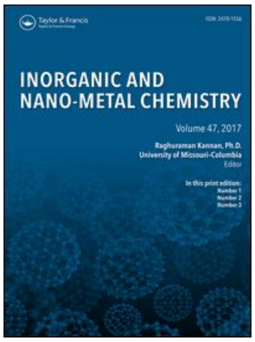


INORGANIC AND NANO-METAL CHEMISTRY

Volume 47, 2017

Inorganic and Nano-Metal Chemistry

ISSN: 2470-1556 (Print) 2470-1564 (Online) Journal homepage: http://www.tandfonline.com/loi/lsrt21

Synthesis, X-ray structural characterization, and catalytic property of binuclear oxidovanadium(V) complex with 2,4-dibromo-6-(5-methylamino-[1,3,4]thiadiazol-2-yl)phenol

Yan Lei & Qiwen Yang

To cite this article: Yan Lei & Qiwen Yang (2017) Synthesis, X-ray structural characterization, and catalytic property of binuclear oxidovanadium(V) complex with 2,4-dibromo-6-(5-methylamino-[1,3,4]thiadiazol-2-yl)phenol, Inorganic and Nano-Metal Chemistry, 47:4, 526-530, DOI: 10.1080/15533174.2016.1186078

To link to this article: http://dx.doi.org/10.1080/15533174.2016.1186078

INORGANIC AND NANO-METAL CHEMISTRY
2017, VOL. 47, NO. 4, 526–530
http://dx.doi.org/10.1080/15533174.2016.1186078

Taylor & Francis
Taylor & Francis Group

Synthesis, X-ray structural characterization, and catalytic property of binuclear oxidovanadium(V) complex with 2,4-dibromo-6-(5-methylamino-[1,3,4]thiadiazol-2-yl) phenol

Yan Lei[a,b] and Qiwen Yang[c]

[a]School of Chemistry and Environmental Engineering, Chongqing Three Gorges University, Chongqing, P. R. China; [b]Key Laboratory of Water Environment Evolution and Pollution Control in Three Gorges Reservoir, Chongqing Three Gorges University, Chongqing, P. R. China; [c]China Huaxi Engineering Design and Construction Co., Ltd., Sichuan, P. R. China

ABSTRACT
A novel binuclear oxidovanadium(V) complex $[V_2O_2(\mu\text{-}O)L_2(OEt)_2]$, where L is the deprotonated form of 2,4-dibromo-6-(5-methylamino-[1,3,4]thiadiazol-2-yl)phenol (HL), was prepared by the reaction of 2-(3,5-dibromo-2-hydroxybenzylidene)-*N*-methylhydrazinecarbothioamide (HL′) and $VO(acac)_2$ in ethanol. The ligand L′ underwent a cyclization during the coordination, to form a new ligand L. Structure of the complex was characterized by physicochemical methods and single-crystal X-ray determination. Crystal of the complex crystallizes in hexagonal space group *R*-3, with $a = b = 33.302(3)$ Å, $c = 15.308(2)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $V = 14702(3)$ Å^3, $Z = 18$, $R_1 = 0.0823$, $wR_2 = 0.2064$, $S = 1.011$. X-ray analysis indicates that the V atom in the complex is in an octahedral coordination environment, constructed by the phenolate O and thiadiazol N atoms of L, one oxido O atom, one bridging O atom, and one deprotonated ethanol O atom. The distance between the two V atoms is 3.365(1) Å. The complex has an effective catalytic property for the oxidation of several olefins.

ARTICLE HISTORY
Received 19 June 2015
Accepted 1 May 2016

KEYWORDS
Vanadium complex; thiadiazol ligand; synthesis; crystal structure; catalytic oxidation

Introduction

The coordination chemistry of vanadium has attracted considerable attention due to its biological importance [1–3] and their application as catalysts in various oxidations reactions.[4–6] Recent reports indicated that vanadium complexes with hydrazone ligands possess efficient catalytic properties in various organic syntheses.[7,8] In addition, vanadium complexes show interesting insulin-like activities.[9,10] In this study, we report the synthesis, X-ray crystal structures, and catalytic oxidation property of a novel oxidovanadium (V) complex, $[V_2O_2(\mu\text{-}O)L_2(OEt)_2]$, where L is the deprotonated form of 2,4-dibromo-6-(5-methylamino-[1,3,4]thiadiazol-2-yl)phenol (HL; Scheme 1). It is interesting that HL was formed during the coordination process of 2-(3,5-dibromo-2-hydroxybenzylidene)-*N*-methylhydrazinecarbothioamide (HL’; Scheme 2) with $VO(acac)_2$ in ethanol.

