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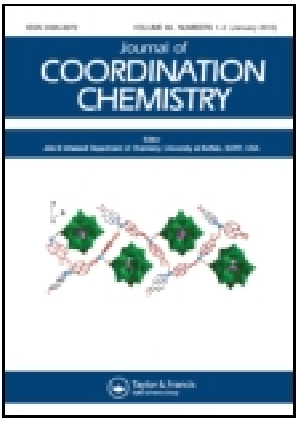

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Hydrogen bond and steric effect directed preparation and structures of dioxovanadium(V) complexes with tridentate Schiff bases

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Hydrogen bond and steric effect directed preparation and structures of dioxovanadium(V) complexes with tridentate Schiff bases

SHAO-SONG QIAN†, ZHONG-LU YOU*‡, YING-NAN LI‡, XUE HU‡, MEI ZHANG‡ and HAI-LIANG ZHU*†

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Three new dioxovanadium(V) complexes, $[VO_2L^1]_2$ (**1**), $[VO_2L^2]$ (**2**) and $[VO_2L^3]$ (**3**) (HL^1 = 2-[(2-ethylaminoethylimino)methyl]-4-methylphenol, HL^2 = 2-[(2-isopropylaminoethylimino)methyl]-6-methylphenol, HL^3 = 5-methoxy-2-[(pyridin-2-ylmethylimino)methyl]phenol), have been prepared and structurally characterized by physico-chemical methods and single crystal X-ray diffraction. Complex **1** is a centrosymmetric dimeric dioxovanadium(V) complex with V···V distance of 3.187(2) Å. V in **1** is octahedral. Complexes **2** and **3** are mononuclear dioxovanadium(V) complexes. V in **2** is in a distorted square-pyramidal coordination and that in **3** is intermediate between square-pyramidal and trigonal bipyramidal. During the synthesis and crystallization of the complexes from oxovanadium(IV) starting material, aerial oxygen probably acts as the oxidizing agent. The final structures of the complexes are directed by hydrogen bonds and steric effects among the Schiff base ligands. The existence of amino groups and small steric effects such as ethyl group can result in the formation of dimeric structures.

Keywords: Schiff base; Oxovanadium complex; Crystal structure; Hydrogen bond; Steric effects

1. Introduction

Considerable interest has focused on Schiff bases and their metal complexes in coordination and biological chemistry [1–3]. Vanadium complexes have interesting biological activities such as normalizing high blood glucose levels and acting as models of haloperoxidases [4–6]. Construction of specific vanadium complexes seems important to explore effective biological agents. Factors that influence the final structures of metal complexes include metal and ligand ratio, solvents, reaction temperature, and weak forces, such as hydrogen bonds and π···π stacking interactions [7, 8]. Mokry and co-workers reported that the steric bulk of the substituent on benzene can be used to modify the coordination geometry and/or number of vanadiums by preventing dimerization [9]. To further explore synthesis of such complexes, three new dioxovanadium(V) complexes, $[VO_2L^1]_2$ (**1**), $[VO_2L^2]$ (**2**) and $[VO_2L^3]$ (**3**) (HL^1 = 2-[(2-ethylaminoethylimino)methyl]

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-4-methylphenol, HL^2 = 2-[(2-isopropylaminoethylimino)methyl]-6-methylphenol, HL^3 = 5-methoxy-2-[(pyridin-2-ylmethylimino)methyl]phenol), respectively, were synthesized and characterized (scheme 1).

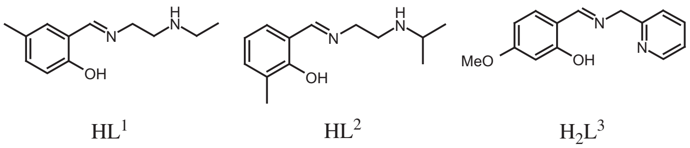
2. Experimental

2.1. *General remarks and physical measurements*

Reagents and solvents were purchased from commercial suppliers and used without purification. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded on a Jasco FT/IR-4000 spectrometer as KBr pellets from 4000–200 cm^{-1}. Molar conductances of the complexes at 10^{-3} M in absolute methanol were measured with a Shanghai DDS–11A conductometer. The conductometer was calibrated before use. First, the temperature compensation was set to 25 °C. Second, the measure switch was set to 'adjust'. Then, by adjusting the constant correction knob, we can make the instrument display the actual coefficient of the conductivity cell. X-ray diffraction was carried out on a Bruker SMART 1000 CCD area diffractometer. ^1H NMR spectra were recorded on a Varian INOVA300 pulse Fourier-transform NMR spectrometer.

