Transition Met Chem (2013) 38:267–273
DOI 10.1007/s11243-012-9687-z

Synthesis, structure and catalytic activity of an oxo-bridged dinuclear oxovanadium complex of an isonicotinohydrazide ligand

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Received: 10 October 2012 / Accepted: 20 December 2012 / Published online: 20 January 2013

Abstract A mononuclear dioxo vanadium(V) complex of a hydrazone ONO donor ligand, $[V^{V}O_2(L^1)]$ (**1**), was synthesized by the reaction of V_2O_5 and terephthalic acid with H_2L^1 in 1:1:1 mol ratio, while an oxo-bridged bis(vanadium(IV)oxo) complex, $[\mu_2\text{–}O\text{–}\{V^{IV}O(L^2)\}_2]$ (**2**), was synthesized by the treatment of isonicotinic acid hydrazide, salicylaldehyde and $CoSO_4{\cdot}7H_2O$ with bis(acetylacetonato)oxovanadium(IV) (H_2L^1 = isonicotinic acid(2-hydroxy-benzylidene)-hydrazide, H_2L^2 = isonicotinic acid (1-methyl-3-oxo-butylidene)-hydrazide). The complexes were characterized by elemental analyses and spectroscopic methods. The crystal structure of complex **2** was determined by X-ray analysis. The complexes were tested as catalysts for the oxidation of cycloalkenes and benzyl alcohol using H_2O_2 as terminal oxidant. Excellent selectivity was achieved in the oxidation of cyclohexene.

Introduction

Vanadium is a versatile bio-essential element [1] capable of existing in a wide range of oxidation states spanning between 3− and 5+. The presence of vanadium(IV) and vanadium(V) compounds in many vanadium-dependent enzymes, including nitrogenases [vanadium nitrogenases with vanadium(II–IV)] [2] and haloperoxidases [3], has stimulated the search for structural and functional models. Furthermore, oxovanadium(IV) and dioxovanadium(V) complexes with N-, O- and S-donor chelating ligands have been studied for their potential insulin-mimetic effects [1, 4–6], tumor growth inhibition and prophylaxis against carcinogenesis [7, 8], as well as their inhibition of several enzymes, including phosphatases, ATPases, nucleases, kinases [9] and antimicrobial activity against mycobacterium tuberculosis [10]. Various organic substrates are oxidized by peroxides in the presence of vanadium complexes with N- and O-donor ligands as epoxidation and oxidation catalysts [11–13]. The use of oxovanadium complexes in oxidation and oxotransfer catalysis has been noted [14–18]. Oxovanadium complexes in catalytic oxidations [19] and the catalytic activity of peroxovanadium complexes have been reviewed recently [20].

Oxo-bridged polynuclear oxo-vanadium complexes have been the subject of considerable interest in recent years [21]. Such complexes may serve as models for studying the role of vanadium in biological systems [22]. Several μ-oxo divanadium compounds containing a $V_2O_3^{n+}$ ($n = 4$, 3 or 2) core have been reported. All these compounds have symmetric structures involving identical ligands around both metal centers. When these compounds have square pyramidal vanadium centers [23–33], the terminal and bridging oxo atoms have a diverse range of arrangements, from anti-linear [31, 32] to syn-angular [23–25] through anti-angular [26–29] and twist angular [33] structures.

On the other hand, hydrazides and hydrazones (Scheme 1a) have interesting ligation properties due to the presence of several potential coordination sites. They can act as bidentate, tridentate or tetradentate ligands depending

Electronic supplementary material The online version of this article (doi:10.1007/s11243-012-9687-z) contains supplementary material, which is available to authorized users.

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on the nature of heterocyclic ring substituents attached to the hydrazone unit, and tend to stabilize the vanadium in its highest oxidation state [34–38]. For example, *N*-salicylidenehydrazides are versatile tridentate ligands and several types of $V^{IV}O$-, $V^{V}O$- and $V^{V}O_2$-complexes have been obtained [39, 40].

Herein, we report the synthesis, crystal structure and catalytic activity of V(IV) and V(V) complexes of an isonicotinohydrazide-based ligand (Scheme 1b).

