Vanadium(V) Complexes with Tridentate Bromo-Substituted Hydrazone Ligands: Synthesis, Characterization, Crystal Structures and Antimicrobial Activity

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Abstract

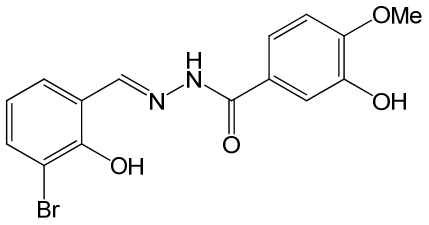
Two new vanadium(V) complexes derived from the bromo-substituted hydrazones *N′*-(3-bromo-2-hydroxybenzylidene)-3-hydroxy-4-methoxybenzohydrazide (H_2L^1), *N′*-(3-bromo-2-hydroxybenzylidene)-3,5-dimethoxybenzohydrazide (H_2L^2), [$VOL^1(OCH_3)(CH_3OH)$] (**1**) and [$VOL^2(OCH_3)(CH_3OH)$] (**2**), were prepared and characterized by IR, UV-Vis and ^{1}H NMR spectra, as well as single crystal X-ray diffraction. The complexes are mononuclear vanadium(V) species, with the V atoms coordinated in octahedral geometry. The free hydrazones and the complexes were studied on their antibacteria activities on *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas fluorescence*, and the fungi *Candida albicans* and *Aspergillus niger*. The existence of the bromo groups in the hydrazone ligands may improve the antibacterial activities.

Keywords: Hydrazone; Vanadium complex; Mononuclear complex; Crystal structure; Antimicrobial activity

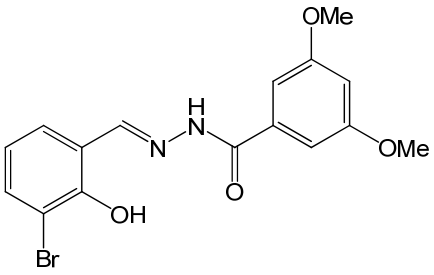
1. Introduction

Hydrazones have attracted remarkable attention because of their wide biological activities, such as antibacterial,[1] antifungal,[2] and antitumor.[3] It was reported that compounds bearing electron-withdrawing groups can improve their antimicrobial activities.[4] Rai and co-workers reported a series of fluoro, chloro, bromo, and iodo-substituted compounds with significant antimicrobial activities.[5] Vanadium complexes with Schiff base ligands have been reported to have interesting

antibacterial activities.[6] In pursuit of novel complex based antimicrobial agents, in this paper, bromo groups are incorporated in hydrazone compounds, and then coordinate with vanadium, to form two new bromo-substituted hydrazone compounds *N′*-(3-bromo-2-hydroxybenzylidene)-3-hydroxy-4-methoxybenzohydrazide (H_2L^1), *N′*-(3-bromo-2-hydroxybenzylidene)-3,5-dimethoxybenzohydrazide (H_2L^2), and two new vanadium(V) complexes, $[VOL^1(OCH_3)(CH_3OH)]$ (1) and $[VOL^2(OCH_3)(CH_3OH)]$ (2), and studied their antimicrobial activities.



H_2L^1



H_2L^2

2. Experimental

2.1. Materials and methods

3-Bromosalicylaldehyde, 3-hydroxy-4-methoxybenzohydrazide, 3,5-dimethoxybenzohydrazide, and $VO(acac)_2$ were purchased from Sigma-Aldrich and used as received. All other reagents were of analytical reagent grade. Elemental analyses of C, H and N were carried out in a Perkin-Elmer automated model 2400 Series II CHNS/O analyzer. FT-IR spectra were obtained on a Perkin-Elmer 377 FT-IR spectrometer with samples prepared as KBr pellets. UV-Vis spectra were obtained on a Lambda 35 spectrometer. ^{1}H NMR data were recorded on a Bruker 300 MHz spectrometer. X-ray diffraction was carried out on a Bruker APEX II CCD diffractometer.

