Scientific paper

Synthesis, X-Ray Crystal Structures and Catalytic Epoxidation of Oxidovanadium(V) Complexes with Aroylhydrazone and Ethyl Maltolate Ligands

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Abstract

Two oxidovanadium(V) complexes, [VOL¹L] (1) and [VOL²L] (2) (L = ethyl maltolate), derived from the aroylhydrazones 4-bromo-*N'*-(2-hydroxy-5-methylbenzylidene)benzohydrazide (H₂L¹) and *N'*-(3,5-dibromo-2-hydroxybenzylidene)-4-methoxybenzohydrazide (H₂L²), respectively, have been synthesized and characterized by elemental analysis, infrared and electronic spectroscopy. Structures of the complexes were further confirmed by single crystal X-ray determination. The V atoms in the complexes are coordinated by the ONO donor atoms of the aroylhydrazone ligand, OO donor atoms of the ethyl maltolate ligand, and one oxido O atom, forming octahedral coordination. The complexes function as effective olefin epoxidation catalysts with hydrogen peroxide as terminal oxidant and sodium hydrogen carbonate as a co-catalyst.

Keywords: Aroylhydrazone; vanadium complex; catalytic activity; crystal structure

1. Introduction

Schiff base complexes have gained remarkable attention due to their interesting applications in the development of new materials like catalysts, and biological applications like DNA cleavage, antibacterial, antiviral and antifungal agents.¹ Metal complexes of hydrazone type Schiff bases were used as catalysts for the organic synthesis, such as olefin polymerization and epoxidation reactions.² Among the various metal ions, the complexes of vanadium have received considerable interest in their biochemical significance and industrial catalytic processes.³ For instance, the use of vanadium complexes in asymmetric synthesis, in C–C bond formation as well as in C–C, C–O and C–H bond cleavages, catalytic oxidation of various olefins, oxidative halogenation and selective epoxidation of unsaturated hydrocarbons and allyl alcohols.⁴ Aroylhydrazones bearing typical –CO–NH–N=CH– group are interesting ligands in the preparation of various metal complexes which have considerable biological and catalytic properties.⁵ To date, a number of vanadium complexes have been obtained. However, the vanadium complexes with hydrazones are rarely reported with catalytic

oxidation of olefins. Recently, our research group has reported some vanadium complexes and their catalytic epoxidation property.⁶ As a continuation of such work, we report in this paper two new vanadium(V) complexes [VOL¹L] (1) and [VOL²L] (2) (L = ethyl maltolate), derived from the aroylhydrazones 4-bromo-*N'*-(2-hydroxy-5-methylbenzylidene)benzohydrazide (H₂L¹) and *N'*-(3,5-dibromo-2-hydroxybenzylidene)-4-methoxybenzohydrazide (H₂L²).

2. Experimental

2. 1. Materials and Methods

5-Methylsalicylaldehyde, 3,5-dibromosalicylaldehyde, 4-bromobenzohydrazide and 4-methoxybenzohydrazide were purchased from Sigma-Aldrich. VO(acac)₂ and the solvents with analytical reagent grade were purchased from Xiya Chemicals Co. Ltd. Microanalyses for C, H, N were carried out using a Perkin Elmer 2400 CHNS/O elemental analyzer. ¹H NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer. FT-IR spectra were recorded on a FT-IR 8400-Shimadzu as KBr discs in

the range of 400–4000 cm^{-1} . UV-Vis spectra were recorded on a Lambda 35 spectrometer. X-ray diffraction data were collected using a Bruker Smart 1000CCD diffractometer.