Experimental

Materials

$VO(acac)_2$, 3,5-dibromosalicylaldehyde, and *N*-methylhydrazinecarbothioamide were purchased from Aldrich. All other reagents were used as received without further purification.

Physical measurements

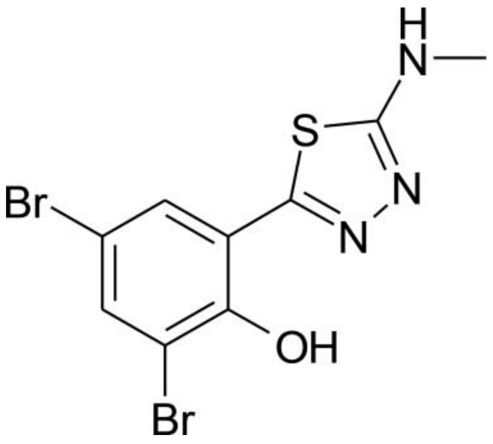
Infrared spectra (4000–400 cm^{-1}) were recorded as KBr discs with an FTS-40 Bio-Rad FT-IR spectrophotometer. Microanalyses (C, H, N) of the ligands and the complexes were carried out on a Carlo-Erba 1106 elemental analyzer. Solution electrical conductivity was measured at 298 K using a DDS-11 conductivity meter. GC analyses were performed on a Shimadzu GC-2010 gas chromatograph.

X-ray crystallography

Crystallographic data of the complex were collected on a Bruker SMART CCD area diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. Absorption corrections were applied using the multi-scan program.[11] The structure was solved by direct methods and successive Fourier difference syntheses (SHELXS-97), and anisotropic thermal parameters for all non-hydrogen atoms were refined by full-matrix least-squares procedure against F^2 (SHELXL-97).[12] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined by a riding mode, with a common thermal parameter. The ethanolate group (C20-C19-O6) is

CONTACT Yan Lei leiyan222@126.com School of Chemistry and Environmental Engineering, Chongqing Three Gorges University, Chongqing 404000, P. R. China

Supplementary data are available from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk; or *via* www.ccdc.cam.ac.uk/conts/retrieving.html) on request, quoting the deposition numbers: CCDC 1404116.



Scheme 1. HL.

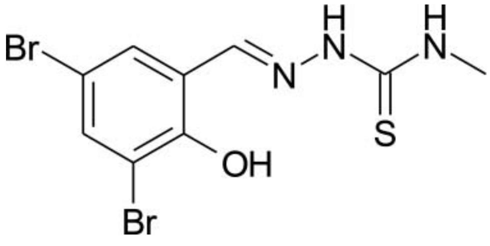
disordered over two sites with occupancies of 0.436(3) and 0.564(3). The crystallographic data and experimental details for the structure analysis are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2.

Preparation of HL′

Hot methanol solutions of 3,5-dibromosalicylaldehyde and *N*-methylhydrazinecarbothioamide (1:1) were stirred under reflux for 1 h and cooled to room temperature. The colorless precipitate was then filtered, washed with methanol, and dried *in vacuo*. Yield: 87%. Anal. calcd. for $C_9H_9Br_2N_3OS$ (%): C, 29.4; H, 2.5; N, 11.4. Found (%): C, 29.6; H, 2.5; N, 11.3. IR data (KBr, cm^{-1}): 3420m, 3151w, 1616s, 1540s, 1440m, 1397m, 1327w, 1258s, 1170m, 1113w, 1037m, 930w, 855w, 741w, 691m, 578w, 471w. ^1H NMR (300 MHz, DMSO) δ 11.59 (s, 1H, N*H*), 10.04 (s, 1H, N*H*), 8.64 (s, 1H, C*H* = N), 8.30 (s, 1H, OH), 8.10 (d, 1H, Ar*H*), 7.76 (d, 1H, Ar*H*), and 3.02 (s, 3H, C*H*$_3$).