2.2. Synthesis of the hydrazones

To the methanolic solution (30 mL) of 3-bromosalicylaldehyde (0.01 mol, 2.01 g) was added a methanolic solution (20 mL) of 3-hydroxy-4-methoxybenzohydrazide (0.01 mol, 1.82 g), or 3,5-dimethoxybenzohydrazide (0.01 mol, 1.96 g) with stirring. The mixtures were stirred for 30 min at room temperature, and left to slowly evaporate to give colorless crystalline product, which were recrystallized from methanol and dried in vacuum containing anhydrous $CaCl_2$.

For H_2L^1: Yield 94%. *Anal.* Calc. for $C_{15}H_{13}BrN_2O_4$: C, 49.3; H, 3.6; N, 7.7. Found:

C, 49.5; H, 3.7; N, 7.6%. IR data (cm^{-1}): 3429, 3195, 1642, 1612. UV-Vis data (MeOH, λ_{max}, nm): 225, 293, 307, 325, 400. ^{1}H NMR (300 MHz, d^6-DMSO): δ 12.76 (s, 1H, O*H*), 12.30 (s, 1H, O*H*), 11.27 (s, 1H, N*H*), 8.63 (s, 1H, C*H*=N), 7.63 (d, 1H, Ar*H*), 7.50-7.40 (m, 3*H*, ArH), 7.13 (d, 1H, Ar*H*), 6.92 (t, 1H, Ar*H*), 3.85 (s, 3H, OCH_3). For H_2L^2: Yield 97%. *Anal.* Calc. for $C_{16}H_{15}BrN_2O_4$: C, 50.7; H, 4.0; N, 7.4. Found: C, 50.5; H, 4.1; N, 7.5%. IR data (cm^{-1}): 3433, 3197, 1644, 1612. UV-Vis data (MeOH, λ_{max}, nm): 225, 295, 307, 328, 400. ^{1}H NMR (300 MHz, d^6-DMSO): δ 12.65 (s, 1H, O*H*), 11.33 (s, 1H, N*H*), 8.63 (s, 1H, C*H*=N), 7.63 (d, 1H, Ar*H*), 7.45 (d, 1*H*, ArH), 6.92 (t, 1H, Ar*H*), 6.71 (s, 1H, Ar*H*), 6.45 (d, 2H, Ar*H*), 3.84 (s, 6H, OCH_3).

2.3. Synthesis of the complexes

The hydrazone compounds (0.1 mmol each) dissolved in methanol were mixed with $VO(acac)_2$ (0.1 mmol, 26.5 mg) dissolved in methanol (10 mL). The mixtures were refluxed for 1 h and then cooled to room temperature. Single crystals of the complexes, suitable for X-ray diffraction, were grown from the solution upon slowly evaporation within a few days. The crystals were isolated by filtration, washed with ethanol and dried in vacuum containing anhydrous $CaCl_2$.

For **1**: Yield 36%. Anal. calc. for $C_{17}H_{18}BrN_2O_7V$: C, 41.4; H, 3.7; N, 5.7; found: C, 41.3; H, 3.7; N, 5.6%. IR data (cm^{-1}): 3454 (w), 1603 (s), 958 (m). UV-Vis data (MeOH, λ_{max}, nm): 272, 335. ^{1}H NMR (300 MHz, d^6-DMSO): δ 12.71 (s, 1H, O*H*), 12.20 (s, 1H, O*H*), 9.39 (s, 1H, Ar*H*), 8.56 (s, 1H, C*H*=N), 7.61 (q, 1H, Ar*H*), 7.51-7.41 (m, 2H, Ar*H*), 7.08 (d, 1H, Ar*H*), 6.91 (t, 1H, Ar*H*), 3.86 (s, 3H, OCH_3), 3.33 (s, 6H, CH_3OH and OCH_3). For **2**: Yield 41%. Anal. calc. for $C_{18}H_{20}BrN_2O_7V$: C, 42.6; H, 4.0; N, 5.5; found: C, 42.7; H, 3.9; N, 5.6%. IR data (cm^{-1}): 3450 (w), 1602 (s), 953 (m). UV-Vis data (MeOH, λ_{max}, nm): 275, 323. ^{1}H NMR (300 MHz, d^6-DMSO): δ 12.56 (s, 1H, O*H*), 9.30 (s, 1H, Ar*H*), 8.59 (s, 1H, C*H*=N), 7.66 (d, 1H, Ar*H*), 7.53 (d, 1H, Ar*H*), 7.17-6.91 (m, 2H, Ar*H*), 6.70 (s, 1H, Ar*H*), 3.84 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.38 (s, 6H, CH_3OH and OCH_3).