2. 2. Synthesis of 4-bromo-*N'*-(2-hydroxy-5-methylbenzylidene)benzohydrazide (H_2L^1)

An ethanolic solution (20 mL) containing 2-hydroxy-5-methylbenzaldehyde (1.0 mmol, 0.14 g) was added dropwise to an ethanolic solution of 4-bromobenzohydrazide (1.0 mmol, 0.22 g) with constant stirring. The mixture was refluxed for 30 min, after which the solvent was removed by rotary evaporator. The white precipitate was re-crystallized from ethanol and obtained by filtration. Yield: 0.25 g, 76%. For $\text{C}_{15}\text{H}_{13}\text{BrN}_2\text{O}_2$: anal. calcd., %: C, 54.07; H, 3.93; N, 8.41. Found, %: C, 54.26; H, 4.02; N, 8.32. FT-IR (KBr), cm^{-1} : $\nu(\text{OH})$ 3427, $\nu(\text{NH})$ 3241, $\nu(\text{CH})$ 2820–3100, $\nu(\text{C=O})$ 1645, $\nu(\text{C=N})$ 1612, $\nu(\text{C-O})$ 1157. UV-Vis data in ethanol (λ , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$)): 231 (19,270), 285 (18,125), 303 (17,430), 345 (12,653). ^1H NMR (500 MHz, $\text{DMSO}-d_6$, ppm): δ = 12.03 (s, 1H; OH), 11.12 (s, 1H; NH), 8.62 (s, 1H; CH=N), 7.87 (d, 2H; ArH), 7.73 (d, 2H; ArH), 7.45 (s, 1H; ArH), 7.12 (d, 1H; ArH), 6.95 (d, 1H; ArH), 2.32 (s, 3H, CH_3).

2. 3. Synthesis of *N'*-(3,5-dibromo-2-hydroxybenzylidene)-4-methoxybenzohydrazide (H_2L^2)

An ethanolic solution (20 mL) containing 3,5-dibromo-2-hydroxybenzaldehyde (1.0 mmol, 0.28 g) was added dropwise to an ethanolic solution of 4-methoxybenzohydrazide (1.0 mmol, 0.17 g) with constant stirring. The mixture was refluxed for 30 min, after which the solvent was removed by rotary evaporator. The white precipitate was re-crystallized from ethanol and obtained by filtration. Yield: 0.31 g, 72%. For $\text{C}_{15}\text{H}_{12}\text{Br}_2\text{N}_2\text{O}_3$: anal. calcd., %: C, 42.09; H, 2.83; N, 6.54. Found, %: C, 41.85; H, 2.92; N, 6.46. FT-IR (KBr), cm^{-1} : $\nu(\text{OH})$ 3447, $\nu(\text{NH})$ 3221, $\nu(\text{CH})$ 2820–3100, $\nu(\text{C=O})$ 1653, $\nu(\text{C=N})$ 1612, $\nu(\text{C-O})$ 1153. UV-Vis data in ethanol (λ , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$)): 221 (21,250), 272 (17,610), 310 (15,455), 332 (16,820). ^1H NMR (500 MHz, $\text{DMSO}-d_6$, ppm): δ = 12.02 (s, 1H; OH), 11.13 (s, 1H; NH), 8.67 (s, 1H; CH=N), 7.88 (d, 2H; ArH), 7.79 (s, 1H; ArH), 7.71 (s, 1H; ArH), 7.13 (d, 2H; ArH), 3.80 (s, 1H, CH_3).

2. 4. Synthesis of the complexes [VOL ^1L] (1) and [VOL ^2L] (2)

The aroylhydrazones H_2L^1 (0.10 mmol, 33 mg) or H_2L^2 (0.10 mmol, 43 mg) was dissolved in ethanol (15 mL). To each solution an ethanolic solution (10 mL) of $\text{VO}(\text{acac})_2$ (0.10 mmol, 26 mg) and ethyl maltol (0.10 mmol, 14 mg) was added with stirring. Mixtures were stirred at room temperature for 30 min to give deep brown

solution. Brown block-shaped single crystals suitable for X-ray analysis were obtained after slow evaporation of the solvent over a few days. The crystals were isolated by filtration.