Results and discussion

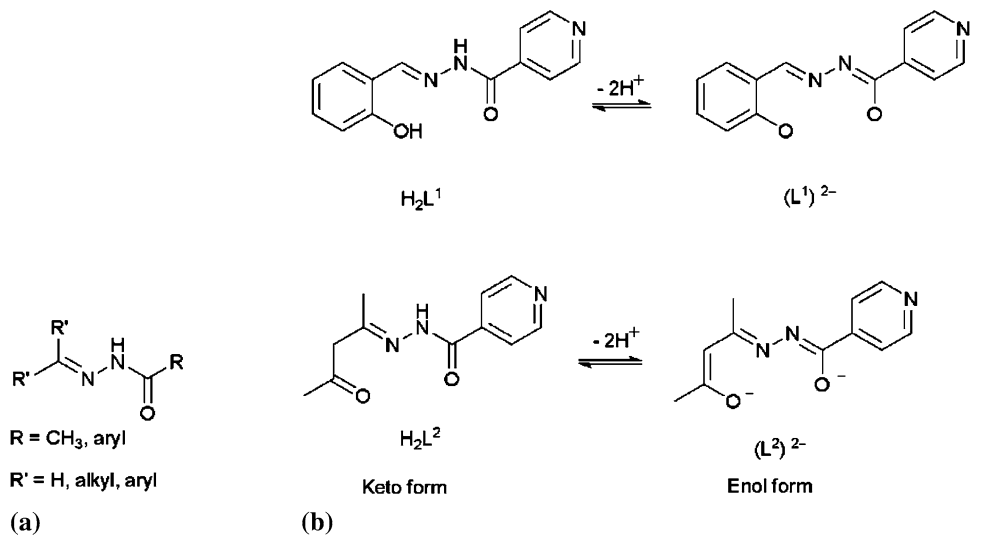
The ligands H_2L^1 and H_2L^2 were synthesized in situ. Complex $[V^{V}(O)_2(L^1)]$ (**1**) was formed in a template reaction of equimolar amounts of salicylaldehyde and isonicotinic acid hydrazide with V_2O_5 in a mixture of MeOH/H_2O and in the presence of terephthalic acid (Scheme 2). The preparation of this complex starting from $[VO(acac)_2]$ in ethanol and in the absence of terephthalic acid has been reported recently [41].

Condensation of isonicotinic acid hydrazide with one of the acetylacetonate groups of $[VO(acac)_2]$ in the presence of cobalt sulfate, added to adjust the pH of the solution to 4.49, led to the formation of $[\mu_2\text{–O–}\{V^{IV}O(L^2)\}_2]$ (**2**) (where H_2L^2 = Schiff base derived from monocondensation of acetylacetone and isonicotinic acid hydrazide), Scheme 2. The combination of cobalt sulfate with vanadylbis(acetylacetonate) is expected to give a bimetallic complex [16].

In the IR spectra, the free ligand H_2L^1 shows stretching bands attributed to C=O, C=N, C–OH (phenolic) and N-H at 1,682, 1,617, 1,287 and 3,178 cm^{-1}, respectively [16, 42]. A band at 3,346 cm^{-1} is assigned to ν(O-H) vibrations involving intramolecular hydrogen bonding, while a band at 1,213 cm^{-1} is attributed to δ(O-H) (phenolic) [43]. The presence of ν(OH) observed for H_2L^1 as a weak band at 3,346 cm^{-1} suggests intramolecular hydrogen bonding (O–H···N) in H_2L^1 [44]. For complex **1**, the absence of an N–H band, together with red shifts in azomethine (–C=N–) and carbonyl bands of the ligand, indicates coordination of H_2L^1 as a dianionic ligand in the enol form (Scheme 1). The absence of the bands at 3,346 and 1,287 cm^{-1} and the presence of the bands at 1,349 and 1,258 cm^{-1} support involvement of the phenolic oxygen in coordination through deprotonation. This is confirmed by the band at 456 cm^{-1} assigned to V-O (phenolic). The IR spectrum of complex **1** also exhibits a broad band at 3,430 cm^{-1} due to hydrogen bonded N-H of the pyridinium group and O-H of the crystal surface adsorbed water. The –C=N-N=C- moiety is observed as a strong band at 1,604 cm^{-1}. Complex **1** shows strong bands at around 970 and 864 cm^{-1} which may be assigned to antisymmetric and symmetric ν(O=V=O) vibrations of the cis-VO_2 group, respectively [45].

