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Synthesis and Crystal Structures of Schiff Base Oxovanadium(V) Complexes $[VO(BN)(OCH_3)]_2$ and $[VO_2(BM)]$

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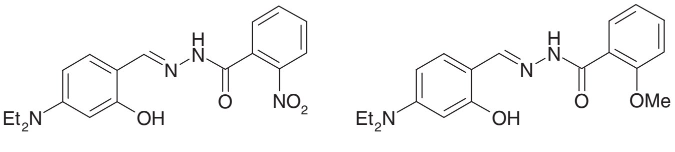
$[VO(acac)_2]$ reacts with the Schiff bases *N'*-(2-hydroxy-4-diethylaminobenzylidene)-2-nitrobenzohydrazide (H_2BN) and *N'*-(2-hydroxy-4-diethylaminobenzylidene)-2-methoxybenzohydrazide (HBM), respectively, in absolute methanol to give the oxovanadium(V) complexes $[VO(BN)(OCH_3)]_2$ (1) and $[VO_2(BM)]$ (2). Both complexes were characterized by elemental analysis, infrared (IR) spectra, and single-crystal x-ray determination. The complex (1) crystallizes in the monoclinic space group $P2_1/c$, with $a = 10.828(2)$, $b = 18.177(4)$, $c = 10.778(2)$ Å, $\beta = 106.914(3)°$, $V = 2029.6(7)$ Å^3, $Z = 4$. The complex (2) crystallizes in the triclinic space group *P*-1, with $a = 8.459(2)$, $b = 10.068(3)$, $c = 11.776(3)$ Å, $\alpha = 88.727(2)$, $\beta = 88.904(3)$, $\gamma = 69.486(3)°$, $V = 939.0(4)$ Å^3, $Z = 2$. Complex (1) is a centrosymmetric methoxy-bridged dimeric oxovanadium(V) compound, and complex (2) is a monomeric dioxovanadium(V) compound.

Keywords crystal structure, coordination compound, oxovanadium(V) complex, Schiff base

INTRODUCTION

Oxovanadium complexes have received considerable attention in the context of the 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 coordination chemistry.[6–8] For the present paper, two new oxovanadium(V) complexes, $[VO(BN)(OCH_3)]_2$ (**1**) and $[VO_2(BM)]$ (**2**), derived from the Schiff bases *N'*-(2-hydroxy-4-diethylaminobenzylidene)-2-nitrobenzohydrazide (H_2BN) and *N'*-(2-hydroxy-4-diethylaminobenzylidene)-2-methoxybenzohydrazide (HBM; Scheme 1), respectively, have been synthesized and characterized.



SCH. 1. H_2BN and HBM.

EXPERIMENTAL

Materials and Methods

4-Diethylaminosalicylaldehyde, 2-nitrobenzohydrazide, and 2-methoxybenzohydrazide were purchased from Alfa Aesar. $[VO(acac)_2]$ was prepared according to the literature method.[9] All chemicals and solvents were of analytical grade and used as obtained. Microanalyses of the Schiff bases and the oxovanadium(V) complexes were performed with a Vario EL III CHNOS elemental analyzer. The infrared spectra were recorded as KBr pellets with an FTS-40 spectrophotometer.

Crystal Structure Determination

Data were collected on a Bruker smart 1000 CCD area diffractometer using a graphite monochromator Mo Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. The data were corrected with SADABS programs and refined on F^2 with Siemens SHELXL software.[10,11] The structures were solved by direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms 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 coordinate bond lengths and angles are listed in Table 2.

Preparation

H_2BN

A mixture of 4-diethylaminosalicylaldehyde (1.93 g, 10 mmol) and 2-nitrobenzohydrazide (1.81 g, 10 mmol) in 100 mL methanol was refluxed for 2 h. After reducing the solvent to

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TABLE 1
Crystallographic data for complexes (**1**) and (**2**)

	(**1**)	(**2**)
Formula	$C_{19}H_{21}N_4O_6V$	$C_{19}H_{22}N_3O_5V$
Formula weight	452.3	423.3
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	P-1
a (Å)	10.828(2)	8.459(2)
b (Å)	18.177(4)	10.068(3)
c (Å)	10.778(2)	11.776(3)
α (°)	90	88.727(2)
β (°)	106.914(3)	88.904(3)
γ (°)	90	69.486(3)
V (Å^3)	2029.6(7)	939.0(4)
Z	4	2
T (K)	298(2)	298(2)
λ (Å)	0.71073	0.71073
$\rho_{\text{calcd.}}$ (g cm^{-3})	1.480	1.497
μ (mm^{-1})	0.533	0.565
Measured reflections	13890	7849
Independent reflections	4291	3908
Observed reflections ($I > 2\sigma(I)$)	3242	3481
R_{int}	0.0369	0.0182
R_1[a]	0.0459	0.0475
wR_2[b]	0.1088	0.1333
GOF on F^2	1.044	1.038

[a] $R_1 = \sum(\|F_o| - |F_c\|)/\sum|F_o|$.

