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

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Hydrogen-Bond Influenced Synthesis and Crystal Structures of (4-Chloro-2-[(2-dimethylaminoethylimino)methyl] phenolato)dioxovanadium(V) and Bis(2-[(2aminoethylimino)methyl]-4-bromophenolato) dioxovanadium(V)

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Hydrogen-Bond Influenced Synthesis and Crystal Structures of (4-Chloro-2-[(2-dimethylaminoethylimino)methyl] phenolato)dioxovanadium(V) and Bis(2-[(2-aminoethylimino)methyl]-4-bromophenolato) dioxovanadium(V)

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A mononuclear vanadium complex, $[VO_2L^a](1)$ ($L^a = 4$ -chloro-2-[(2-dimethylaminoethylimino)methyl]phenolate), and a binuclear vanadium complex, $[VO_2L^b]_2$ (2) ($L^b = 2$ -[(2-aminoethyl imino)methyl]-4-bromophenolate), were prepared and characterized by physical chemical methods (IR and UV-Vis spectra, elemental analysis), and single crystal X-ray diffraction. The V coordinate center in (1) is ligated by three NNO donor atoms of the Schiff base ligand L^a , and two oxo groups, generating pyramidal coordination. Each V coordinate center in (2) is ligated by three NNO donor atoms of the Schiff base ligand L^b , and three oxo groups, generating octahedral coordination. Close examination on the relationship between structures of Schiff base ligands and the final complexes, hydrogen bonds are the substantial influence factors in the self-assembly processes.

Keywords hydrogen bonding, self-assembly, Schiff base, vanadium, X-ray diffraction

INTRODUCTION

In the last few decades, tremendous attention has been focused on Schiff bases and their complexes in the fields of coordination chemistry and bioinorganic chemistry.^[1–3] Vanadium compounds present innumerous pharmacological applications as antitumorals, antimicrobials, and insulin-mimics.^[4–6] It has been demonstrated that the insulin effects of promoting glucose uptake and inhibiting lipolysis can be duplicated by vanadium. It has been known that there exists trigonal bipyramidal vanadium within the phosphate-metabolizing enzyme.^[7,8] The design and self-assembly of complexes with predicated structures is a hot topic in supramolecular chemistry. To further explore the role in the self-assembly and structures of vanadium complexes, a mononuclear vanadium complex, $[VO_2L^a]$ (1) (L^a = 4chloro-2-[(2-dimethylaminoethylimino)methyl]phenolate), and a binuclear vanadium complex, $[VO_2L^b]_2$ (2) (L^b = 2-[(2aminoethylimino)methyl]-4-bromophenolate), were prepared and discussed.

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 (Taizhou University, China). The IR spectra were measured with a Nicolet FT-IR 170-SX spectrophotometer (Liaoning Normal University, China) using KBr pellets in the 4000–400 cm⁻¹ region. UV-Vis spectra were recorded on a Perkin-Elmer Lambda 9 instrument (Taizhou University, China). The EPR spectra of the complexes were measured using a Bruker EMX Micro Premium X spectrometer (Liaoning Normal University, China).

Synthesis of the Schiff Bases HL^a and HL^b

The two Schiff bases were synthesized according to the general method. A methanol solution (50 mL) of aldehyde (1.0 mmol) was added dropwise to a stirred methanol solution (50 mL) of primary amine (1.0 mmol). The mixture was stirred for 30 minutes and the solvent was then evaporated to give yellow oil product with quantitative yield. Anal. Calcd. for HL^a (%) C, 58.3; H, 6.7; N, 12.4. Found (%): C, 58.2; H, 6.6; N, 12.3. Anal. Calcd. for HL^b (%): C, 44.5; H, 4.6; N, 11.5. Found (%): C, 44.3; H, 4.7; N, 11.5. Characteristic IR data (KBr, cm⁻¹): HL^a, 1637 ($\nu_{C=N}$); HL^b, 3221 (ν_{N-H}), 1632 ($\nu_{C=N}$).

