Synthesis and Crystal Structures of the Dioxovanadium Complexes $[VO_2L^1]$ and $[VO_2L^2]_2^1$

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Abstract—Two new oxovanadium complexes, $[VO_2L^1]$ (I) and $[VO_2L^2]_2$ (II), where L¹ and L² are the deprotonated forms of 4-bromo-2-[(2-diethylaminoethylimino)methyl]phenol (HL¹) and 4-bromo-2-{[2-(2-hydroxyethylamino)ethylimino]methyl}phenol (HL²), respectively, have been synthesized and characterized by IR spectra and single crystal X-ray diffraction. The crystal of I is monoclinic: space group $P2_1/n$, a = 14.300(3), b = 7.010(2), c = 15.460(2) Å, $\beta = 107.401(2)^\circ$, V = 1478.7(5) Å³, Z = 4. The crystal of II is monoclinic: space group $P2_1/c$, a = 7.270(2), b = 15.373(3), c = 11.893(3) Å, $\beta = 99.302(2)^\circ$, V = 1311.8(5) Å³, Z = 2. Complex I is a mononuclear dioxovanadium(IV) complex. Complex II is a centrosymmetric dinuclear dioxovanadium(V) complex with a V…V distance of 3.117(2) Å. The V atom in I is in a distorted square-pyramidal coordination, and that in II is in an octahedral coordination. The difference in the structures of the complexes is largely induced by the hydrogen bonds during the self-assembly process.

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INTRODUCTION

Much attention has been focused on the Schiff bases and their complexes in the fields of coordination chemistry and biological chemistry [1-3]. Vanadium compounds present innumerous pharmacological applications as antitumorals, antimicrobials and insulinmimics [4-6]. It has been demonstrated that the insulin effects of promoting glucose uptake and inhibiting lipolysis can be duplicated by vanadium. It is known that there is trigonal bipyramidal vanadium within the phosphate-metabolizing enzyme [7, 8]. Mokry and coworkers reported that the steric bulk of the substituent of the benzene ring can be used to modify the coordination geometry and/or a number of vanadium atoms by preventing dimerization pathways [9]. To further explore the role in the synthesis of such complexes [10], in this paper two new oxovanadium complexes, $[VO_2L^1]$ (I) and $[VO_2L^2]_2$ (II), where L^1 and L^2 are the deprotonated forms of 4-bromo-2-[(2-diethylaminoethylimino)methyl]phenol (HL¹) and 4-bromo-2-{[2-(2-hydroxyethylamino)ethylimino]methyl}phenol (HL²), respectively, were synthesized and characterized:





EXPERIMENTAL

Materials and measurements. All chemicals used were commercially available with AR grade. Elemental analyses (CHN) were performed using a Perkin-Elmer 240 elemental analyzer. IR spectra

Synthesis of the schiff bases HL¹ and HL². Two Schiff bases were synthesized according to the general method. A methanol solution (50 mL) of 5-bromosal-

were measured with a Nicolet FT-IR 170-SX spectrophotometer using KBr pellets in the $4000-400 \text{ cm}^{-1}$ region.

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icylaldehyde (1.0 mmol, 156.6 mg) was added dropwise to a stirred methanol solution (50 mL) of organic amine (1.0 mmol, N,N-diethylethane-1,2-diamine for HL¹ and 2-(2-aminoethylamino)ethanol for HL²). The mixture was stirred for 30 min, and the solvent was then evaporated to give and orange oil product in quantitive yield.

For $C_{13}H_{19}N_2OBr$ (HL¹) anal. calcd., %: C, 52.2; H, 6.4; N, 9.4. Found, %: C, 52.0; H, 6.5; N, 9.3. For $C_{11}H_{15}N_2O_2$ Br (HL²) C, 46.0; anal. calcd., %: H, 5.3; N, 9.8. Found, %: C, 46.1; H, 5.3; N, 9.7.

IR spectrum (KBr; v, cm⁻¹): HL¹ 1635 v (C=N); HL² 3232 v(N-H), 1633 v(C=N).

Synthesis of $[VO_2L^1]$ (I). A methanol solution (5 mL) of VO(Acac)₂ (0.1 mmol, 26.5 mg) was added to a methanol solution (10 mL) of HL¹ (0.1 mmol, 30.0 mg) under stirring. The mixture was stirred at room temperature for 30 min to give a brown solution. The resulting solution was allowed to stand in air for a few days. The brown block-shaped crystals suitable for X-ray single-crystal diffraction were formed on the bottom of the vessel. The isolated product was washed with cold methanol and dried in air. The yield was 67%.