[b] $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$, $w_{(1)} = 1/[\sigma^2(F_o{}^2) + (0.058P)^2 + 0.3908P]$, $w_{(2)} = 1/[\sigma^2(F_o{}^2) + (0.0836P)^2 + 0.4924P]$, where $P = (F_o{}^2 + 2F_c{}^2)/3$.

TABLE 2
Selected bond lengths (Å) and angles (°) for the complexes (**1**) and (**2**)

(**1**)			
V1–O1	1.8121 (17)	V1–O2	1.9329 (16)
V1–O5	1.5810 (19)	V1–O6	1.8103 (15)
V1–O6A	2.4474 (17)	V1–N1	2.0840 (19)
O5–V1–O6	103.72 (9)	O5–V1–O1	102.54 (10)
O6–V1–O1	104.31 (7)	O5–V1–O2	99.71 (9)
O6–V1–O2	88.83 (7)	O1–V1–O2	150.47 (8)
O5–V1–N1	96.47 (9)	O6–V1–N1	155.86 (8)
O1–V1–N1	83.72 (7)	O2–V1–N1	74.67 (7)
O5–V1–O6A	178.56 (8)	O6–V1–O6A	74.84 (7)
O1–V1–O6A	77.95 (7)	O2–V1–O6A	80.29 (6)
N1–V1–O6A	84.93 (7)		
(**2**)			
V1–O1	1.9034 (17)	V1–O2	2.0293 (17)
V1–O4	1.6220 (17)	V1–O5	1.621 (2)
V1–N1	2.1439 (19)		
O5–V1–O4	110.13 (10)	O5–V1–O1	104.26 (9)
O4–V1–O1	98.05 (8)	O5–V1–O2	97.95 (9)
O4–V1–O2	91.71 (8)	O1–V1–O2	150.81 (8)
O5–V1–N1	107.54 (9)	O4–V1–N1	140.97 (9)
O1–V1–N1	82.12 (7)	O2–V1–N1	73.19 (7)

20 mL and cooling to room temperature, the precipitated yellow solid was filtered off, washed with methanol, and dried. Recrystallization from methanol yielded pure product of H_2BN as a yellow solid. Yield 2.62 g (88%). Anal.: Calcd. for $C_{15}H_{13}N_3O_4$ (%): C, 60.2; H, 4.4; N, 14.0. Found (%): C, 59.9; H, 4.4; N, 14.1. Infrared (IR) (KBr, ν_{max}/cm^{-1}): 3356 (OH), 3227 (NH), 1655 (C=O), 1643 (C=N).

HBM

This ligand was prepared by following the same procedure outlined for H_2BN, with 2-nitrobenzohydrazide replaced with 2-methoxybenzohydrazide (1.66 g, 10 mmol), yielding a colorless solid product. Yield 2.71 g (95%). Anal.: Calcd. for $C_{16}H_{16}N_2O_3$ (%): C, 67.6; H, 5.7; N, 9.8. Found (%): C, 67.4; H, 5.8; N, 10.0. IR (KBr, ν_{max}/cm^{-1}): 3355 (OH), 3223 (NH), 1651 (C=O), 1645 (C=N).

*[VO(BN)(OCH$_3$)]$_2$ (**1**)*

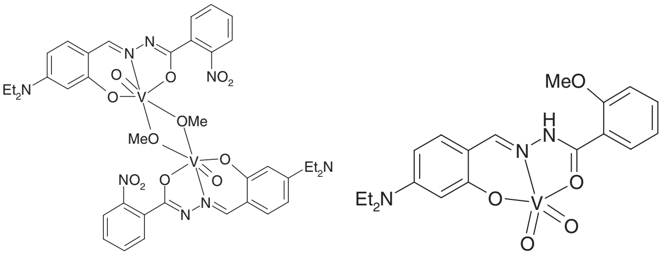
A stirred solution of H_2BN (0.299 g, 1 mmol) in absolute methanol (20 mL) was mixed with [VO(acac)$_2$] (0.265 g, 1 mmol), and the resulting reaction mixture was refluxed on a water bath for 1 h, and then cooled to room temperature, yielding a deep brown solution. The solution was allowed to stand still at ambient temperature to slow evaporation of the solvent, yielding brown crystals of (**1**). Yield 0.378 g (84%). Anal.: Calcd. for $C_{19}H_{21}N_4O_6V$ (%): C, 50.5; H, 4.7; N, 12.4. Found (%): C, 50.3; H, 4.9; N, 12.6. IR (KBr, ν_{max}/cm^{-1}): 1608 (C=N), 1504 (NO$_2$, *asym*), 1352 (NO$_2$, *sym*), 1338 (C–O, enolic), 1218 (C–O, phenolate), 1023 (N–N), 973 (V=O), 495, 446 (V–O, V–N).