2.4. X-ray crystallography

X-ray diffraction was carried out at a Bruker APEX II CCD area diffractometer equipped with MoKα radiation (λ = 0.71073 Å). The collected data were reduced with SAINT,[7] and multi-scan absorption correction was performed using SADABS.[8] The structures of the complexes were solved by direct method, and refined against F^2 by full-matrix least-squares method using SHELXTL.[9] All of the non-hydrogen atoms

were refined anisotropically. The hydrogen atoms of the methanol ligands were located from electronic density maps and refined isotropically. The remaining hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data and refinement parameters for the complexes are listed in Table 1. Selected bond lengths and angles are listed in Table 2.

Table 1. Crystallographic and refinement data for the complexes

Complex	H_2L^1	**1**	**2**
Formula	$C_{15}H_{13}BrN_2O_4$	$C_{17}H_{18}BrN_2O_7V$	$C_{18}H_{20}BrN_2O_7V$
Formula weight	365.18	493.18	507.21
Crystal shape/color	Block/colorless	Block/brown	Block/brown
T (K)	298(2)	298(2)	298(2)
Crystal dimensions (mm^3)	0.18 × 0.15 × 0.15	0.19 × 0.17 × 0.17	0.22 × 0.20 × 0.18
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	P-1	$P2_1/n$
a (Å)	17.2603(13)	7.6101(9)	13.5326(10)
b (Å)	7.2902(12)	10.3404(13)	9.3050(7)
c (Å)	12.1706(19)	13.1269(16)	16.1808(13)
α (º)	90	81.517(1)	90
β (º)	104.431(1)	75.965(1)	94.621(1)
γ (º)	90	68.939(1)	90
V ($Å^3$)	1483.1(4)	933.1(2)	2030.9(3)
Z	4	2	4
D_{calc} (g cm^{-3})	1.635	1.755	1.659
μ (Mo Kα) (mm^{-1})	2.791	2.716	2.499
F(000)	736	496	1024
Measured reflections	8532	8761	18003
Unique reflections	2764	3455	3606
Observed reflections ($I \geq 2\sigma(I)$)	1896	2906	2900
Min. and max.	0.6335 and 0.6795	0.6264 and 0.6552	0.6094 and 0.6619

transmission			
Parameters	205	260	269
Restraints	1	1	1
Goodness of fit on F^2	1.025	1.030	1.039
R_1, wR_2 $[I \geq 2\sigma(I)]^a$	0.0437, 0.1036	0.0285, 0.0679	0.0345, 0.0776
R_1, wR_2 (all data)^a	0.0717, 0.1159	0.0378, 0.0721	0.0498, 0.0857