Complex 1: Yield: 0.18 g, 33%. For $\text{C}_{22}\text{H}_{18}\text{BrN}_2\text{O}_6\text{V}$: anal. calcd., %: C, 49.18; H, 3.38; N, 5.21. Found, %: C, 49.35; H, 3.31; N, 5.12. FT-IR (KBr), cm^{-1} : $\nu(\text{C=N})$ 1611, $\nu(\text{C-O})$ 1176, $\nu(\text{V=O})$ 971. UV-Vis data in ethanol (λ , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$)): 271 (18,223), 325 (10,370), 410 (2,738). **Complex 2:** Yield: 0.26 g, 41%. For $\text{C}_{22}\text{H}_{17}\text{Br}_2\text{N}_2\text{O}_7\text{V}$: anal. calcd., %: C, 41.80; H, 2.71; N, 4.43. Found, %: C, 41.61; H, 2.83; N, 4.51. FT-IR (KBr), cm^{-1} : $\nu(\text{C=N})$ 1608, $\nu(\text{C-O})$ 1173, $\nu(\text{V=O})$ 972. UV-Vis data in ethanol (λ , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$)): 265 (19,560), 332 (12,451), 413 (3,890).

2. 5. X-Ray Structure Determination

Crystal structures of complexes were measured on a Bruker SMART 1000CCD diffractometer using Mo-K α radiation (λ = 0.71073 Å) and a graphite monochromator at 25 °C. Unit cell and reflection data were obtained by standard methods and are summarized in Table 1.⁷ The structures were solved, refined, and prepared for publication using the SHELXTL package (structure solution refinements and molecular graphics),⁸ and using full-matrix least-squares techniques by using F^2 with anisotropic displacement factors for all non-hydrogen atoms. The amino H atoms were located from difference Fourier maps and

Table 1. Crystal data and structure refinement for the complexes

Parameters	1	2
Molecular formula	$\text{C}_{22}\text{H}_{18}\text{BrN}_2\text{O}_6\text{V}$	$\text{C}_{22}\text{H}_{17}\text{Br}_2\text{N}_2\text{O}_7\text{V}$
Formula weight	537.23	632.13
Crystal system	Triclinic	Triclinic
Space group	$P-1$	$P-1$
a (Å)	7.4116(9)	9.7299(8)
b (Å)	11.8466(11)	11.1554(10)
c (Å)	13.2718(12)	11.4937(11)
α (°)	107.525(1)	69.303(1)
β (°)	93.496(1)	88.575(1)
γ (°)	90.253(1)	88.952(1)
V (Å ³)	1108.8(2)	1166.6(2)
Z	2	2
D_{calc} (g/cm ³)	1.609	1.800
μ (mm ⁻¹)	2.290	3.897
$F(000)$	540	624
Reflections collected	5921	10918
Independent reflection (R_{int})	4075 (0.0134)	4312 (0.0405)
Reflections observed ($I > 2\sigma(I)$)	3102	3227
Data/restraints/parameters	4075/0/291	4312/0/309
Goodness-of-fit on F^2	1.025	1.049
Final R indices ($I > 2\sigma(I)$)	0.0537, 0.1333	0.0399, 0.0829
R indices (all data)	0.0740, 0.1465	0.0644, 0.0926
Max/min $D\rho$ (e Å ⁻³)	1.034, -1.007	0.530, -0.449

refined isotropically, with N–H distances restrained to 0.90(1) Å. Positions of the remaining hydrogen atoms were calculated from the structure of the molecular skeleton and their displacement parameters were refined isotropically on a group-wise basis.

3. Results and Discussion

3. 1. Synthesis and Spectral Characterization

The two complexes were readily prepared from the reaction of the corresponding aroylhydrazone ligands and VO(acac)₂. The single crystals of the complexes are stable at ambient condition.

