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A novel 2D vanadium(V)-isonicotinohydrazide coordination polymer, $C_{15}H_{16}AgN_4O_8V$: Synthesis, structure, catalytic activity and DFT calculation

Hassan Hosseini Monfared^{a,*}, Sohaila Alavi^a, Afsaneh Farrokhi^a, Morteza Vahedpour^a, Peter Mayer^b

^a Department of Chemistry, Zanjan University, 45195-313 Zanjan, Iran

^b Fakultät für Chemie und Pharmazie, Ludwig-Maximilians-Universität, München, Butenandtstr. 5-13, Haus D, D-81377 München, Germany

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ABSTRACT

A novel two-dimensional 3d–4d transition metal-based coordination polymer [VO(OCH₃)(OHCH₃) (L)Ag(NO₃)]_{∞} (**1**) has been synthesized and characterized by single crystal X-ray diffraction and fluorescence spectroscopy (H₂L = (*E*)-*N*'-(2-hydroxybenzylidene)isonicotinohydrazide). The coordination sphere of each V center is octahedral and chelates to a tridentate ligand L, while the tetrahedral conformation of Ag center consists of two O and two N atoms. Infinite zigzag chains of Ag-tetrahedrals are formed. The hydrazinide L^{2–} ligands of octahedral-V centers link adjacent chains to form an undulated heterometal based 2D layer. DFT calculations on **1** reproduced the geometric parameters and the electronic absorptions were predicted. The coordination polymer **1** showed very selective heterogeneous catalytic activity with 77–89% conversion in oxidation of alkenes, cyclooctane and benzyl alcohol by H₂O₂.

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1. Introduction

Coordination polymers have been widely studied in synthetic chemistry and materials science. The synthesis of coordination polymers with different metal ions and ligands [1] has led to a wide range of potential application-oriented properties, including catalysis, conductive, luminescent, magnetic, porous, or chiral materials [2]. Coordination polymers with moderate stability and high lability are efficient catalysts in a vast range of chemical and biochemical processes [3,4]. Most of them focused on the polymers containing 3d transition metals rather than 3d–4f or 3d–4d mixed ones [5,6]. To our best knowledge, only several examples of V(V)–Ag complexes have been reported in the literatures [7–11].

The most useful strategy to construct such polymers is to employ appropriate bridging ligands. Some multidentate ligands showed ditopic bridging capability *via* simultaneous ligations to the two metal ions in two different directions [12,13]. A potential pentadentate ligand, *N*-arylideneisonicotinohydrazide (Fig. 1), acts as a ditopic bridging ligand *via* two different coordination modes, tridentate chelation and bridging binding modes, toward three metal ions. Transition metal ions and *N*-arylidenebenzohydrazides show the potential to form mono and multi-nuclear structures in solution and solid state [14,15]. The catalytic properties of manganese [14], iron [16] and oxovanadium [17,18] *N*-arylidenebenzohydrazides complexes were recently paid considerable attention. Taking the advantage of coordination ability of *N*-arylidenebenzohydrazides with transition metals, and changing the benzohydrazide moiety to isonicotinohydrazide, we synthesized a new 3d–4d heterometal-based 2D polymeric complex.

On the other hand there is a lot of interest for the development of new efficient oxygenation catalysts to functionalize feedstock hydrocarbons to raw oxygen-containing chemicals. Heterogeneous catalysts which are friendly to the environment have the inherent advantages of the easier handling, separation and recovery from the reaction mixture over the homogeneous catalysts. In addition, for obvious environmental constraints, classical stoichiometric oxidants, such as dichromate or permanganate, should be replaced by new environment friendly catalytic processes using clean oxidants like molecular oxygen or hydrogen peroxide [19,20]. Hydrogen peroxide is particularly attractive oxidant as it is cheap, reasonably stable, readily available, and gives only water as a by-product.

