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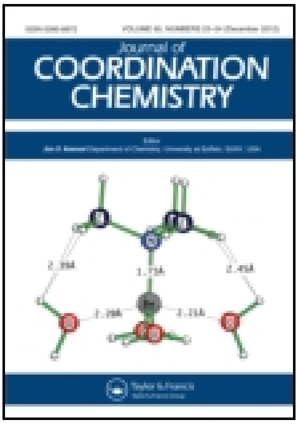

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Synthesis and structures of 3-chloro-*N′*-(2-hydroxybenzylidene)benzohydrazide and its oxovanadium(V) complex

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A new Schiff-base 3-chloro-*N′*-(2-hydroxybenzylidene)benzohydrazide (H_2BBH) and its oxovanadium(V) complex $[VO(BBH)(OCH_3)]_2$ have been synthesized and characterized by elemental analysis, infrared (IR) spectra, and single-crystal X-ray determination. Both the ligand and the complex crystallized in the monoclinic space group $P2_1/c$. The Schiff-base coordinates to V through the phenolate O, the imine N, and the enolic O. In the centrosymmetric dimeric oxovanadium(V) complex, the V atom is six-coordinate in an octahedral geometry. The bond lengths related to the donor atoms in the complex are different from those in the ligand. The coordination of the ligand to V is also supported by IR spectra.

Keywords: Schiff base; Oxovanadium(V) complex; Crystal structure; Coordination compound

1. Introduction

Oxovanadium complexes have received considerable attention for their role in living organisms [1–3]. This interest stems from the discovery of two kinds of vanadium enzymes, vanadium-nitrogenases and vanadate-dependent haloperoxidases [4, 5]. The insulin-like effect of vanadium complexes is another intriguing and promising feature that has further stimulated vanadium chemistry [6–8]. Schiff bases are versatile ligands in coordination chemistry and biological chemistry [9, 10]. Oxovanadium complexes derived from Schiff bases have been reported to possess insulin-enhancing properties [11, 12]. However, the number of oxovanadium complexes with Schiff-bases containing –C = N–NH–C(O)– functional groups are relatively few. In this work, a new Schiff-base 3-chloro-*N′*-(2-hydroxybenzylidene)benzohydrazide (H_2BBH) and its oxovanadium(V) complex $[VO(BBH)(OCH_3)]_2$ (scheme 1) have been synthesized and characterized. This particular interest is to investigate the coordination and the structures between the Schiff base and the oxovanadium(V) complex.

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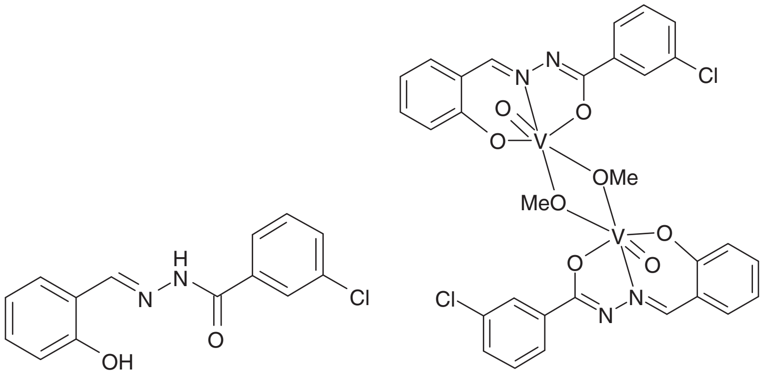

Scheme 1. H_2BBH and $[VO(BBH)(OCH_3)]_2$.

2. Experimental

2.1. *Materials and methods*

Salicylaldehyde and 3-chlorobenzohydrazide were purchased from Alfa Aesar. $[VO(acac)_2]$ was prepared according to the literature method [13]. All chemicals and solvents were of analytical grade and used as obtained. Microanalyses of the Schiff base and the oxovanadium(V) complex were performed with a Vario EL III CHNOS elemental analyzer. Infrared (IR) spectra were recorded as KBr pellets with a FTS-40 spectrophotometer.