The $\nu(\text{C}=\text{N})$ absorptions are observed at 1611 cm^{−1} for **1** and 1608 cm^{−1} for **2**.⁹ The intense bands indicative of the C=O vibrations and the sharp bands indicative of the N–H vibrations are absent in the complexes, indicating the enolization of the aroylhydrazone ligands. The weak peaks in the low wave numbers in the region 450–700 cm^{−1} may be attributed to V–O and V–N bonds in the complexes. The complexes exhibit typical bands at 971–972 cm^{−1}, which are assigned to the V = O vibrations.¹⁰

The UV-Vis spectra of the complexes were recorded in 10^{−5} mol L^{−1} in ethanol, in the range 200–500 nm. The weak bands centered at 325–332 nm for the complexes are attributed to intramolecular charge transfer transitions from the p_π orbital on the nitrogen and oxygen to the empty d orbitals of the metal.¹⁰ The intense bands observed at 265–270 nm are assigned to intraligand π – π^* transition. The bands centered at about 410 nm are attributed to the ligand-to-metal charge transfer transitions (LMCT).¹¹

3. 2. Structure Description of the Complexes

The molecular structures of complexes **1** and **2** are shown in Figs. 1 and 2, respectively. Selected bond lengths

Fig. 1. An ORTEP diagram of complex **1** with atom labeling scheme and 30% probability thermal ellipsoids for all non-hydrogen atoms.

and angles are reported in Table 2. The V atoms in both complexes are six-coordinated in octahedral geometry, with the phenolate oxygen (O(1)), the enolate oxygen (O(2)) and the imine nitrogen (N(1)) of the aroylhydrazone ligands, and the hydroxylate oxygen (O(5)) of the ethyl maltolate ligand in the equatorial plane, and with the oxido group (O(3)) and the carbonyl oxygen (O(4)) in the axial positions. The V atoms deviated from the least-squares planes defining by the four equatorial donor at-

Fig. 2. An ORTEP diagram of complex **2** with atom labeling scheme and 30% probability thermal ellipsoids for all non-hydrogen atoms.

Fig. 3. Hydrogen bonds linked structures of complex **1**, viewed along the a axis. Hydrogen bonds are shown as dashed lines.

Fig. 4. Hydrogen bonds linked structures of complex 2, viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

oms by 0.295(2) Å for **1** and 0.290(2) Å for **2**. The bond lengths related to the V atoms are comparable to the similar vanadium complexes.^{6b,12} The benzene rings C(1)–C(6) and C(9)–C(14) form dihedral angles of 2.1(3)° for **1** and 2.7(3)° for **2**. There exists weak Br(1)···O(7)ⁱ (*i*: $-1 + x, y, 1 + z$) contact with distance of 2.96(5) Å representing 87.8 % of the sum of van der Waals radii in complex **2**.

In the crystal structure of complex **1**, the vanadium complex molecules are linked through C–H···O hydrogen bonds (Table 3) to form layers along the *ab* plane (Fig. 3). In the crystal structure of complex **2**, the vanadium complex molecules are linked through C–H···O and C–H···Br hydrogen bonds (Table 3) to form three-dimensional network (Fig. 4).

Table 3. Hydrogen bonding interactions (Å, °)

<i>D</i> –H··· <i>A</i>	<i>d</i> (<i>D</i> –H)	<i>d</i> (H··· <i>A</i>)	<i>d</i> (<i>D</i> ··· <i>A</i>)	Angle(<i>D</i> –H··· <i>A</i>)
1				
C(6)–H(6)···O(3) ⁱⁱ	0.93	2.50(3)	3.367(5)	154(6)
C(7)–H(7)···O(3) ⁱⁱⁱ	0.93	2.53(3)	3.143(5)	124(6)
C(14)–H(14)···O(6) ^{iv}	0.93	2.57(3)	3.399(5)	148(6)
C(21)–H(21)···O(4) ^v	0.93	2.42(3)	3.246(5)	148(6)
2				
C(6)–H(6)···O(3) ^{vi}	0.93	2.56(3)	3.237(4)	130(5)
C(11)–H(11)···Br(2) ^{vii}	0.93	2.80(3)	3.563(4)	140(5)
C(19)–H(19)···O(7) ^{viii}	0.93	2.47(3)	3.340(4)	156(5)

Symmetry codes: ii) $1 + x, y, z$; iii) $1 - x, 1 - y, 1 - z$; (iv) $-x, -y, 1 - z$; (v) $1 - x, -y, 1 - z$; (vi) $-x, 1 - y, 1 - z$; (vii) $1 + x, -1 + y, z$; (viii) $x, y, 1 + z$.