Herein we report the synthesis, crystal structure, fluorescent properties, DFT calculations and catalytic activity of the new 2D polymeric complex, $[VO(OCH_3)(OHCH_3)(L)Ag(NO_3)]$ (1), $H_2L = (E)-N'-(2-hydroxybenzylidene)$ isonicotinohydrazide.

2. Experimental

Bis(acetylacetonato)oxovanadium(IV), [VO(acac)₂], solvents and other materials with high purity were purchased from Merck and Fluka and used as received. IR spectra were recorded as KBr disks with a Matson 1000 FT-IR spectrophotometer in the range of 4000–450 cm⁻¹. UV–Vis spectra of solution were recorded on a Shimadzu 160 spectrometer. UV–Vis absorption spectra and emission spectra (Photoluminescence) of the solid **1** were recorded on



^{*} Corresponding author. Tel.: +98 241 5152576; fax: +98 241 5283203. *E-mail address:* monfared@znu.ac.ir (H.H. Monfared).

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Fig. 1. The coordination environment of **1**. Selected interatomic bond distances (Å) and angles (°): Ag1–06, 2.518(2); Ag1–N2, 2.246(2); Ag1–06^{#b}, 2.621(2); Ag1–N3^{#c}, 2.248(3); V1–01, 1.8556(19); V1–02, 1.9810(19); V1–03, 1.586(2); V1–04, 1.758(2); V1–05, 2.304(2); V1–N1, 2.130(2); 01–C1, 1.332(3); 02–C8, 1.292(3); N2–C8, 1.313(3); 01–C1, 1.332(3); N1–N2, 1.399(3); O6–Ag1–N2, 106.06(8); O6–Ag1–06^{#b}, 101.26(8); O6–Ag1–N3^{#c}, 98.66(8); O6^{#b}–Ag1–N2, 87.08(7); N2–Ag1–N3^{#c}, 136.89(8); O6^{#b}–Ag1–N3^{#c}, 122.24(8); O1–V1–O2, 153.22(9); O1–V1–O3, 100.39(10); O1–V1–O4, 102.20(9); O1–V1–O5, 81.34(8); O1–V1–N1, 83.98(8); O2–V1–O3, 96.75(9); O2–V1–O4, 94.27(9); O2–V1–O5, 79.78(8); O2–V1–N1, 74.05(8); 83.29(9); O4–V1–N1, 160.60(10); O5–V1–N1, 79.46(8).

HR4000 and USB2000 Ocean Optics spectrophotometers by absorption and emission modes, respectively. The reaction products of oxidation were determined and analyzed by HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane $30 \text{ m} \times 320 \text{ µm} \times 0.25 \text{ µm}$) and gas chromatograph-mass spectrometry (Hewlett–Packard 5973 Series MS-HP gas chromatograph with a mass-selective detector). The elemental analyses (carbon, hydrogen, and nitrogen) of compounds were obtained from Carlo ERBA Model EA 1108 analyzer. Vanadium percentages of complexes were measured by a Varian spectrometer AAS-110.

2.1. Synthesis of (E)-N'-(2-hydroxybenzylidene) isonicotinohydrazide $({\rm H}_2{\rm L})$

A methanol solution (10 ml) of isonicotinohydrazide (0.146 mmol) and salicylaldehyde (0.146 mmol) was refluxed for 3 h. The solution was then evaporated on a steam bath to 5 cm³ and cooled to room temperature. Yellow crystals of H₂L was separated and filtered off, washed with cooled methanol and then dried in air. Yield: 95%. M.p.: 273 °C. Element analysis (%) *Anal.* Calc. for C₁₃H₁₁N₃O₂ (MW: 241.25): C, 64.72; H, 4.60; N, 17.42. Found: C, 64.60; H, 4.65; N, 17.00%. IR (KBr, cm⁻¹): 3346 (w, O–H), 3178 (m, N–H), 3000 (s), 2837 (m), 1682 (vs C=O), 1619 (s, C=N). λ_{max} (ε , dm³ mol⁻¹ cm⁻¹) = 217 (24 000), 290 (17 000), 300 sh (16 000), 334 nm (15 000).

