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ORIGINAL PAPER

Synthesis and Crystal Structures of *N*′-3,5-Dibromo-2-Hydroxybenzylidene)-2-Hydroxy-3-Methylbenzohydrazide and its Oxovanadium(V) Complex [*N*′-(3,5-Dibromo-2-Oxidobenzylidene-*κO*)-2-Hydroxy-3-Methylbenzohydrazidato-$\kappa^2 N',O$](Methanol-*κO*)(Methanolato-*κO*)Oxidovanadium(V)

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Abstract A new hydrazine ligand *N*′-3,5-dibromo-2-hydroxybenzylidene)-2-hydroxy-3-methylbenzohydrazide (**1**) and its oxovanadium(V) complex [*N*′-(3,5-dibromo-2-oxidobenzylidene-*κO*)-2-hydroxy-3-methylbenzohydrazidato-$\kappa^2 N',O$](methanol-*κO*)(methanolato-*κO*)oxidovanadium(V) (**2**), were prepared and were structurally characterized by elemental analysis, IR spectra and single-crystal X-ray diffraction. Compound **1** crystallizes in the triclinic space group $P{-}1$, with unit cell dimensions $a = 7.813(2)$ Å, $b = 8.748(2)$, $c = 26.071(6)$ Å, $\alpha = 85.763(2)°$, $\beta = 81.521(2)°$, $\gamma = 89.358(3)°$, $V = 1757.6(7)$ Å^3, $Z = 4$, $R_1 = 0.0587$, and $wR_2 = 0.1054$. Compound **2** crystallizes in the triclinic space group *P*-1, with unit cell dimensions $a = 7.777(3)$ Å, $b = 11.594(3)$, $c = 12.363(3)$ Å, $\alpha = 107.965(3)°$, $\beta = 103.190(2)°$, $\gamma = 96.656(2)°$, $V = 1011.3(5)$ Å^3, $Z = 2$, $R_1 = 0.0634$, and $wR_2 = 0.1480$. The hydrazine ligand coordinates to the V atom through the phenolic O, imino N, and ethanolic O atoms. The V atom in the complex is in an octahedral coordination, with the three donor atoms of the hydrazine ligand and one methanolato O atom defining the equatorial plane, and with one methanol O and one oxo O atoms occupying the axial positions. The displacement of the V atom from the equatorial plane towards the axial oxo O atom is 0.305(2) Å.

Keywords Hydrazine · Oxovanadium complex · Synthesis · Crystal structure

Introduction

The coordination chemistry of oxovanadium complexes with multidentate ligands has attracted much interest both for their structures and biological activities [1–5]. In the recent years, a large number of oxovanadium complexes have been reported; however, the oxovanadium complexes with hydrazine ligands are relatively rare [6–8]. In this paper, a new hydrazine ligand *N*′-3,5-dibromo-2-hydroxybenzylidene)-2-hydroxy-3-methylbenzohydrazide (**1**, Scheme 1) was prepared. Based on the ligand, a new oxovanadium(V) complex, [*N*′-(3,5-dibromo-2-oxidobenzylidene-*κO*)-2-hydroxy-3-methylbenzohydrazidato-$\kappa^2 N',O$](methanol-*κO*)(methanolato-*κO*)oxidovanadium(V) (**2**), was successful prepared. The structures of the hydrazine ligand and the complex were characterized by elemental analysis, IR spectra, and single-crystal X-ray diffraction.

Experimental

Materials and Measurements

3,5-Dibromosalicylaldehyde and 2-hydroxy-3-methylbenzohydrazide were purchased from Aldrich. Other chemicals and solvents were of reagent grade and were used as obtained. Elemental analyses were performed on a Carlo-Erba EA microanalyser. Infrared spectra were recorded as KBr discs on a Bruker IFS-66V spectrometer. The ^{1}H NMR spectrum of the hydrazine ligand was recorded on a Bruker 400 MHz spectrometer with $CDCl_3$ as the solvent.