Table 2. Selected bond lengths (Å) and angles (°) for the complexes

	1	2
Bond lengths (Å)		
V(1)–O(1)	1.841(3)	1.847(2)
V(1)–O(3)	1.580(3)	1.583(3)
V(1)–O(5)	1.871(3)	1.863(2)
V(1)–O(2)	1.941(3)	1.921(2)
V(1)–O(4)	2.261(3)	2.259(3)
V(1)–N(1)	2.097(3)	2.090(3)
Bond angles (°)		
O(3)–V(1)–O(1)	100.96(19)	99.93(13)
O(1)–V(1)–O(5)	98.68(13)	100.77(11)
O(1)–V(1)–O(2)	155.11(14)	154.62(11)
O(3)–V(1)–N(1)	101.16(14)	99.60(13)
O(5)–V(1)–N(1)	160.03(12)	160.64(12)
O(3)–V(1)–O(4)	173.29(17)	175.04(13)
O(5)–V(1)–O(4)	77.53(10)	77.60(10)
N(1)–V(1)–O(4)	82.89(11)	84.41(11)
O(3)–V(1)–O(5)	97.98(14)	98.05(12)
O(3)–V(1)–O(2)	95.33(17)	97.23(12)
O(5)–V(1)–O(2)	97.53(12)	95.16(10)
O(1)–V(1)–N(1)	83.29(13)	83.99(11)
O(2)–V(1)–N(1)	75.14(12)	74.78(11)
O(1)–V(1)–O(4)	84.75(14)	83.34(11)
O(2)–V(1)–O(4)	80.45(12)	80.93(11)

3. 3. Catalytic Property

The catalytic experiment was carried out according to the literature method.^{6b} A mixture of CH₃OH/CH₂Cl₂ (V:V = 7:3, 1.2 mL) was used for the reactions at 25 °C. The molar ratios for the catalyst:substrate:NaHCO₃:H₂O₂ are 1:298:117:1170. The conversion was measured after 74.5 min. Both vanadium complexes have good property in the olefin oxidation processes with epoxides as the products. The results are summarized in Table 4. Interestingly, both complexes have similar catalytic properties with high epoxide yields and good selectivity toward the aliphatic and aromatic substrates. However, when H₂O₂ was used as single oxidant the catalytic efficiency is not good. When NaHCO₃ was added as a co-catalyst to the above reactions,

Table 4. The catalytic oxidation results

Substrate	Product		Conversion (%) (TON) ^a
1	> 99 (351)
		2	> 99 (367)
1	98 (343)
		2	> 99 (327)
1	93 (310)
		2	96 (307)
1	95 (282)
		2	97 (291)

^a TON = (mmol of product)/mmol of catalyst.

the efficiency of the catalytic property can increase obviously. This might be attributed to the equilibrium process between H₂O₂ and hydrogen carbonate to produce peroxydicarbonate, HCO₄[−], which is a more reactive nucleophile than H₂O₂ and facilitated the epoxidation reactions. The two vanadium complexes have better catalytic properties than the cobalt(II) complex derived from 2-bromo-*N*'-(2-hydroxy-5-methylbenzylidene)benzohydrazide,¹³ and similar catalytic properties with the oxido-vanadium(V) and dioxidomolybdenum(VI) complexes of hydrazones and Schiff bases.¹⁴

4. Conclusion

Two new similar oxido vanadium(V) complexes with aroylhydrazone ligands have been prepared and structurally characterized using X-ray structure analysis. The complexes have octahedral geometry with positions around the central atom being occupied with donor atoms of the aroylhydrazone ligand, the ethyl maltolate ligand and one oxido group. The complexes show effective catalytic property in the oxidation of various olefins to their corresponding epoxides.

