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Synthesis and Crystal Structures of Dimeric Schiff Base Oxovanadium(V) Complexes with Antimicrobial Activity[1]

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Abstract—Two new dimeric oxovanadium(V) complexes, $[VO_2L^1]_2 \cdot 2H_2O$ (**I**) and $[VO_2L^2]_2$ (**II**), where L^1 and L^2 are the monoanionic form of 5-methoxy-2-[(2-methylaminoethylimino)methyl]phenol (HL^1) and 5-diethylamino-2-[(2-methylaminoethylimino)methyl]phenol (HL^2), respectively, have been synthesized and characterized by elemental analysis, FT-IR spectra, and single crystal X-ray determination. The crystal of **I** is monoclinic: space group $P2_1$, $a = 6.858(2)$, $b = 16.630(3)$, $c = 12.306(2)$ Å, $\beta = 103.985(2)°$, $V = 1361.9(5)$ Å^3, $Z = 2$. The crystal of **II** is triclinic: space group $P\bar{1}$, $a = 7.378(2)$, $b = 8.838(2)$, $c = 13.312(3)$ Å, $\alpha = 102.576(2)°$, $\beta = 92.044(2)°$, $\gamma = 113.017(2)°$, $V = 772.7(3)$ Å^3, $Z = 2$. The V···V distances are 3.140(1) Å in **I** and 3.254(1) Å in **II**. The V atoms in the complexes are in octahedral coordination. The effect of the complexes on the antimicrobial activity against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans* was studied.

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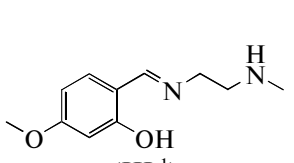
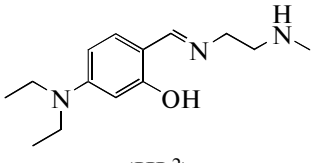
INTRODUCTION

The coordination chemistry of oxovanadium complexes with multidentate ligands has received considerable attention in recent years for their biological and medicinal applications [1–4]. Among the multidentate 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, 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 and characterization of two new dimeric oxovanadium(V) complexes, $[VO_2L^1]_2 \cdot 2H_2O$ (**I**) and $[VO_2L^2]_2$ (**II**), where L^1 and L^2 are the deprotonated form of 5-methoxy-2-[(2-methylaminoethylimino)methyl]phenol (HL^1) and 5-diethylamino-2-[(2-methylaminoethylimino)methyl]phenol (HL^2), respectively:



(HL^1)



(HL^2)

The preliminary antimicrobial activity of the complexes was studied.

EXPERIMENTAL

Materials and methods. 4-Methoxysalicylaldehyde, 4-diethylaminosalicylaldehyde, and N-methylethane-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 PerkinElmer Model 240B automatic analyzer. The vanadium content was determined as V_2O_5. IR spectra were recorded on an IR-408 Shimadzu 568 spectrophotometer.

Synthesis of HL^1. 4-Methoxysalicylaldehyde (1.52 g, 0.01 mmol) and N-methylethane-1,2-diamine (0.74 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 HL^1, which was collected by filtration

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and dried in vacuum containing anhydrous $CaCl_2$. The yield was 1.72 g (82.7%).

For $C_{11}H_{16}N_2O_2$			
anal. calcd., %:	C, 63.4;	H, 7.7;	N, 13.4.
Found, %:	C, 63.2;	H, 7.8;	N, 13.5.

Synthesis of HL². 4-Diethylaminosalicylaldehyde (1.93 g, 0.01 mmol) and N-methylethane-1,2-diamine (0.74 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 HL^2, which was collected by filtration and dried in vacuum containing anhydrous $CaCl_2$. The yield was 2.13 g (85.5%).

For $C_{14}H_{23}N_3O$			
anal. calcd., %:	C, 67.4;	H, 9.3;	N, 16.8.
Found, %:	C, 67.6;	H, 9.3;	N, 16.9.

Synthesis of I. HL^1 (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 was 0.08 g (51.9%).

For $C_{22}H_{34}N_4O_{10}V_2$				
anal. calcd., %:	C, 42.9;	H, 5.6;	N, 9.1;	V, 16.5.
Found, %:	C, 42.7;	H, 5.5;	N, 9.0;	V, 16.7.

