Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

Synthesis, Structures, and Antimicrobial Activities of Dimeric Oxovanadium(V) Complexes with Tridentate Schiff Bases

Xiao-Jun Zhao [a] , Ling-Wei Xue [a] & Gan-Qing Zhao [a]

[a] College of Chemistry and Chemical Engineering, Pingdingshan University, Pingdingshan Henan, 467000, P.R. China

Accepted author version posted online: 07 Mar 2013.

To cite this article: Xiao-Jun Zhao , Ling-Wei Xue & Gan-Qing Zhao (2013): Synthesis, Structures, and Antimicrobial Activities of Dimeric Oxovanadium(V) Complexes with Tridentate Schiff Bases, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, DOI:10.1080/15533174.2012.751420

To link to this article: http://dx.doi.org/10.1080/15533174.2012.751420

Synthesis, Structures, and Antimicrobial Activities of Dimeric Oxovanadium(V) Complexes with Tridentate Schiff Bases

Xiao-Jun Zhao, Ling-Wei Xue*, Gan-Qing Zhao

College of Chemistry and Chemical Engineering, Pingdingshan University, Pingdingshan Henan 467000, P.R. China

** Corresponding author. E-mail: pdsuchemistry@163.com*

Abstract

Two new dimeric oxovanadium(V) complexes, $[VO_2L^1]_2$ (**1**) and $[VO_2L^2]_2$ (**2**), where L^1 and L^2 are the mono-anionic form of 2-{1-[2-(2-hydroxyethylamino)ethylimino]ethyl}phenol (HL^1) and 2-[1-(2-ethylaminoethylimino)ethyl]phenol (HL^2), respectively, have been synthesized and characterized by elemental analysis, FT-IR spectra, and single crystal X-ray determination. The crystal of complex (**1**) is orthorhombic: space group *Pbca*, a = 9.284(1), b = 12.733(2), c = 21.626(3) Å, V = 2556.5(7) $Å^3$, Z = 4. The crystal of complex (**2**) is orthorhombic: space group *Pbca*, a = 9.618(2), b = 12.416(3), c = 21.370(3) Å, V = 2552.0(9) $Å^3$, Z = 4. The V···V distances are 3.138(1) Å in complex (**1**) and 3.141(1) Å in complex (**2**). The V atoms in the complexes are octahedrally coordinated. The antimicrobial activity of the free Schiff bases and the complexes were studied. The complexes have potential activities against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans*.

Keywords oxovanadium, Schiff base, crystal structure, dimeric complex, antimicrobial activity

INTRODUCTION

Coordination chemistry of oxovanadium complexes with multi-dentate ligands has received considerable attention in recent years for their biological and medicinal applications.[1-4] Among the multi-dentate ligands, Schiff bases are considered as a very important class of organic compounds which have wide applications in many biological aspects. Some Schiff bases were reported to possess antibacterial, antifungal and antitumor activities.[5-7] Schiff base complexes have been used as drugs. Moreover, it is well known that some biological activities, when administered as metal complexes, are being increased.[8,9] The literature reveals that oxovanadium complexes with Schiff bases have been less studied. We report herein the synthesis, characterization, and antimicrobial activities of two new dimeric oxovanadium(V) complexes, $[VO_2L^1]_2$ (**1**) and $[VO_2L^2]_2$ (**2**), where L^1 and L^2 are the deprotonated form of 2-{1-[2-(2-hydroxyethylamino)ethylimino]ethyl}phenol (HL^1; Chart 1) and 2-[1-(2-ethylaminoethylimino)ethyl]phenol (HL^2; Chart 1), respectively.

EXPERIMENTAL

Materials and methods

2-Acetylphenol, 2-(2-aminoethylamino)ethanol, and *N*-ethylethane-1,2-diamine were purchased from Fluka. Other reagents and solvents were analytical grade and used without further purification. Elemental (C, H, and N) analyses were made on a Perkin-Elmer Model 240B automatic analyzer. Vanadium content of the complexes was determined as V_2O_5. IR spectra were recorded on an IR-408 Shimadzu 568 spectrophotometer.