For $C_{13}H_{18}N_2O_3BrV$ anal. calcd., %: C, 41.0; H, 4.8; N, 7.3. Found, %: C, 40.8; H, 4.8; N, 7.4.

IR spectrum (v, cm⁻¹): 1636 s, 1597 m, 1519 s, 1454 s, 1417 m, 1380 s, 1322 w, 1309 w, 1271 m, 1208 m, 1157 s, 1101 w, 1071 w, 1023 m, 957 s, 895 w, 871 m, 776 m, 745 m, 683 w, 663 w, 617 w, 575 m, 543 w, 471 m, 440 m.

Synthesis of $[VO_2L^2]_2$ (II). A methanol solution (5 mL) of VO(Acac)₂ (0.1 mmol, 26.5 mg) was added to a methanol solution (10 mL) of HL² (0.1 mmol, 28.7 mg) under stirring. The mixture was stirred at room temperature for 30 min to give a brown solution.

The resulting solution was allowed to stand in air for a few days. The brown block-shaped crystals suitable for X-ray single-crystal diffraction were formed at the bottom of the vessel. The isolated product was washed with cold methanol and dried in air. The yield was 73%.

For C₂₂H₂₈N₄O₈Br₂V₂

anal. calcd., %:	C, 35.8;	Н, 3.8;	N, 7.6.
Found, %:	C, 35.7;	Н, 3.9;	N, 7.5.

IR data (cm⁻¹): 3227 sh. m, 1638 s, 1596 m, 1521 s, 1457 s, 1416 m, 1381 s, 1281 s, 1202 w, 1182 w, 1145 w, 1076 w, 1037 m, 932 s, 875 m, 862 s, 813 m, 723 m, 672 w, 567 w, 471 m, 437 w.

X-ray single-crystal diffraction. Diffraction intensities for the complexes were collected at 298(2) K using a Bruker SMART 1000 CCD area-detector with Mo K_{α} radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the SAINT program [11]. Empirical absorption corrections were applied using the SADABS program [12]. The structures were solved by direct methods and refined against F^2 by fullmatrix least-squares methods using the SHELXTL package [13]. All of the non-hydrogen atoms were refined anisotropically. The H(2) atom attached to N(2) in II was located from a difference Fourier map and refined isotropically with an N-H distance restrained to 0.90(1) Å and with $U_{iso}(H)$ set to 0.08 Å². Other H atoms in the complexes were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data for the complexes are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. Supplementary material for structures I and II has been deposited with the Cambridge Crystallographic Data Centre (nos. 820387 for (I) and 820388 for (II); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The Schiff bases HL^1 and HL^2 were prepared via the reaction of equimolar quantities of 5-bromosalicylaldehyde and N,N-diethylethane-1,2-diamine and 2-(2-aminoethylamino)ethanol, respectively, in methanol. The two complexes were readily synthesized according to the standard procedure:

Description	Value			
Parameter	Ι	II		
Formula	$C_{13}H_{18}N_2O_3BrV$	$C_{22}H_{28}N_4O_8Br_2V_2$		
FW	381.1	738.2		
Crystal shape/color	Block/brown	Block/brown		
Crystal system	Monoclinic	Monoclinic		
Space group	$P2_1/n$	$P2_{1}/c$		
a, Å	14.300(3)	7.270(2)		
b, Å	7.010(2)	15.373(3)		
<i>c</i> , Å	15.460(2)	11.893(3)		
β, deg	107.401(2)	99.302(2)		
<i>V</i> , Å ³	1478.7(5)	1311.8(5)		
Ζ	4	2		
Т, К	298(2)	298(2)		
$\rho_{calcd}, g \ cm^{-3}$	1.712	1.869		
<i>F</i> (000)	768	736		
$\mu(MoK_{\alpha}), mm^{-1}$	3.381	3.813		
Crystal size, mm	$0.27 \times 0.23 \times 0.22$	$0.27 \times 0.23 \times 0.23$		
θ Range, deg	2.32-27.00	2.65-27.00		
Index range (h, k, l)	-18, 18; -8, 8; -19, 19	-9, 8; -19, 17; -15, 8		
Type of scan	Multi-scan	Multi-scan		
T_{\min}, T_{\max}	0.462, 0.523	0.426, 0.474		
Reflections collected	11439	6659		
Independent reflections (R_{int})	3228 (0.0417)	2777 (0.0383)		
Reflections with $I \ge 2\sigma(I)$	2305	1967		
Parameters	183	176		
Restraints	0	1		
Goodness-of-fit on F^2	0.995	1.005		
Final <i>R</i> indeces $(I \ge 2\sigma(I))^*$	$R_1 = 0.0331, wR_2 = 0.0680$	$R_1 = 0.0372, wR_2 = 0.0790$		
<i>R</i> indeces (all data)*	$R_1 = 0.0590, wR_2 = 0.0763$	$R_1 = 0.0639, wR_2 = 0.0874$		
Largest diff. peak and hole, $e/Å^3$	0.292, -0.317	0.388, -0.528		