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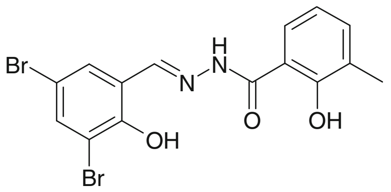

Scheme 1 *N*′-3,5-Dibromo-2-hydroxybenzylidene)-2-hydroxy-3-methylbenzohydrazide

Synthesis of *N*′-3,5-Dibromo-2-Hydroxybenzylidene)-2-Hydroxy-3-Methylbenzohydrazide (**1**)

A methanolic solution (30 mL) of 3,5-dibromosalicylaldehyde (2.0 mmol, 560 mg) was added dropwise to a stirred methanolic solution (20 mL) of 2-hydroxy-3-methylbenzohydrazide (2.0 mmol, 332 mg). The mixture was stirred at room temperature for 1 h to give clear colorless solution. The solution was slowly evaporated in air to give colorless solid product of the hydrazine ligand. Yield: 93%. Analysis calculated for $C_{15}H_{12}Br_2N_2O_3$: C, 42.1; H, 2.8; N, 6.5%; found: C, 42.3; H, 2.8; N, 6.6%. ^{1}H NMR data ($CDCl_3$, ppm): $\delta = 2.15$ (s, 3H), 6.92 (q, 1H), 7.31 (d, 1H), 7.66 (d, 1H), 7.73 (s, 1H), 7.81 (s, 1H), 8.15 (s, 1H), 8.73 (s, 1H), 10.3 (b, 2H). Single crystals of the compound were obtained by recrystallization of the product in methanol.

Synthesis of [*N*′-(3,5-Dibromo-2-Oxidobenzylidene-*κO*)-2-Hydroxy-3-Methylbenzohydrazidato-κ^2N',O](Methanol-*κO*)(Methanolato-*κO*) Oxidovanadium(V) (**2**)

To a stirred methanolic solution (5 mL) of the hydrazine ligand (0.5 mmol, 214 mg) was added dropwise a methanolic solution (5 mL) of $VO(acac)_2$ (0.5 mmol, 132 mg). The mixture was stirred for 1 h at room temperature to give brown solution. Brown crystals of the complex, suitable for X-ray diffraction, were obtained after one weak for slow evaporation of the solution in air. Yield: 61%. Analysis calculated for $C_{17}H_{17}Br_2N_2O_6V$: C, 36.7; H, 3.1; N, 5.0%; found: C, 36.5; H, 3.2; N, 5.1%.

X-ray Crystallography

Each single crystal of the compounds was mounted on a glass fiber. Intensity data were collected on a BRUKER SMART 1000 CCD diffractometer. Intensities and lattice parameters were obtained with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). All data were corrected for Lorentz and polarization effects. Empirical absorption corrections were also applied for both crystal structures [9]. Complex scattering factors were taken from the SHELXTL program [10]. The structures of the compounds were solved by direct method, which revealed the positions of all non-hydrogen atoms. Both structures of the compounds were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms. The amino H atoms in the hydrazine ligand and the methanol H atom in the complex were located from difference Fourier maps and refined isotropically, with N–H and O–H distances restrained to 0.90(1) and 0.85(1) Å, respectively. The remaining hydrogen atoms were located in their calculated positions and refined using a riding model. The crystals were weakly diffracting so that the ratio of observed to unique reflections is low (43% for **1** and 42% for **2**). The details of the X-ray crystal