Preparation of the complex

To a stirred solution of H_2L' (0.37 g, 1 mmol), 30-mL ethanol was added $VO(acac)_2$ (0.26 g, 1 mmol). The resulting mixture was refluxed for 1 h. The deep brown reaction solution was filtered and the solvent removed under reduced pressure, yielding brown solid of the complex. Yield: 63%. Brown single crystals suitable for X-ray diffraction were obtained by recrystallization of the solid from ethanol. Anal. calcd. for $C_{22}H_{22}Br_4N_6O_7S_2V_2$ (%): C, 27.3; H, 2.3; N, 8.7. Found (%): C, 27.1; H, 2.4; N, 8.6. IR data (KBr, cm^{-1}): 3265m, 1575s, 1530w, 1496w, 1450m, 1427s, 1393s, 1349w, 1304m, 1286s, 1239s, 1190m, 1172w, 1132w, 1087m, 1042s, 959s, 907m, 862m, 750m, 703m, and 686m.



Scheme 2. HL′.

Table 1. Crystallographic data for the single crystal of the complex.

Parameters	Value
Empirical formula	$C_{22}H_{22}Br_4N_6O_7S_2V_2$
Formula weight	968.1
Temperature (K)	298(2)
Crystal system	Hexagonal
Space group	*R*–3
a (Å)	33.302(3)
b (Å)	33.302(3)
c (Å)	15.308(2)
α (°)	90
β (°)	90
γ (°)	120
V (Å^3)	14702(3)
Z	18
F(000)	8460
Data/restraints/parameters	5698/43/412
Goodness-of-fit on F^2	1.011
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0823$
$wR_2 = 0.2064$	

Results and discussion

Synthesis

HL′ was prepared by condensation reaction of 3,5-dibromosalicylaldehyde with *N*-methylhydrazinecarbothioamide in methanol. The stoichiometric reaction of HL′ with VO(acac)$_2$ in refluxing ethanol yielded the binuclear oxidovanadium(V) complex with a ligand change from L′ to L. We have attempted to prepare and cultivate diffraction quality crystals of the complex from various solvents; yet, only ethanol is suitable. The molar conductance value of the complex measured in absolute ethanol at the concentration of 10^{-3} M is 25 Ω^{-1} cm^2 mol^{-1}, indicating the non-electrolytic nature of the complex in solution.[13] The VO(IV) in VO(acac)$_2$ was oxidized to VO(V) in the complex, which was due to the

Table 2. Selected bond distances (Å) and bond angles (°) for the complex.

V(1)-O(1)	1.968(9)	V(1)-O(3)	1.822(8)
V(1)-O(4)	1.621(10)	V(1)-O(6)	1.714(12)
V(1)-N(1)	2.169(11)	V(1)-N(5)	2.387(10)
V(2)-O(2)	1.951(8)	V(2)-O(3)	1.787(9)
V(2)-O(5)	1.583(8)	V(2)-O(7)	1.767(8)
V(2)-N(2)	2.374(11)	V(2)-N(4)	2.185(9)
O(4)-V(1)-O(6)	102.5(6)	O(4)-V(1)-O(3)	102.9(5)
O(6)-V(1)-O(3)	101.0(5)	O(4)-V(1)-O(1)	95.9(5)
O(6)-V(1)-O(1)	92.8(5)	O(3)-V(1)-O(1)	153.6(4)
O(4)-V(1)-N(1)	92.4(5)	O(6)-V(1)-N(1)	163.5(5)
O(3)-V(1)-N(1)	82.4(4)	O(1)-V(1)-N(1)	78.4(4)
O(4)-V(1)-N(5)	169.9(5)	O(6)-V(1)-N(5)	87.4(5)
O(3)-V(1)-N(5)	76.7(4)	O(1)-V(1)-N(5)	81.6(4)
N(1)-V(1)-N(5)	77.6(3)	O(5)-V(2)-O(7)	102.4(4)
O(5)-V(2)-O(3)	101.8(4)	O(7)-V(2)-O(3)	101.9(4)
O(5)-V(2)-O(2)	96.5(4)	O(7)-V(2)-O(2)	92.0(4)
O(3)-V(2)-O(2)	153.9(3)	O(5)-V(2)-N(4)	95.1(4)
O(7)-V(2)-N(4)	160.7(4)	O(3)-V(2)-N(4)	82.0(4)
O(2)-V(2)-N(4)	77.9(4)	O(5)-V(2)-N(2)	172.0(4)
O(7)-V(2)-N(2)	84.9(4)	O(3)-V(2)-N(2)	79.5(4)
O(2)-V(2)-N(2)	79.8(4)	N(4)-V(2)-N(2)	77.2(3)