2.2. *Synthesis of 3-chloro-N′-(2-hydroxybenzylidene)benzohydrazide (H_2BBH)*

A mixture of salicylaldehyde (1.22 g, 10 mmol) and 3-chlorobenzohydrazide (1.70 g, 10 mmol) in 100 mL methanol was refluxed for 2 h, and cooled to room temperature. The colorless solution was left in air for about a month until most of the solvent was evaporated, yielding needle-shaped single crystals of H_2BBH, which were isolated by filtration, and dried in air. Yield 2.53 g (92%). Anal. Calcd for $C_{14}H_{11}ClN_2O_2$ (%): C, 61.2; H, 4.0; N, 10.2. Found (%): C, 60.9; H, 4.1; N, 10.3. IR (KBr, ν_{max}/cm^{-1}): 3446 (OH), 3164 (NH), 1650 (C = O), 1622 (C = N).

2.3. *Synthesis of the oxovanadium(V) complex $[VO(BBH)(OCH_3)]_2$*

A stirred solution of H_2BBH (0.274 g, 1 mmol) in absolute methanol (20 mL) was mixed with $[VO(acac)_2]$ (0.265 g, 1 mmol), and the resulting reaction mixture was refluxed on a water bath for 1 h, and then cooled to room temperature, yielding a deep-brown solution. The solution was left at ambient temperature for slow evaporation of the solvent for a week, yielding brown block-shaped single crystals of the complex. Yield 0.273 g (74%). Anal. Calcd for $C_{30}H_{24}Cl_2N_4O_8V_2$: C, 48.6; H, 3.3; N, 7.6. Found (%): C, 48.9; H, 3.3; N, 7.4. IR (KBr, ν_{max}/cm^{-1}): 1602 (C = N), 1339 (C–O, enolic), 1216 (C–O, phenolate), 1024 (N–N), 914 (V = O), 481, 437 (V–O, V–N).

Table 1. Crystallographical and experimental data for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{14}H_{11}ClN_2O_2$	$C_{30}H_{24}Cl_2N_4O_8V_2$
Formula weight	274.7	741.3
Temperature (K)	298(2)	298(2)
Crystal shape/color	Needle/colorless	Block/brown
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	10.855(3)	11.481(3)
b	13.587(2)	8.081(2)
c	8.893(2)	19.035(3)
β	95.326(3)	117.240(2)
Volume (Å^3), Z	1305.9(5), 4	1570.2(6), 2
Calculated density (g cm^{-3})	1.397	1.568
Absorption coefficient, μ (Mo-Kα) (cm^{-1})	0.291	0.822
$F(000)$	568	752
Crystal size (mm^3)	0.18 × 0.17 × 0.15	0.30 × 0.27 × 0.26
R_{int}	0.0621	0.0804
Unique reflections	2823	3755
Observed reflections $I \geq 2\sigma(I)$	1398	1974
Min. and max. transmission	0.9495/0.9577	0.7905/0.8147
Parameters	176	208
Restraints	1	0
Goodness-of-fit on F^2	1.040	0.941
R_1, wR_2 $[I \geq 2\sigma(I)]$[a]	0.0624, 0.1481	0.0660, 0.1563
R_1, wR_2 (all data)[a]	0.1359, 0.1820	0.1280, 0.1909
Largest difference peak and hole (e Å^{-3})	0.390/ − 0.316	0.712/ − 0.526

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w_{(1)} = [\sigma^2(F_o)^2 + (0.0649(F_o^2 + 2F_c^2)/3)^2 + 0.1444(F_o^2 + 2F_c^2)/3)]^{-1}$, $w_{(2)} = [\sigma^2(F_o)^2 + (0.0910(F_o^2 + 2F_c^2)/3)^2]^{-1}$.

2.4. *X-ray structural determination*

Data were collected on a Bruker SMART 1000 CCD area diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. The data were corrected with SADABS and refined on F^2 with Siemens SHELXL software [14, 15]. The structures were solved by direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. H2 attached to N2 in H_2BBH was located from a difference Fourier map and refined isotropically, with N–H distance restrained to 0.90(1) Å. The other hydrogens were placed in calculated positions and included in the last cycles of refinement. Crystal data and details of the data collection and refinement are listed in table 1. Selected bond lengths and angles are listed in table 2. The intramolecular O1–H1···N1 and intermolecular N2–H2···O2 hydrogen bond parameters are given in table 3.

