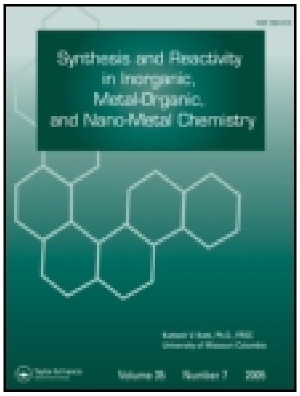

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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Synthesis and Crystal Structures of Dioxovanadium Complexes With Schiff Bases

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Two new dioxovanadium complexes, $[VO_2L^1]_2$ (1) and $[VO_2L^2]_2$ (2), where L^1 and L^2 are the deprotonated forms of 2-bromo-4-chloro-6-{[2-(2-hydroxyethylamino)ethylimino)methyl]phenol (HL^1) and 2-{[2-(2-hydroxyethylamino)ethylimino]methyl}phenol (HL^2), respectively, have been synthesized and characterized by IR, UV-Vis spectra, and single-crystal X-ray diffraction. Both complexes are centrosymmetric dimeric dioxovanadium(V) compounds, with the V···V distances of 3.251(2) Å and 3.127(2) Å, respectively. The V atoms in the complexes are in octahedral coordination.

Keywords crystal structure, dioxovanadium complex, Schiff base, synthesis

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 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] 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 number of vanadium atoms by preventing dimerization pathways.[9] To further explore the role in the synthesis of such complexes,[10] in this study, two new oxovanadium complexes, $[VO_2L^1]_2$ (1) and $[VO_2L^2]_2$ (2), where L^1 and L^2 are the deprotonated forms of 2-bromo-4-chloro-6-{[2-(2-hydroxyethylamino)ethylimino)methyl]phenol (HL^1) and 2-{[2-(2-hydroxyethylamino)ethylimino]methyl}phenol (HL^2), 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 (Waltham, MA, USA. The IR spectra were measured with a Nicolet FT-IR 170-SX spectrophotometer (Liaoning Normal University) using KBr pellets in the 4000–400 cm^{-1} region. UV-Vis spectra were recorded on a Perkin-Elmer Lambda 9 instrument. The EPR spectra of the complexes were measured using a Bruker EMX Micro Premium X spectrometer (Madison, WI, USA).

Synthesis of the Schiff Bases HL^1 and HL^2

The two Schiff bases were synthesized according to the general method. A methanol solution (50 mL) of 2-(2-aminoethylamino)ethanol (1.0 mmol, 104.1 mg) was added dropwise to a stirred methanol solution (50 mL) of aldehydes (1.0 mmol; salicylaldehyde for HL^1 and 3-bromo-5-chlorosalicylaldehyde for HL^2). The mixture was stirred for 30 min and the solvent was then evaporated to give orange oil product with quantitative yield. Anal. Calcd. for HL^1: C, 63.4; H, 7.7; N, 13.4%. Found: C, 63.2; H, 7.8; N, 13.5%. Anal. Calcd. for HL^2: C, 41.1; H, 4.4; N, 8.7%. Found: C, 41.2; H, 4.5; N, 8.6%. Selected IR data (KBr, cm^{-1}): HL^1, 3237 ($\nu_{N\text{-}H}$), 1633 ($\nu_{C=N}$); HL^2, 3233 ($\nu_{N\text{-}H}$), 1637 ($\nu_{C=N}$).

Synthesis of the Complex $[VO_2L^1]_2$ (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^1 (0.1 mmol, 20.8 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.

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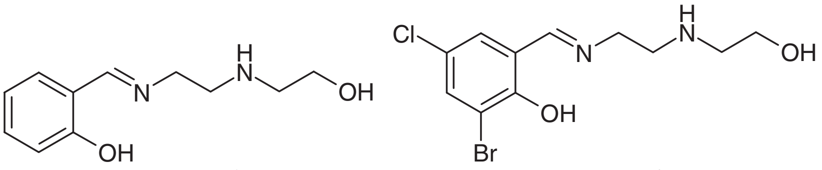


HL[1] HL[2]

SCH. 1. HL^1 and HL^2.