2.2. *Synthesis of the Schiff bases*

To a methanolic solution (50 cm^3) of substituted salicylaldehyde (2.0 mmol) a methanolic solution (30 cm^3) of primary amine (2.0 mmol) was added with continuous stirring. The mixture was stirred for 30 min at room temperature to give yellow solution. The solvent was evaporated to give yellow paste of the Schiff base, which was washed with methanol and dried in air. Yields: 80–90%. Anal. Calcd for $C_{12}H_{18}N_2O$ (HL^1): C, 69.9; H, 8.8; N, 13.6%. Found: C, 69.7; H, 8.8; N, 13.7%. IR data: 3372 (br, w) ν(O–H), 3211 (w) ν(N–H), 1645 (s) ν(C=N), 1207 (s) ν(C–O). ^1H NMR (DMSO-d_6, ppm): δ 1.07 (t, 3H), 2.25 (s, 3H), 2.64 (q, 2H), 2.91 (s, 2H), 3.69 (s, 2H), 6.83 (d, 1H), 7.00 (s, 1H), 7.07 (d, 1H), 7.25 (s, 1H), 8.30 (s, 1H), 9.81 (s, 1H). Anal. Calcd for $C_{13}H_{20}N_2O$ (HL^2): C, 70.9; H, 9.2; N, 12.7%. Found: C, 70.6; H, 9.1; N, 12.8%. IR data: 3365 (br, w) ν(O–H), 3205 (w) ν(N–H), 1645 (s) ν(C=N), 1205 (s). ^1H NMR (DMSO-d_6, ppm): δ 1.08 (d, 6H), 2.23 (s, 3H), 2.81 (m, 1H), 2.91 (m, 2H), 3.70 (t, 2H), 6.78 (t, 1H), 7.08 (d, 1H), 7.17 (d, 1H), 7.25 (s, 1H), 8.36 (s, 1H), 13.5 (s, 1H). Anal. Calcd for $C_{14}H_{14}N_2O_2$ (HL^3): C, 69.4; H, 5.8; N, 11.6%. Found: C, 69.5; H, 5.9; N, 11.4%. IR data: 3327 (br, w) ν(O–H), 1627 (s) ν(C=N), 1193 (s) ν(C–O). ^1H NMR (DMSO-d_6, ppm): δ 3.78 (s, 3H), 4.86 (s, 1H), 6.49 (m, 2H), 7.19 (m, 3H), 7.40 (m, 1H), 7.65 (m, 1H), 8.37 (s, 1H), 8.54 (d, 1H).



HL^1 HL^2 H_2L^3

Scheme 1. The Schiff bases.

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2.3. *Synthesis of the complexes*

A methanolic solution (20 cm^3) of the Schiff base (0.5 mmol) was added with stirring to a methanolic solution (20 cm^3) of $VO(acac)_2$ (0.5 mmol, 0.133 g). The mixtures were stirred at room temperature for 30 min to give yellow solutions. X-ray quality single crystals were formed by slow evaporation of the solutions in air after a few days.

2.3.1. bis(μ_2-Oxo)bis(2-[(2-ethylaminoethylimino)methyl]-4-methylphenolato)dioxo divanadium(V) (1). Yellow single crystals. Yield: 76.4 mg (53%). Anal. Calcd for $C_{24}H_{34}N_4O_6V_2$: C, 50.0; H, 5.9; N, 9.7%. Found: C, 49.8; H, 6.1; N, 9.6%. IR data: 3228 (w) *ν*(N–H), 1636 (s) *ν*(C=N), 1292 (s) *ν*(C–O), 933 (m) *ν*(V=O), 849 (s) *ν*(V=O), 562 (w) *ν*(V–N), 445 (w) *ν*(V–O). ^1H NMR (DMSO-d_6, ppm): δ 1.30 (t, 3H), 2.25 (m, 3H), 2.59 (d, 1H), 2.82 (m, 1H), 3.30 (s, 2H), 3.91 (s, 1H), 4.09 (m, 1H), 5.57 (s, 1H), 6.70 (d, 1H), 7.30 (m, 2H), 8.84 (s, 1H). $\Lambda_M = 12\ \Omega^{-10}\ cm^2\ mol^{-1}$.