Table 1 Crystallographic data for **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{16}H_{16}Br_2N_2O_4$	$C_{17}H_{17}Br_2N_2O_6V$
Formula weight	460.1	556.1
Crystal shape/colour	Block/colorless	Block/brown
Crystal size (mm)	0.23 × 0.20 × 0.20	0.27 × 0.23 × 0.23
Crystal system	Triclinic	Triclinic
Space group	$P-1$	$P-1$
a (Å)	7.813(2)	7.777(3)
b (Å)	8.748(2)	11.594(3)
c (Å)	26.071(6)	12.363(3)
α (°)	85.763(2)	107.965(3)
β (°)	81.521(2)	103.190(2)
γ (°)	89.358(3)	96.656(2)
V (Å^3)	1757.6(7)	1011.3(5)
Z	4	2
D_{calc} (g/cm^3)	1.739	1.826
T (K)	298(2)	298(2)
μ (mm^{-1})	4.634	4.477
F(000)	912	548
Range of h, k, l	−9/9, −10/10, −31/27	−9/9, −14/14, −15/15
Max. and min. transmission	0.415 and 0.458	0.378 and 0.426
Unique reflections	6442	4290
Observed reflections $I > 2\sigma(I)$	2746	1806
Data/restraints/ parameters	6442/4/451	4290/1/261
Goodness-of-fit on F^2	0.932	0.899
R_{int}	0.0662	0.0723
R_1 [$I \geq 2\sigma(I)$]	0.0587	0.0634
wR_2 [$I \geq 2\sigma(I)$]	0.1054	0.1480
R_1 (all data)	0.1698	0.1694
wR_2 (all data)	0.1404	0.2089

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

1			
Bond lengths			
N1–C7	1.273(9)	N1–N2	1.373(8)
N3–C22	1.265(9)	N3–N4	1.378(8)
2			
Bond lengths			
N1–C7	1.274(9)	N1–N2	1.390(9)
V1–O1	1.865(6)	V1–O2	1.955(6)
V1–O4	1.577(6)	V1–O5	2.308(6)
V1–O6	1.746(5)	V1–N1	2.134(6)
Bond angles			
O4–V1–O6	102.5(3)	O4–V1–O1	100.0(3)
O6–V1–O1	100.4(3)	O4–V1–O2	97.5(3)
O6–V1–O2	97.1(2)	O1–V1–O2	151.8(2)
O4–V1–N1	95.7(3)	O6–V1–N1	161.0(3)
O1–V1–N1	81.9(2)	O2–V1–N1	74.6(2)
O4–V1–O5	176.4(3)	O6–V1–O5	80.3(2)
O1–V1–O5	81.6(2)	O2–V1–O5	79.8(2)
N1–V1–O5	81.4(2)		

data, and the structure solution and refinement for both compounds are given in Table 1. Selected bond lengths and angles are given in Table 2. Crystallographic data for both compounds have been deposited in the Cambridge Crystallographic Data Centre (CCDC 817824 and 817825).

Results and Discussion

The hydrazine ligand and the oxovanadium(V) complex are stable in air at room temperature. They are soluble in methanol, ethanol and acetonitrile. The elemental analyses are in good agreement with the chemical formulae proposed for the compounds.

The hydrazine compound *N*′-3,5-dibromo-2-hydroxybenzylidene)-2-hydroxy-3-methylbenzohydrazide is a flexible multidentate ligand, which coordinates to the metal atoms through the phenolic O, imino N, and enolic O atoms. The V atoms usually adopt octahedral and square-pyramidal coordination [11–13]. The methanol was proved to be a preferred solvent for the preparation of such complexes.

Structure of 1

The molecular structure of the hydrazine ligand is shown in Fig. 1. The compound consists of two hydrazine molecules and two methanol molecules of crystallization. The hydrazine molecules are approximately coplanar, with mean deviation from the least squares planes defined by the non-hydrogen atoms of 0.062(1) and 0.039(1) Å, respectively. The dihedral angles between the two benzene rings are 6.6(2) and 4.4(2)°. The intramolecular O–H···N hydrogen bonds (Table 3) may contribute to the formation of the planar geometry of the molecules. The hydrazine molecule adopts a *trans* configuration about the C7–N1 and C22–N3 bonds. The long C7–N1 and C22–N3 bonds and the short N1–N2 and N3–N4 bonds suggest the delocalization of the acetohydrazide moieties. All the bond distances in the compound are within normal ranges [14], and are comparable to those in the similar compounds [15, 16].

In the crystal structure of the compound (Fig. 2), the adjacent two hydrazine molecules are linked by two methanol molecules through two intermolecular C31—H31B···O2 hydrogen bonds (Table 3) and two intermolecular O7—H7···O1 hydrogen bonds (Table 3), to form dimers. There are no obvious short contacts among the dimers.