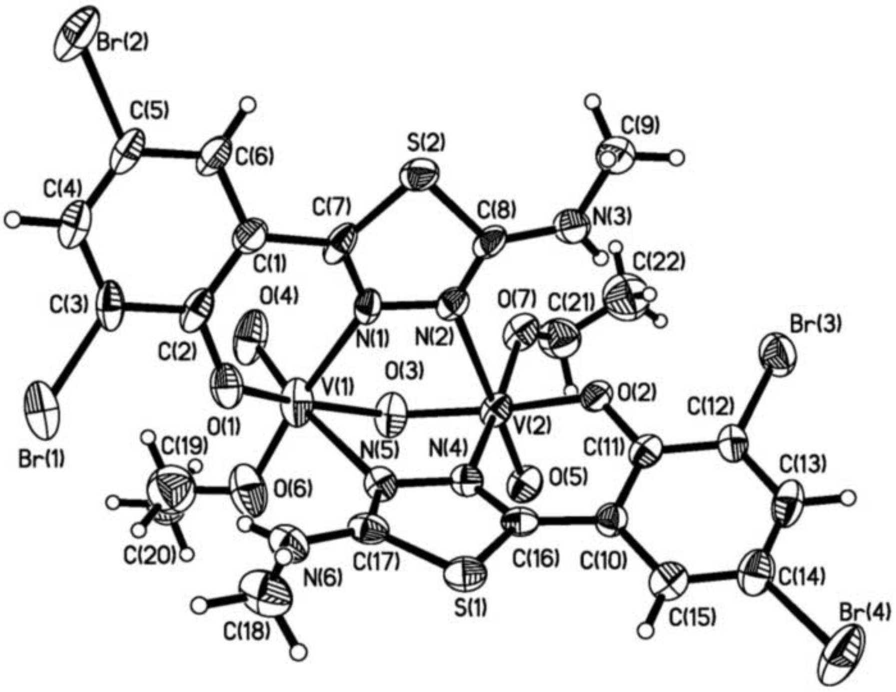


Figure 1. ORTEP diagram of the complex with 30% thermal ellipsoid.

oxidation of the oxygen in air, because no other oxidant was added during the preparation.

Description of the structure of the complex

The perspective view of the complex is shown in Figure 1. The two V atoms are bridged by one O group, and two thiadiazol groups of L, with a separation of 3.365(1) Å. The ligand L coordinates to the V atoms in its deprotonated form, with the deprotonated phenolate oxygen and thiadiazol nitrogen donor atoms. The dihedral angles between the benzene ring and the thiadiazol ring in L are 25.3(3)° and 30.0(3)°. The V atoms in the complex are in octahedral geometry, with the phenolate oxygen and thiadiazol nitrogen of L, the deprotonated ethanol oxygen, and the bridging oxygen group defining the equatorial plane, and with the thiadiazol nitrogen of another L and the oxido oxygen occupying the axial positions. The equatorial donor atoms for V(1) and V(2) form high degree of planarity, with mean deviations from the least-squares planes of 0.038(3) and 0.004(3) Å, respectively. The V(1) and V(2) atoms are displaced by 0.292(2) and 0.307(3) Å, respectively, toward the axial oxido oxygen from the least-squares planes defined by the equatorial donor atoms. The V–O and V–N bonds in the complex are comparable to those observed in other vanadium complexes.[14,15] The rather long V(1)-O(6) and V(2)-O(7) bonds and consequently weak bonding are due to the *trans* influence of the oxido groups. The distortion of the octahedral coordination of both structures can also be observed from the bond angles related to the V atoms. The N(5)–V(1)–O(3) and N(4)–V(2)–O(3) bond angles are much less than the ideal value of 90°, as a result of the strain created by the five-membered chelate ring V(1)–N(5)–N(4)–V(2)–O(3). Molecules of the complex are linked by weak Br···O and Br···S interactions, to form a three-dimensional network (Figure 2).