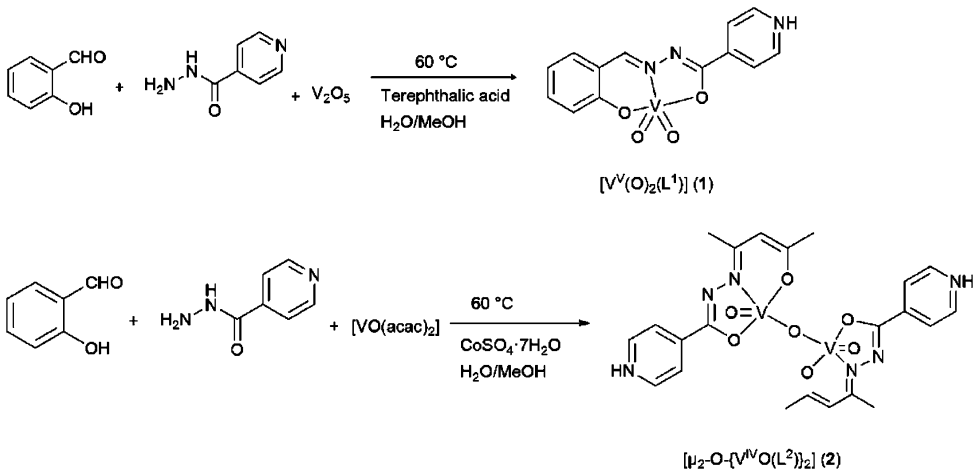
The presence of bands for *ν*(C=O) at 1,666 cm^{-1} and *ν*(N–H) at 3,214 cm^{-1} in the IR spectrum of complex **2** provides evidence for the coordination of H_2L^2 to vanadium in the keto form (Scheme 1). The IR spectrum also exhibits a broad band at 3,364 cm^{-1} due to hydrogen bonded N-H of the pyridinium group and O-H of adsorbed water at 3,516 cm^{-1}. The –C=N-N=C- unit is also observed as a very strong band at 1,615 cm^{-1}. The spectrum shows *ν*(C=C, C=N) vibrations in the range 1,307 and 1,267 cm^{-1} and a strong *ν*(V=O) band at 851 cm^{-1} could be clearly identified for complex **2** [46].

The UV–Vis spectra were recorded in MeOH/H_2O for both complexes. The two spectra are quite similar. The spectrum of compound **1** displays absorption peaks at



Scheme 1 (**a**) Acyl and aroyl hydrazones general formula, (**b**) the keto and enol form of the in situ synthesized ligand H_2L^1 = (*E*)-*N*′-(2-hydroxybenzylidene)isonicotinohydrazide and H_2L_2 = (*E*)-*N*′-(4-oxopentan-2-ylidene)isonicotinohydrazide

Scheme 2 The synthesis of complexes **1** and **2**



216, 279, 325 and 399 nm. The band at 216 nm can be attributed to internal ligand $\pi \rightarrow \pi^*$ and the absorptions at 279 and 325 nm are due to $n \rightarrow \pi^*$ internal transitions of H_2L^1. The band at 399 nm can be assigned to ligand to metal O/N → V charge transfer. For complex **2**, the intense bands at 228 and 279/325 nm were assigned to intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. The band at 379 nm was attributed to ligand to metal O/N → V charge transfer transitions. The weak d–d transition of **2** was observed at 569 nm. For complex **1**, no d–d bands are expected as there are no d electrons.

Description of the structure

The molecular structure and labeling of the atoms for complex **2** are displayed in Fig. 1 along with selected bond lengths and angles. The structure of **1** has been reported already [41].