Structure of 2

The molecular structure of the oxovanadium(V) complex is shown in Fig. 3. The dianionic hydrazine ligand coordinates to the V atom through the phenolic O, imino N, and enolic O atoms, forming a five-membered and a six-membered chelate rings with bite angles of 74.6(2) and 81.9(2)°. The V atom in the complex is in an octahedral coordination, with the three donor atoms of the hydrazine ligand and one methanolato O atom defining the equatorial plane, and with one methanol O and one oxo O atoms occupying the axial positions. The displacement of the V atom from the equatorial plane towards the axial oxo O atom is 0.305(2) Å. The coordinate bond lengths and angles in the complex are similar to those reported elsewhere [11–13]. The formation of the coordinate bonds with the V atom for the hydrazine ligand, together with the

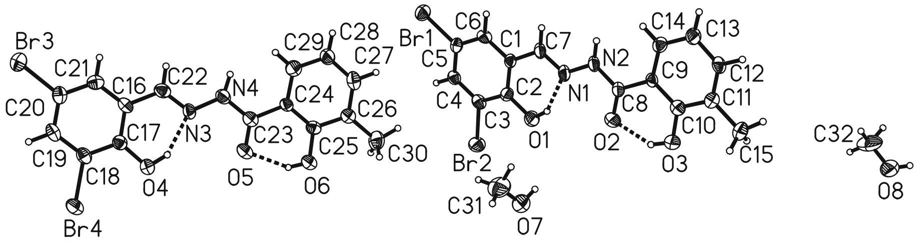

Fig. 1 Molecular structure of **1** with 30% probability ellipsoids. Hydrogen bonds are shown as *dashed lines*

Table 3 Hydrogen geometries for **1** and **2**

D–H···*A*	*d*(*D*–H, Å)	*d*(H···*A*, Å)	*d*(*D*···*A*, Å)	Angle (*D*–H···*A*, °)
1				
O7–H7···O1$^{\#1}$	0.82	2.61	3.056(9)	116
O6–H6···O5	0.82	1.83	2.545(8)	145
N4–H4A···O8$^{\#2}$	0.90(1)	2.17(5)	2.901(10)	138(7)
O3–H3···O2	0.82	1.84	2.547(8)	143
O1–H1···N1	0.85(1)	1.82(5)	2.567(8)	146(8)
N2–H2···O7$^{\#3}$	0.90(1)	2.02(3)	2.878(9)	161(7)
O4–H4C···N3	0.85(1)	1.82(4)	2.582(8)	148(8)
C31–H31B···O2$^{\#4}$	0.96	2.50	3.423(8)	161(8)
2				
O5–H5···O3$^{\#5}$	0.85(1)	1.90(2)	2.733(8)	166(8)
O3–H3···N2	0.82	1.81	2.536(9)	146
C7–H7···O4$^{\#6}$	0.93	2.54	3.225(8)	131(8)

Symmetry codes: #1: 1 − *x*, −*y*, 1 − *z*; #2: *x*, *y*, −1 + *z*; #3: *x*, 1 + *y*, *z*; #4: −*x*, 1 − *y*, 1 − *z*; #5: 2 − *x*, 1 − *y*, 1 − *z*; #6: 1 − *x*, 1 − *y*, 1 − *z*

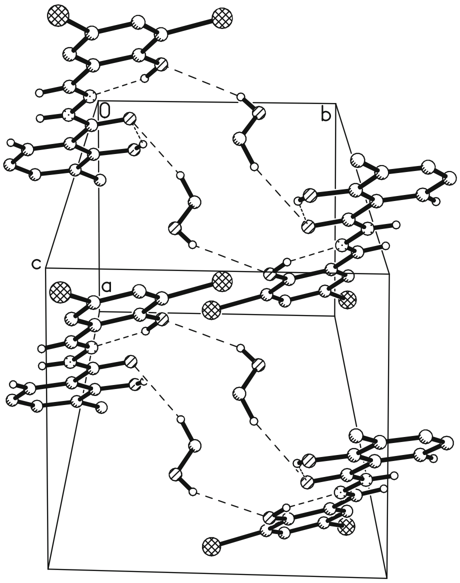

Fig. 2 Molecular packing diagram of **1**. Hydrogen bonds are shown as *dashed lines*

existence of the intramolecular O–H···N hydrogen bond (Table 3), leads to the planarity of the hydrazine ligand. The dihedral angle between the C1–C6 and C9–C14 benzene rings is 5.6(2)°.