Synthesis of L^1

2-Acetylphenol (1.36 g, 0.01 mmol) and 2-(2-aminoethylamino)ethanol (1.04 g, 0.01 mol) were mixed in methanol (60 mL). The mixture was stirred at reflux for 30 min and three quarter of the solvent was evaporated, to give yellow solid product of L^1, which was collected by filtration and dried in vacuum containing anhydrous $CaCl_2$. The yield is 1.89 g (85.1%). Analysis calculated for $C_{12}H_{18}N_2O_2$: C, 64.8; H, 8.2; N, 12.6%; found: C, 64.5; H, 8.2; N, 12.7%.

Synthesis of L^2

2-Acetylphenol (1.36 g, 0.01 mmol) and *N*-ethylethane-1,2-diamine (0.88 g, 0.01 mol) were mixed in methanol (60 mL). The mixture was stirred at reflux for 30 min and three quarter of the solvent was evaporated, to give yellow solid product of L^2, which was collected by filtration and dried in vacuum containing anhydrous $CaCl_2$. The yield is 1.21 g (58.8%). Analysis calculated for $C_{12}H_{18}N_2O$: C, 69.9; H, 8.8; N, 13.6%; found: C, 69.7; H, 8.9; N, 13.7%.

*Synthesis of complex (**1**)*

L^1 (0.5 mmol, 0.11 g) in methanol (20 mL) was added with stirring to $VO(acac)_2$ (0.5 mmol, 0.13 mg) in methanol (10 mL). The mixture was stirred at refluxed for 30 min to give a brown solution. The solution was left still at room temperature in air to give brown block-shaped single crystals, which were collected by filtration and dried in vacuum containing anhydrous $CaCl_2$. The yield is 0.11 g (72.4%). Analysis calculated for $C_{24}H_{34}N_4O_8V_2$: C, 47.4; H, 5.6; N, 9.2; V, 16.7%; found: C, 47.6; H, 5.7; N, 9.3; V, 16.9%.

*Synthesis of complex (**2**)*

L^2 (0.5 mmol, 0.10 g) in methanol (20 mL) was added with stirring to $VO(acac)_2$ (0.5 mmol, 0.13 mg) in methanol (10 mL). The mixture was stirred at refluxed for 30 min to give a brown solution. The solution was left still at room temperature in air to give brown block-shaped single

crystals, which were collected by filtration and dried in vacuum containing anhydrous $CaCl_2$. The yield is 0.09 g (62.5%). Analysis calculated for $C_{24}H_{34}N_4O_6V_2$: C, 50.0; H, 5.9; N, 9.7; V, 17.7%; found: C, 49.7; H, 5.9; N, 9.6; V, 17.9%.

X-ray crystal determination

Data were collected from selected crystals mounted on glass fibers. The data for the complexes were processed with SAINT[10] and corrected for absorption using SADABS.[11] Semi-empirical absorption corrections were applied with ψ scans.[12] The structures of the complexes were solved by direct method using the SHELXS-97 program and refined by full-matrix least-squares techniques on F^2 using anisotropic displacement parameters.[13] All non-hydrogen atoms were refined anisotropically. Amino H atoms in the complexes were located from difference Fourier maps and refined isotropically, with N–H distances restrained to 0.90(1) Å. The remaining hydrogen atoms were placed at the calculated positions. Crystallographic data for the complexes are listed in Table 1. Selected bond lengths and angles are given in Table 2. Hydrogen bonding information is listed in Table 3.

RESULTS AND DISCUSSION

The synthesis of the complexes is shown as Chart 2.