The dimeric complex **2**, which lies on a crystallographic center of symmetry, is formed by a bridging oxo atom with a V1–O4 bond length of 1.7915(4) Å. It is evident from the thermal ellipsoids that the oxo bridge is probably slightly disordered around the center of inversion—this will have small bond length/angle implications for the geometry. The lattice is triclinic with *P*1 bar symmetry, and the molecule is situated on a center of inversion with $Z' = 0.5$. The centrosymmetric dimer is formed via the bridging oxo connecting two vanadium atoms. Hence, the vanadium atoms adopt a distorted square pyramidal geometry. The V-O distance is 1.7915(4) Å and the angle V1–O4–V1^i is 180.00° (translation of symmetry code to equiv.pos $i = 1 - x, -y, 2 - z$ which is very similar to reported oxo-bridged hydrazone complexes) [31, 32]. The H_2L^2 ligand binds the vanadium meridionally in its fully deprotonated $(L^2)^{2-}$ form through the acac O, imine N and deprotonated amide O in its enol form, giving two chelate rings; a folded six-membered and an almost planar five-membered. The corresponding bite angles are 85.10(8)° and 76.13(7)° which are very similar to other reported hydrazone complexes [15, 16]. The acetonate O, enolate O

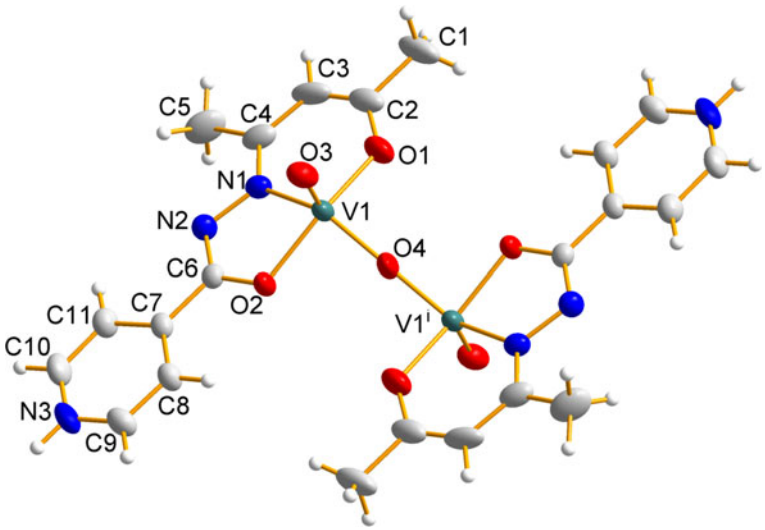


Fig. 1 Thermal ellipsoid plot (50 % probability) of [μ_2-O-$\{V^{IV}O(L^2)\}_2$] (**2**) with atom numbering (symmetry code $i = 1 - x, -y, 2 - z$); Selected bond distances (Å) and angels (°): V1-O1 1.9243(17), V1-O2 1.9424(14), V1-O3 1.6046(17), V1-O4 1.7915(4), V1-N1 2.0581(17), O2-C6 1.308(2), N2-C6 1.295(3), V1-O4-V1^i 180.00, O1-V1-O2 151.40(9), O1-V1-O3 103.26(9), O1-V1-O4 92.44(5), O1-V1-N1 85.10(8), O2-V1-O3 103.19(7), O2-V1-O4 88.62(5), O2-V1-N1 76.13(7), O3-V1-O4 109.99(6), O3-V1-N1 109.14(8), O4-V1-N1 140.29(5)

Table 1 Oxidation of hydrocarbons with aqueous 30 % H_2O_2 in the presence of catalysts **1** and **2**

No.	Substrate	Cat.	Solvent	Temp. (°C)	Conv. (%)	Epoxide/allyl alcohol selectivity (%)
1	Cyclooctene	2	$CHCl_3$	80	3	100
2	Cyclooctene	2	EtOH	80	10	100
3	Cyclooctene	2	MeOH	80	79	100
4	Cyclooctene	2	CH_3CN	80	87	100
5	Cyclooctene	2	CH_3CN	25	12	100
6	Cyclooctene	2	CH_3CN	60	51	100
7	Cyclohexene	2	CH_3CN	80	100	89[a]
8	Benzyl alcohol	2	CH_3CN	80	44	100
9	Cyclooctene	1	CH_3CN	80	80	100
10	Cyclohexene	1	CH_3CN	80	89	95[b]

Conditions: catalyst 1.71 μ mol (0.001 g/MW), substrate 1.0 mmol, H_2O_2 3.0 mmol, CH_3CN 3.0 ml, chlorobenzene (internal standars) 0.1 g, temperature 80 °C, time 5 h