[a] $R_1 = F_o - F_c/F_o$, $wR_2 = [\sum w(F_o^2 - Fc^2)/\sum w(F_o^2)^2]^{1/2}$

Table 2. Selected bond distances (Å) and angles (°) for the complexes

	1	**2**
V1-O1	1.8676(16)	1.8594(18)
V1-O2	1.9309(15)	1.9445(18)
V1-O5	1.5831(17)	1.581(2)
V1-O6	2.4343(17)	2.407(2)
V1-O7	1.7698(16)	1.7559(19)
V1-N1	2.1330(18)	2.129(2)
O5-V1-O7	102.51(8)	103.79(11)
O5-V1-O1	99.01(9)	99.96(10)
O7-V1-O1	98.66(7)	99.68(9)
O5-V1-O2	100.53(8)	97.85(10)
O7-V1-O2	97.74(7)	96.05(9)
O1-V1-O2	151.03(7)	152.61(9)
O5-V1-N1	96.04(8)	96.01(10)
O7-V1-N1	160.86(7)	159.01(9)
O1-V1-N1	82.88(7)	83.45(8)
O2-V1-N1	74.00(6)	74.12(8)
O5-V1-O6	177.35(8)	174.54(9)
O7-V1-O6	80.15(7)	80.79(8)
O1-V1-O6	80.48(7)	82.00(8)
O2-V1-O6	79.01(6)	78.55(8)
N1-V1-O6	81.32(6)	79.10(7)

2.5. Antimicrobial assay

The antibacterial activities of the hydrazone compounds and the vanadium complexes were tested against *B. subtilis*, *S. aureus*, *E. coli*, and *P. fluorescence* using MH (Mueller–Hinton) medium. The antifungal activities of the compounds were tested against *C. albicans* and *A. niger* using RPMI-1640 medium. The MIC values of the tested compounds were determined by a colorimetric method using the dye MTT.[10] A stock solution of the compound (150 $\mu g \cdot mL^{-1}$) in DMSO was prepared and graded quantities (75 $\mu g \cdot mL^{-1}$, 37.5 $\mu g \cdot mL^{-1}$, 18.8 $\mu g \cdot mL^{-1}$, 9.4 $\mu g \cdot mL^{-1}$, 4.7 $\mu g \cdot mL^{-1}$, 2.3 $\mu g \cdot mL^{-1}$, 1.2 $\mu g \cdot mL^{-1}$, 0.59 $\mu g \cdot mL^{-1}$) were incorporated in specified quantity of the corresponding sterilized liquid medium. A specified quantity of the medium containing the compound was poured into micro-titration plates. Suspension of the microorganism was prepared to contain approximately 1.0×10^5 cfu$\cdot mL^{-1}$ and applied to microtitration plates with serially diluted compounds in DMSO to be tested and incubated at 37 °C for 24 h and 48 h for bacteria and fungi, respectively. Then the MIC values were visually determined on each of the microtitration plates, 50 μL of PBS (phosphate buffered saline 0.01 mol$\cdot L^{-1}$, pH = 7.4) containing 2 mg of MTT$\cdot mL^{-1}$ was added to each well. Incubation was continued at room temperature for 4–5 h. The content of each well was removed and 100 μL of isopropanol containing 5% 1 mol$\cdot L^{-1}$ HCl was added to extract the dye. After 12 h of incubation at room temperature, the optical density was measured with a microplate reader at 550 nm.

3. Results and Discussion

3.1. Synthesis and characterization

The hydrazones H_2L^1 and H_2L^2 were readily prepared by the condensation reaction of a 1:1 molar ratio of 3-bromosalicylaldehyde with 3-hydroxy-4-methoxybenzohydrazide and 3,5-dimethoxybenzohydrazide, respectively in ethanol. The complexes were prepared by the reaction of the hydrazones H_2L^1 and H_2L^2 with $VO(acac)_2$ in methanol, followed by re-crystallization. Elemental analysis of the complexes are in accordance with the molecular structures determined by the single crystal X-ray analysis.