Crystal structure description of the complexes

The molecular structures of complexes (**1**) and (**2**) are shown in Figs. 1 and 2, respectively. The two complexes crystallize as centrosymmetric dimeric structures, with the inversion center located at the midpoint of the two V atoms. The V···V distances are 3.138(1) Å in complex (**1**) and 3.141(1) Å in complex (**2**). The V atom in each complex is octahedrally coordinated, with

phenolic O, imino N, and amine N atoms of the Schiff base ligand and one oxo O atom defining the equatorial plane, and two oxo O atoms occupying the two axial positions. The V atoms deviate from the least-squares planes defined by the four equatorial donor atoms are 0.332(1) Å in complex (**1**), and 0.354(1) Å in complex (**2**). The V–O and V–N coordinate bond lengths in the complexes are comparable to each other, as well as the corresponding values observed in other similar oxovanadium(V) complexes with Schiff bases.[14-17] There exist two N−H···O hydrogen bonds between the two [VO_2L] units, which might contribute to the formation of dimeric structures.

Infrared spectra

In the infrared spectra of the free Schiff bases, weak ν(O–H) bands were observed at about 3420–3450 cm^{-1}. The bands are absent after chelation, suggesting coordination through the deprotonated form. In the infrared spectra of the free Schiff bases, ν(C=N) bands are at about 1643 cm^{-1}, which are located at lower wave numbers for the complexes, 1612–1615 cm^{-1}, indicating that the Schiff bases are coordinated to the V atoms through azomethine N atoms. The middle ν(C–O) bands in the spectra of the complexes are located at 1125–1129 cm^{-1}. The characteristic ν(V=O) and ν(V–O) bands can be monitored at 985 and 435-470 cm^{-1}, respectively.

Antimicrobial activity

Qualitative determination of antimicrobial activity was done using the disk diffusion method.[18,19] The results are summarized in Table 4. A comparative study of minimum inhibitory concentration (MIC) values of the Schiff bases and the two complexes indicate that the cobalt complexes have better activity than the free Schiff bases. Generally, this is caused by the

greater lipophilic nature of the complexes than the ligand. Such increased activity of the metal chelates can be explained on the basis of chelating theory.[20] On chelating, the polarity of the metal atoms will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charge of the metal atoms with donor atoms. Further, it increases the delocalization of *p*-electrons over the whole chelate ring and enhances the lipophilicity of the complexes. This increased lipophilicity enhances the penetration of the complexes into lipid membrane and blocks the metal binding sites on enzymes of micro-organisms.

From Table 4, it is obvious that the complexes showed greater antimicrobial and antifungi activities against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans* when compared to the free Schiff bases. The structures of the tested compounds seem to be the principal factor influencing the antimicrobial activity. For *Staphylococcus aureus* and *Escherichia coli*, the activities of complex (**1**) are stronger than complex (**2**). And for *Candida albicans*, both complexes have similar activities. It is somewhat disappointed that even though the activities for *Staphylococcus aureus* and *Escherichia coli* of the complexes are stronger than those of the free Schiff bases, they are still much less than the control drug Tetracycline. But for *Candida albicans*, both complexes showed stronger activities than the Schiff bases and Tetracycline.

CONCLUSION

In summary, two new centrosymmetric dimeric oxovanadium(V) complexes have been prepared by reaction of the tridentate Schiff bases 2-{1-[2-(2-hydroxyethylamino)ethylimino]ethyl}phenol and 2-[1-(2-ethylaminoethylimino)ethyl]phenol

with $VO(acac)_2$. The structures of the complexes have been characterized by elemental analysis, infrared spectra and single crystal X-ray diffraction. The Schiff bases coordinate to the V atoms through the NNO donor atoms. The existence of N−H···O hydrogen bonds between two $[VO_2L]$ units might contributes to the formation of dimeric structures. Antimicrobial test shows that both complexes have potential activities against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans*.

SUPPLEMENTARY MATERIAL

CCDC-846536 for complex (**1**) and 846537 for complex (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

ACKNOWLEDGMENTS

This research was supported by the National Sciences Foundation of China (No. 20676057 and 20877036) and Top-class foundation of Pingdingshan University (No. 2008010).

REFERENCES

1. Li, X.; Lah, M.S.; Pecoraro, V.L. Vanadium complexes of the tridentate Schiff-base ligand *N*-salicylidene-*N'*-(2-hydroxyethyl)ethylenediamine-acid-base and redox conversion between vanadium(IV) and vanadium(V) imino phenolates. *Inorg. Chem.* **1988**, *27*, 4657-4664.