2.2. Synthesis of $[VO(OCH_3)(OHCH_3)(L)Ag(NO_3)]_{\infty}$ (1)

 H_2L (0.14 mmol), vanadium(IV) oxide bis(acetylacetonate) (0.15 mmol) and silver(I) nitrate (0.15 mmol) were placed in the main arm of a branched tube. Methanol was added to fill the arms. The tube was sealed and the arm containing the reagents immersed in an oil bath at 60 °C while the other arm was kept at ambient temperature. After 24 h, red crystals of [VO(OCH₃) (OHCH₃)(L)Ag(NO₃)]_∞ (1) suitable for X-ray analysis were deposited in the cooler arm in yield 80%. Element analysis (%) *Anal.* Calc.

Та	hl	le	1	

Crystal data and structure refinement for $[VO(OCH_3)(OHCH_3)(L)Ag(NO_3)]_{\infty}$ (1).

Compound	1
Net formula	C ₁₅ H ₁₆ AgN ₄ O ₈ V
$M_{ m r}$ (g mol ⁻¹)	539.119
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	8.7440(7)
<i>b</i> (Å)	7.5417(5)
<i>c</i> (Å)	29.0459(17)
α (°)	90
β (°)	96.892(6)
γ (°)	90
$V(Å^3)$	1901.6(2)
Ζ	4
D_{calc} (g cm ⁻³)	1.88313(20)
$\mu (\mathrm{mm}^{-1})$	1.574
Absorption correction	'multi-scan'
Transmission factor range	0.88151-1.00000
Reflections measured	7324
R _{int}	0.0261
Mean $\sigma(I)/I$	0.0505
θ Range	4.24-26.33
Observed reflections	2828
x, y (weighting scheme)	0.0245, 0
Hydrogen refinement	mixed
Reflections in refinement	3843
Parameters	264
Restraints	1
$R(F_{\rm obs})$	0.0291
$R_{\rm w}(F^2)$	0.0593
S	0.928
Shift/error _{max}	0.001
Maximum electron density (e Å ⁻³)	0.601
Minimum electron density (e Å ⁻³)	-0.382

for **1**: C, 33.42; H, 2.99; N, 10.39. Found: C, 33.50; H, 3.00; N, 10.35%. IR (KBr, cm⁻¹): 3442 (s, br), 2922 (w), 1607 (s, C=O), 1537 (m, C=N), 1381 (vs), 1292 (w), 968 (w, V=O).

2.3. X-ray crystallography

X-ray quality crystals of $[VO(OCH_3)(OHCH_3)(L)Ag(NO_3)]_{\infty}$ (1) could be grown from methanol. Red crystals of 1 (0.35 × 0.14 × 0.07 mm) was investigated in a diffraction experiment at 173(2) K on an Oxford XCalibur diffractometer and with monochromated Mo K α radiation (λ = 0.71073) obtained from a graded multilayer X-ray optics. The structure was solved by direct methods with siR97 [21], and refined with full-matrix least-squares techniques on F^2 with shelxL-97 [22]. The C-bonded hydrogen atoms were calculated in idealized geometry riding on their parent atoms. The O- and N-bonded hydrogen atoms were located from the difference map with $U(H) = 1.5 \times U_{iso}(O)$ and $U(H) = 1.2 U_{iso}(N)$. Graphics were drawn with DIAMOND [23]. The crystal data and refinement parameters are presented in Table 1.