IR spectral characterization

The weak bands centered at 3151 cm^{-1} for HL′ and 3265 cm^{-1} for the complex can be attributed to the ν_{NH} vibrations. The hydrazone ligand shows stretching bands attributed to C=N and C—OH at 1616 and 1258 cm^{-1}, respectively.[16] The corresponding absorptions of the complex are observed at 1575 and 1239 cm^{-1}, respectively. The V=O stretching mode in the complex occurs as a single and strong band at 959 cm^{-1}.[17]

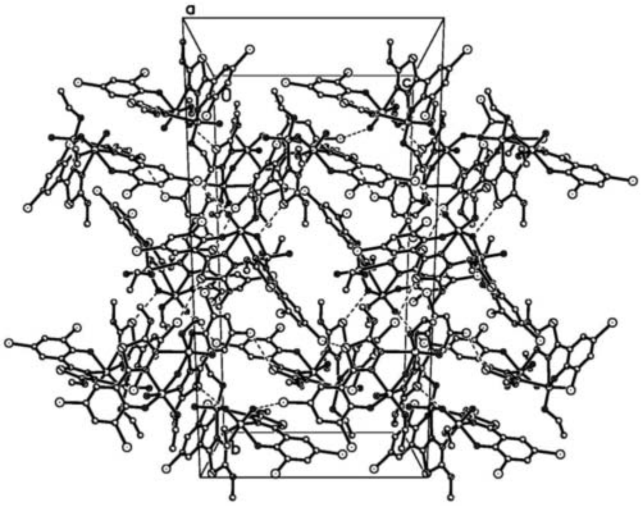
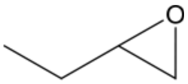
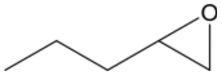
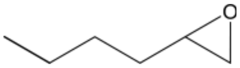
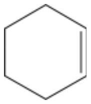
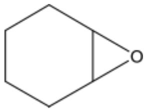
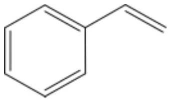
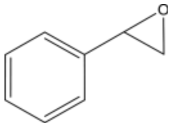
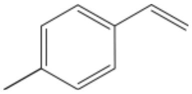
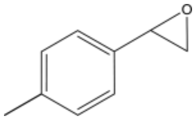
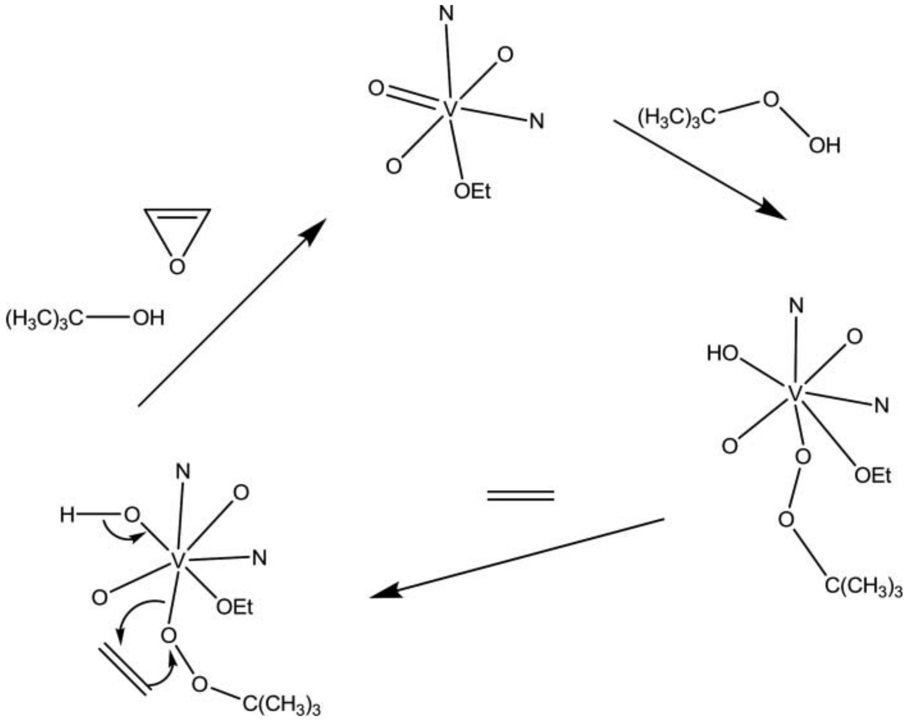