Synthesis of the Complex [VO₂L^a] (1)

A methanol solution (5 mL) of $VO(acac)_2$ (0.1 mmol, 26.5 mg) was added to a methanol solution (10 mL) of HL^a

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(0.1 mmol, 22.6 mg) under stirring at room temperature for 30 min to give a yellow solution. The resulting solution was allowed to stand in air for a few days. Yellowish brown needle-like 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. Yield: 37%. Anal. Calcd. for C₁₁H₁₄ClN₂O₃V (%): C, 42.8; H, 4.6; N, 9.1. Found (%): C, 42.6; H, 4.7; N, 9.0%. IR data (cm⁻¹): 3438 (m), 3327 (w), 3125 (m), 1656 (s), 1612 (s), 1453 (m), 1398 (s), 1165 (w), 1123 (w), 1073 (w), 927 (w), 823 (w), 770 (w), 712 (w), 590 (w), 534 (w), 449 (w). UV-Vis spectra data in DMSO [nm (ε , M⁻¹ cm⁻¹)]: 261 (1.27 × 10⁴), 376 (3.1 × 10³), 535 (213).

Synthesis of the Complex $[VO_2L^b]_2$ (2)

Needle-like single crystals of (2) was prepared and crystallized according to the same method as presented for (1), with HL^a replaced by HL^b (0.1 mmol, 24.3 mg). Yield: 41%. Anal. Calcd. for C₁₈H₂₀Br₂N₄O₆V₂ (%): C, 33.3; H, 3.1; N, 8.6. Found (%): C, 33.2; H, 3.1; N, 8.7. IR data (cm⁻¹): 3443 (br, m), 3278 (w), 3198 (w), 2923 (w), 1625 (s), 1527 (w), 1453 (m), 1380 (m), 1294 (s), 1184 (w), 963 (w), 920 (w), 834 (m), 804 (w), 688 (w), 651 (w), 485 (w), 461 (w). UV-Vis spectra data in DMSO [nm (ε , M⁻¹ cm⁻¹)]: 253 (1.36 × 10⁴), 362 (3.5 × 10³), 546 (171).

TABLE 1 Crystal data for the complexes

	(1)	(2)
Formula	C ₁₁ H ₁₄ ClN ₂ O ₃ V	$C_{18}H_{20}Br_2N_4O_6V_2$
FW	308.6	650.1
Crystal shape/color	Block/yellow	Block/yellow
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_{1}/c$
a/Å	6.672 (1)	10.301 (3)
b/Å	11.693 (2)	14.667 (4)
c/Å	16.485 (2)	7.370 (2)
β / $^{\circ}$	98.624 (2)	100.442 (3)
$V/Å^3$	1271.5 (3)	1095.0 (5)
Z	4	2
T/K	298 (2)	298 (2)
$D_c/\mathrm{g}~\mathrm{cm}^{-3}$	1.612	1.972
<i>F</i> (000)	632	640
μ/mm^{-1} (Mo-K α)	0.991	4.546
T_{\min}	0.819	0.342
$T_{\rm max}$	0.826	0.373
Reflections/parameters	2744/165	2366/145
Independent reflections	2240	1807
Restraints	0	0
Goodness of fit on F^2	1.028	1.023
$R_1, wR_2 [I \ge 2\sigma(I)]^a$	0.0329, 0.0847	0.0312, 0.0647
R_1, wR_2 (all data) ^{<i>a</i>}	0.0426, 0.0913	0.0480, 0.0715

$$\label{eq:arrow} \begin{split} {}^aR_1 &= \sum ||Fo| - |Fc|| / \sum |Fo|, \ wR_2 = [\sum w(Fo^2 - Fc^2)^2 / \sum w(Fo^2)^2]^{1/2}, \\ w_1 &= [\sigma^2 \ Fo^2 + (0.0431(Fo^2 + 2Fc^2)/3)^2 + 0.5496(Fo^2 + 2Fc^2)/3]^{-1}, \\ w_2 &= [\sigma^2 \ Fo^2 + (0.0280(Fo^2 + 2Fc^2)/3)^2 + 0.4812(Fo^2 + 2Fc^2)/3]^{-1}. \end{split}$$