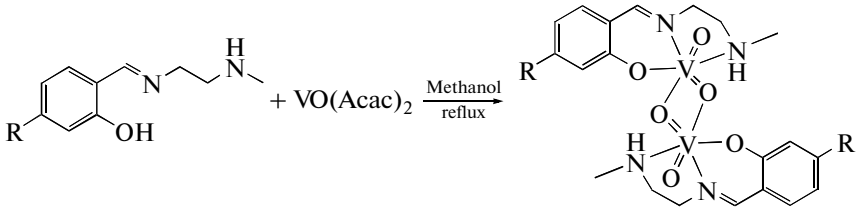
Synthesis of II. HL^2 (0.5 mmol, 0.12 g) in methanol (20 mL) was added with stirring to $VO(Acac)_2$ (0.5 mmol, 0.13 mg) in methanol (10 mL). The mixture was stirred at refluxed for 30 min to give a brown solution. The solution was left still at room temperature in air to give brown block-shaped single crystals, which were collected by filtration and dried in vacuum containing anhydrous $CaCl_2$. The yield was 0.12 g (72.7%).

For $C_{14}H_{22}N_3O_3V$				
anal. calcd., %:	C, 50.8;	H, 6.7;	N, 12.7;	V, 15.4.
Found, %:	C, 50.6;	H, 6.8;	N, 12.6;	V, 15.7.

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]. Semiempirical absorption corrections were applied with ψ scans [12]. The structures 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. The 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. The 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. Supplementary materials have been deposited with the Cambridge Crystallographic Data Centre (nos. 846538 (**I**) and 846539 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The synthesis of the complexes is shown as the following:



I: R = OCH_3; II: R = $N(CH_2CH_3)_2$

The molecular structures of the complexes **I** and **II** are shown in Figs. 1 and 2, respectively. Complex **I** contains a dimeric oxovanadium(V) complex and one disordered water molecules of crystallization. Complex **II** crystallizes as a centrosymmetric dimeric structure with the inversion center located at the mid-

Table 1. Crystallographic data and structure refinement summary for complexes **I** and **II**

Parameter	Value	
	I	**II**
Habit, colour	Block, brown	Block, brown
Formula weight	598.4	331.29
Temperature, K	298(2)	298(2)
Crystal size, mm	0.20 × 0.17 × 0.15	0.28 × 0.27 × 0.26
Radiation, λ, Å	MoK_α (0.71073)	MoK_α (0.71073)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1$	$P\bar{1}$
Unit cell dimensions:		
a, Å	6.858(2)	7.378(2)
b, Å	16.630(3)	8.838(2)
c, Å	12.306(2)	13.312(3)
α, deg		102.576(2)
β, deg	103.985(2)	92.044(2)
γ, deg	90	113.017(2)
V, Å^3	1361.9(5)	772.7(3)
Z	2	2
ρ_{calcd}, mg cm^{-3}	1.459	1.424
F(000)	620	348
Absorption coefficient, mm^{-1}	0.741	0.655
θ Range for data collection, deg	2.45–27.00	2.59–26.99
Index ranges	$-8 \le h \le 7$, $-21 \le k \le 21$, $-15 \le l \le 13$	$-9 \le h \le 9$, $-11 \le k \le 11$, $-15 \le l \le 16$
Reflections collected	8239	6251
Independent reflections	5629	3277
Reflections with $I > 2\sigma(I)$	4109	2739
Parameters	353	196
Restraints	13	1
Final R indices ($I > 2\sigma(I)$)	0.0527	0.0382
R indices (all data)	0.1320	0.0930
Goodness-of-fit	1.035	1.078
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	0.607, –0.359	0.475, –0.278

point of the two V atoms. The V···V distances are 3.139(1) Å in **I** and 3.254(1) Å in **II**. The V atom in each complex is in an octahedral coordination with the phenolate O, imine N, and amine N atoms of the Schiff base ligand and one oxo O atom defining the equatorial plane, and with 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 0.344(1) and 0.326(1) Å in **I** and 0.370(1) Å in **II**. The V–O and V–N coordinate bond lengths in the complexes are comparable to each other and are also comparable to the corresponding values observed in other similar oxovanadium(V) complexes with Schiff bases [14–17]. There exist two N–H···O hydrogen bonds between two $[VO_2L]$ units, which might contribute to the formation of dimeric structures.

In the infrared spectra of the free Schiff bases, the weak ν(O–H) bands were observed at about 3400–3450 cm^{-1}. The bands are absent after chelation, suggesting the coordination through the deprotonated form. In the infrared spectra of the free Schiff bases, the ν(C=N) bands are at about 1645 cm^{-1}, which are located at lower wave numbers for the comlexes, 1615–1618 cm^{-1}, indicating that the Schiff bases are coordinated to the V atoms through the azomethine N atoms. The middle ν(C–O) bands in the spectra of the complexes are located at 1123–1133 cm^{-1}. The characteristic ν(V=O) and ν(V–O) bands can be monitored at 985 and 433–478 cm^{-1}, respectively.