2. Monga, V.; Thompson, K.H.; Yuen, V.G.; Sharma, V.; Patrick, B.O.; McNeill, J.H.; Orvig, C. Vanadium complexes with mixed O,S anionic ligands derived from maltol: Synthesis, characterization, and biological studies. *Inorg. Chem.* **2005**, *44*, 2678-2688.
3. del Rio, D.; Galindo, A.; Tejedo, J.; Bedoya, F.J.; Lenco, A.; Mealli, C. Synthesis, antiapoptotic biological activity and structure of an oxo-vanadium(IV) complex with an OOO ligand donor set. *Inorg. Chem. Commun.* **2000**, *31*, 32-34.
4. Grüning, C.; Schmidt, H.; Rehder, D. A water-soluble, neutral {aqua-V^{V}}$_2$ complex with a biomimetic ONO ligand set. *Inorg. Chem. Commun.* **1999**, *2*, 57-59.
5. Sonmez, M.; Celebi, M.; Berber, I. Synthesis, spectroscopic and biological studies on the new symmetric Schiff base derived from 2,6-diformyl-4-methylphenol with *N*-aminopyrimidine. *Eur. J. Med. Chem.*, **2010**, *45*, 1935-1940.
6. Mohamed, G.G.; Omar, M.M.; Ibrahim, A.A. Biological activity studies on metal complexes of novel tridentate Schiff base ligand. Spectroscopic and thermal characterization. *Eur. J. Med. Chem.* **2009**, *44*, 4801-4812.
7. Sinha, D.; Tiwari, A.K.; Singh, S.; Shukla, G.; Mishra, P.; Chandra, H.; Mishra, A.K. Synthesis, characterization and biological activity of Schiff base analogues of indole-3-carboxaldehyde. *Eur. J. Med. Chem.* **2008**, *43*, 160-165.
8. Bagihalli, G.B.; Avaji, P.G.; Patil, S.A.; Badami, P.S. Synthesis, spectral characterization, in vitro antibacterial, antifungal and cytotoxic activities of Co(II), Ni(II) and Cu(II) complexes with 1,2,4-triazole Schiff bases. *Eur. J. Med. Chem.* **2008**, *43*, 2639-2649.
9. Sun, Y.-X. Synthesis, crystal structures and antibacterial activities of two Schiff base copper(II) complexes. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **2006**, *36*, 621-625.

10. Bruker, SMART and SAINT. *Area Detector Control and Integration Software*; Bruker Analytical X-ray Instruments Inc.: Madison, WI, USA, **1997**.

11. Sheldrick, G. M. SADABS. *Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Göttingen, Germany, **1997**.

12. North, A. C. T.; Phillips, D. C.; Mathews, F. S. A semi-empirical method of absorption correction. *Acta Crystallogr.*, **1968**, *A24*, 351-359.

13. Sheldrick, G. M. SHELXL-97. *Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, **1997**.

14. Duncan, C.A.; Copeland, E.P.; Kahwa, I.A.; Quick, A.; Williams, D.J. Unusual formation and crystal structure of a new stable dinuclear vanadium(V) amino-imino-acetal. *J. Chem. Soc. Dalton Trans.* **1997**, *6*, 917-919.

15. Mokry, L.M.; Carrano, C.J. Steric control of vanadium(V) coordination geometry - a mononuclear structural model for transition-state-analog rnase inhibitors. *Inorg. Chem.* **1993**, *32*, 6119-6121.

16. Mondal, S.; Mukherjee, M.; Dhara, K.; Ghosh, S.; Ratha, J.; Banerjee, P.; Mukherjee, A.K. Supramolecular architecture in an oxovanadium(V)-schiff base complex: Synthesis, Ab initio structure determination from X-ray powder diffraction, DNA binding and cleavage activity. *Cryst. Growth Des.* **2007**, *7*, 1716-1721.