 TABLE 2

 Coordinate bond lengths (Å) and bond angles (°) for the

complexes							
	(1)					
V1-O1	1.899 (2)	V1-O2	1.612 (2)				
V1-O3	1.624 (2)	V1-N1	2.159 (2)				
V1-N2	2.161 (2)						
O2-V1-O3	109.3 (1)	O2-V1-O1	104.6 (1)				
03-V1-01	98.6 (1)	O2-V1-N1	108.6 (1)				
O3-V1-N1	140.0(1)	01-V1-N1	83.7 (1)				
O2-V1-N2	96.3 (1)	O3-V1-N2	88.5 (1)				
01-V1-N2	154.1 (1)	N1-V1-N2	75.1 (1)				
	(2	2)					
V1-O1	1.903 (2)	V1-O2	1.617 (2)				
V1-O3	1.669 (2)	V1-N1	2.176 (2)				
V1-N2	2.130 (2)	V1-O3 ⁱ	2.385 (2)				
O2-V1-O3	108.2 (1)	O2-V1-O1	102.1 (1)				
03-V1-01	99.4 (1)	O2-V1-N2	92.4 (1)				
O3-V1-N2	92.6 (1)	O1-V1-N2	157.1 (1)				
02-V1-N1	95.6 (1)	O3-V1-N1	154.4 (1)				
01-V1-N1	84.3 (1)	N2-V1-N1	76.7 (1)				
02-V1-O3 ⁱ	169.1 (1)	O3-V1-O3 ⁱ	79.2 (1)				
01-V1-O3 ⁱ	84.2 (1)	N2-V1-O3 ⁱ	79.0 (1)				
N1-V1-O3 ⁱ	75.9 (1)						

Symmetry code: (i) 1 - x, -y, -z.

Crystal Structure Determination

Diffraction intensities for the complexes were collected at 298(2) K using a Bruker APEX2 CCD area-detector (Liaoning Normal University, China) with MoK α radiation ($\lambda = 0.71073$ Å). The collected data were reduced by SAINT software,^[9] and empirical absorption corrections were performed by SADABS software.^[10] The final structures of both complexes were solved by direct methods and refined against F^2 by full-matrix leastsquares methods by SHELXTL software.[11] All non-hydrogen atoms were refined anisotropically. The amino H atoms in (2)were located from an electronic density map and refined isotropically, with N-H and H···H distances restrained to 0.90(1) and 1.43(2) Å, respectively, and with $U_{iso}(H)$ set to 0.08 Å². All 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. Hydrogen bonds are presented in Table 3.

TABLE 3Hydrogen-bond geometry (Å, $^{\circ}$) for (2)

	-			
$D-H\cdots A$	D-H	$H \cdots A$	$D \cdots A$	$D-H\cdots A$
$N2-H2A\cdotsO1^{i}$ $N2-H2B\cdotsO2^{ii}$	0.90 0.90	2.31 2.08	3.024 (3) 2.896 (3)	136 150

Symmetry codes: (i) 1 - x, -y, -z; (ii): 1 - x, -y, 1 - z.



FIG. 1. View of the molecular structure of (1) with atom labels. Displacement ellipsoids are shown at 30% probability level.