[a] Other product was 2-cyclohexen-1-ol (11 %)

[b] Other product was 2-cyclohexen-1-ol (5 %)

and imine N atoms of $(L^2)^{2-}$ and the bridging oxo O atom (lying trans to the imine N) form the basal plane of the pyramid, such that the vanadium atom lies 0.540 Å above the O1/N1/O2/O4 plane toward O3. The apical position is occupied by the oxo O(3). The disposition of the oxovanadium groups is anti-coplanar which has also been observed in other dimeric oxovanadium complexes [31, 32]. The V=O distance V1-O3 is only 1.6046(17) Å which is very similar to another reported (oxo)vanadium(IV) complex [47]. The four V-O bond lengths follow the order: V-O(oxo) < V-O(bridging oxo) < V-O(acetonate) < V–O(enolate).

Catalytic activity

For our catalytic investigation, we chose alkene oxidation with the aim of obtaining the epoxide as a target product, since epoxides are one of the most useful synthetic intermediates for the preparation of oxygen-containing natural products or the production of epoxy resins, etc. The catalytic efficiency of complex **2** was studied in the oxidation of *cis*-cyclooctene in a variety of solvents (Table 2). The activity of **2** was lowest in chloroform, with a conversion of 3 % after 5 h, while the best performance of was observed in acetonitrile (conversion 87 % after 5 h), possibly due to its dielectric constant ($\varepsilon/\varepsilon_0 = 37.5$) which is the highest of all the solvents used. The optimum polarity of acetonitrile that dissolves both the alkene and H_2O_2 might be facilitating the epoxidation reaction in this case. The improvement in the conversion on changing the solvent from methanol ($\varepsilon/\varepsilon_0 = 32.7$) to acetonitrile suggests the possible involvement of acetonitrile in the oxidation. However, this idea was not supported by the absence of acetamide in the GC analyses and ^{1}H NMR spectrum of the oxidation product.

The performance of the catalyst **2** decreased at temperatures lower than 80 °C (Table 1, numbers 5 and 6). The catalytic activity of complex **1** in the oxidation of cis-cyclooctene and cyclohexene was lower than complex **2**, but its selectivity toward cyclohexene epoxide was higher (Table 1, no. 10). Cyclohexene is more prone to both epoxidation and allylic oxidation [48]. To provide evidence for or against a radical mechanism and to evaluate the catalyst selectivity, oxygenation of cyclohexene was performed (Table 1, no. 7). After 5 h, quantitative conversion of cyclohexene was obtained with excellent selectivity toward epoxide (89 %), with 2-cyclohexen-1-ol as the by-product.

Complex **2** also catalyzed the oxidation of benzyl alcohol to benzaldehyde with 100 % selectivity and conversion of 44 % (Table 1, no. 8).

Conclusions

Two complexes of V^{IV}=O and V^{V}=O with tridentate Schiff base ligands were synthesized and characterized by spectroscopic methods and X-ray analysis. The catalytic potential of the complexes were evaluated in oxidation of cycloalkenes by aqueous H_2O_2, and excellent selectivity toward epoxide was observed. Various V(IV)/V(V) catalysts have been used for the oxidation of cyclooctene and cyclohexene with H_2O_2 and TBHP (Table 2). None of the reported catalysts show such high activity and/or selectivity as the present complexes.

Experimental

Bis(acetylacetonato)oxovanadium(IV), $[VO(acac)_2]$, $CoSO_4 \cdot 7H_2O$, isonicotinic acid hydrazide, salicylaldehyde, terephthalic

Table 2 Oxidation characteristics of cyclooctene and cyclohexene by different oxovanadium complexes

