, 6H, CH₂). ¹³C NMR (100 MHz, DMSO-*d*₆, ppm): δ_C 175.95, 164.21, 154.38, 132.66, 132.20, 119.47, 116.57, 78.82, 41.56, 40.11, 39.06, 30.72, 23.00.

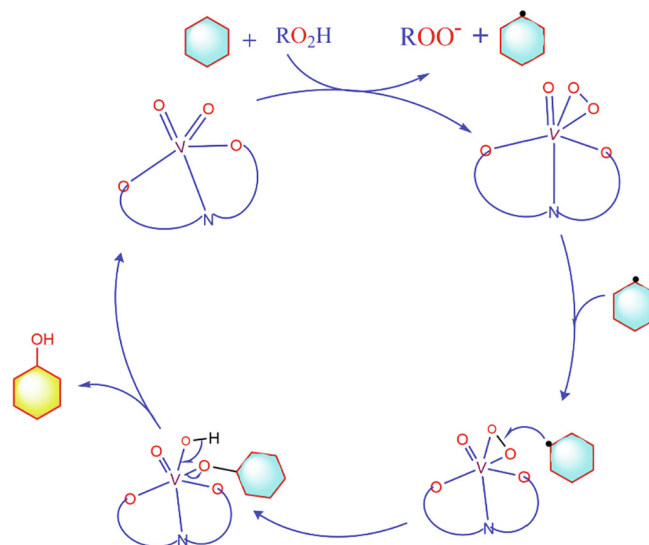
Table 4

Oxidation of cyclohexane and cyclopentane catalyzed by bimetallic vanadium(V) complex^a.

Entry	Catalyst	Time / h	Yield % ^{b,c}		Yield % ^{b,c}	
			Cyclohexanol	Cyclohexanone	Cyclopentanol	Cyclopentanone
1	1.0 mg	2	7	2	5	3
2	1.5 mg	2	13	7	10	5
3	2.0 mg	2	23	12	19	9
4	2.5 mg	2	41	37	30	27
5	3.0 mg	2	29	18	24	17

^a Reaction conditions (unless stated otherwise): Catalyst (2.5 mg); cyclohexane (5 mL, 5 mmol); cyclohexane: mCPBA mole ratio (1:4); Temperature (100 °C), under solvents free condition.

^b, ^cGC yield.



Scheme 3. The possible reaction mechanism for oxidation of cyclohexane.

2.5. Oxidation of cyclohexane

The alkane oxidations were typically carried out in air, in 50 mL round bottom flask, cyclohexane (0.08 g, 1 mmol), *m*-chloroperoxybenzoic acid (0.69 g, 4 mmol), VO₂LG (0.01 mmol) were added and stirred vigorously. The reaction mixtures were stirred at ambient temperature for 20 min and then were raised to 100 °C for 2 h. The oxidation reactions were monitored by withdrawing small aliquots after different periods of time, which were then cooled, extract and dried over anhydrous sodium sulfate. The oxidized product was purified by column chromatography. The product was ascertained by comparison with the authentic sample using ¹H NMR spectroscopy.

3. Results and discussion

The vanadium(V) complex was obtained by reaction of hydrazone ligand with one equivalent of vanadium pentoxide and sodium carbonate, in methanol (Scheme 2). VO₂LG is insoluble in methanol, ethanol, benzene, toluene, acetone, ether, and acetonitrile but soluble in dimethylformamide (DMF) and dimethylsulfoxide (DMSO). The characterization of VO₂LG has been carried out using elemental analysis, IR, NMR spectroscopy, and single crystal X-ray diffraction. The IR spectrum of VO₂LG exhibit a strong band in the ranges of 950–960 cm⁻¹, which are the signature of oxidovanadium(V) compounds and are assigned to ν(O=V=O) [31,32]. The characteristic bands at 1613 cm⁻¹ and 1560 cm⁻¹ are assigned to ν(C=C) and ν(C=N) of the coordinated hydrazone ligand. The ¹H NMR spectrum of VO₂LG exhibits a peaks at δ = 8.85 ppm, which is assigned to methylene proton (H-C=N), the peaks at δ = 7.95–6.73 ppm appeared as multiplets, which are assigned

to aromatic protons. Similarly, the $-\text{CH}_2$ protons appeared at the expected position and resonates at $\delta = 2.99\text{--}2.34$.

3.1. Crystal structure description

The X-ray quality crystal structure of VO_2LG was obtained upon slow evaporation of DMF solution of the compound, at room temperature. VO_2LG consists of two vanadium ions, bridging sodium ions, and hydrazone ligand. The crystal structure is shown in Fig. 1, crystallographic data are summarized in Table 1, whereas selected bond lengths and bond angles are presented in Tables 2 and 3. The compound crystallized in triclinic with $P\bar{1}$ space group. The hydrazone ligand acts as bis(tridentate) N_2O_4 chelating ligand to two vanadium ions. The basal positions are occupied by O-naphtholic, O-enolic and the N-imine atoms of chelating ligand, whereas the terminal positions are occupied by two oxido groups. The metal ligand bond distances are 1.867(5) Å (V1–O1), 1.959(5) Å (V1–O2), 2.126(7) Å (V1–N1), 1.653(6) Å (V1=O4), 1.999(6) Å (V2–O6), 1.630(6) Å (V2=O7), 1.614(6) Å (V2=O8), and 2.115(7) Å (V2–N4). The trans angles in VO_2LG are O4–V1–N1 (145.7(3)°) and O1–V1–O2 (144.3(3)°) around V1 with geometrical index, $\tau = 0.02$, whereas the trans angles around V1 are O5–V2–O6 (154.6(3)°) and O7–V2–N4 (128.2(3)°), with $\tau = 0.44$, respectively. Hence, vanadium ions adopted a square pyramidal geometry with slight distortion. The geometrical bond lengths and bond angles of the vanadium(V) complex are compared with the literature reports containing the similar complexes and found to be similar [31,32].