RESULTS AND DISCUSSION

Preparation of the Schiff Bases and the Complexes

The Schiff bases were prepared via the reaction of equimolar quantities of 5-chlorosalicylaldehyde with N,N-dimethylethane-1,2-diamine, and 5-bromosalicylaldehyde with ethane-1,2diamine, respectively, in methanol. It should be reminded that the ligand HL^b can only be produced by 5-bromosalicylaldehyde added dropwise to ethane-1,2-diamine in a highly diluted solution. If ethane-1,2-diamine was added dropwise to 5bromosalicylaldehyde, it can give a mixture of mono-Schiff base HL^b and *bis*-Schiff base *N*,*N*'-bis(5-bromosalicylidene)ethane-1,2-diamine. Both vanadium complexes were readily prepared by the standard procedure as widely described in literature. Both complexes crystallized as yellowish brown needle-like single crystals, which are stable in air at room temperature. Single crystals of the complexes are soluble in DMSO, DMF, MeCN, MeOH, and EtOH. The valence of the vanadium in both complexes is +5 oxidation state and therefore EPR silent.

Structure Description of (1)

The molecular structure of (1) is presented in Figure 1. The complex is a mononuclear dioxovanadium(V) compound. The V atom in the complex is five-coordinated in a distorted square pyramidal geometry. The basal plane of the coordination is composed of the three donor atoms the Schiff base ligand, and an oxo group, O3. The apical position is occupied by a second oxo group, O2. The V atom lies 0.483(2) Å from the mean plane defined by the basal donor atoms, in the direction of the apical oxo group. The V1-O2 and V1-O3 distances in the complex are 1.612(2) and 1.624(2) Å, respectively, indicating they are typical V=O double bonds. The distortion of the square pyramidal coordination can be observed by the coordinate bond angles, ranging from 96.3(1) to $109.3(1)^{\circ}$ for the vertical angles, and from 140.0(1) to $154.1(1)^{\circ}$ for the diagonal angles. The coordinate bond lengths in the complex are comparable to those in

other similar dioxovanadium complexes.^[12,13] The τ value for the complex is 0.24, indicating a distorted square pyramidal coordination.^[14]

Structure Description of (2)

The molecular structure of (2) is presented in Figure 2. The complex is a centrosymmetric dinuclear dioxovanadium(V) compound, with the inversion center located at the midpoint of the two V atoms, which has a distance of 3.156(1) Å. Each V atom in the complex is six-coordinated through three bonds to oxo groups and through bonds to L^b, generating an octahedral geometry. The V atom lies 0.340(2) Å from the mean plane defined by the equatorial donor atoms, in the direction of the axial oxo group, O2. The V1-O2 and V1-O3 distances in the complex are 1.617(2) and 1.669(2) Å, respectively, indicating they are typical V=O double bonds. The O3 atom is involved in the bridge between V1 and V1A, strongly coordinated to O3 and weakly coordinated to O3A. The coordinate bond lengths are comparable to those observed in (1) and other similar dimeric oxovanadium complexes.^[15-17] The distortion of the octahedral coordination can be observed by the coordinate bond angles, ranging from 75.9(1) to $108.2(1)^{\circ}$ for the vertical angles, and from 154.4(1) to $169.1(1)^{\circ}$ for the diagonal angles. There form two intermolecular N-H--O hydrogen bonds between the two $[VO_2L^b]$ units in the complex. In the crystal structure of (2), the dinuclear $[VO_2L^b]_2$ molecules are linked through intermolecular N-H--O hydrogen bonds, to form 1D chains running along the *c*-axis, as presented in Figure 3.

SUPPLEMENTARY MATERIALS

Crystallographic data in CIF format have been deposited with the Cambridge Structural Database (CCDC-858862 and CCDC-858863 for (1) and (2), respectively). Copies of the data can be obtained free of charge, on application to CCDC, 12



FIG. 2. View of the molecular structure of (2) with atom labels. Displacement ellipsoids are shown at 30% probability level. Atoms labeled with suffix A and those unlabeled are related to the symmetry operation 1 - x, -y, -z. Hydrogen bonds are drawn as dotted lines.



FIG. 3. Hydrogen bond (dotted lines) linked 1D chain structure of (2). Viewed down the b axis.

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