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Synthesis, Crystal Structure, and Antibacterial Activity of a Dinuclear Oxidovanadium(V) Complexes Derived from 2-[(2-Methylaminoethylimini)methyl]-4-Trifluoromethoxyphenol[1]

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Abstract—A new dinuclear oxidovanadium(V) complex, $[V_2O_2(\mu\text{-}O)_2L_2]$, where L is the monoanionic form of 2-[(2-methylaminoethylimini)methyl]-4-trifluoromethoxyphenol (HL), was prepared and characterized by IR, UV-Vis and ^{1}H NMR spectra, as well as single crystal X-ray diffraction (CIF file CCDC no. 1567062). The complex crystallizes as the monoclinic space group $P2_1/c$ with unit cell dimensions a = 12.974(3), b = 6.572(2), c = 17.205(3) Å, β = 107.300(3)°, V = 1400.7(5) Å^3, Z = 2, R_1 = 0.0879, wR_2 = 0.1208, GOOf = 1.068. X-ray analysis indicates that the complex is a centrosymmetric dinuclear oxidovanadium(V) species with the V atoms in octahedral coordination. The Schiff base and the complex were evaluated for their antibacterial (*Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas fluorescence*) activities. The complex has the most activity against *B. subtilis* with the MIC value of 1.2 μg mL^{-1}.

Keywords: Schiff base, oxidovanadium complex, dinuclear complex, crystal structure, antibacterial activity

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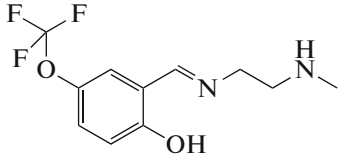
INTRODUCTION

Schiff bases are a kind of biological active compound, which can be prepared by the condensation reaction of carbonyl-containing compounds with various amines. The compounds have attracted considerable attention for their wide range of biological activities [1–7]. It was reported that compounds bearing electron-withdrawing groups can improve their antimicrobial activities [8, 9]. Rai and co-workers reported a series of fluoro, chloro, bromo, and iodo-substituted compounds, and found that they have significant antimicrobial activities [10]. Vanadium complexes with Schiff bases have been reported to have interesting antibacterial activities [11–14]. In the present work, a new dinuclear oxidovanadium(V) complex, $[V_2O_2(\mu\text{-}O)_2L_2]$, where L is the monoanionic form of 2-[(2-methylaminoethylimini)methyl]-4-trifluoromethoxyphenol (HL), is reported (Scheme 1).



Scheme 1.

[1] The article is published in the original.

EXPERIMENTAL

Materials and methods. 5-Trifluoromethoxysalicylaldehyde, *N*-methylethane-1,2-diamine, and vanadyl acetylacetonate were purchased from Sigma-Aldrich and used as received. All other reagents were of analytical reagent grade. Elemental analyses of C, H, and N were carried out in a Perkin-Elmer automated model 2400 Series II CHNS/O analyzer. FT-IR spectra were obtained on a Perkin-Elmer 377 FT-IR spectrometer with samples prepared as KBr pellets. UV-Vis spectra were obtained on a Lambda 900 spectrometer. ^{1}H NMR data was recorded on a Bruker 300 MHz spectrometer. X-ray diffraction was carried out on a Bruker APEX II CCD diffractometer.

Synthesis of the complex. 5-Trifluoromethoxysalicylaldehyde (0.01 mol, 2.06 g) and *N*-methylethane-1,2-diamine (0.01 mol, 0.74 g) were dissolved in methanol. Then, vanadyl acetylacetonate (0.01 mol, 2.65 g) was added and stirred for 1 h to give brown solution. Single crystals of the complex, suitable for X-ray diffraction, were grown from the solution upon slowly evaporation for a week. The yield was 1.22 g (35%).

Table 1. Crystallographic and structure refinement for the complex

Parameter	Value
Formula weight	688.33
Crystal shape/color	Block/brown
T, K	298(2)
Crystal dimensions, mm	0.17 × 0.15 × 0.15
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	12.974(3)
b, Å	6.572(2)
c, Å	17.205(3)
β, deg	107.300(3)
V, Å^3	1400.7(5)
Z	2
ρ_{calcd}, g cm^{-3}	1.632
$\mu(MoK_\alpha)$, mm	0.759
$F(000)$	696
Measured reflections	4932
Unique reflections	2254
Observed reflections ($I \geq 2\sigma(I)$)	1600
Mininimum and maximum transmission	0.8818 and 0.8947
Parameters	222
Restraints	67
Goodness of fit on F^2	1.072
R_1, wR_2 ($I \geq 2\sigma(I)$)*	0.0879, 0.2065
R_1, wR_2 (all data)*	0.1209, 0.2378

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

IR data (ν, cm^{-1}): 3233 w ν(N–H), 1635 s ν(C=N), 937 m ν(V=O), 453 w ν(V–O). UV-Vis data (CH_3CN; λ_{max}, nm): 270, 350, 435.