3.2. Spectroscopic studies

In the spectra of the hydrazone compounds and the complexes, the weak and broad bands in the range 3400-3500 cm^{-1} are assigned to the vibration of O–H bonds. The weak and sharp bands of the hydrazone compounds located at about 3195 cm^{-1} are

assigned to the vibration of N–H bonds. The intense bands at 1643 cm^{-1} of the hydrazone compounds are generated by ν(C=O) vibrations, whereas the bands at 1612 cm^{-1} by the ν(C=N) ones. The non-observation of the ν(C=O) and ν(N–H) bands, present in the spectra of the hydrazone compounds, indicates the enolization of the amide functionality upon coordination to the V-center. Instead strong bands at 1602 cm^{-1} are observed, which can be attributed to the asymmetric stretching vibration of the C=N bonds, characteristic for the coordination of the enolate form of the compounds. The strong ν(V=O) bands at about 955 cm^{-1} for the complexes could be clearly identified for the complexes.[11]

In the electronic spectra of the hydrazones and the complexes, the bands in the range of 320-340 nm are attributed to the intra-ligand $\pi\rightarrow\pi^*$ absorption. In the electronic spectra of the complexes, the lowest energy transition bands are observed at 400 nm, which are attributed to LMCT transition as charge transfer from *p*-orbital on the lone-pair of ligands' oxygen atoms to the empty *d*-orbital of the vanadium atoms. The other mainly LMCT and to some extent $\pi\rightarrow\pi^*$ bands appear at 275 nm for the complexes are due to the oxygen donor atoms bound to vanadium(V).[11]

3.3. Structure description of H_2L^1

Molecular structure of H_2L^1 is shown in Figure 1. The molecule of the compound adopts *E* configuration with respect to the methylidene unit. The distance of the methylidene bond C7-N1, 1.281(5) Å, confirms it as a typical double bond. The shorter distance of the C8-N2 bond (1.356(4) Å) and the longer distance of the C8-O2 bond (1.230(4) Å) for the –C(O)–NH– unit than usual, suggests the presence of conjugation effects in the molecule. All bond lengths in the compound are within normal values.[4a] The dihedral angle between the two aromatic rings is 39.0(3)°. The crystal structure (Figure 2) of the compound is stabilized by hydrogen bonds [N3–H2 = 0.90(1) Å, H2···O3^{i} = 2.00(1) Å, N2···O3^{i} = 2.885(3) Å, N2–H2···O3^{i} = 169(4)º; O3–H3 = 0.82 Å, H3···O2^{ii} = 1.84 Å, O3···O2^{ii} = 2.654(3) Å, O3–H3···O2^{ii} = 172(4)º; O1–H1 = 0.82 Å, H1···N1 = 1.87 Å, O1···N1 = 2.577(4) Å, O1–H1···N1 = 144(4)º; symmetry codes: (i) $1-x$, $1-y$, $1-z$; (ii) x, $1/2-y$, $1/2+z$].

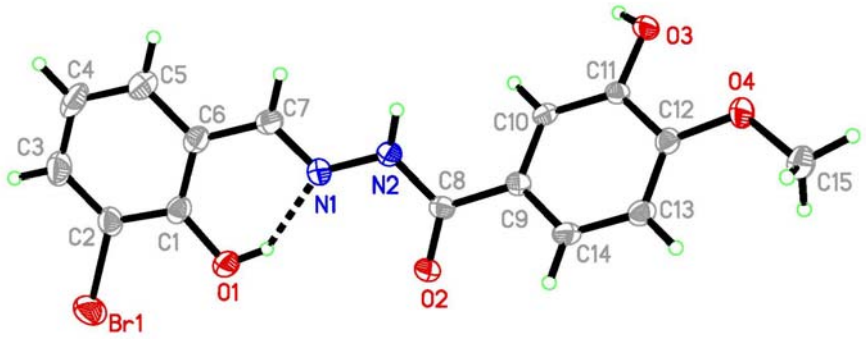


Figure 1. A perspective view of H_2L^1 with the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen bond is shown as a dotted line.