Yield: 49%. Anal. Calcd. for $C_{22}H_{30}N_4O_8V_2$: C, 45.5; H, 5.2; N, 9.7%. Found: C, 45.3; H, 5.3; N, 9.5%. IR data (cm^{-1}): 3343 (br, m), 3209 (sh, m), 1645 (vs), 1599 (s), 1549 (m), 1472 (m), 1448 (m), 1417 (w), 1397 (w), 1334 (w), 1297 (s), 1208 (w), 1148 (m), 1128 (w), 1088 (m), 1049 (m), 1029 (m), 1005 (m), 968 (w), 939 (s), 840 (s), 803 (w), 770 (s), 628 (m), 569 (w), 447 (w). UV-Vis spectra data in DMSO [nm (ε, M^{-1} cm^{-1})]: 254 (1.3 × 10^4), 372 (3.4 × 10^3), 552 (173).

Synthesis of the Complex [VO$_2$L^2]$_2$ (2)

The complex was prepared and crystallized according to the same method as that described for (**1**), with HL^1 replaced with HL^2 (0.1 mmol, 32.1 mg). Yield: 62%. Anal. Calcd. for $C_{22}H_{26}Br_2Cl_2N_4O_8V_2$: C, 32.7; H, 3.2; N, 6.9%. Found: C, 32.4; H, 3.3; N, 7.1%. IR data (cm^{-1}): 3345 (br, m), 3213 (sh, m), 1647 (vs), 1597 (s), 1545 (m), 1471 (m), 1448 (m), 1417 (w), 1398 (w), 1331 (w), 1297 (s), 1210 (w), 1146 (m), 1128 (w), 1088 (m), 1048 (m), 1029 (m), 1012 (m), 973 (w), 937 (s), 845 (s), 802 (w), 770 (s), 621 (m), 568 (w), 439 (w). UV-Vis spectra data in DMSO [nm (ε, M^{-1} cm^{-1})]: 259 (1.4 × 10^4), 367 (3.2 × 10^3), 561 (187).

TABLE 1
Crystal data for the complexes

	(**1**)	(**2**)
Formula	$C_{22}H_{30}N_4O_8V_2$	$C_{22}H_{26}Br_2Cl_2N_4O_8V_2$
FW	580.4	807.1
Crystal shape/color	Block/brown	Block/brown
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	11.259 (2)	14.003 (2)
b (Å)	6.843 (2)	6.802 (1)
c (Å)	16.094 (3)	16.446 (2)
β (°)	105.356 (3)	112.391 (2)
V (Å^3)	1195.7 (4)	1448.4 (3)
Z	4	2
T (K)	298 (2)	298 (2)
D_c (g cm^{-3})	1.612	1.851
F(000)	600	800
μ/mm^{-1} (Mo-Kα)	0.838	3.640
$T_{\min}$	0.831	0.488
$T_{\max}$	0.850	0.530
Reflections/parameters	2594/169	3139/187
Independent reflections	1841	1576
Restraints	2	2
Goodness of fit on F^2	1.023	0.976
R_1, wR_2 [$I \geq 2\sigma(I)$]^a	0.0435, 0.0957	0.0603, 0.1145
R_1, wR_2 (all data)^a	0.0681, 0.1070	0.1483, 0.1478

$^a R_1 = \sum||Fo| - |Fc||/\sum|Fo|$, $wR_2 = [\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$, $w_1 = [\sigma^2 Fo^2 + (0.0483(Fo^2 + 2Fc^2)/3)^2]^{-1}$, $w_2 = [\sigma^2 Fo^2 + (0.0602(Fo^2 + 2Fc^2)/3)^2]^{-1}$.

Crystal Structure Determination

Diffraction intensities for the complexes were collected at 298(2) K using a Bruker SMART 1000 CCD area-detector