For $C_{22}H_{24}F_6N_4O_8V_2$			
Anal. calcd., %	C, 38.39	H, 3.51	N, 8.14
Found, %	C, 38.23	H, 3.63	N, 8.25

X-ray crystallography. X-ray diffraction was carried out at a Bruker APEX II CCD area diffractometer equipped with MoK_α radiation (λ = 0.71073 Å). The collected data were reduced with SAINT [15], and multi-scan absorption correction was performed using SADABS [16]. The structures of the complexes were solved by direct method, and refined against F^2 by full-matrix least-squares method using SHELXTL [17]. All of the non-hydrogen atoms were refined anisotropically. The amino hydrogen atoms were located from electronic density maps and refined isotropically with N–H distances restrained to 0.90(1) Å. The remaining hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The trifluoromethyl group is disordered over two sites with occupancies of 0.431(2) and 0.569(2). The crystallographic data and refinement parameters for the compounds are listed in Table 1. Selected bond lengths and angles are listed in Table 2.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1567062; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Antimicrobial assay. The antibacterial activities of the compounds were tested against *B. subtilis*, *S. aureus*, *E. coli*, and *P. fluorescence* using MH (Mueller–Hinton) medium. The MIC values of the tested compounds were determined by a colorimetric method using the dye MTT [18]. A stock solution of the compound (150 μg mL^{-1}) in DMSO was prepared and graded quantities (75, 37.5, 18.8, 9.4, 4.7, 2.3, 1.2, 0.59 μg mL^{-1}) were incorporated in specified quantity of the corresponding sterilized liquid medium. A spec-

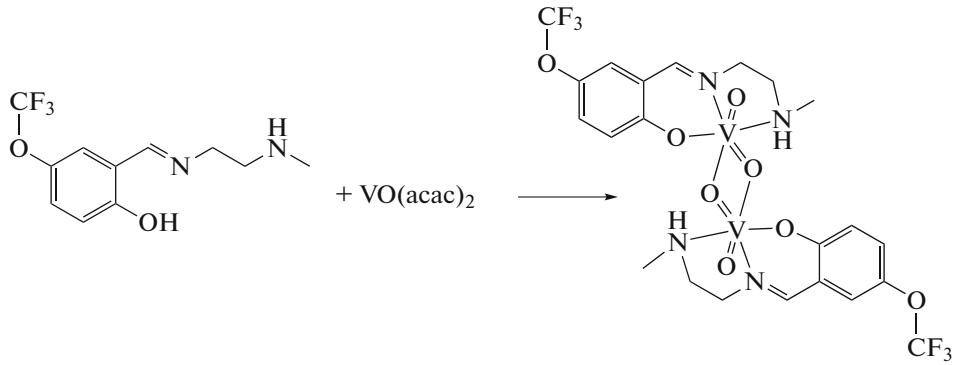
Table 2. Selected bond distances (Å) and angles (deg) for the complexes

Bond	*d*, Å	Bond	*d*, Å
V(1)–O(1)	1.918(5)	V(1)–O(3*A*)	1.672(4)
V(1)–O(3)	2.330(4)	V(1)–O(4)	1.605(5)
V(1)–N(1)	2.178(5)	V(1)–N(2)	2.144(6)
Angle	ω, deg	Angle	ω, deg
O(4)V(1)O(3*A*)	107.6(2)	O(4)V(1)O(1)	102.0(2)
O(3)V(1)O(1*A*)	98.3(2)	O(4)V(1)N(2)	92.9(2)
O(3)V(1)N(2*A*)	94.3(2)	O(1)V(1)N(2)	156.6(2)
O(4)V(1)N(1)	95.3(2)	O(3)V(1)N(1*A*)	156.1(2)
O(1)V(1)N(1)	83.0(2)	N(2)V(1)N(1)	77.7(2)
O(4)V(1)O(3)	169.3(2)	O(3)V(1)O(3*A*)	79.25(19)
O(1)V(1)O(3)	84.87(18)	N(2)V(1)O(3)	78.12(19)
N(1)V(1)O(3)	77.12(16)		

ified quantity of the medium containing the compound was poured into micro-titration plates. Suspension of the microorganism was prepared to contain approximately 1.0×10^5 cfu mL^{-1} and applied to microtitration plates with serially diluted compounds in DMSO to be tested and incubated at 37°C for 24 and 48 h for bacterial and fungi, respectively. Then the MIC values were visually determined on each of the microtitration plates, 50 μL of PBS (phosphate buffered saline 0.01 mol L^{-1}, pH 7.4) containing 2 mg of MTT mL^{-1} was added to each well. Incubation was continued at room temperature for 4–5 h. The content of each well was removed and 100 μL of isopropanol containing 5% 1 mol L^{-1} HCl was added to extract the dye. After 12 h of incubation at room temperature, the optical density was measured with a microplate reader at 550 nm.