2.3.2. (2-[(2-Isopropylaminoethylimino)methyl]-6-methylphenolato)dioxovanadium (V) (2). Yellow single crystals. Yield: 107.2 mg (71%). Anal. Calcd for $C_{13}H_{19}N_2O_3V$: C, 51.7; H, 6.3; N, 9.3%. Found: C, 51.5; H, 6.4; N, 9.1%. IR data: 3187 (w) *ν*(N–H), 1643 (s) *ν*(C=N), 1292 (s) *ν*(C–O), 927 (s) *ν*(V=O), 848 (s) *ν*(V=O), 589 (w) *ν*(V–N), 458 (w) *ν*(V–O). ^1H NMR (DMSO-d_6, ppm): δ 1.22 (d, 3H), 1.42 (d, 3H), 2.11 (s, 3H), 2.59 (d, 1H), 3.07 (s, 1H), 3.34 (s, 1H), 3.97 (m, 2H), 5.54 (m, 1H), 6.71 (t, 1H), 7.38 (t, 2H), 8.87 (s, 1H). $\Lambda_M = 30\ \Omega^{-1}\ cm^2\ mol^{-1}$.

2.3.3. bis(5-Methoxy-2-[(pyridin-2-ylmethylimino)methyl]phenolato)dioxovanadium(V) (3). Yellow single crystals. Yield: 90.7 mg (56%). Anal. Calcd for $C_{14}H_{13}N_2O_4V$: C, 51.9; H, 4.0; N, 8.6%. Found: C, 51.6; H, 4.1; N, 8.7%. IR data: 1611 (s) *ν*(C=N), 1231 (s) *ν*(C–O), 925 (s) *ν*(V=O), 563 (w) *ν*(V–N), 438 (w) *ν*(V–O). ^1H NMR (DMSO-d_6, ppm): δ 4.02 (s, 3H), 5.03 (m, 1H), 6.57 (m, 2H), 6.63 (t, 1H), 7.36 (m, 3H), 7.57 (m, 2H), 8.86 (s, 1H). $\Lambda_M = 25\ \Omega^{-1}\ cm^2\ mol^{-1}$.

2.4. *X-ray crystallography*

Diffraction intensities for the complexes were collected at 298(2) K using a Bruker SMART 1000 CCD area diffractometer with Mo*Kα* radiation ($\lambda = 0.71073$ Å). The collected data were reduced using SAINT [10] and multi-scan absorption correction was performed using SADABS [11]. The structures were solved by direct methods and refined against F^2 by full-matrix least-squares using the SHELXTL package [12]. All non-hydrogen atoms were refined anisotropically. The amino hydrogens in **1** and **2** 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. The remaining hydrogens in the complexes were placed in calculated positions and constrained to ride on their parent. The crystallographic data for the complexes are summarized in table 1. Selected bond lengths and angles are listed in table 2.

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Table 1. Crystallographic and experimental data for **1**–**3**.

Complex	**1**	**2**	**3**
Formula	$C_{24}H_{34}N_4O_6V_2$	$C_{13}H_{19}N_2O_3V$	$C_{14}H_{13}N_2O_4V$
Formula weight	576.4	302.2	324.2
T (K)	298(2)	298(2)	298(2)
Crystal shape/color	Block/yellow	Block/yellow	Block/yellow
Crystal size (mm^3)	0.17 × 0.15 × 0.15	0.20 × 0.17 × 0.15	0.17 × 0.15 × 0.15
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	$P2_1/n$	$P2_1/n$
a (Å)	7.6441(6)	12.724(2)	11.594(2)
b (Å)	8.5500(7)	6.779(1)	10.380(3)
c (Å)	11.3268(9)	17,082(3)	12.014(3)
α (°)	78.838(1)	90	90
β (°)	78.566(1)	104.261(3)	109.679(2)
γ (°)	67.047(1)	90	90
V (Å^3)	662.58(9)	1427.9(4)	1361.4(5)
Z	1	4	4
D_c (g cm^{-3})	1.445	1.406	1.582
μ (Mo-Kα) (mm^{-1})	0.750	0.700	0.746
F(000)	300	632	664
Data collected	3902	6481	6326
Unique data	2822	2345	2520
Observed data ($I \geqslant 2\sigma(I)$)	2499	1672	1884
Parameters	169	178	191
Restraints	1	1	0
Min. and max. transmission	0.883 and 0.896	0.873 and 0.902	0.884 and 0.896
Goodness-of-fit on F^2	1.055	1.039	1.037
R_1, wR_2 [$I \geqslant 2\sigma(I)$]^a	0.0325, 0.0790	0.0453, 0.1057	0.0384, 0.0874
R_1, wR_2 (all data)^a	0.0389, 0.0833	0.0683, 0.1196	0.0574, 0.0974
Large diff. peak and hole (eÅ^{-3})	0.347 and −0.233	0.377 and −0.249	0.279 and −0.251