Figure 2. Molecular packing diagram of the complex.

Table 3. Catalytic oxidation results[a].

Substrate	Product	Conversion (%)[b]	Selectivity (%)
		90	100
		89	100
		85	100
		100	100
		100	100
		100	100

[a] The molar ratio of catalyst:substrate:TBHP is 1:300:1000. The reactions were performed in mixture of CH_3OH/CH_2Cl_2 (V:V = 7:3; 1.5 mL).
[b] The GC conversion (%) was measured relative to the starting substrate after 1 h.



Scheme 3. Proposed catalytic oxidation mechanism.

Catalytic epoxidation results

The catalytic experiment was carried out according to the literature method using *tert*-butyl hydrogen peroxide (TBHP) as the oxidant.[18] The results are summarized in Table 3. Oxidation of cyclohexene, vinylbenzene, and 1-methyl-4-vinylbenzene gave the corresponding epoxides in 100% yields, while in the oxidation of pent-1-ene, hex-1-ene, and hept-1-ene, the yields are less than 100%. Thus, it is obvious that the terminal double bonds are less reactive than the conjugated double bonds. This is in agreement with those reported in the literature.[18] The selectivity of the complexes for the oxidation of all substrates is 100%. The proposed catalytic mechanism is depicted in Scheme 3. At the first step, TBHP was activated by coordination to the V atoms and formation of hepta-coordinated vanadium intermediate. Then, olefin as a nucleophile attacked the electrophile oxygen atom of the coordinated TBHP. Finally, the epoxides were formed, and TBHP was reduced as *tert*-butyl alcohol.

Conclusion

A novel binuclear oxidovanadium(V) complex with 2,4-dibromo-6-(5-methylamino-[1,3,4]thiadiazol-2-yl)phenol as ligands was prepared by the reaction of 2-(3,5-dibromo-2-hydroxybenzylidene)-*N*-methylhydrazinecarbothioamide and $VO(acac)_2$ in ethanol. The original hydrazone underwent a cyclization during the coordination process, to form a new thiadiazol ligand. The complexes show effective catalytic property in the oxidation of olefins to their corresponding epoxides.

Funding

This project was supported by the Scientific and Technological Research Program of Chongqing Municipal Education Commission (Grant No. KJ1401025), the Science and Technology of Wanzhou Science Committee (Grant No. 201403062), and the Youth Foundation of Three Georges University (Grant No. 13QN13).