RESULTS AND DISCUSSION

The complex was readily prepared by the reaction of a 1 : 1 : 1 molar ratio of 5-trifluoromethoxysalicylaldehyde, *N*-methylethane-1,2-diamine and vanadyl acetylacetonate in methanol (Scheme 2). Elemental analyses of the complex are in accordance with the molecular structure proposed by the X-ray analysis.



Scheme 2.

In the spectrum of HL, the weak and broad band centered at 3432 cm^{-1} is assigned to the vibration of O–H bonds, which is absent after chelation, suggesting the coordination through the deprotonated form. The weak and sharp band located at 3233 cm^{-1} of complex is assigned to the vibration of N–H bonds. The intense band at 1635 cm^{-1} in the spectrum of the complex can be attributed to the stretching vibration of the azomethine groups C=N. The corresponding absorption of HL is observed at 1647 cm^{-1}, indicating

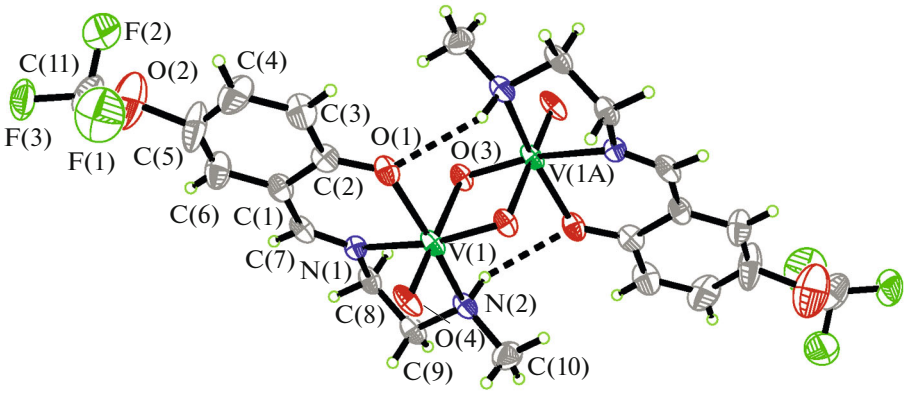


Fig. 1. A perspective view of the complex with the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.

the coordination via the imino groups. The characteristic ν(V=O) and ν(V–O) bands can be monitored at 937 and 453 cm^{-1}, respectively [19].

In the electronic spectrum of the complex, the lowest energy transition band is observed at 435 nm, which is attributed to LMCT transition as charge transfer from *p*-orbital on the lone-pair of ligands' oxygen atoms to the empty *d* orbital of the vanadium atom. The other strong bands in the range of 330–370 nm in the spectrum of the complex is similar to the absorption band in the spectrum of the free Schiff base, so it is attributed to the intra-ligand $\pi \rightarrow \pi^*$ absorption peak of the ligand. The other mainly LMCT and to some extent $\pi \rightarrow \pi^*$ band appears at 270 nm, and this is due to the oxygen donor atoms bound to vanadium(V) [19].

The molecular structure of the complex is shown in Fig. 1. The complex crystallizes as centrosymmetric dinuclear structure, with the inversion center located at the midpoint of the two V atoms. The V···V distance is 3.111(1) Å. The V atom in the 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 plane defined by the four equatorial donor atoms by 0.335(2) Å. The V–O and V–N coordinate bond lengths in the complex are comparable to the corresponding values observed in other similar oxovanadium(V) complexes with Schiff bases [20–24]. There exist two N–H···O hydrogen bonds between the two $[VO_2L]$ units, which might contribute to the formation of dimeric structure.

The hydrazone compound and the vanadium complex were screened for antibacterial activities against two Gram (+) bacterial strains (*Bacillus subtilis* and *Staphylococcus aureus*) and two Gram (–) bacterial strains (*Escherichia coli* and *Pseudomonas fluorescence*) by MTT method. The MIC (minimum inhibitory concentration, μg mL^{-1}) values of the compounds against four bacteria are listed in Table 3. Penicillin G was used as the standard drug. The hydrazone compound shows strong activity against *B. subtilis*, medium activities against *S. aureus* and *E. coli*, while no activity against *P. fluorescence*. The complex is in general stronger than the hydrazone for the antibacterial activities on *B. subtilis*, *E. coli*, and *P. fluorescence*. As for *S. aureus*, even though the MIC values are the same, it is in fact that the complex is more active than the hydrazone. It is noticeable that the complex has the most activity against *B. subtilis* as compared to Penicillin G.

Table 3. Antibacterial activities of the hydrazone and the complex (MIC, μg mL^{-1})

Tested material	*B. subtilis*	*S. aureus*	*E. coli*	*P. fluoresence*
H_2L	4.7	9.4	37.5	>75
The complex	1.2	9.4	18.8	37.5
Penicillin G	2.3	4.7	>75	>75

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