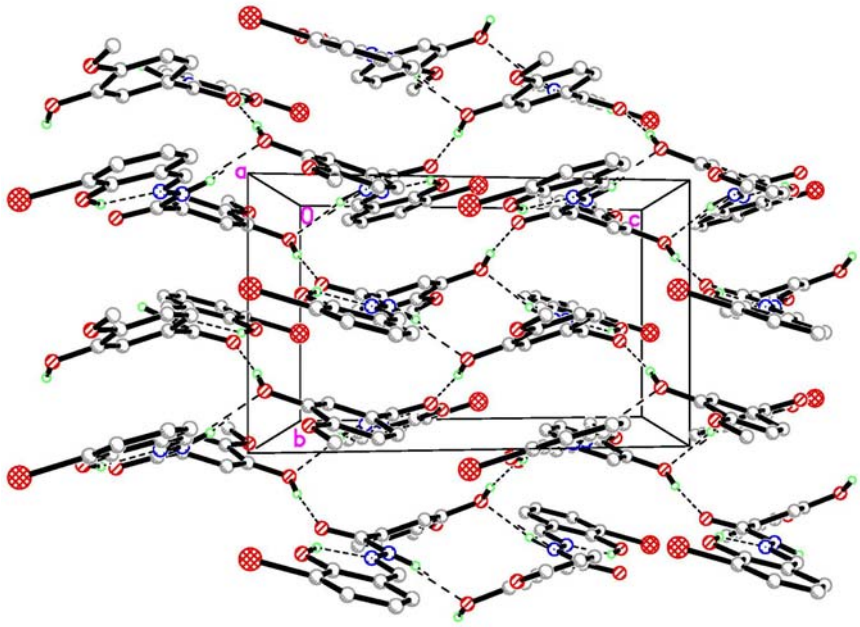


Figure 2. Molecular packing structure of H_2L^1, with hydrogen bonds shown as dotted lines.

3.4. Structure description of the complexes

Molecular structures of the complexes are shown in Figures 3 and 4, respectively. The coordination geometry around the vanadium atoms can be described as distorted octahedral with the tridentate hydrazone ligand coordinated in meridional fashion, forming five- and six-membered chelate rings with bite angles of 74.0-74.2° and 82.8-83.5°, respectively, typical for this type of ligand systems.[13] Each chelating hydrazone ligand lies in a plane with one hydroxylato ligand which lies *trans* to the

hydrazone imino N atom. One O atom of the methanol ligand *trans* to the oxo group completes the distorted octahedral coordination sphere at rather elongated distances of 2.40-2.44 Å, due to the *trans* influence of the oxo group. This is accompanied by significant displacements of the vanadium atoms from the planes defined by the four basal donor atoms toward the apical oxo oxygen atoms by 0.32-0.33Å. As expected, the hydrazone compounds coordinate in their doubly deprotonated enolate form which is consistent with the observed O2–C8 and N2–C8 bond lengths of about 1.29-1.32 Å. This agrees with reported vanadium complexes containing the enolate form of this ligand type.[12]

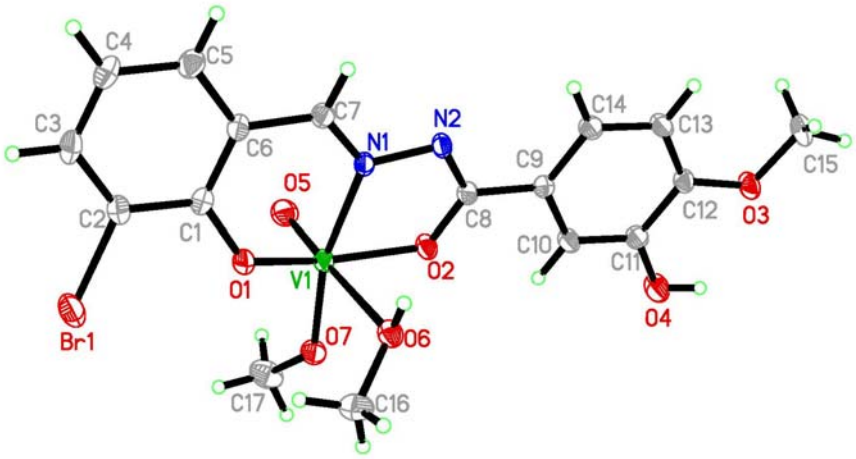


Figure 3. A perspective view of complex **1** with the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.