Table 1.	Crystallographic	data and experiment	details for complexes I	and II
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* $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \right]^{1/2}$, $w_1 = [\sigma^2 F_o^2 + (0.0379(F_o^2 + 2F_c^2)/3)^2]^{-1}$, $w_2 = [\sigma^2 F_o^2 + (0.0402(F_o^2 + 2F_c^2)/3)^2]^{-1}$.

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	()	···· · · · · · · · · · · · · · · · · ·				
Bond	d, Å	Bond	d, Å			
I						
V(1)–O(1)	1.9206(18)	V(1)–O(2)	1.618(2)			
V(1)–O(3)	1.6227(18)	V(1)–N(1)	2.154(2)			
V(1)–N(2)	2.209(2)					
\mathbf{I}						
V(1)–O(1)	1.917(2)	V(1)–O(3)	1.613(2)			
V(1)–O(4)	1.666(2)	V(1)–O(4) ⁱ	2.319(2)			
V(1)–N(1)	2.158(3)	V(1)-N(2) ⁱ	2.174(3)			
$V(1)\cdots V(1)^i$	3.1169(12)					
Angle	ω, deg	Angle	ω, deg			
]	[
O(2)V(1)O(3)	110.62(11)	O(2)V(1)O(1)	102.55(9)			
O(3)V(1)O(1)	97.41(9)	O(2)V(1)N(1)	113.76(9)			
O(3)V(1)N(1)	134.53(9)	O(1)V(1)N(1)	82.41(8)			
O(2)V(1)N(2)	93.92(9)	O(3)V(1)N(2)	90.88(8)			
O(1)V(1)N(2)	157.50(8)	N(1)V(1)N(2)	76.93(8)			
	I	I				
O(3)V(1)O(4)	106.59(12)	O(3)V(1)O(1)	100.95(11)			
O(4)V(1)O(1)	99.59(10)	O(3)V(1)N(1)	95.73(11)			
O(4)V(1)N(1)	155.74(10)	O(1)V(1)N(1)	85.04(10)			
O(3)V(1)N(2)	94.55(11)	O(4)V(1)N(2)	92.35(10)			
O(1)V(1)N(2)	156.76(10)	N(1)V(1)N(2)	76.21(10)			
O(3)V(1)O(4) ⁱ	173.22(10)	O(4)V(1)O(4) ⁱ	78.35(10)			
O(1)V(1)O(4) ⁱ	82.53(9)	N(1)V(1)O(4) ⁱ	78.68(9)			
N(2)V(1)O(4) ⁱ	80.45(9)					

Table 2. Selected bond lengths (Å) and bond angles (deg) for the complexes I and II^\ast

* Symmetry code: ${}^{i} 1 - x, 1 - y, 1 - z$.



Prepared brown crystals of I and II are stable in air at room temperature and soluble in DMSO, DMF, MeCN, MeOH, and EtOH and are insoluble in water.

It is very interesting that even if the Schiff bases are very similar and the synthetic procedure is identical, the final structures of the complexes are different. By contrast with HL¹, HL² possesses the hydrogen atom attached to the amino N(2) atom, which participates in the formation of the N–H…O hydrogen bond with the adjacent ligand. The two N–H…O hydrogen bonds, as well as the oxo bridges in II, made the two $[VO_2L^2]$ moieties more closely and formed a dimer. For I, there is no such hydrogen bond, which leads to the formation of a mononuclear dioxovanadium(V) complex.

The molecular structure of complex I is shown in Fig. 1. The V atom is five-coordinate in a distorted square pyramidal geometry. The basal plane is com-

posed of the phenolate O, imine N, and amine N atoms of the deprotonated Schiff base ligand L¹, and an oxo ligand O(3). The apical position is occupied by the second oxo ligand O(2). The V atom lies 0.489(2) Å from the mean plane of the basal atoms in the direction of the apical oxo ligand. The coordinate bond lengths in the complex are comparable with those observed in other similar dioxovanadium complexes [14– 16]. The τ value for the complex is 0.38, indicating a severely distorted square pyramidal coordination [17].