Supplementary Material

CCDC reference numbers 2043121 and 2043122 contain the supplementary crystallographic data for this article. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk>, or from Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk.

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5. References

- (a) H. Zakeri, S. Rayati, G. Zarei, A. Parsa, F. Adhami, *Iran. J. Catal.* **2020**, *10*, 71–78;
(b) M. Gillard, J. Weynand, H. Bonnet, F. Loiseau, A. Decotignies, J. M. Dejeu, E. Defrancq, B. Elias, *Chem. Eur. J.* **2020**, *26*, 13849–13860; DOI:10.1002/chem.202001409
(c) A. Arunadevi, N. Raman, *J. Coord. Chem.* **2020**, *73*, 2095–2116; DOI:10.1080/00958972.2020.1824293
(d) J. M. Galvan-Hidalgo, D. M. Roldan-Marchan, A. Gonzalez-Hernandez, T. Ramirez-Apan, A. Nieto-Camacho, S. Hernandez-Ortega, E. Gomez, *Med. Chem. Res.* **2020**, *29*, 2146–2156; DOI:10.1007/s00044-020-02630-4
(e) S. Kumari, S. Ray, *New J. Chem.* **2020**, *44*, 14953–14963; DOI:10.1039/D0NJ01590C
(f) S. Q. T. Pham, C. Richardson, C. Kelso, A. C. Willis, S. F. Ralph, *Dalton Trans.* **2020**, *49*, 10360–10379. DOI:10.1039/D0DT01370F
- (a) R. Ramachandran, G. Prakash, P. Viswanathamurthi, J. G. Malecki, *Inorg. Chim. Acta* **2018**, *477*, 122–129; DOI:10.1016/j.ica.2018.03.007
(b) M. Ghorbanloo, A. M. Alamooti, *J. Porous Mater.* **2017**, *24*, 769–777; DOI:10.1007/s10934-016-0314-9
(c) S. Selvamurugan, R. Ramachandran, G. Prakash, P. Viswanathamurthi, J. G. Malecki, A. Endo, *J. Organomet. Chem.* **2016**, *803*, 119–127; DOI:10.1016/j.jorganchem.2015.11.017
(d) S. Muthumari, R. Ramesh, *RSC Advances* **2016**, *6*, 52101–52112; DOI:10.1039/C6RA06734D
(e) Y.-J. Cai, Y.-Y. Wu, F. Pan, Q.-A. Peng, Y.-M. Cui, *Acta Chim. Slov.* **2020**, *67*, 896–903; DOI:10.17344/acs.2020.5895
(f) S. Aslkhademi, N. Noshiranzadeh, M. S. Sadjadi, K. Mehriani, N. Farhadyar, *Polyhedron* **2019**, *160*, 115–122. DOI:10.1016/j.poly.2018.12.023
- (a) J. Szklarzewicz, A. Jurowska, M. Hodorowicz, R. Grybos, K. Kruczala, M. Gluch-Lutwin, G. Kazek, *J. Coord. Chem.* **2020**, *73*, 986–1008; (b) L.-P. Lu, F.-Z. Suo, Y.-L. Feng, L.-L. Song, Y. Li, Y.-J. Li, K.-T. Wang, *Eur. J. Med. Chem.* **2019**, *176*, 1–10; (c) F. Heidari, S. J. A. Fatemi, S. Y. Ebrahimipour, H. Ebrahimnejad, J. Castro, M. Dusek, V. Eigner, *Inorg. Chem. Commun.* **2017**, *76*, 1–4; (d) M. Sutradhar, L. M. D. R. S. Martins, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Coord. Chem. Rev.* **2015**, *301–302*, 200–239.
- (a) L. Schober, M. Sako, S. Takizawa, H. Groger, H. Sasai, *Chem. Commun.* **2020**, *56*, 10151–10154; DOI:10.1039/D0CC02621B
(b) U. Das, P. Pattanayak, M. K. Santra, S. Chattopadhyay, *J. Chem. Res.* **2018**, *1*, 57–62; DOI:10.3184/174751918X15168821806597
(c) Y. Sekiguchi, K. Arashiba, H. Tanaka, A. Eizawa, K. Na-