2.4. Computational details

The ground state geometries were obtained in the gas phase by full geometry optimization. The basis set used throughout this study is the LANL2DZ. The electronic spectrum of **1** was calculated with the TDDFT method [24]. Ground-state electronic structure calculations of **1** have been performed using density functional theory (DFT) [25] methods employing the GAUSSIAN-O3 software package [26]. The functional used throughout this study was the B3LYP, consisting of a hybrid exchange functional as defined by Becke's three-parameter equation [27] and the non-local Lee– Yang–Parr correlation functional [28] (B3LYP/LANL2DZ).

2.5. Experimental set up for catalytic oxidation

The liquid phase catalytic oxidations were carried out under air (atmospheric pressure) in a 25 ml round bottom flask equipped with a magnetic stirrer and immersed in a thermostated oil bath at 60 ± 1 °C. In a typical experiment, H_2O_2 (3 mmol) was added to a flask containing the catalyst 1 (1 mg) and a representative alkene, namely cyclooctene (1 mmol) in a solvent (3 ml). The course of the reaction was monitored using a gas chromatograph equipped with a capillary column and a flame ionization detector. The oxidation products were identified by comparing their retention times with those of authentic samples or alternatively by ¹H NMR and GC–Mass analyses. Yields based on the added substrate were determined by a calibration curve. Control reactions were carried out in the absence of catalyst, under the same conditions as the catalytic runs. No products were detected.

At the end of the reaction, the solution and catalyst changed to yellow-brown solution and white solid, respectively. The solid coordination polymer was not dissolved and it was recoverable.

3. Results and discussion

3.1. Characterization

The N-arylideneisonicotinohydrazide pro-ligand H₂L was obtained by the condensation of isonicotinohydrazide and salicylaldehyde. In reaction with basic vanadium(IV) oxide bis (acetylacetonate) and silver(I) nitrate, V(IV) is oxidized to V(V) by air and H₂L forms a dinegative ligand and occupies V(V) and Ag(I) coordination sites. Elemental analyses confirmed the composition of H₂L and **1**. The IR spectrum of **1** shows one broad and strong band due to the coordinated methanol at 3442 cm⁻¹ and one strong band at 1607 cm^{-1} due to the stretching of C=O groups. The V=O stretching vibration is observed at 968 cm⁻¹, similar with the polymer Zhao [6] reported. No band is seen for the N-H stretching vibration of the L^{2-} . The V=O stretching vibration in **1** occurs at a lower energy compared to the reported vanadium(V) complexes [17]. The IR spectrum of **1** indicates that the (*E*)-1-isonicotinoyl-2-(2-oxidobenzylidene)hydrazin-1-ide (L²⁻) acts as a tridentate chelating ligand being bonded to the V(V) acceptor center via the deprotonated oxygen atom of the phenol, imine nitrogen and carbonyl oxygen of isonicotinoyl moieties [16].