TABLE 2
Selected bond lengths (Å) and bond angles (°) for the complexes

(**1**)			
V1-O1	1.9084 (19)	V1-O3	1.606 (2)
V1-O4	1.6775 (18)	V1-N1	2.139 (2)
V1-N2	2.161 (2)	V1-O4^{i}	2.4519 (19)
O3-V1-O4	107.83 (10)	O3-V1-O1	101.43 (9)
O4-V1-O1	100.34 (9)	O3-V1-N1	98.43 (9)
O4-V1-N1	151.75 (9)	O1-V1-N1	84.11 (8)
O3-V1-N2	93.38 (9)	O4-V1-N2	91.41 (9)
O1-V1-N2	157.16 (9)	N1-V1-N2	76.53 (8)
O3-V1-O4^{i}	171.94 (9)	O4-V1-O4^{i}	77.76 (8)
O1-V1-O4^{i}	82.92 (7)	N1-V1-O4^{i}	75.12 (7)
N2-V1-O4^{i}	80.51 (7)		
(**2**)			
V1-O1	1.923 (4)	V1-O3	2.322 (4)
V1-O4	1.605 (4)	V1-N1	2.135 (5)
V1-N2	2.191 (5)	V1-O3^{ii}	1.686 (4)
O4-V1-O3^{ii}	107.3 (2)	O4-V1-O1	101.26 (19)
O3^{ii}-V1-O1	98.56 (19)	O4-V1-N1	96.7 (2)
O3^{ii}-V1-N1	155.08 (19)	O1-V1-N1	83.06 (19)
O4-V1-N2	91.8 (2)	O3^{ii}-V1-N2	93.9 (2)
O1-V1-N2	158.3 (2)	N1-V1-N2	78.2 (2)
O4-V1-O3	170.72 (18)	O3-V1-O3^{ii}	78.63 (18)
O1-V1-O3	84.64 (16)	N1-V1-O3	76.77 (16)
N2-V1-O3	80.46 (17)		

Symmetry codes: (i) 1 – x, 2 – y, – z; (ii) 1 – x, 2 – y, 2 – z.

TABLE 3
Hydrogen bond geometry (Å, °) for the complexes

D–H···A	D–H	H···A	D···A	D–H···A
(**1**)				
N2–H2···O1$^{\#1}$	0.894(10)	2.31(2)	3.116(3)	149(3)
O2–H2A···O4$^{\#2}$	0.848(10)	2.103(11)	2.948(3)	174(4)
O2–H2A···N1$^{\#3}$	0.848(10)	2.69(3)	3.137(3)	114(3)
(**2**)				
O2–H2A···O3$^{\#4}$	0.852(10)	1.93(2)	2.768(7)	168(8)
N2–H2···O1$^{\#4}$	0.897(10)	2.31(5)	3.066(6)	141(7)

Symmetry codes: #1: $1 - x, 2 - y, -z$; #2: $1/2 - x, -1/2 + y, -1/2 - z$; #3: $-1/2 + x, 3/2 - y, -1/2 + z$; #4: $1 - x, 2 - y, 2 - z$.

with Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the SAINT program,[11] and empirical absorption corrections were performed using the SADABS program.[12] The structures were solved by direct methods and refined against F^2 by full-matrix least-squares methods using the SHELXTL package.[13] All of the non-hydrogen atoms were refined anisotropically. H2 atoms attached to N2 in both complexes were located from difference Fourier maps and refined isotropically, with N–H distances restrained to 0.90(1) Å, and with U_{iso}(H) set to 0.08 Å^2. 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 listed in Table 3.

RESULTS AND DISCUSSION

Preparation of the Schiff Bases and the Complexes

The Schiff bases HL^1 and HL^2 were prepared *via* the reaction of equimolar quantities of 2-(2-aminoethylamino)ethanol with salicylaldehyde and 3-bromo-5-chlorosalicylaldehyde, respectively, in methanol. The two complexes were readily synthesized according to the standard procedure (Scheme 2), crystallized as brown crystals, which are stable in air at room temperature. The crystals of the complexes are soluble in DMSO, DMF, MeCN, MeOH, and EtOH, insoluble in water. The vanadium in both complexes are +5 oxidation state and therefore EPR silent.

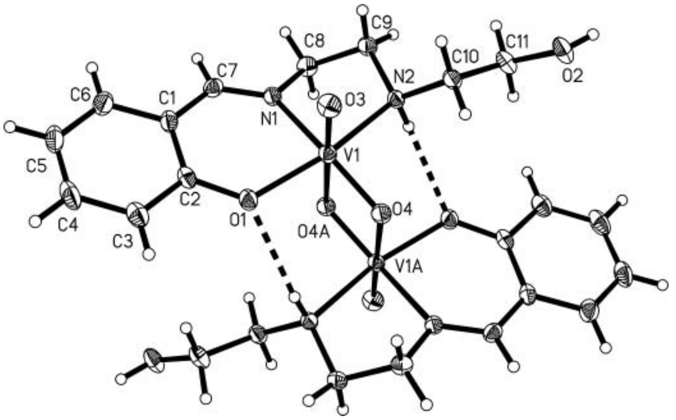
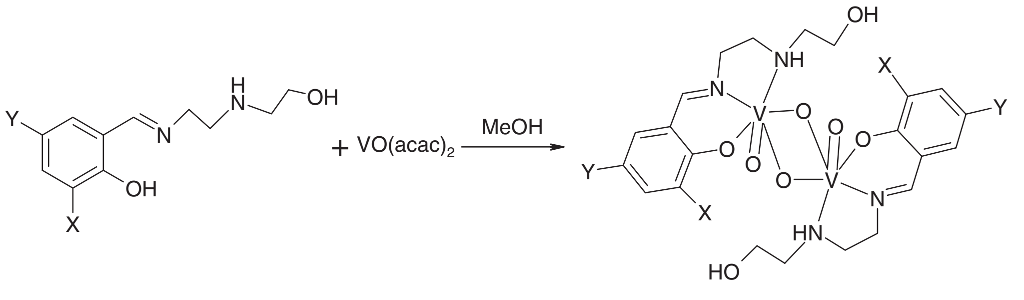