$^aR_1 = F_o - F_c/F_o$, $wR_2 - [\Sigma w(F_o{}^2 - F_c{}^2)/\Sigma w(F_o{}^2)^2]^{1/2}$.

3. Results and discussion

The Schiff bases were synthesized by reaction of equimolar quantities of substituted salicylaldehydes with primary amines in methanol. All complexes were synthesized by reaction of methanol solution of the Schiff bases with $VO(acac)_2$. The compounds were characterized by elemental analysis and IR spectra. Structures of the complexes were further confirmed by X-ray crystallography. The molar conductance values of **1**, **2**, and **3** measured in methanol at 10^{-3} M are 12, 30, and 25 $\Omega^{-1}\,cm^2\,mol^{-1}$, indicating the non-electrolytic nature of the complexes [13]. Vanadium in the complexes is + 5 oxidation state and therefore EPR silent. During the synthesis and crystallization of the complexes from oxovanadium(IV) starting material, aerial oxygen must act as the oxidizing agent.

The three Schiff bases coordinate to V through phenolate O, imino N, and amino/pyridine N. The hydroxy groups deprotonate upon coordination. In dimeric **1**, there are four N–H···O hydrogen bonds (table 3) between the two [VO_2L^1] units, while in mononuclear **2**, there are two N–H···O hydrogen bonds. The difference might be caused by the steric effects of the terminal groups, ethyl for **1**, and isopropyl for **2**. As for **3**, there are no hydrogen bonds among the molecules, leading to formation of mononuclear complex.

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Table 2. Selected bond lengths (Å) and angles (°) for **1**–**3**.

1			
V1–O1	1.909(1)	V1–O2	1.610(2)
V1–O3	1.664(1)	V1–N1	2.156(2)
V1–N2	2.152(2)	V1–O3A	2.396(1)
O2–V1–O3	107.6(1)	O2–V1–O1	102.0(1)
O3–V1–O1	98.8(1)	O2–V1–N2	92.5(1)
O3–V1–N2	92.0(1)	O1–V1–N2	158.3(1)
O2–V1–N1	98.5(1)	O3–V1–N1	152.1(1)
O1–V1–N1	84.8(1)	N2–V1–N1	77.0(1)
O2–V1–O3A	169.7(1)	O3–V1–O3A	78.1(1)
O1–V1–O3A	85.3(1)	N2–V1–O3A	78.6(1)
N1–V1–O3A	74.6(1)		
2			
V1–O1	1.896(2)	V1–O2	1.598(2)
V1–O3	1.703(2)	V1–N1	2.125(3)
V1–N2	2.130(3)		
O2–V1–O3	109.6(1)	O2–V1–O1	109.0(1)
O3–V1-O1	93.1(1)	O2–V1–N1	105.1(1)
O3–V1–N1	144.1(1)	O1–V1–N1	83.7(1)
O2–V1–N2	101.9(1)	O3–V1–N2	88.6(1)
O1–V1–N2	146.4(1)	N1–V1–N2	75.7(1)
3			
V1–O1	1.911(2)	V1–O3	1.617(2)
V1–O4	1.618(2)	V1–N1	2.125(2)
V1–N2	2.115(2)		
O3–V1–O4	109.1(1)	O3–V1–O1	101.8(1)
O4–V1–O1	98.1(1)	O3–V1–N2	93.5(1)
O4–V1–N2	90.7(1)	O1–V1–N2	158.6(1)
O3–V1–N1	120.2(1)	O4–V1–N1	129.0(1)
O1–V1–N1	84.2(1)	N2–V1–N1	75.1(1)
V1–O5	1.578(2)	V1–O6	1.744(2)
V1–N1	2.094(2)		
O5–V1–O6	109.2(1)	O5–V1–O1	105.4(1)
O6–V1–O1	99.7(1)	O5–V1–O3	102.5(1)
O6–V1–O3	88.0(1)	O1–V1–O3	146.6(1)
O5–V1–N1	99.9(1)	O6–V1–N1	148.7(1)
O1–V1–N1	83.0(1)	O3–V1–N1	74.4(1)

Table 3. Hydrogen-bond geometry (Å, °) of **1** and **2**.