No	Substrate to product	Conv. (%)	Selectivity (%)	Time (h)	Oxidant/Catalyst	TOF (h^{-1})[a]	Ref.
1	cyclooctene oxide	80	100	5	$H_2O_2/[V^VO_2(L^1)]$ (**1**)	259	This work
2		87	100	5	$H_2O_2/[\mu_2–O–\{V^{IV}O(L^2)\}_2]$ (**2**)	509	This work
3		84	100	4.5	$TBHP/V^{IV}O(L^3)_2$[b]	7	[12]
4		29	100	6	$H_2O_2/[V^VOL^4Cl]$[c]	5	[13]
5		39	100	6	$H_2O_2/[V^VOL^5Cl]$[d]	7	[13]
6	cyclohexene oxide	89	95	5	$H_2O_2/[V^VO_2(L^1)]$ (**1**)	58	This work
7		100	89	5	$H_2O_2/[\mu_2–O–\{V^{IV}O(L^2)\}_2]$ (**2**)	117	This work
8		96	2	6	$H_2O_2/[V^VO_2$(pydx-aepy)]-Y[e]	314	[49]
9		60	6	24	$H_2O_2/V^{IV}O(bpy)_2^{2+}$-Y[f]	4	[50]
10		95	7	6	H_2O_2/V^VO_2(pydx-dmen)-Y[g]	670	[51]

[a] Turnover frequency (moles of product per moles of metal catalyst per hour)

[b] TBHP = tert-butylhydroperoxide, L^3 = N-salicylidin-2-chloroethylamine

[c] $L^4 = Me_2NCH_2CH_2N(CH_2\text{-}2\text{-}O\text{-}3,5\text{-}C_6H_2^tBu_2)_2$

[d] $L^5 = Me_2NCH_2CH(CH_3)N(CH_2\text{-}2\text{-}O\text{-}3,5\text{-}C_6H_2^tBu_2)_2$

[e] Hpydx-aepy = Schiff base of pyridoxal and 2-aminoethylpyridine condensation, Y = zeolite-Y

[f] bpy = bipyridine, Y = zeolite-Y

[g] Hpydx-dmen = (E)-4-[(2-(dimethylamino)ethylimino]methyl-5-(hydroxymethyl)-2-methylpyridin-3-ol, Y = zeolite-Y

acid, alkenes, 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 FTIR spectrophotometer in the range of 4,000–400 cm^{-1}. UV–Vis spectra of solutions were recorded on a Shimadzu 160 spectrometer. The reaction products of oxidation were determined and analyzed with an HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m × 320 μm × 0.25 μm) and GC–MS (Hewlett-Packard 5973 Series MS-HP gas chromatograph with a mass-selective detector). Elemental analyses were determined on a CHN Perkin-Elmer 2400 analyzer. The vanadium content of the complexes was determined with a Varian spectrometer AAS-110.

Synthesis of $[V(O)_2(L^1)]$ (**1**)

Salicylaldehyde (18.3 mg, 0.15 mmol), isonicotinic acid hydrazide (20.6 mg, 0.15 mmol), V_2O_5 (39.8 mg, 0.15 mmol) and terephthalic acid (24.9 mg, 0.15 mmol) were placed in the main arm of a branched tube. A mixture of methanol and water (50:50, v/v) was carefully added to fill both 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 4 days, yellow crystals of $[V^V(O)_2(L^1)]$ (**1**) suitable for X-ray analysis were deposited in the cooler arm in yield 74 % (35 mg). Calc. for $C_{13}H_{10}N_3O_4V$ (323.18): C 48.3, H 3.1, N 13.0, V 15.8. Found C 48.3, H 3.3, N 12.9, V 15.9. IR (KBr, cm^{-1}): 3430 (s, vbr), 3,092 (w), 2,922 (w), 2,853 (w), 1,636 (w, C=O), 1,604 (s, -C=N-N=C-), 1,537 (m, C=N), 1,501 (m), 1,441 (s), 1,349 (s), 1,290 (m), 1,076 (m), 970 (m, V=O), 864 (vs, V=O), 765 (s), 679 (m), 617 (m), 567 (m), 456 (s). UV/Vis (in CH_3OH/H_2O, 50:50 v/v, $c = 3.1 \times 10^{-5}$ mol dm^{-3}, λ_{max} [nm] with ε [dm^3 mol^{-1} cm^{-1}]): 216 (11,600), 279 (39,400), 325 (36,000), 399 (19,516).