The molecular structure of the complex II is shown in Fig. 2. The compound is a centrosymmetric dimeric dioxovanadium(V) complex with the inversion center located at the midpoint of the two V atoms. The V…V distance is 3.117(2) Å. Each V atom in the complex is six-coordinated through three bonds to oxo groups and through bonds to the tridentate Schiff base ligand L², forming an octahedral geometry. The distance be-



Fig. 1. Molecular structure of complex I at 30% probability displacement.

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Fig. 2. Molecular structure of complex II at 30% probability displacement. Atoms labeled with the suffix A are at the symmetry position 1 - x, 1 - y, 1 - z.



Fig. 3. Molecular packing of complex II viewed along the x axis. Intermolecular hydrogen bonds are drawn as thin dashed lines.

tween atoms V(1) and O(3) is 1.613(2) Å, indicating a typical V=O bond. The O(4) atom is involved in the bridge between V(1) and V(1*A*) strongly coordinated to O(4) (1.666(2) Å) and weakly coordinated to O(4*A*) (2.319(2) Å). The coordinate bond lengths are comparable to those observed in I and other similar oxovanadium complexes [18–20]. The distortion of the octahedral coordination can be observed by the coordinate bond angles ranging from 76.2(1)° to 106.6(1)° for the perpendicular angles and from 155.7(1)° to 173.2(1)° for the diagonal angles. They form two intermolecular N–H···O hydrogen bonds between the two [VO₂L²] moieties in the complex.

In the crystal structure of complex II, the molecules are linked through intermolecular $N-H\cdots O$ and $O-H\cdots O$ hydrogen bonds to form a 3D network as shown in Fig. 3.

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REFERENCES

- 1. Shi, L., Mao, W.-J., Yang, Y., et al., *J. Coord. Chem.*, 2009, vol. 62, no. 21, p. 3471.
- Cheng, K., Zheng, Q.-Z., Qian, Y., et al., *Bioorg. Med. Chem.*, 2009, vol. 17, no. 23, p. 7861.
- 3. You, Z.-L., Shi, D.-H., Xu, C., et al., *Eur. J. Med. Chem.*, 2008, vol. 43, no. 4, p. 862.
- Xie, M., Gao, L., Li, L., et al., J. Inorg. Biochem., 2005, vol. 99, no. 2, p. 546.
- 5. Orvig, C., Caravan, P., Gelmini, L., et al., *J. Am. Chem. Soc.*, 1995, vol. 117, no. 51, p. 12759.
- Bastos, A.M.B., Silva, J.G., da Maia, P.I.S., et al., *Polyhedron*, 2008, vol. 27, no. 6, p. 1787.

- 7. Borah, B., Chen, C.W., Egan, W., et al., *Biochemistry*, 1985, vol. 24, no. 8, p. 2058.
- Wlodawer, A., Miller, M., and Sjolin, L., *Proc. Natl. Acad. Sci. USA*, 1983, vol. 80, no. 12, p. 3628.
- 9. Mokry, L.M. and Carrano, C.J., *Inorg. Chem.*, 1993, vol. 32, no. 26, p. 6119.
- 10. Liu, S.-Y., Zheng, R.-H., Ma, Y.-P., et al., *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, 2011, vol. 41, no. 1, p. 22.
- Smart and Saint, Area Detector Control and Integration Software, Madison (WI, USA): Siemens Analytical X-Ray Systems, Inc., 1996.
- 12. Sheldrick, G.M., SADABS, Program for Empirical Absorption Correction of Area Detector Data, Göttingen (Germany): Univ. of Göttingen, 1996.

- Sheldrick, G.M., SHELXTL, Version 5.1, Software Reference Manual, Madison (WI, USA): Bruker AXS, Inc., 1997.
- 14. Mokry, L.M. and Carrano, C.J., *Inorg. Chem.*, 1993, vol. 32, no. 26, p. 6119.
- 15. Baruah, B., Rath, S.P., and Chakravorty, A., *Eur. J. Inorg. Chem.*, 2004, no. 9, p. 1873.
- 16. Root, C.A., Hoeschele, J.D., Cornman, C.R., et al., *Inorg. Chem.*, 1993, vol. 32, no. 18, p. 3855.
- 17. Addison, A.W., Rao, T.N., Reedijk, J., et al., *Dalton Trans.*, 1984, no. 7, p. 1349.
- 18. Rayati, S., Sadeghzadeh, N., and Khavasi, H.R., *Inorg. Chem. Commun.*, 2007, vol. 10, no. 12, p. 1545.
- 19. Seena, E.B., Mathew, N., Kuriakose, M.R., et al., *Polyhedron*, 2008, vol. 27, no. 5, p. 1455.
- 20. Maurya, M.R., Agarwal, S., Abid, M., et al., *Dalton Trans.*, 2006, no. 7, p. 937.