- kajima, K. Yoshizawa, Y. Nishibayashi, *Angew. Chem. Int. Ed.* **2018**, 57, 9064–9068; DOI:10.1002/anie.201802310
- (d) M. R. Maurya, N. Jangra, F. Avecilla, I. Correia, *Eur. J. Inorg. Chem.* **2019**, 2, 314–329; DOI:10.1002/ejic.201801243
- (e) J. C. Pessoa, M. R. Maurya, *Inorg. Chim. Acta* **2017**, 455, 415–428. DOI:10.1016/j.ica.2016.04.012
5. (a) D. Sadhukhan, A. Ray, G. Pilet, C. Rizzoli, G. M. Rosair, C. J. Gomez-Garcia, S. Signorella, S. Bellu, S. Mitra, *Inorg. Chem.* **2011**, 50, 8326–8339; DOI:10.1021/ic200846j
- (b) M. Bagherzadeh, M. Zare, T. Salemnoush, S. Ozkar, S. Akbayrak, *Appl. Catal. A-General* **2014**, 475, 55–62; DOI:10.1016/j.apcata.2014.01.020
- (c) V. Vrdoljak, J. Pisk, D. Agustin, P. Novak, J. P. Vukovic, D. Matkovic-Calogovic, *New J. Chem.* **2014**, 38, 6176–6185; DOI:10.1039/C4NJ01394H
- (d) M. Ghorbanloo, R. Bikas, G. Malecki, *Inorg. Chim. Acta* **2016**, 445, 8–16; DOI:10.1016/j.ica.2016.02.018
- (e) Z. Moradi-Shoeili, M. Zare, S. Akbayrak, S. Ozkar, *Transition Met. Chem.* **2017**, 42, 357–363. DOI:10.1007/s11243-017-0139-7
6. (a) D.-H. Zou, N. Sun, W. Chen, *J. Struct. Chem.* **2019**, 60, 1101–1109; DOI:10.1134/S0022476619070114
- (b) M. Liang, D.-H. Zou, *Acta Chim. Slov.* **2016**, 63, 180–185; DOI:10.17344/acsi.2015.2169
- (c) M. Liang, D.-H. Zou, *Inorg. Nano-Met. Chem.* **2017**, 47, 110–115; DOI:10.1080/15533174.2016.1149730
- (d) M. Liang, N. Sun, D.-H. Zou, *Acta Chim. Slov.* **2018**, 65, 964–969. DOI:10.17344/acsi.2018.4625
7. Bruker, SMART (Version 5. 624) and SAINT (Version 6. 04) programs using the windows NT system, Bruker AXS Inc., Madison, WI, USA, **2001**.
8. G. M. Sheldrick, *Acta Crystallogr.* **2008**, A64, 112–122. DOI:10.1107/S0108767307043930
9. D. Sadhukhan, M. Maiti, E. Zangrando, S. Pathan, S. Mitra, A. Patel, *Polyhedron* **2014**, 69, 1–9. DOI:10.1016/j.poly.2013.11.007
10. A. Sarkar, S. Pal, *Polyhedron* **2006**, 25, 1689–1694. DOI:10.1016/j.poly.2005.11.009
11. S. Roy, T. N. Mandal, K. Das, R. J. Butcher, A. L. Rheingold, S. K. Kar, *J. Coord. Chem.* **2010**, 63, 2146–2157. DOI:10.1080/00958972.2010.499457
12. (a) J.-X. Lei, J. Wang, Y. Huo, Z. You, *Acta Chim. Slov.* **2016**, 63, 670–677;