In the crystal structure of the complex (Fig. 4), the adjacent two complex molecules are linked by two intermolecular C7−H7···O4 hydrogen bonds (Table 3), to form a dimer. The adjacent dimers are further linked by two methanol ligands through two intermolecular O5−H5···O3 hydrogen bonds (Table 3), to form chains along the *a* axis.

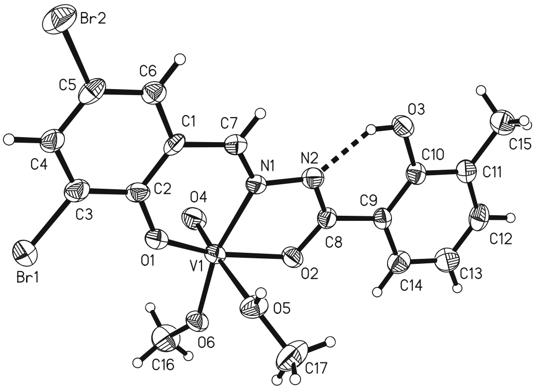

Fig. 3 Molecular structure of **2** with 30% probability ellipsoids. Hydrogen bonds are shown as *dashed lines*

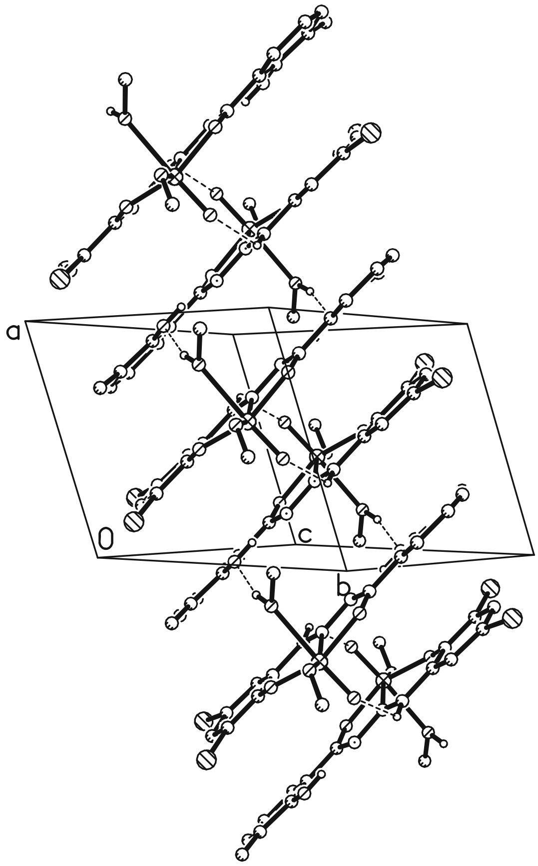

Fig. 4 Molecular packing diagram of **2**. Hydrogen bonds are shown as *dashed lines*

IR Spectra

The typical band centered at 3432 cm^{-1} of the hydrazine ligand can be attributed to the phenolic O–H stretch. The *ν*(C=O) absorption band at 1653 cm^{-1} and the sharp *ν*(NH) band at 3223 cm^{-1} in the IR spectrum of the hydrazine ligand are absent in the complex, indicating the enolisation of the amide functionality and subsequent proton replacement by the V atom. The middle absorption band at 1328 cm^{-1} in the spectrum of the complex is assigned to the v(C–O)(enolic) vibration. The intense absorption at 1628 cm^{-1} in the hydrazine ligand can be assigned to the –C=N– group, which is observed at lower frequency (1602 cm^{-1}) in the spectrum of the complex, indicating the coordination of the imino N atom to the V atom. The band indicative of the V=O vibration is at 916 cm^{-1}. And the lower frequencies in the range 430–480 cm^{-1} can be attributed to the V–O and V–N vibrations.

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