3. Results and discussion

Reaction between equimolar quantities of $[VO(acac)_2]$ with H_2BBH in absolute methanol afforded $[VO(BBH)(OCH_3)]_2$. The BBH adopts an enolic tautomeric form on complexation. On aerial oxidation in methanol, the V^{IV} in $VO(acac)_2$ is changed to

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

1			
N1–C7	1.274(4)	N1–N2	1.386(3)
N2–C8	1.352(4)	C8–O2	1.227(3)
C2–O1	1.360(4)	–	–
2			
V1–O1	1.818(3)	V1–O2	1.925(3)
V1–O3	2.381(3)	V1–O3^{i}	1.820(3)
V1–O4	1.591(3)	V1–N1	2.112(3)
N1–C7	1.283(5)	N1–N2	1.406(4)
N2–C8	1.304(5)	C8–O2	1.313(5)
C2–O1	1.336(5)	–	–
O4–V1–O1	101.54(15)	O4–V1–O3^{i}	101.93(15)
O1–V1–O3^{i}	103.34(13)	O4–V1–O2	97.00(13)
O1–V1–O2	153.24(14)	O3^{i}–V1–O2	91.38(12)
O4–V1–N1	99.17(16)	O1–V1–N1	83.38(13)
O3^{i}–V1–N1	155.98(13)	O2–V1–N1	74.69(13)
O4–V1–O3	174.34(14)	O1–V1–O3	83.04(12)
O3–V1–O3^{i}	73.58(12)	O2–V1–O3	79.84(11)
N1–V1–O3	84.59(11)	–	–

Symmetry code: $^{i}-x$, $1-y$, $-z$.

Table 3. Hydrogen bonding for **1**.

D–H···A	$d(D$–H) (Å)	d(H···A) (Å)	$d(D$···A) (Å)	∠(D–H···A) (°)
O1–H1···N1	0.82	1.93	2.645(3)	146
N2–H2···O2^{ii}	0.893(10)	1.939(13)	2.818(3)	167(3)

Symmetry code: ^{ii}x, $1/2-y$, $1/2+z$.

V^V in the complex. The Schiff base crystallizes as colorless crystals, and the oxovanadium(V) complex crystallizes as brown crystals, both of which are stable in air at room temperature, and soluble in common polar organic solvents, such as DMSO, DMF, MeOH, EtOH, and MeCN, but insoluble in water.

3.1. *IR spectra*

IR spectra of the Schiff base and the oxovanadium(V) complex provide information about the metal–ligand bonding. Assignments are based on typical group frequencies. The weak and broad band centered at 3446 cm^{-1} of the Schiff base is assigned to the ν(O–H). The ν(C = O) vibration at 1650 cm^{-1} and the sharp ν(NH) vibration of 3164 cm^{-1} for H_2BBH are absent in the complex, indicating enolization of the amide functionality and subsequent proton replacement by the vanadium, in accord with the results from X-ray determination. The ν(C–O)(enolic) of the complex is at 1339 cm^{-1}. The strong band at 1622 cm^{-1} in the Schiff base is assigned to the azomethine group, observed at lower frequency (1602 cm^{-1}) in the complex, indicating coordination of azomethine to V. The band observed at 914 cm^{-1} for the complex is assigned to V = O stretch, and the bands indicative of V–O and V–N vibrations are at 437–481 cm^{-1}.

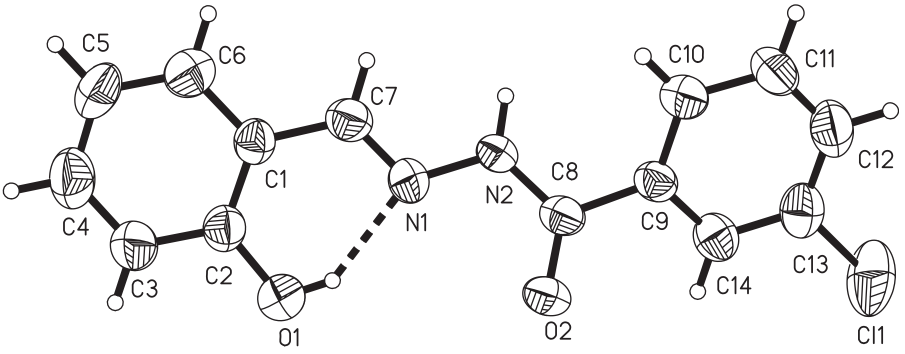

Figure 1. ORTEP plot (50% probability level) and numbering scheme for **1**.