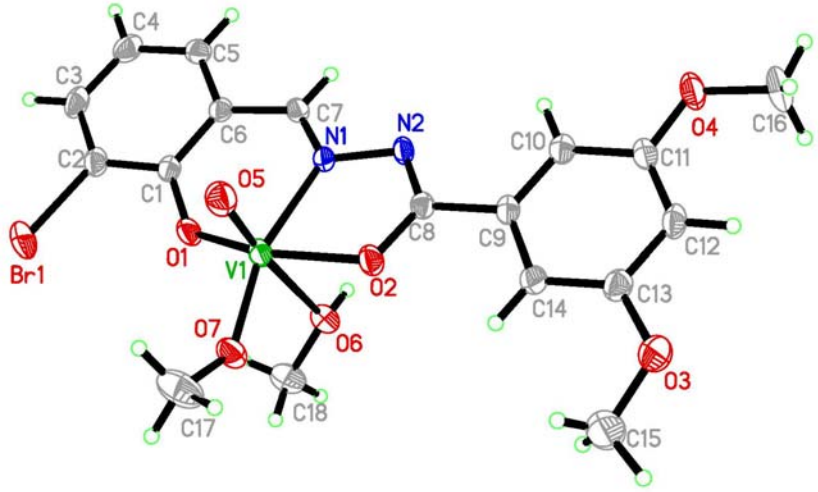


Figure 4. A perspective view of complex **2** with the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.

In the crystal packing structure of complex **1**, the complex molecules are linked by hydrogen bonds [O4–H4 = 0.82 Å, H4···O6^{iii} = 2.39 Å, O4···O6^{iii} = 3.009(2) Å,

O4–H4···O6^{iii} = 133(5)º; O6–H6 = 0.84(1) Å, H6···N2 = 2.06(1) Å, O6···N2 = 2.893(2) Å, O6–H6···N2 = 171(3)º; C7–H7 = 0.93 Å, H7···O4^{iv} = 2.58 Å, C7···O4^{iv} = 3.381(2) Å, C7–H7···O4^{iv} = 144(5)º; symmetry codes: (iii) x, 1 + y, z; (iv) x, –1 + y, z], leading to the formation of 3D network (Figure 5). In the crystal packing structure of complex **2**, the complex molecules are linked by hydrogen bonds [O6–H6 = 0.85(1) Å, H6···N2^{v} = 2.07(1) Å, O6···N2^{v} = 2.911(3) Å, O6–H6···N2^{v} = 172(4)º, symmetry code for v: 1 – x, 1 – y, – z], leading to the formation of dimers (Figure 6).