D–H···*A*	*d*(*D*–H) (Å)	*d*(H···*A*) (Å)	*d*(*D*···*A*) (Å)	(*D*–H···*A*) (°)
1				
N2–H2···O3^{i}	0.90(1)	2.43(2)	2.886(2)	112(2)
N2–H2···O1^{i}	0.90(1)	2.32(2)	3.037(2)	138(2)
2				
N2–H2···O3^{ii}	0.90(1)	2.00(1)	2.890(4)	170(4)

Symmetry codes: (i) $-x$, $1-y$, $-z$; (ii) $1/2-x$, $-1/2+y$, $3/2-z$.

3.1. *Structure description of 1*

The molecular structure of **1** is shown in figure 1. X-ray crystallography reveals that the complex is a centrosymmetric dimeric oxovanadium(V) compound, with inversion center located at the midpoint between the two vanadiums. The V···V distance is 3.187(2) Å. Each V in the complex is six-coordinate through three bonds to oxo groups and three

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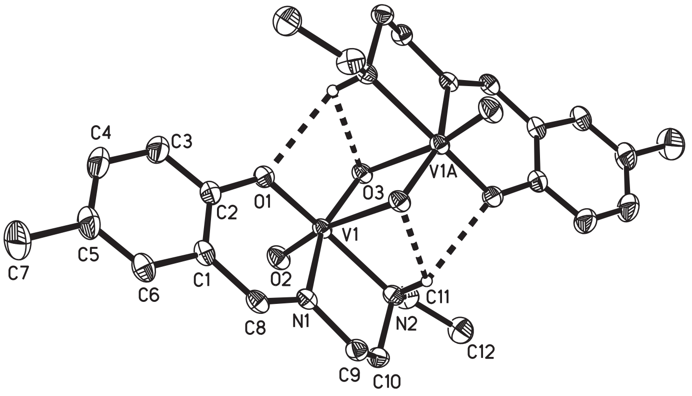

Figure 1. A perspective view of the molecular structure of **1** with the atom labeling scheme. The thermal ellipsoids are drawn at the 30% probability level. Hydrogen bonds are shown as dashed lines. Unlabeled atoms are related to the symmetry position –*x*, 1–*y*, –*z*.

bonds to the tridentate Schiff base, forming an octahedral geometry. The distance between V1 and O2 is 1.609(2) Å, indicating it is a typical V=O bond [14, 15]. O3 in the complex is a bridging group, linking two different but symmetry related vanadiums. The V1–O3 distance of 1.664(1) Å is longer than V1–O2, in accord with those observed in similar structures [14–18]. The V–O and V–N bonds (table 2) agree well with those observed in other Schiff base oxovanadium complexes [14–18]. The V1–O1 bond length of 1.909(1) Å confirms the Schiff base ligand is a monoanion [15, 16]. Distortion of octahedral coordination can be observed by coordinate bond angles, ranging from 74.6(1) to 107.6(1)° for the perpendicular angles and from 152.1(1) to 169.7(1)° for diagonal angles. Four N−H*cdots*O hydrogen bonds form between the two [VO_2L^1] units. Examination of the complex and dimeric oxovanadium(V) complexes reported previously show most exist with intramolecular hydrogen bonds [14–18]. The molecules are further stacked along the *a* axis (figure 2).