*[VO$_2$(BM)] (**2**)*

This complex was prepared by following the same procedure outlined for (**1**), yielding light green single crystals. Yield 0.272 g (64%). Anal.: Calcd. for $C_{19}H_{22}N_3O_5V$ (%): C, 53.9; H, 5.2; N, 9.9. Found (%): C, 54.3; H, 5.4; N, 9.8. IR (KBr, ν_{max}/cm^{-1}): 3184 (NH), 1606 (C=N), 1422 (C=O), 924 (V=O), 456, 404 (V–O, V–N).

RESULTS AND DISCUSSION

The overview of the two complexes is shown in Scheme 2. Reaction between equimolar quantities of [VO(acac)$_2$] with H_2BM and HBN, respectively, in absolute methanol, afforded [VO(BN)(OCH$_3$)]$_2$ and [VO$_2$(BM)]. The ligands BN and BM adopt enolic tautomeric form on complexation. On aerial oxidation in methanol, the V$^{\text{IV}}$ atom in VO(acac)$_2$ is changed to V$^{\text{V}}$ in the complexes.



SCH. 2. $[VO(BN)(OCH_3)]_2$ and $[VO_2(BM)]$.

Structure Description

$[VO(BN)(OCH_3)]_2$ (1)

The crystal structure of (**1**) with atom numbering scheme is shown in Figure 1. The complex is a centrosymmetric dimeric oxovanadium(V) compound, with V···V distance of 3.404(1) Å. The ligand BN forms one five-membered ring and one six-membered chelate ring with bite angles of 74.7(1) and 83.7(1)°. The V atom is in a distorted octahedral O_5N coordination sphere. The phenolate O, imine N, and enolic O atoms of BN and one methoxy O atom constitute the equatorial plane, with mean deviation of 0.016 Å. The two axial positions are occupied by one oxo O atom and another methoxy O atom. The displacement of the V atom from the equatorial plane toward the axial oxo group is 0.360(2) Å. The *cis* bond angles are in the range 74.8(1)–104.3(1)°, and the *trans* bond angles are within 150.5(1)–178.6(1)°. The V–O and V–N bond lengths in the complex are comparable with the bond lengths reported for oxovanadium(V) complexes with similar ligands.[12–14] As commonly observed in analogous species, the elongated V1–O6A (symmetry code for A: 2 – *x*, 2 – *y*, 1 – *z*) bond *trans* to the oxo group in the complex indicates weak coordination of the O6A atom at the axial position.

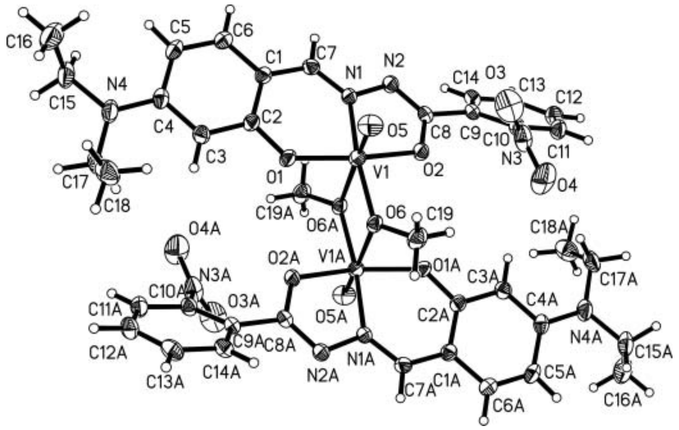


FIG. 1. ORTEP plots (30% probability level) and numbering scheme for (**1**).

In the crystal structure of the complex (Figure 2), the molecules are stacked together by weak $\pi\cdots\pi$ and C–H···π interactions among the molecules (Tables 3 and 4).