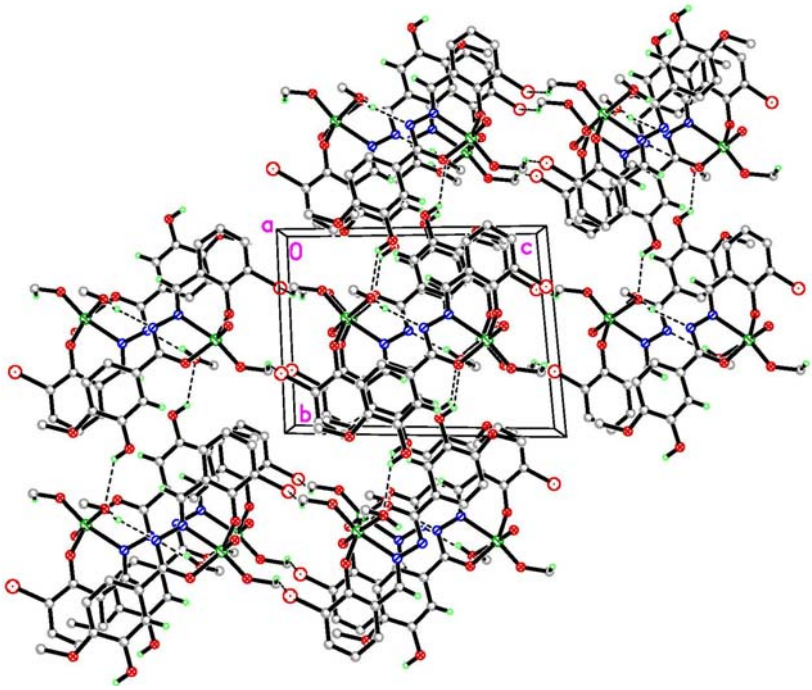


Figure 5. Molecular packing structure of complex **1**, with hydrogen bonds shown as dotted lines.

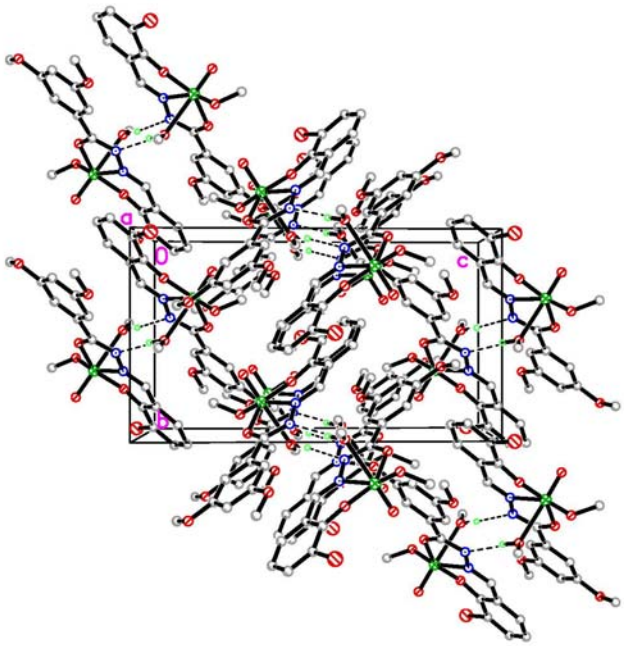


Figure 6. Molecular packing structure of complex **2**, with hydrogen bonds shown as dotted lines.

3.5. Antimicrobial activity

The hydrazone compounds and the vanadium complexes were screened for antibacterial activities against two Gram (+) bacterial strains (*Bacillus subtilis* and *Staphylococcus aureus*) and two Gram (–) bacterial strains (*Escherichia coli* and *Pseudomonas fluorescence*) by MTT method. The MIC (minimum inhibitory concentration, $\mu g \cdot mL^{-1}$) values of the compounds against four bacteria are listed in Table 3. Penicillin G was used as the standard drug. Both hydrazone compounds show medium activity against *B. subtilis* and *S. aureus*, weak activity against *P. fluorescence*, and no activity against *E. coli*. The vanadium complexes, in general, have stronger activities against the bacteria than the free hydrazones. The complexes have strong activities against *B. subtilis*, *S. aureus* and *E. coli* which are comparable to Penicillin G. Complex **1** has no activity against *P. fluoresence*, while complex **2** has weak activity. Both complexes have no activity on the fungal strains *Candida albicans* and *Aspergillus niger*. From the results, we can conclude that the existence of the bromo groups in the hydrazone ligands may improve the antibacterial activities.

Table 3. Antimicrobial activities of the compounds with minimum inhibitory concentrations ($\mu g \cdot mL^{-1}$)

Tested material	*B. subtilis*	*S. aureus*	*E. coli*	*P. fluorescence*
H_2L^1	37.5	18.8	75	> 150

H_2L^2	18.8	18.8	75	> 150
1	4.6	9.4	9.4	> 150
2	2.3	9.4	9.4	75
Penicillin G	2.3	4.7	>150	> 150

4. Supplementary Data

CCDC 1913947 (H_2L^1), 1913948 (**1**) and 1913949 (**2**) contain the supplementary crystallographic data for the compounds. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

5. Acknowledgments

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6. References

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