Synthesis of $[\mu_2–O–\{V^{IV}O(L^2)\}_2]$ (**2**)

A mixture of salicylaldehyde (35.4 mg, 0.29 mmol), i-sonicotinic acid hydrazide (39.8 mg, 0.29 mmol), vanadium(IV) oxide bis(acetylacetonate) (39.8 mg, 0.15 mmol) and cobalt(II) sulfate heptahydrate (41.0 mg, 0.15 mmol) was placed in the main arm of a branched tube. A mixture of methanol and water (50:50 v/v) was carefully added to fill both 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 4 days, light orange-red crystals of $[\mu_2–O–\{VO(L^2)\}_2]$ (**2**) suitable for X-ray analysis were deposited in the cooler arm in yield 88 % (75 mg). Calc. for C22H24N6O7V2 (586.34): C 45.1, H 4.1, N 14.3, V 17.4. Found C 45.1, H 4.1, N 14.4, V 17.7. IR (KBr, cm^{-1}): 3,515 (m), 3,364 (m, N–H), 3,215 (w, N-H), 2,992 (m), 2,927 (m), 2,869 (m), 1,663 (vs, C=O), 1,615 (m, C=N), 1,485 (m), 1,408 (m), 1,376 (s), 1,308 (vs), 1,267 (s), 1,200 (w), 1,153 (w), 1,031 (s), 979 (m, V=O), 851 (s), 754 (s), 734 (s), 699 (s), 475 (vs, V-N), 449 (s, V-O-V). UV/Vis (in CH_3OH/H_2O, 50:50 v/v,

$c = 2.0 \times 10^{-5}$ mol dm^{-3}, λmax [nm] with ε [dm^3 mol^{-1} cm^{-1}]): 228 (12,650), 279 (53,000), 325 (49,550), 397 (23,500), 569 (100, d-d).

General procedure for the oxidation of alkenes

The epoxidation of alkenes with hydrogen peroxide was performed in a 25 ml round-bottom flask. In a typical experiment, the flask was charged with 3.0 ml of CH_3CN, 1.0 mmol alkene, 0.1 g chlorobenzene as internal standard and 1.71 μmol of catalyst. To this mixture, 3 mmol of a 30 % aqueous solution of hydrogen peroxide was added. The reactant mixture was stirred vigorously for 5 h at the desired temperature. At appropriate intervals, aliquots were removed and analyzed immediately by GC. The reaction products were quantified by gas chromatography and identified by comparison with the retention time and spectral data to those of an authentic sample. Alkene conversion and oxidation product yields based on the starting substrate were quantified by comparison with chlorobenzene. In some instances, reactions were carried out on a larger scale and the epoxides were isolated to allow further confirmation of their identity and yields by NMR.

X-ray structure determination

Single crystals of **1** and **2** were selected under a polarizing microscope. X-ray quality crystals of $[\mu_2\text{–O–}\{V^{IV}O(L^2)\}_2]$ (**2**) could be grown from methanol/water (50:50 v/v). A light red crystal of **2** (0.21 × 0.07 × 0.05 mm) was used for the diffraction experiment at 173(2) K on a KappaCCD diffractometer and with monochromated Mo *K*a radiation ($\lambda = 0.71073$ Å). The structures were solved by Direct Methods with SIR97 [49] and refined with full-matrix least-squares techniques on F^2 with SHELXL-97 [50]. Crystal data for $C_{22}H_{23}N_6O_7V_2$ (**2**): $M = 585.34$, *Triclinic*, *P*1 bar, $a = 7.6360(3)$ Å, $b = 8.8857(3)$ Å, $c = 9.9135(5)$ Å, $\alpha = 86.299(3)°$, $\beta = 77.702(2)°$, $\gamma = 73.878(3)°$, $Z = 1$, μ (MoKa) = 0.794 mm^{-1}. Of the 4,291 reflections measured, 2,285 independent reflections were used to solve the structure. Based on all these data and 171 refined parameters, final $R_1 = 0.0331$, w$R_2 = 0.0858$, and the goodness-of-fit on F^2 is 1.046. The C-bonded hydrogen atoms were calculated in idealized geometries riding on their parent atoms. The O-bonded hydrogen atoms were located from the difference map and refined freely. Graphics were drawn with DIAMOND [51].

Supplementary data

Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Center (CCDC) as Supplementary Publication CCDC-887289 for **2**. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments This work was financially supported by the University of Zanjan, the Faculty of Chemistry and Biochemistry of the Ludwig-Maximilians-Universität München, and the School of Chemistry.

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