3.2. Description of crystal structure

Single crystal X-ray diffraction revealed that the asymmetric unit of **1** consists of a V(V)O, a Ag(I), a L^{2-} , OHCH₃, OCH₃⁻ and NO₃⁻ ligands. The coordination environment and selected bond lengths and angles of 1 are shown in Fig. 1. Polyhedral representation of the 2D layer along different axis of the 2D grid coordination polymer in the solid state is shown in Fig. 2. The ligand L^{2-} , coordinates to a V and two Ag centers. In 1 the vanadium atom has a six-coordinated structure as a VO(ONO)(O)(O)-type. The V(V) atom is meridionally coordinated by the phenoxo oxygen atom O1, imine nitrogen atom N1 and carbonyl oxygen atom O2 donor set of (E)-1-isonicotinoyl-2-(2-oxidobenzylidene)hydrazin-1-ide (L²⁻) ligand. Two cis-coordinated methoxylato and a methanol and oxo ligands complete the distorted octahedral vanadium coordination sphere. The metal center in **1** is displaced by 0.29 Å out of the least-squares plane defined by the donor atoms O1, N1, O2 and O4 towards the V=O moiety. Moreover, the nitrogen atom N1 of the L²⁻ ligand is located *trans* to the methoxylato group O4 with an angle of O4-V1-N1, 160.60(10)°. The vanadium to terminal oxo group (O3) bond lengths for complexes 1 (V1-O3, 1.586(2) Å) are at the lower end of the typically observed range for oxovanadium(V) complexes [29,30], which is consistent with the reported values of analogous hydrazone complexes [31]. The short V–O3 distance (1.586(2)-Å) indicates the presence of a vanadium-oxygen double bond which is commonly found in the VO³⁺ complexes. The L²⁻ ligand forms one six-membered and one fivemembered chelate ring with bite angles of about 83.98(8)° (01-V1-N1) and 74.05(8)° (O2-V1-N1), respectively. Two resonance forms are possible for doubly deprotonated H₂L: hydrazonate and hydrazinide (Scheme 1). N-arylidenebenzohydrazide analogues of H₂L coordinate as monotopic tridentate ligand in the monoanionic (as phenoxo) [16] or dianionic (as hydrazonate) [15,32] forms. Unlike to its analogues, the coordination mode of the H₂L is very interesting and behaves as a ditopic bridging ligand in hydrazinide form via two different coordination modes, tridentate chelation to V center and bridging binding toward two Ag center (Fig. 1). The ditopic action of L^{2-} forms a grid 2D coordination polymer (Fig. 2). Hydrazinide form of the H_2L is consistent with the observed O2-C8 and N2-C8 bond lengths of 1.292(3) and 1.313(3)-Å, respectively in 1. The O2-C8 bond length is similar to considerably short O2-C8 bond length for reported ligand and Mn complex (1.233 and 1.244-Å, respectively) with the coordinated keto form of the N-arylidenebenzohydrazide system [14].

The vanadium to oxygen bond lengths follows the order V-O3 (oxo) < V-O4 (methoxylato oxygen) < V-O1 (phenoxo oxygen) < V-O2 (carbonyl oxygen) < V-O5 (methanol oxygen). On the other hand, the V-N bond length to nitrogen atom N1 of the L^{2-} is considerably elongated due to the *trans* influence of the methoxylato group O4. The dihedral angle between vanadium coordinated atoms plane (O1, N1, O2, O4) and isonicotinoyl plane (C9–C13, N3) in **1** is 44.86°. The nitrate μ_2 - κ O bridge spans two Ag centers with distance Ag–Ag 4.932(2)-Å. The nearly tetrahedral conformation of each Ag center consists of two μ_2 - κ O atoms from two NO₃⁻ ligands with distances 2.518 (Ag-O6) and 2.621-Å (Ag- $O6^{\#}$) and two N atoms from L^{2-} ligands (Ag1-N2, 2.246(2) and Ag1-N3[#], 2.248(3)). The one-dimensional zigzag chains along *b*-axis are built up from corner-sharing tetrahedrals in which silver exhibits tetrahedral and fourfold coordination (Fig. 2a). The adjacent one-dimensional zigzag chains are linked (Fig. 2b) by the Narvlideneisonicotinohydrazide L^{2-} ligands via N2 and N3 (μ_{2-} κ N2: κ N3) to form an undulated heterometal based 2D layer in [0 0 1] planes with thickness of 17.95 Å (Fig. 2c).

3.3. Photoluminescence study

In common sense, silver(I) complex may emit weak photoluminescence at low temperature [33]. At ambient temperature, the synthesized complex **1** in the solid state shows photoluminescence with emission maximum at 475 nm upon excitation at 400 nm. Fig. 3 shows the photo-induced emission spectrum of the synthesized complex. Owing to the blue emission of **1**, it may be potential materials for blue light-emitting diode devices. The condensed polymeric materials may be good candidates for thermally stable and solvent-resistant blue fluorescent material because **1** is insoluble in the common solvents such as ethanol, chloroform, acetone, acetonitrile, benzene, and water.