17. Abe, Y.; Lyoda, A.; Seto, K.; Moriguchi, A.; Tanase, T.; Yokoyama, H. Synthesis, structures and ion-association properties of a series of Schiff base oxidovanadium(V) complexes with 4-substituted long alkoxy chains. *Eur. J. Inorg. Chem.* **2008**, *13*, 2148-2157.

18. Barry, A. Procedures and theoretical considerations for testing antimicrobial agents in agar media. in: Lorian (Ed.), Antibiotics in Laboratory Medicine, fifth ed. Williams and Wilkins, Baltimore, 1991.

19. Rosu, T.; Negoiu, M.; Pasculescu, S.; Pahontu, E.; Poirier, D.; Gulea, A. Metal-based biologically active agents: Synthesis, characterization, antibacterial and antileukemia activity evaluation of Cu(II), V(IV) and Ni(II) complexes with antipyrine-derived compounds. *Eur. J. Med. Chem.* **2010**, *45*, 774-781.

20. Searl, J.W.; Smith, R.C.; Wyard, S. Electron spin resonance absorption for polycrystalline substances. *J. Proc. Phys. Soc.* **1961**, *78*, 1174-1176.

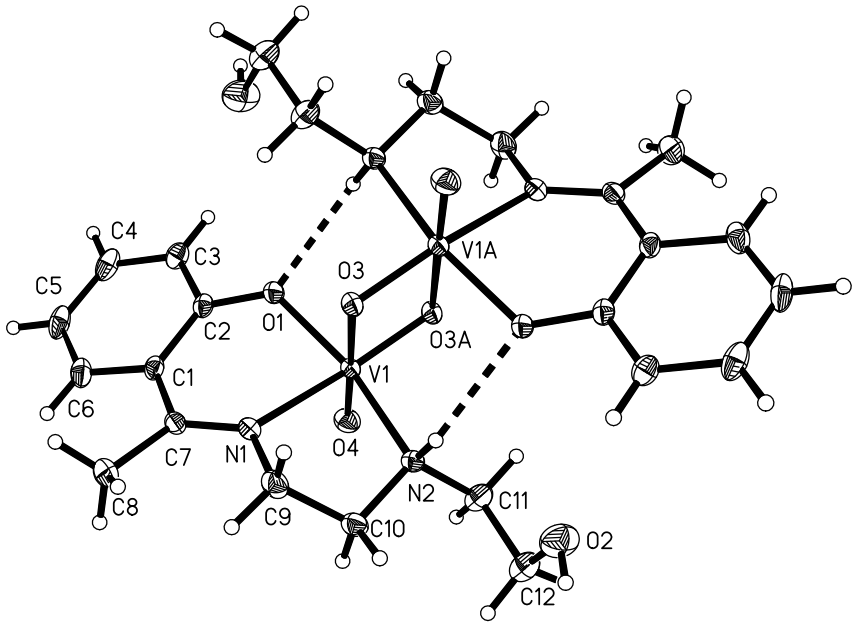

FIG. 1. Molecular structure of (**1**) at 30% probability displacement. Symmetry code for A: 2 – *x*, – *y*, – *z*.