FIG. 1. Molecular structure of the complex (**1**) at 30% probability displacement. Atoms labeled with the suffix A are at the symmetry position $1 - x, 2 - y, -z$. Hydrogen bonds are drawn as dashed lines.

Structure Description of the Complexes

The molecular structures of the complexes (**1**) and (**2**) are shown in Figures 1 and 2, respectively. Both compounds are centrosymmetric dimeric dioxovanadium(V) complexes, with the inversion center located at the midpoint of the two V atoms. The V atom in each complex is six-coordinated through three bonds to oxo groups and through bonds to the tridentate Schiff base ligand, forming an octahedral geometry. The V1-O3 distance in (**1**) and the V1-O4 distance in (**2**) are about 1.605 Å, indicating them as typical V=O bonds. The O4 atom in (**1**) and O3 atom in (**2**) are involved in the bridge between V1 and V1A. The coordinate bond lengths are comparable to those observed in other similar oxovanadium complexes.[14–16] The distortion of the octahedral coordination can be observed by the coordinate bond angles, ranging from 75.1(1)° to 107.8(1)° for the perpendicular angles, and from 151.8(1)° to 171.9(1)° for the diagonal angles. In complex (**1**), there form two intermolecular



SCH. 2. The synthesis of the complexes. (**1**) X = Y = H; (**2**) X = Br, Y = Cl.

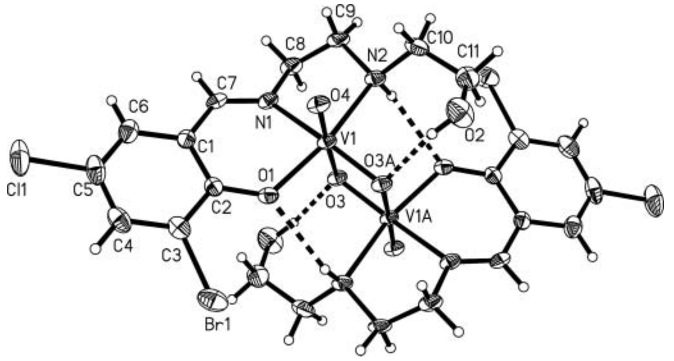


FIG. 2. Molecular structure of the complex (**2**) at 30% probability displacement. Atoms labeled with the suffix A are at the symmetry position 1 – *x*, 2 – *y*, 2 – *z*. Hydrogen bonds are drawn as dashed lines.

N−H· · ·O hydrogen bonds between the two [VO$_2$L^1] moieties, while in complex (**2**), there form two intermolecular N−H· · ·O hydrogen bonds and two intermolecular O−H· · ·O hydrogen bonds between the two [VO$_2$L^2] moieties. This might be the reason that the V· · ·V distance of 3.127(2) Å in (**2**) is shorter than that of 3.251(2) Å in (**1**).

In the crystal structure of the complex (**1**), the molecules are linked through intermolecular O−H· · ·O, N−H· · ·O, and O−H· · ·N hydrogen bonds, to form a 3D network, as shown in Figure 3. In the crystal structure of the complex (**2**), there are no obvious short contacts among the dimers, as shown in Figure 4.