3.2. *Structure description of 2 and 3*

Molecular structures of **2** and **3** are shown in figures 3 and 4, respectively. The two Schiff base ligands for **2** and **3** are coordinated in a similar manner. L^2 in **2** coordinates to V

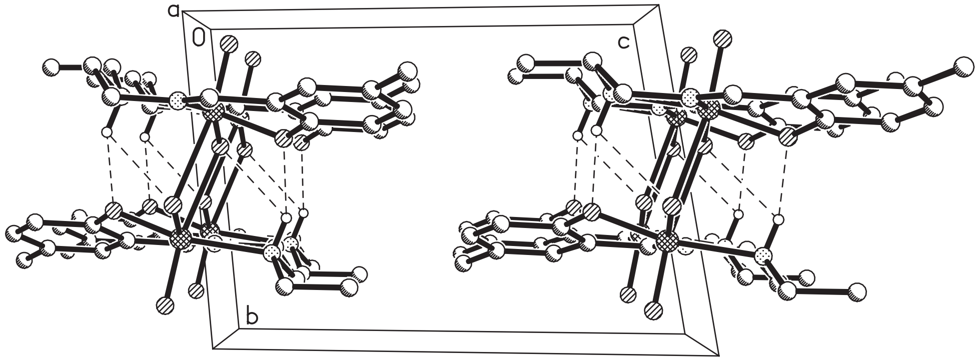

Figure 2. Molecular packing of **1** viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

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through phenolate O, imine N, and amine N. L^3 in **3** coordinates to V through phenolate O, imine N, and pyridine N. In each complex V is coordinated by the Schiff base ligand and two oxo. V in **2** is distorted square-pyramidal coordination, while **3** is intermediate between square-pyramidal and trigonal bipyramidal. The extent of distortion of a square-pyramidal geometry toward a trigonal-bipyramidal geometry can be measured by the value of τ which is defined as $(\beta - \alpha)/60°$, where α and β are the two largest coordinate bond angles [19]. For an ideal square-pyramidal geometry τ is 0 and for an ideal trigonal-bipyramidal geometry τ is 1. The values of τ are 0.039 for **2** and 0.493 for **3**. The V1–O1 and V1–N1 lengths are comparable to each other and also to those observed in similar oxovanadium complexes [20, 21]. V1–N2 in **2** is longer than in **3**, which might be influenced by formation of N2–H2*cdots*O3 hydrogen bonds in **2**, and also might be influenced by the different geometries of N2. It is not unusual that $M–N_{amino}$ bonds are longer than $M–N_{pyridine}$ bonds [9, 16, 17, 22]. Molecules in **2** are linked through intermolecular $N-H\cdots O$ hydrogen bonds, forming zigzag chains running along the *b* axis, as shown in figure 5.

3.3. *IR and NMR spectra*

IR spectra of HL^1, HL^2, **1** and **2** exhibit sharp bands at 3150–3250 cm^{-1}, assigned to ν(N–H). Weak and broad absorptions at 3300–3400 cm^{-1} in spectra of the free Schiff bases

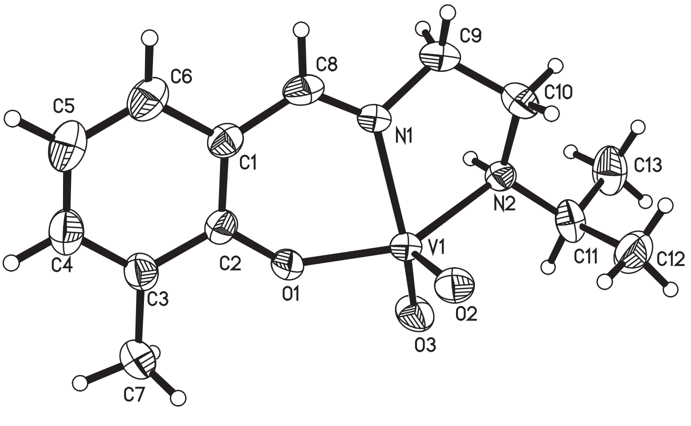

Figure 3. A perspective view of the molecular structure of **2** with the atom labeling scheme. The thermal ellipsoids are drawn at the 30% probability level.

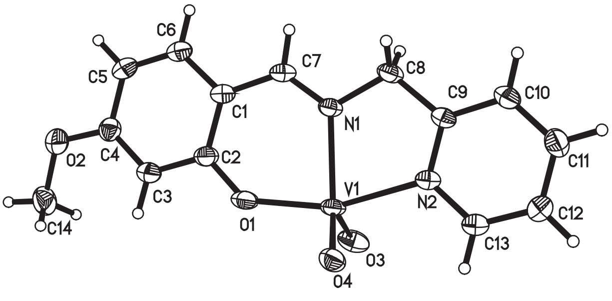

Figure 4. A perspective view of the molecular structure of **3** with the atom labeling scheme. The thermal ellipsoids are drawn at the 30% probability level.