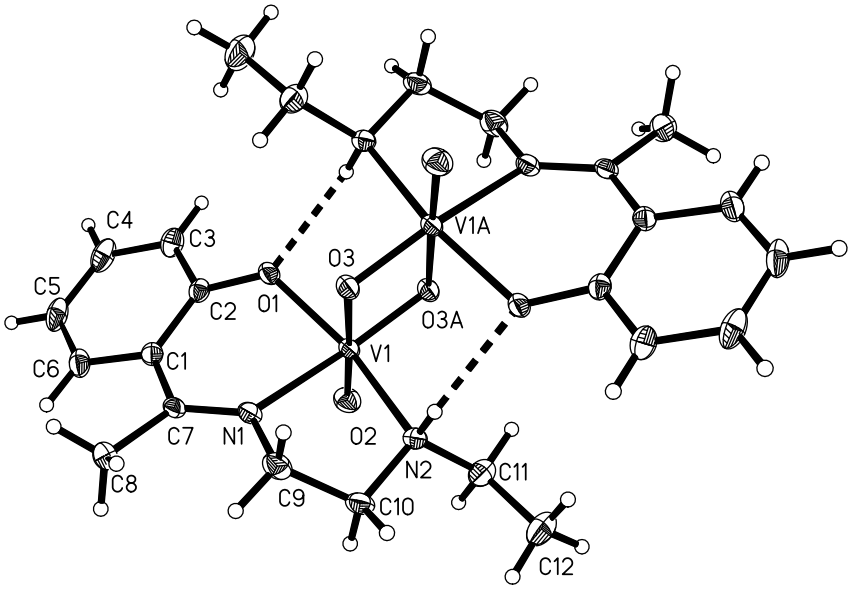

FIG. 2. Molecular structure of (**2**) at 30% probability displacement. Symmetry code for A: 2 – *x*, 1 – *y*, – *z*.

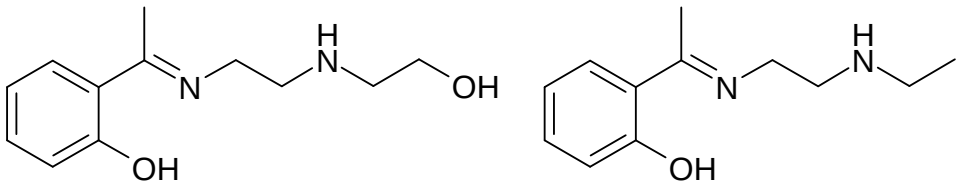

Chart 1. The Schiff bases HL^1 and HL^2

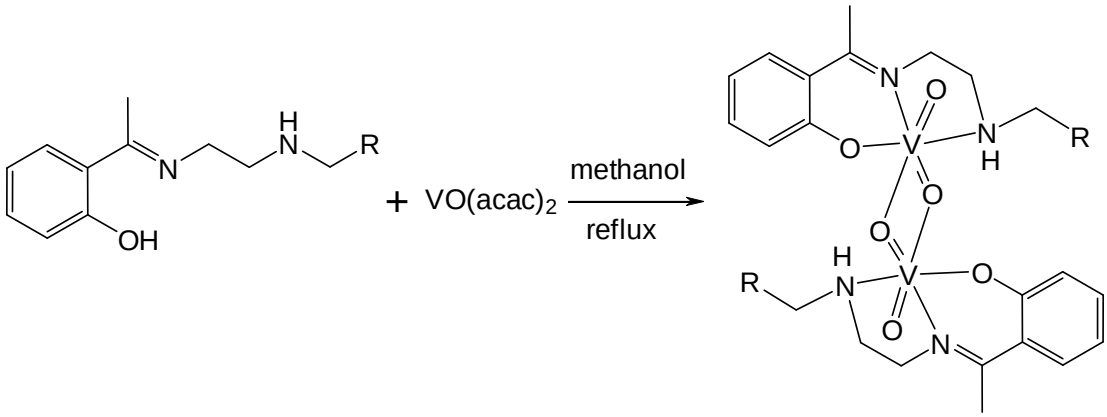

Chart 2. The preparation of the complexes [R = CH_2OH for complex (**1**) and CH_3 for complex (**2**)]

TABLE 1 Crystal and structure refinement data for (**1**) and (**2**)

Compound	(**1**)	(**2**)
CCDC	846536	846537
Molecular formula	$C_{24}H_{34}N_4O_8V_2$	$C_{24}H_{34}N_4O_6V_2$
Molecular weight	608.4	576.4
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*
a /Å	9.284(1)	9.618(2)
b /Å	12.733(2)	12.416(3)
c /Å	21.626(3)	21.370(3)
V /Å^3	2556.5(7)	2552.0(9)
Z	4	4