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 complexes indicates that the complexes have much better activity than the free Schiff bases. Generally, this is caused by the greater lipophilic nature of the complex 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 derealization of *p*-electrons over the whole chelate ring and enhances the lipophilicity of the complex. This increased lipophilicity enhances the penetration of the complex into the lipid membrane and blocks the metal binding sites on enzymes of microorganisms.

From Table 4, it is obvious that the complexes show greater antimicrobial activities against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans*, when compared to the free Schiff bases. As for the complexes, there are no obvious difference for the activities

Table 2. Coordinate bond distances (Å) and angles (deg) for complexes **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
	I		
V(1)–O(1)	1.909(4)	V(1)–O(5)	1.609(4)
V(1)–O(7)	1.689(3)	V(1)–N(1)	2.156(4)
V(1)–N(2)	2.158(5)	V(1)–O(6)	2.339(4)
V(2)–O(3)	1.927(4)	V(2)–O(6)	1.680(3)
V(2)–O(8)	1.605(4)	V(2)–O(7)	2.331(4)
V(2)–N(3)	2.151(4)	V(2)–N(4)	2.167(5)
	II		
V(1)–O(1)	1.917(2)	V(1)–O(2)	1.612(2)
V(1)–O(3)	1.664(2)	V(1)–N(1)	2.153(2)
V(1)–N(2)	2.146(2)	V(1)–O(3*A*)	2.458(2)
Angle	ω, deg	Angle	ω, deg
	I		
O(5)V(1)O(7)	106.8(2)	O(5)V(1)O(1)	102.2(2)
O(7)V(1)O(1)	98.2(2)	O(5)V(1)N(1)	97.6(2)
O(7)V(1)N(1)	154.1(2)	O(1)V(1)N(1)	84.4(2)
O(5)V(1)N(2)	92.6(2)	O(7)V(1)N(2)	93.1(2)
O(1)V(1)N(2)	157.7(2)	N(1)V(1)N(2)	77.2(2)
O(5)V(1)O(6)	170.4(2)	O(7)V(1)O(6)	78.3(2)
O(1)V(1)O(6)	84.8(2)	N(1)V(1)O(6)	76.3(2)
N(2)V(1)O(6)	78.8(2)	O(8)V(2)O(6)	105.7(2)
O(8)V(2)O(3)	101.8(2)	O(6)V(2)O(3)	99.4(2)
O(8)V(2)N(3)	96.2(2)	O(6)V(2)N(3)	156.7(2)
O(3)V(2)N(3)	83.6(2)	O(8)V(2)N(4)	92.7(2)
O(6)V(2)N(4)	94.0(2)	O(3)V(2)N(4)	156.7(2)
N(3)V(2)N(4)	76.8(2)	O(8)V(2)O(7)	171.0(2)
O(6)V(2)O(7)	78.7(2)	O(3)V(2)O(7)	85.0(2)
N(3)V(2)O(7)	78.5(2)	N(4)V(2)O(7)	79.1(2)
	II		
O(2)V(1)O(3)	107.4(1)	O(2)V(1)O(1)	102.9(1)
O(3)V(1)O(1)	98.3(1)	O(2)V(1)N(2)	92.7(1)
O(3)V(1)N(2)	91.5(1)	O(1)V(1)N(2)	158.0(1)
O(2)V(1)N(1)	100.1(1)	O(3)V(1)N(1)	150.7(1)
O(1)V(1)N(1)	85.1(1)	N(2)V(1)N(1)	77.0(1)
O(2)V(1)O(3*A*)	169.2(1)	O(3)V(1)O(3*A*)	77.4(1)
O(1)V(1)O(3*A*)	85.7(1)	N(2)V(1)O(3*A*)	77.3(1)
N(1)V(1)O(3*A*)	73.8(1)		

* Symmetry code for *A*: $1-x, -y, -z$.