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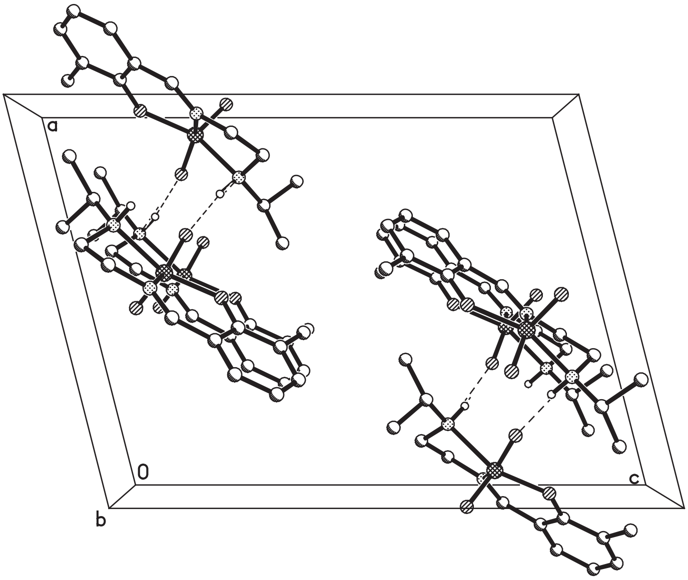

Figure 5. Molecular packing of **2** viewed along the *b* axis. Hydrogen bonds are shown as dashed lines.

are absent in the complexes, indicating that the three Schiff bases coordinate to V through deprotonated phenolate. This is also supported by the shift of *ν*(C–O) of free Schiff bases and corresponding complexes. Strong absorptions at 1636 cm^{-1} in **1**, 1643 cm^{-1} in **2**, and 1611 cm^{-1} in **3** are attributed to *ν*(C=N) [23], which are shifted to lower wavenumbers when compared to those of the free Schiff bases. This is caused by coordination of imino N. Bands at 933 and 849 cm^{-1} in **1**, 927 and 848 cm^{-1} in **2**, and 925 cm^{-1} in **3** are assigned to *ν*(V=O) [16]. There are two distinct bands attributed to V=O stretches in spectra of **1** and **2**. However, there is only one band attributed to V=O stretch in **3**. This can be explained by V=O bond distances. The V=O bonds in **1** and **2** are 1.610(1) and 1.664(1) Å, and 1.598(2) and 1.703(2) Å, respectively. However, in **3**, the two V=O bonds are very similar, *viz.* 1.617(2) and 1.618(2) Å.

The DMSO-d_6 solutions of the Schiff bases and their complexes were used to record proton NMR spectra. The aromatic protons appear as multiplets at δ 6.7–7.7 ppm. For HL^1 and HL^2 and their complexes, methyl groups attached to aromatic rings resonate as a singlet near δ 2.2 ppm, while those of the ethyl or isopropyl groups are δ 1.1 ppm for HL^1 and HL^2, and δ 1.30 ppm for **1** and δ 1.22 ppm for **2**. The singlet observed at δ 3.78 ppm for HL^3 and δ 4.02 ppm for **3** are attributed to methyl of the methoxy substituents on the salicylidene fragments. The –NH– protons of HL^1 and HL^2 are broad singlets at δ 9.8 ppm and δ 13.5 ppm, respectively. The azomethine (–CH=N–) protons in the Schiff bases are singlets at δ 8.3–8.6 ppm, while in the complexes they are observed at δ 8.8–8.9 ppm. These chemical shifts are not unusual for complexes containing the oxovanadium(V) units [21, 24, 25].

4. Conclusion

This paper reports the synthesis and structures of three new dioxovanadium(V) complexes with Schiff bases. The hydrogen bonds and steric effects of the Schiff bases influence the final structures of the complexes. The amino group, which readily forms intermolecular hydrogen bonds with adjacent ligand, and the presence of small steric effects of ethyl can result in formation of dimeric structures. Besides the amino group, sizes of the groups attached to the amino groups are very sensitive. Comparing **1** and **2** the small adjustment from ethyl to isopropyl, only mononuclear complex can be obtained.

Supplementary material

CCDC 891283 for **1**, 891287 for **2**, and 891285 for **3** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/data_request/cif.

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