D_{calc} (g cm^{-3})	1.581	1.500
Crystal dimensions (mm)	0.20 × 0.20 × 0.17	0.17 × 0.15 × 0.15
μ (mm^{-1})	0.788	0.779
Radiation λ	Mo Kα (0.71073 ´)	Mo Kα (0.71073 ´)
T_{min}/T_{max}	0.8583/0.8777	0.8789/0.8921
Reflections measured	12786	14239
Range/indices (h, k, l)	-11, 11; -16, 10; -27, 23	-12, 12; -13, 15; -27, 18
θ limit (°)	2.87–27.00	2.84-27.00
Unique reflections	2778 [R_{int} = 0.0408]	2771 [R_{int} = 0.0342]
Observed reflections (I > 2σ(I))	2104	2240
Parameters	178	168
Restraints	1	1
Goodness of fit on F^2	1.046	1.050
R_1, wR_2 [$I \geq 2\sigma(I)$][a]	0.0364, 0.0893	0.0341, 0.0824
R_1, wR_2 (all data)[a]	0.0542, 0.0982	0.0458, 0.0883

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

TABLE 2 Selected bond lengths (Å) and angles (°) for (**1**) and (**2**)

(**1**)

Bond lengths			
V1-O1	1.889(2)	V1-O3	2.347(2)
V1-O3A	1.683(2)	V1-O4	1.603(2)
V1-N1	2.179(2)	V1-N2	2.169(2)
Bond angles			
O4-V1-O3A	107.1(1)	O4-V1-O1	101.8(1)
O3-V1-O1A	99.8(1)	O4-V1-N2	93.3(1)
O3-V1-N2A	92.7(1)	O1-V1-N2	156.6(1)
O4-V1-N1	95.3(1)	O3-V1-N1A	156.3(1)
O1-V1-N1	82.8(1)	N2-V1-N1	78.0(1)
O4-V1-O3	170.9(1)	O3-V1-O3A	79.0(1)
O1-V1-O3	83.5(1)	N2-V1-O3	79.5(1)
N1-V1-O3	77.8(1)		

Symmetry code for A: $2 - x, - y, - z$

(**2**)

Bond lengths			
V1-O1	1.907(2)	V1-O2	1.614(2)
V1-O3A	1.669(1)	V1-O3	2.364(2)
V1-N1	2.188(2)	V1-N2	2.161(2)
Bond angles			
O2-V1-O3A	107.7(1)	O2-V1-O1	101.8(1)
O3-V1-O1A	99.5(1)	O2-V1-N2	94.8(1)

O3-V1-N2A	91.8(1)	O1-V1-N2	155.9(1)
O2-V1-N1	95.9(1)	O3-V1-N1A	155.1(1)
O1-V1-N1	82.9(1)	N2-V1-N1	78.0(1)
O2-V1-O3	170.4(1)	O3-V1-O3A	79.1(1)
O1-V1-O3	83.3(1)	N2-V1-O3	78.0(1)
N1-V1-O3	76.6(1)		

Symmetry code for A: 2 – *x*, 1 – *y*, – *z*

TABLE 3 Hydrogen geometries for (**1**) and (**2**)

D–H···*A*	*d*(*D*–H) (Å)	*d*(H···*A*) (Å)	*d*(*D*···*A*) (Å)	Angle(*D*–H···*A*) (°)
(**1**)				
N2–H2A···O1^{i}	0.88(1)	2.33(2)	3.027(2)	136(2)
O2–H2···O3^{ii}	0.82	2.05	2.841(3)	161
(**2**)				
N2–H2···O1^{iii}	0.89(1)	2.21(2)	2.959(2)	142(3)

Symmetry codes: i) 2 – *x*, – *y*, – *z*; ii) 3/2 – *x*, 1/2 + *y*, *z*; iii) 2 – *x*, 1 – *y*, – *z*.

TABLE 4 MIC values (μg/mL) for the antimicrobial activities of the tested compounds

	Staphylococcus	*Escherichia coli*	*Candida albicans*

	aureus		
HL[1]	64	256	> 1024
HL[2]	256	128	> 1024
(**1**)	2	16	256
(**2**)	8	32	128
Tetracycline	0.32	2.12	> 1024