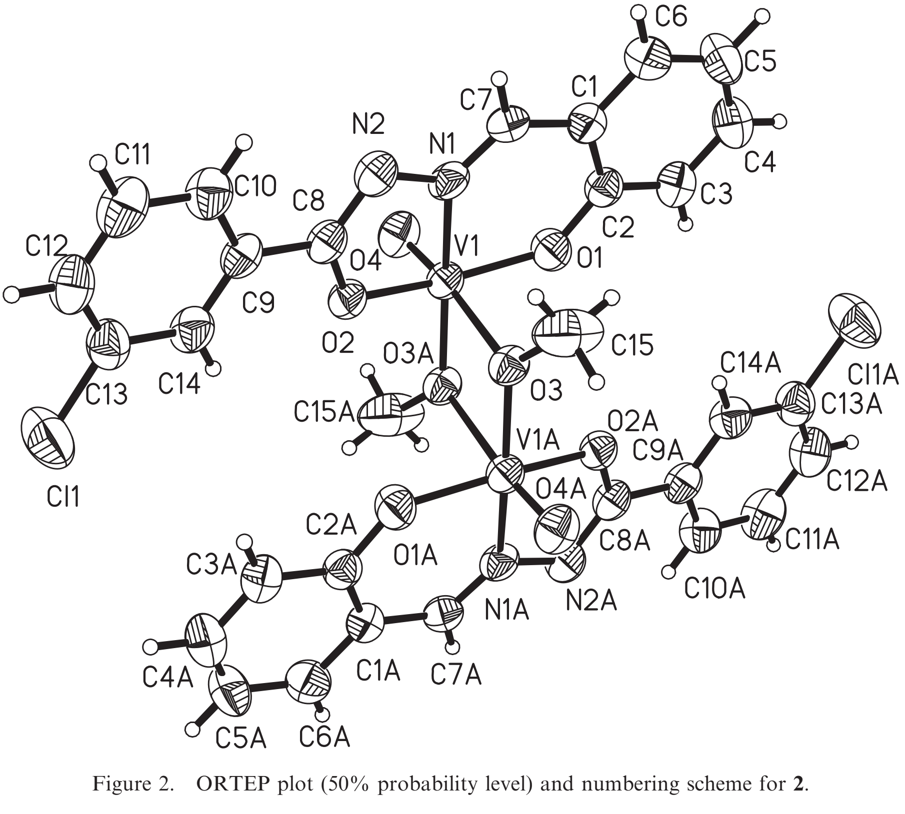

Figure 2. ORTEP plot (50% probability level) and numbering scheme for **2**.

3.2. *Structures of the Schiff base and oxovanadium(V) complex*

Figures 1 and 2 give perspective views of the Schiff base and the oxovanadium(V) complex together with the atom-labeling systems. There is an intramolecular O1–H1···N1 hydrogen bond in the ligand, and the dihedral angle between the two benzene rings is 16.2(2)°. All the bond lengths in the Schiff-base ligand are comparable

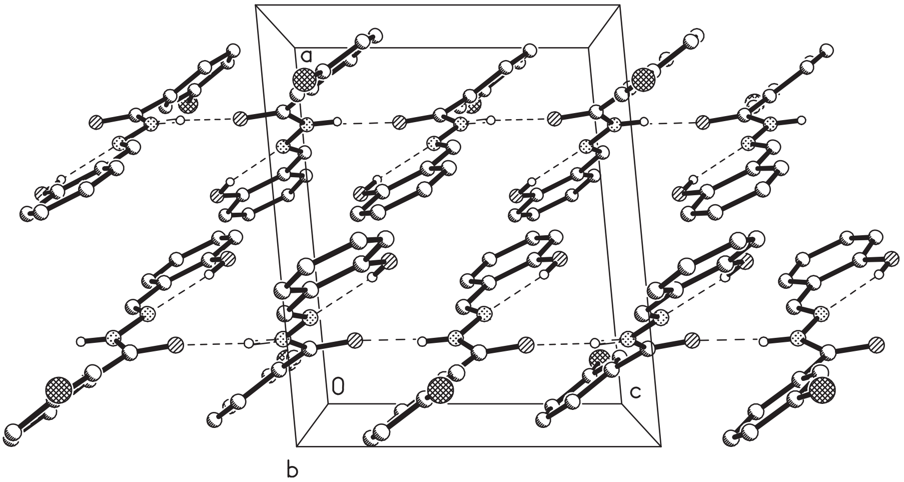

Figure 3. Molecular packing diagram for **1**, viewed along the *c*-axis.