3.4. Theoretical results: geometry optimization, electronic structure

With the aim to approach the origin of some properties of the complex, geometry optimizations and electronic spectrum calculations within the density functional theory (DFT) were carried out for **1**. We studied correlations between DFT and experimental data. These correlations allowed the assignments of particular electronic transitions. DFT calculations were performed in the gas phase on **1** starting from crystallographic data (Fig. 1). The geometry of the asymmetric unit was optimized in a singlet state by the DFT/B3LYP method using the basis set LANL2DZ. In the optimized



Fig. 2. Polyhedral representation of the 2D grid layer along (a) *a*-axis, (b) *b*-axis and (c) *c*-axis showing the connection of VO₅N octahedrals and AgN₂(µ-O)₂ tetrahedrals (four-fold coordination).



Scheme 1. Schematic drawing of the reactions for the preparation of H₂L and the 3d–4d coordination polymer 1.

structure, in addition to the asymmetric unit of **1**, two neutral molecules namely H_2O and NH_3 coordinated to Ag were also considered to fulfill its coordination number four. The optimized and experimental values of selected geometrical parameters are listed in Table 2. In general, the predicted bond lengths and angles are in good agreement with the values based upon the X-ray crystal structure data. The compound **1** is polymeric and some interactions between the neighboring building blocks are present. Since in the geometrical optimization of **1**, only the coordinated atoms and a few of the second neighbor atoms of the vanadium and silver centers were considered, the effects of the polymeric network or other weak interactions on the coordination environment (V and Ag) parameters are negligible. For this reason the theoretical study was performed on the building block without taking into account these weak interactions between neighboring building blocks. The results of the DFT calculations (Table 2) confirmed the reliability of our assumption. DFT calculations on **1** reproduced the geometric parameters that are in good agreement with the values



Fig. 3. Photo-induced emission spectrum of 1 in the solid state at room temperature with excitation at 400 nm.

based upon the X-ray crystal structure data. Thereby we may conclude that the effects of the weak interactions in the polymeric solid state network on the geometric parameters of the building unit are negligible. The value of gas phase calculations is useful for extended network structures and gives valuable information about polymers [34], including nature of bonds and predicting UV–Vis.

Frontier molecular orbitals of **1** with the energy eigenvalues are presented in Fig. 4. The HOMO-LUMO gap equals 3.37 eV. The

Table 2					
The experimental	and optimized	bond lengths	(Å) and	angles (°) for '

HOMO is of contributions from $p\pi L^{2-}/Ag$ center and the LUMO is localized on the vanadium center/ligand L^{2-} . In order to investigate the lowest lying singlet states of 1, the UV–Vis spectrum of 1 was calculated by the TDDFT/B3LYP [35]. Selected calculated states, together with their vertical excitation wavelength and oscillator strength are displayed in Table 3. The highest in energy transition (292 nm) can be ascribed as HOMO $-3 \rightarrow$ LUMO and HOMO-1 \rightarrow LUMO, and is due to charge transfer from the Schiff base ligand to vanadium(V) and the intra molecular transition of the ligand H₂L. The absorption band at 310 nm is similar to the intra molecular transition of the corresponding ligand H₂L. These assignments well match with the observed bands for H₂L if scaling factor 0.70 is considered [36]. Consideration of the contour plots of the valence orbitals (Fig. 4) helps to assign it to $\pi \rightarrow \pi^*$ of the ligand and, to a minor extent, to a LMCT. The lowest in energy transition (361 nm) is assigned to HOMO \rightarrow LUMO, that is mainly due to charge transfer from the Schiff base ligand to vanadium(V) and probably matches with the observed very broad band of observed 400 nm for **1**. The weak interactions between the neighboring building blocks do not affect the geometric parameters of the coordination environment but they are important for the absorption properties. The compound **1** shows a very broad absorption band about 400 nm due to ligand to metal charge transfer. Since the whole structure of the ligand is influenced by weak interactions between the building units, the calculated energy transitions values are not matched well with the observed one. However, the