References

1. Sinha, A; Banerjee, K.; Banerjee, A.; Das, S.; Choudhuri, S. K. Synthesis, characterization and biological evaluation of a novel vanadium complex as a possible anticancer agent. *J. Organomet. Chem.* **2014**, *772*, 34–41.
2. Rivadeneira, J.; Barrio, D. A.; Arrambide, G.; Gambino, D.; Bruzzone, L.; Etcheverry, S. B. Biological effects of a complex of vanadium(V) with salicylaldehyde semicarbazone in osteoblasts in culture: Mechanism of action. *J. Inorg. Biochem.* **2009**, *103*, 633–642.
3. Guilherme, L. R.; Massabni, A. C.; Cuin, A.; Oliveira, L. A. A.; Castellano, E. E.; Heinrich, T. A.; Costa-Neto, C. M. Synthesis, characterization, crystal structure, and biological studies of vanadium complexes with glycolic acid. *J. Coord. Chem.* **2009**, *62*, 1561–1571.
4. Pisk, J.; Daran, J. C.; Poli, R.; Agustin, D. Pyridoxal based ONS and ONO vanadium(V) complexes: Structural analysis and catalytic application in organic solvent free epoxidation. *J. Mol. Catal. A* **2015**, *403*, 52–63.
5. Ebrahimipour, S. Y.; Abaszadeh, M.; Castro, J.; Seifi, M. Synthesis, X-ray crystal structure, DFT calculation and catalytic activity of two new oxido-vanadium(V) complexes containing ONO tridentate Schiff bases. *Polyhedron* **2014**, *79*, 138–150.
6. Romanowski, G.; Kira, J.; Wera, M. Five- and six-coordinate vanadium(V) complexes with tridentate Schiff base ligands derived from S (+)-isoleucinol: Synthesis, characterization and catalytic activity in the oxidation of sulfides and olefins. *Polyhedron* **2014**, *67*, 529–539.
7. Chalapathi, P. V.; Prathima, B.; Rao, Y. S.; Ramesh, G. N.; Reddy, A. V. Catalytic and kinetic spectrophotometric method for determination of vanadium(V) by 2,3,4-trihydroxyacetophenonephenylhydrazone. *J. Saudi Chem. Soc.* **2014**, *18*, 882–892.
8. Li, A.-M. Vanadium(V) complexes with hydrazone and benzohydroxamate ligands: Synthesis, structures and catalytic epoxidation. *J. Coord. Chem.* **2014**, *67*, 2076–2085.
9. Sostarecz, A. G.; Gaidamauskas, E.; Distin, S.; Bonetti, S. J.; Levinger, N. E.; Crans, D. C. Correlation of insulin-enhancing properties of vanadium-dipicolinate complexes in model membrane systems: Phospholipid langmuir monolayers and AOT reverse micelles. *Chem. Eur. J.* **2014**, *20*, 5149–5159.
10. Pillai, S. I.; Subramanian, S. P.; Kandaswamy, M. A novel insulin mimetic vanadium-flavonol complex: Synthesis, characterization and in vivo evaluation in STZ-induced rats. *Eur. J. Med. Chem.* **2013**, *63*, 109–117.
11. Blessing, R. H. An empirical correction for absorption anisotropy. *Acta Crystallogr. A.* **1995**, *51*, 33–38.
12. Sheldrick, G. M. *SHELXTL97, Program for Refining Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.
13. Geary, W. J. Use of conductivity measurements in organic solvents for characterisation of coordination compounds. *Coord. Chem. Rev.* **1971**, *7*, 81–122.
14. Ren, J.-Q.; Jiao, Q.-Z.; Wang, Y.-N.; Xu, F.-Y.; Cheng, X.-S.; You, Z.-L. Synthesis, structures and *Helicobacter pylori* urease inhibition of Schiff base vanadium complexes containing acetohydroxamate ligands. *Chinese J. Inorg. Chem.* **2014**, *30*, 640–648.
15. Qu, D.; Niu, F.; Zhao, X. L.; Yan, K.-X.; Ye, Y.-T.; Wang, J.; Zhang, M.; You, Z. Synthesis, crystal structures, and urease inhibition of an acetohydroxamate-coordinated oxovanadium(V) complex derived from N0-(3-bromo-2-hydroxybenzylidene)-4-methoxybenzohydrazide. *Bioorg. Med. Chem.* **2015**, *23*, 1944–1949.
16. El-Tabl, A. S.; Aly, F. A.; Shakdofa, M. M. E.; Shakdofa, A. M. E. Synthesis, characterization, and biological activity of metal complexes of azohydrazone ligand. *J. Coord. Chem.* **2010**, *63*, 700–712.
17. Prathapachandra Kurup, M. R.; Seena, E. B.; Kuriakose, M. Synthesis, spectral and structural studies of oxovanadium(IV/V) complexes derived from 2-hydroxyacetophenone-3-hydroxy-2-naphthoylhydrazone: Polymorphs of oxovanadium(V) complex [VOL(OCH3)]. *Struct. Chem.* **2010**, *21*, 599–605.
18. Rayati, S.; Rafiee, N.; Wojtczak, A. cis-Dioxo-molybdenum(VI) Schiff base complexes: Synthesis, crystal structure and catalytic performance for homogeneous oxidation of olefins. *Inorg. Chim. Acta* **2012**, *386*, 27–35.