- (b) L. Xu, Y. Li, M. Duan, Y. Li, M. Han, J. Wu, Y. Wang, K. Dong, Z. You, *Polyhedron* **2019**, 165, 138–142; DOI:10.1016/j.poly.2019.03.016
- (c) Q.-C. Zhou, T.-R. Wang, H. Li, L. Chen, J.-J. Xin, S. Guo, G.-H. Sheng, Z.-L. You, *J. Inorg. Biochem.* **2019**, 196, 110680; DOI:10.1016/j.jinorgbio.2019.03.020
- (d) Z.-Q. Sun, S.-F. Yu, X.-L. Xu, X.-Y. Qiu, *Acta Chim. Slov.* **2020**, 67, 1281–1289; DOI:10.17344/acsi.2020.6236
- (e) D. L. Peng, *Russ. J. Coord. Chem.* **2020**, 46, 276–282; DOI:10.1134/S1070328420040065
- (f) L. Li, K.-W. Lu, Y.-T. Li, G.-F. Jiang, Y. Xin, L. Ye, Y. Zhang, H. Liu, C.-N. Shang, Z.-L. You, *Chin. J. Inorg. Chem.* **2017**, 33, 905–912; DOI:10.1007/s40242-017-7240-5
- (g) Y. M. Cui, Y. Q. Wang, X. X. Su, H. Huan, P. Zhang, *J. Struct. Chem.* **2019**, 60, 1299–1305. DOI:10.1134/S0022476619080092
13. F.-M. Wang, *Acta Chim. Slov.* **2016**, 63, 406–410. DOI:10.1109/TCSII.2015.2505038
14. (a) H.-Y. Liu, Y.-S. Yin, L.-J. Yang, X.-L. Zhou, Y.-F. Ye, *Acta Chim. Slov.* **2020**, 67, 130–136; DOI:10.17344/acsi.2019.5286
- (b) Q.-A. Peng, X.-P. Tan, Y.-D. Wang, S.-H. Wang, Y.-X. Jiang, Y.-M. Cui, *Acta Chim. Slov.* **2020**, 67, 644–650; DOI:10.17344/acsi.2019.5650
- (c) Q. Yang, P. Wang, Y. Lei, *Acta Chim. Slov.* **2020**, 67, 927–933; DOI:10.17344/acsi.2020.5932
- (d) M. Abdi, A. F. Shojaei, M. Ghadermazi, Z. Moradi-Shoeili, *Acta Chim. Slov.* **2020**, 67, 476–486. DOI:10.17344/acsi.2019.5466

Povzetek

Sintetizirali smo dva oksidovanadijeva(V) kompleksa, [VOL¹L] (1) in [VOL²L] (2) (L = etil maltolat), pripravljena z aroilhidrazonom 4-bromo-N²-(2-hidroksi-5-metilbenziliden)benzohidrazidom (H₂L¹) in N²-(3,5-dibromo-2-hidroksibenzilidene)-4-metoksibenzohidrazidom (H₂L²) ter ju okarakterizirali z elementno analizo, infrardečo in elektronsko spektroskopijo. Strukturi kompleksov smo nadalje potrdili z monokristalno rentgensko difrakcijo. Vanadijev atom v obeh kompleksih je koordiniran z ONO donorskimi atomi aroilhidrazonskega liganda, OO donorskimi atomi etil maltolatnega liganda in z enim oksido O atomom, ki skupaj tvorijo oktaedrično koordinacijo. Kompleksa sta učinkovita katalizatorja za epoksidacijo olefinov z vodikovim peroksidom kot oksidantom in natrijevim hidrogenkarbonatom kot kokatalizatorjem.

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