to those observed in similar Schiff-base compound [16]. The complex, derived from the Schiff-base ligand, is a centrosymmetric dimeric oxovanadium(V) structure, with V···V distance of 3.381(1) Å. The ligand BBH forms one five-membered and one six-membered chelate rings with bite angles of 74.7(1) and 83.4(1)°. The V is in a distorted octahedral O_5N coordination sphere. The phenolate O, imine N, and enolic O of BBH, and one methoxy constitute the equatorial plane, with mean deviation of 0.030 Å. The two axial positions are occupied by one oxo and another methoxy. The displacement of V from the equatorial plane toward the axial oxo is 0.335(2) Å. The *cis* bond angles are in the range 73.6(1)–103.3(1)°, and the *trans* bond angles are 153.2(1)–174.3(1)°. The V–O and V–N bond lengths in the complex are comparable with bond lengths reported for oxovanadium(V) complexes with similar ligands [17–21]. As commonly observed in analogous species, the elongated V1–O3 bond *trans* to the oxo group in the complex indicates weak coordination of O3 at the axial position. The dihedral angle between the two benzene rings in the complex is 7.0(2)°.

The Schiff-base ligand coordinates to V through the phenolate O1, the imine N1, and enolic O2. The bond lengths of C7 = N1 [1.283(2) Å] and N1–N2 [1.406(2) Å] in the complex are longer than those [1.274(2) and 1.386(2) Å] in the Schiff ligand, indicating the imine N of the azomethine group is coordinated to V. The bond lengths of C2–O1 [1.336(2) Å] in the complex is a little shorter than that [1.360(2) Å] in the Schiff-base ligand, which is due to the intramolecular O1–H1···N1 hydrogen bond in the ligand. The distance between C8 and N2 [1.304(2) Å] in the complex is shorter than that [1.352(2) Å] in the ligand, and the distance between C8 and O2 [1.313(2) Å] in the complex is longer than that [1.227(2) Å] in the ligand, indicating the enolization of the N2–C8–O2 group in the complex.

In the crystal structure of the Schiff base, molecules are linked *via* intermolecular N–H···O hydrogen bonds, forming chains running along the *c*-axis, as shown in figure 3. In the crystal structure of the complex, molecules are stacked together by weak $\pi \cdots \pi$ interactions among the molecules, as shown in figure 4.

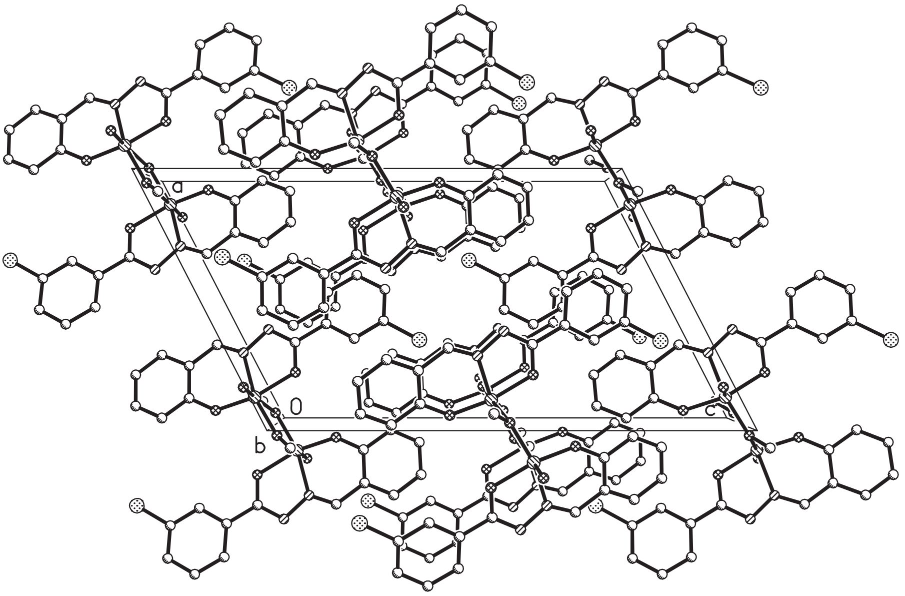

Figure 4. Molecular packing diagram for **2**, viewed along the *c*-axis.

4. Conclusion

Using the new tridentate Schiff-base ligand prepared from salicylaldehyde with 3-chlorobenzohydrazide in methanol, the new dimeric methoxy-bridged centrosymmetric oxovanadium(V) complex has been synthesized. The structures of the Schiff-base ligand and the complex were determined. The dianionic Schiff base coordinates to V through the phenolate-O, the imine-N, and the enolic-O.

Supplementary material

CCDC 806699 and 806700 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgment

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