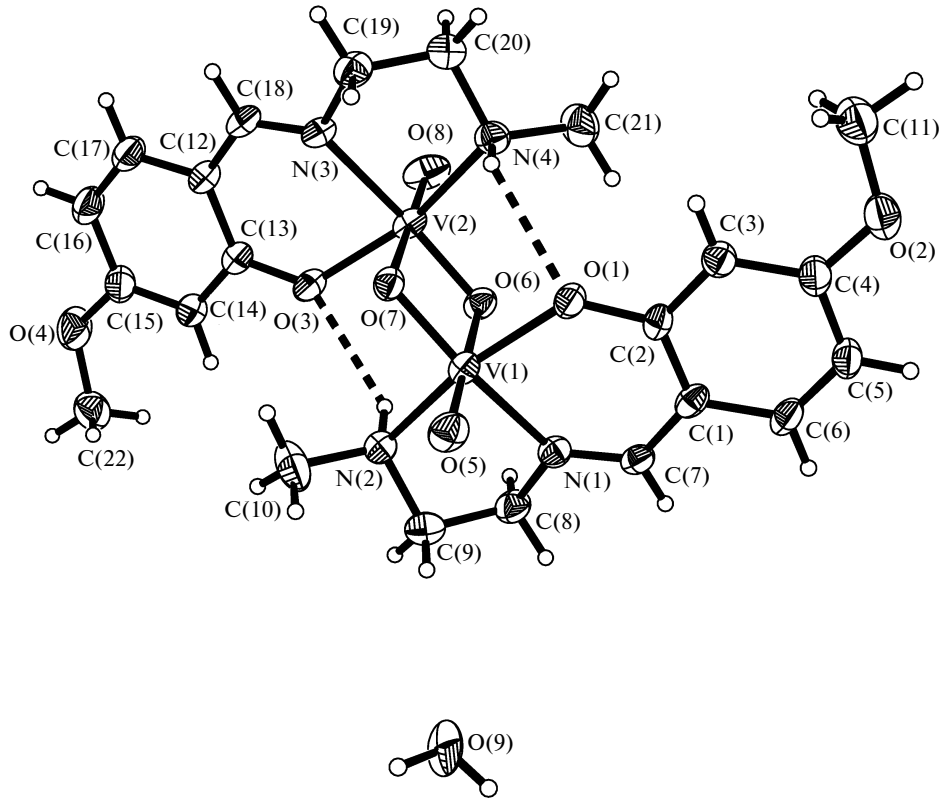


Fig. 1. Molecular structure of **I** at 30% probability displacement.

against *Staphylococcus aureus* and *Escherichia coli*, however, **II** shows stronger activity than **I** for *Candida albicans*.

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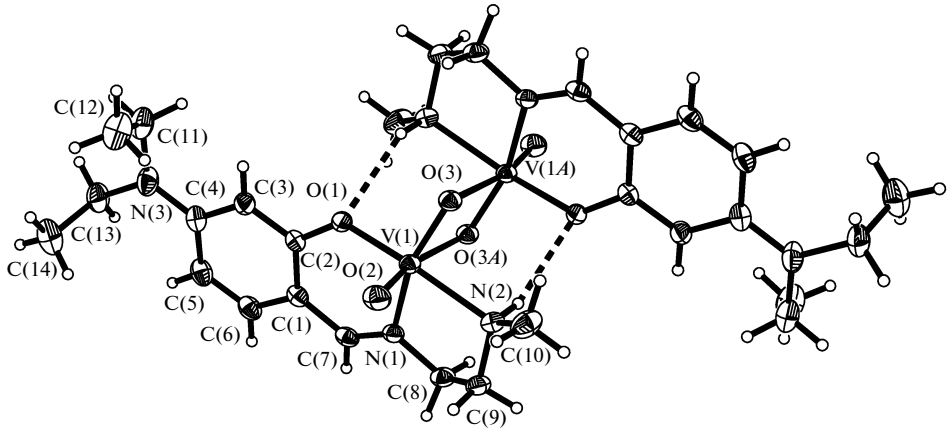

Fig. 2. Molecular structure of **II** at 30% probability displacement.

Table 3. Geometric parameters of hydrogen bonds for complexes **I** and **II***

Contect D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
		I		
O(9)–H(9D)···O(6)[i]	0.85	2.02	2.771(8)	146
N(2)–H(2)···O(6)	0.93(8)	2.22(7)	2.858(6)	126(6)
N(2)–H(2)···O(3)	0.93(8)	2.35(7)	3.067(6)	134(6)
N(4)–H(4)···O(7)	0.83(7)	2.37(8)	2.866(6)	119(6)
N(4)–H(4)···O(1)	0.83(7)	2.43(7)	3.022(6)	129(6)
		II		
N(2)–H(2)···O(3)[ii]	0.90(1)	2.39(3)	2.886(3)	115(2)
N(2)–H(2)···O(1)[ii]	0.90(1)	2.31(2)	3.050(3)	139(3)

* Symmetry code: [i] $-x, 1/2 + y, 1 - z$; [ii] $1 - x, -y, -z$.

Table 4. MIC values (μg/mL) for antimicrobial activities of the compounds

Compound	*Staphylococcus aureus*	*Escherichia coli*	*Candida albicans*
HL^1	32	64	>512
HL^2	32	128	>512
I	4	8	128
II	4	8	64
Tetracycline	0.32	2.12	>512

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