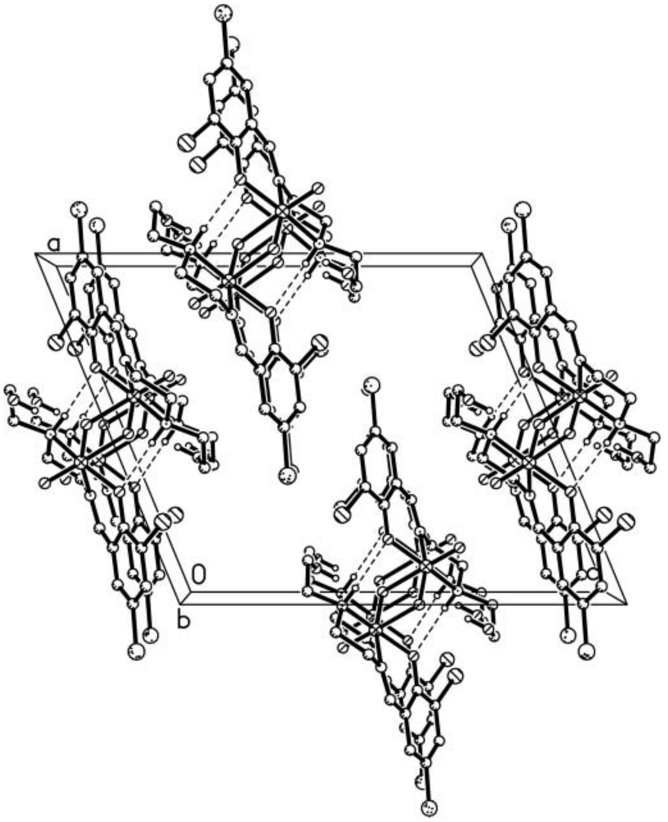


FIG. 4. Molecular packing of the complex (**2**), viewed along the *b* axis. Hydrogen bonds are drawn as thin dashed lines.

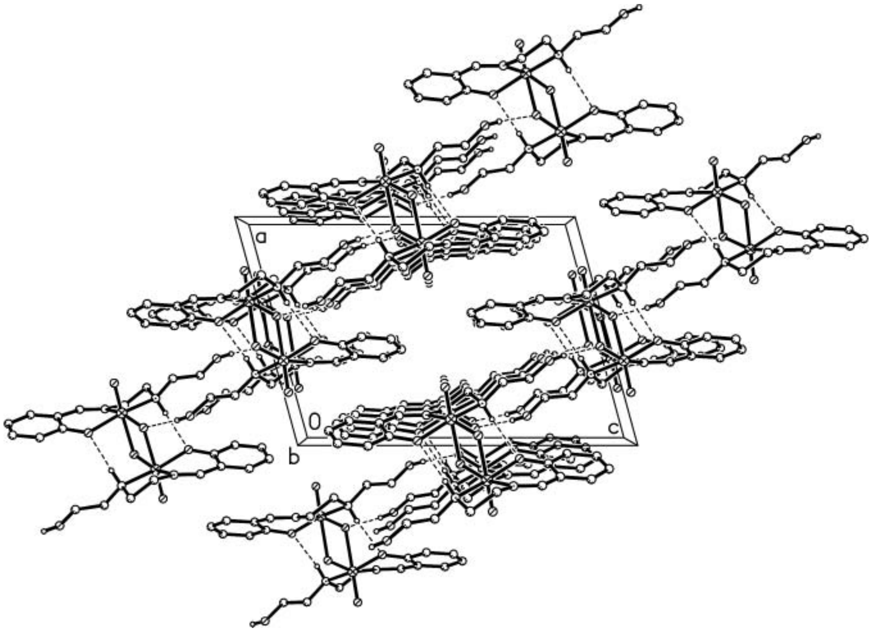


FIG. 3. Molecular packing of the complex (**1**), viewed along the *b* axis. Hydrogen bonds are drawn as thin dashed lines.

CONCLUSIONS

In the present study, two new dioxovanadium complexes have been synthesized and characterized by X-ray diffraction. The Schiff bases 2-bromo-4-chloro-6-{[2-(2-hydroxyethylamino)ethylimino)methyl]phenol and 2-{[2-(2-hydroxyethylamino)ethylimino]methyl}phenol coordinate to the V atoms through the phenolate O, imine N, and amine N atoms. The hydrogen bonds play an important role in the self-assembly of the final packing structures of the complexes.

SUPPLEMENTARY MATERIALS

Supplementary crystallographic data are available from the CCDC, Union Road, Cambridge CB2 1EZ, UK on request quoting the deposition numbers CCDC 820406 for (1) and 820407 for (2) (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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