3.2. Packing diagram

The crystal packing diagram of VO_2LG , shows supramolecular interaction as shown in Fig. 2, the molecular packing involves a classical hydrogen bonding and pi-pi staging interactions. The geometrical hydrogen bond lengths and their symmetry codes are O(9)–H(9A)···O(8), 3.028(10) Å [1 + x, y, z]; O(9)–H(9B)···O(13), 2.845(11) Å [1 – x, – y, 1 – z]; O(11)–H(11A)···O(4), 2.971(11) Å [– x, – y, 1 – z]; O(11)–H(11B)···O(16), 2.822(11) Å [x, – 1 + y, z]; O(13)–H(13A)···O(9), 2.846(11) Å [1 – x, – y, 1 – z]; O(16)–H(16A)···O(12), 2.840(10) Å [x, 1 + y, z] and O(16)–H(16B)···O(3), 2.836(9) Å [1 – x, 1 – y, 1 – z] with their corresponding geometrical bond angles ranging from 134 to 155°, respectively. The crystal structure of VO_2LG was found to be stabilized by intermolecular hydrogen bonding (O – H···O) and pi-pi stacking interactions. These intermolecular interactions also strengthen and facilitate the O···O interactions in the complex. These packing may be arises as a result of the overall packing of the molecules in the crystal lattice. The O···O intermolecular distance in VO_2LG is 2.794 Å, (O₄···O₁₄). Clearly, the O···O intermolecular distance in the O-linked complex is less than the sum of van der Waals atomic radii of oxygen 3.00 Å (r_{vdW} (O) = 1.50 Å). These interactions are analogous with recently reported in the literature [33,34].

3.3. Oxidation of cyclohexane

The oxidation processed for the catalytic oxidation of cyclohexane to cyclohexanol and cyclohexanone was carried out under the favourable optimisation reaction conditions. The reaction conditions for selective oxidation of cyclohexane such as effect of solvents, amounts of catalyst, cyclohexane, mCPBA molar ratios, and reaction time were optimized. Hence, in most of the catalytic oxidation of cyclohexane, solvents play a very important role in the activity of catalyst. The effects of solvents was evaluated on the model reactions and summarized in Fig. 3. It is evident from Fig. 3, the reaction proceeded well under solvents free conditions. It was also noticed that, no cyclohexane oxidation takes place in the absence of the metal complex or the oxidant. Further, there was an increase in percentage yield of the product on increasing the amount of catalyst by 1.5–3 mg. However, varying the amounts of catalyst from 3 to 5 mg, there was no such augmentation in

the yield.

The further probe the potential of $\text{VO}_2\text{LG}/\text{mCPBA}$ catalytic system, the effects of different type of oxidant and oxidant/catalyst ratios was also studied. It was observed that increase the oxidant/catalyst molar ratios increases the rate of oxidation. Other oxidants such as hydrogen peroxide, benzoyl peroxide and ter-butyl hydroperoxide (TBHP) were also tested, but it was found that mCPBA gave highest yield. Further, it was also notice that using m-chloroperoxybenzoic acid as an oxidizing agent, there was an enhancement in product formation. This behaviour may be due to the strongest oxidizing character of m-chloroperoxybenzoic acid (mCPBA) [35]. Hence, from the above standardized protocols we observed that the catalytic systems proceed well using the following reaction condition, using catalyst (2.5 mg), cyclohexane (5 mL, 5 mmol), cyclohexane: mCPBA mole ratio (1:4) under solvents free condition. Screening of the temperature indicated that, 100 °C is the best choice yielded 37% of cyclohexone and 41% cyclohexanol, lowering the reaction temperature to 30 °C gave rise to a much lower yield (Fig. 4). The products yields for catalytic oxidation of cyclohexane to cyclohexanol and cyclohexone are given in Table 4. Hence, using the above standardization protocols, we also carried out the catalytic studies for the oxidation of cyclopentane. Similarly, it was found that the complex also catalyse the oxidation of cyclopentane to the corresponding cyclopentanone and cyclopentanol, but their catalytic activity is lower than that for the oxidation of cyclohexane (Table 4).

To account for the transformation, a proposed catalytic cycle for the catalytic oxidation of cyclohexane is shown in Scheme 3. In the first step, cyclohexane is activated by m-CPBA to produce cyclohexyl radical. In the second step, the cyclohexyl radical interact with the peroxy group of the catalyst, which results in proton transfer resulting in the formation of cyclohexanol and further oxidation which lead to formation cyclohexanone [35].

4. Conclusion

In summary, we have successfully investigated and compared the catalytic activity of homobimetallic vanadium(V) complex containing dihydrazone ligand with tridentate $-\text{ONO}-$ donors ligand. The catalytic activity was carried out successfully using m-chloroperbenzoic acid as an oxidizing agent under solvent free condition. The advantages of these present protocols are mild and environmentally benign, which are the significant features towards the development of a sustainable chemical process for oxidations. In view of the whole process involved and the literatures report available, vanadium(V) complex found to be a promising candidates for catalytic oxidation of cyclohexane and cyclopentane.

Conflict of interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ica.2020.119837>.

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