Bond length	Experimental	Optimized	Bond angle	Experimental	Optimized
V1-01	1.855	1.825	∠03V101	100.39	100.73
V1-02	1.981	1.981	∠03V102	96.57	95.02
V1-03	1.581	1.592	∠03V104	101.57	102.95
V1-04	1.758	1.768	∠03V105	174.29	173.97
V1-05	2.304	2.334	∠N1V101	83.98	83.46
V1-N1	2.130	2.142	∠N1V102	74.05	74.49
Ag1-06	2.518	2.589	∠N1V1O3	95.27	97.77
Ag1-N2	2.246	2.216	∠N1V1O4	160.60	155.58
N1-C7	1.292	1.313	∠N1V105	79.46	79.30
02-C8	1.292	1.315	∠O6Ag1N2	106.06	103.21
C8-N2	1.313	1.335			
N2-N1	1 399	1 422			



Fig. 4. Frontier molecular orbitals of 1 with the energy eigenvalues in eV.

 Table 3

 Calculated (TDDFT method) λ_{max} values for 1 and observed λ_{max} values for 1 and H₂L.

Orbital excitations	Calculated ^a λ (nm)	Observed λ (nm) for 1	Observed λ (nm) for H ₂ L	f ^b	Character
HOMO → LUMO, 68% HOMO → LUMO+1, 13%	361	400 (very broad)		0.004	$L \rightarrow V$ (LMCT), π - π^* $L \rightarrow V$ (LMCT)
HOMO → LUMO, 11% HOMO → LUMO+1, 14% HOMO → LUMO+3, 69%	310		334 300	0.016	L, Ag \rightarrow V (LMCT) L \rightarrow V (LMCT) L \rightarrow V (LMCT), π - π *
HOMO-3 → LUMO, 49% HOMO-3 → LUMO+1, 14% HOMO-2 → LUMO, 18% HOMO-1 → LUMO, 37% HOMO → LUMO+2, 16%	292		290	0.007	L, Ag \rightarrow V (LMCT) L, Ag \rightarrow V (LMCT) Ag(NO ₃) \rightarrow V Ag(NO ₃) \rightarrow V L \rightarrow V (LMCT)

^a Scaling factor = 0.7.

^b Calculated oscillator strength.

Table 4

Catalytic oxidation of cyclooctene with the catalyst 1/H₂O₂.^a

Entry	Catalyst	Cocatalyst	Oxidant	Temp. (°C)	Time (h)	Con. (%) ^b
1	1	NaHCO ₃	H_2O_2	25	3	0
2	1	$NaHCO_3$	H_2O_2	60	1	42
3	1	-	H_2O_2	60	1	41 (73) ^c

 $^a\,$ Ag–V catalyst (1) 1 mg (contain 1.85 μmol V), cyclooctene – 1 mmol, CH_3CN – 3 ml, NaHCO3 – 1 mmol and aqueous H2O2 – 3 mmol.

^b Conversions are based on the starting cyclooctene.

^c After 5 h.

calculation method shows the advantageous to predict some transitions that are covered by charge transfer and could not be seen experimentally.

3.5. Catalytic reactivity

Catalytic potential of **1** was established in the oxidation of various hydrocarbons. At first oxidation of cyclooctene as representative alkene was studied with hydrogen peroxide in the presence of **1**. All reactions were carried out with 1 mmol of cyclooctene in CH₃CN in the presence of catalyst **1** at 60 °C. Cyclooctene oxide was the sole product. The results of control experiments revealed that the presence of catalyst and oxidant are essential for the oxidation. The oxidation of cyclooctene in the absence H₂O₂ was not occured and in the absence of catalyst the oxidation proceeded only up to 6% after 24 h. While the reaction at room temperature was negligible (Table 4, entry 1), increasing the reaction temperature to 60 °C remarkably increased the cyclooctene conversion up to 42% after 1 h (Table 4, entry 2). Further experiment proved that the complex **1** was able to oxidize cyclooctene without the presence of a co-catalyst like NaHCO₃ (Table 4, entries 3).

In search of suitable reaction conditions to achieve the maximum oxidation of cyclooctene, the effect of solvent was studied. Fig. 5 illustrates the influence of the solvent nature in the catalytic epoxidation of cyclooctene by **1**. Methanol, acetonitrile and chloroform were used as solvents. The highest conversion was obtained in acetonitrile, 69% after 4 h. It was observed that the catalytic activity of **1** decreased in order acetonitrile (relative dielectric constants [37], $\epsilon/\epsilon_0 = 37.5$) > methanol (32.7) > chloroform (4.9). In general, there was a good correlation between the solvent polarity (ϵ/ϵ_0) and cyclooctene conversion percent. The highest conversion in acetonitrile possibly is caused by its high dielectric constant.

The catalytic activity of **1** was also examined in oxidation of various hydrocarbons under the optimized conditions (acetonitrile, reaction temperature 60 °C) and the results are shown in Table 5. Cyclooctene was converted to the corresponding epoxide with 100% selectivity. Cyclohexene was mainly oxidized to 2-



Fig. 5. Solvent effect on oxidation of cyclooctene by 1. Catalyst (1) 1 mg, cyclooctene 1 mmol, solvent 3 ml, H_2O_2 3 mmol at 60 $^\circ C.$

cyclohexene-1-ol (22%) and 2-cyclohexene-1-one (66%) and cyclohexene oxide was minor product (1%) (Table 3, entry 2). Allylic oxidation has been reported in the metalloporphyrin systems [38] in the oxidation of alkenes such as cyclohexene and represents radical nature of the active oxidizing species. Catalyst 1 oxidized cyclooctane to cyclooctanol and cyclooctanone with yields 42% and 31%, respectively (Table 5, entry 3). Oxidation of benzylalcohol by 1 produced benzaldehyde with high yield and 100% selectivity (Table 5, entry 4). The profile of products show the oxidation reaction was rather selective and over oxidation products were not produced. Our findings proved that the coordination polymer 1 has the potential to oxidize a reactive alcohol like benzylalcohol, alkenes and relatively uncreative alkane to approximately the same extent with conversions of 73-81%. The total mechanism of the reaction is not fully clear. However, on the basis of the oxidation products of the various hydrocarbons (Table 5), it is predicted that the oxidation reactions proceed by intermediacy of a peroxo-vanadiumhydrazone Schiff base species formed in the reaction mixture in the presence of hydrogen peroxide [17].

4. Conclusions

We isolated a novel 3d–4d heterometal-based coordination polymer, which exhibits a novel 2D grid motif. This work has revealed pentadentate chelating behaviors of the hydrazone Schiff base ligand towards oxovanadium and silver. DFT calculations on the coordination polymer **1** reproduced the geometric parameters and the UV–Vis spectrum of **1** was predicted. Catalytic potential of

Table 5

Oxidation of various substrates with $1/H_2O_2/CH_3CN^a$.

Entry	Substrate	Product(s)	Yield (%) ^b	Conversion (%)	Time (h)
1			73	73	5
2	$\overline{\bigcirc}$	$\bigcirc \circ$	1	89	5
	·	он	22		
			66		
3		ОН	42	77	3
		F°.	31		
4	ОН	СНО	81	81	5
	\checkmark				

^a Reaction conditions: catalyst – 1 mg, CH₃CN – 3 ml, substrate – 1 mmol, aqueous H₂O₂ – 3 mmol and temperature 60 ± 1 °C.

^b Yields are based on the starting substrate.

1 was established in the oxidation of various hydrocarbons by using the environmentally benign and clean oxidant H_2O_2 .

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Appendix A. Supplementary data

CCDC 795784 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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