$[VO_2(BM)]$ (2)

The crystal structure of (**2**) with atom numbering scheme is shown in Figure 3. The ligand BM forms one five-membered ring and one six-membered chelate ring with bite angles of 73.2(1) and 82.1(1)°. The V atom is five-coordinate in an O_4N square pyramidal coordination, as evidenced by the value of τ (0.16), which is defined as $(\beta - \alpha)/60$,[15] where α and β are the two largest angles subtended at the V atoms. For an ideal square-pyramidal geometry τ is 0, and for an ideal

TABLE 3
$\pi\cdots\pi$ Interactions for (**1**) and (**2**)

Cg(I)···Cg(J)[a]	Distance between ring centroids (Å)	Dihedral angle (°)	Perpendicular distance of Cg(I) on Cg(J) (Å)	Perpendicular distance of Cg(J) on Cg(I) (Å)
(**1**)				
$Cg(1)\cdots Cg(1)^{\#1}$	5.370	0.03	2.925	2.925
$Cg(1)\cdots Cg(2)^{\#2}$	4.833	18.06	2.675	3.762
$Cg(2)\cdots Cg(3)^{\#3}$	4.766	50.58	1.705	4.498
$Cg(2)\cdots Cg(3)^{\#2}$	5.995	50.58	4.442	3.378
$Cg(3)\cdots Cg(1)^{\#4}$	5.821	32.96	0.030	3.102
(**2**)				
$Cg(4)\cdots Cg(4)^{\#5}$	4.110	0.00	3.274	3.274
$Cg(4)\cdots Cg(5)^{\#6}$	3.902	2.01	3.500	3.558
$Cg(4)\cdots Cg(5)^{\#5}$	4.957	2.01	3.580	3.647
$Cg(5)\cdots Cg(5)^{\#6}$	4.770	0.03	3.277	3.277
$Cg(5)\cdots Cg(6)^{\#5}$	3.766	10.49	3.556	3.705

[a] *Cg*(1), *Cg*(2), and *Cg*(3) are the centroids of the V(1)-O(2)-C(8)-N(2)-N(1), C(1)-C(2)-C(3)-C(4)-C(5)-C(6), and C(9)-C(10)-C(11)-C(12)-C(13)-C(14) of (**1**). *Cg*(4), *Cg*(5), and *Cg*(6) are the centroids of the V(1)-O(2)-C(8)-N(2)-N(1), C(1)-C(2)-C(3)-C(4)-C(5)-C(6), and C(9)-C(10)-C(11)-C(12)-C(13)-C(14) of (**2**). Symmetry codes: #1, – *x*, – *y*, 1 – *z*; #2, 1 – *x*, – *y*, 1 – *z*; #3, *x*, *y*, –1 + *z*; #4, 1 – *x*, – *y*, 2 – *z*; #5, 1 – *x*, 1 – *y*, – *z*; #6, – *x*, 1 – *y*, – *z*.

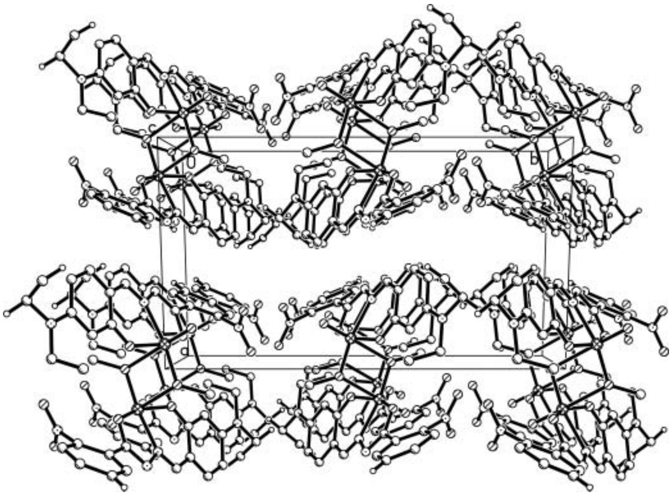


FIG. 2. Molecular packing diagram for (**1**), viewed along the *c* axis.

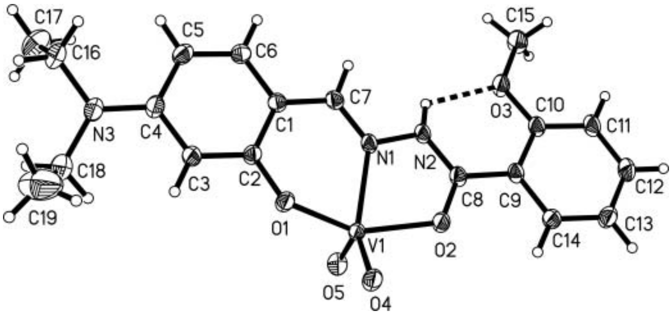


FIG. 3. ORTEP plots (30% probability level) and numbering scheme for (**2**).

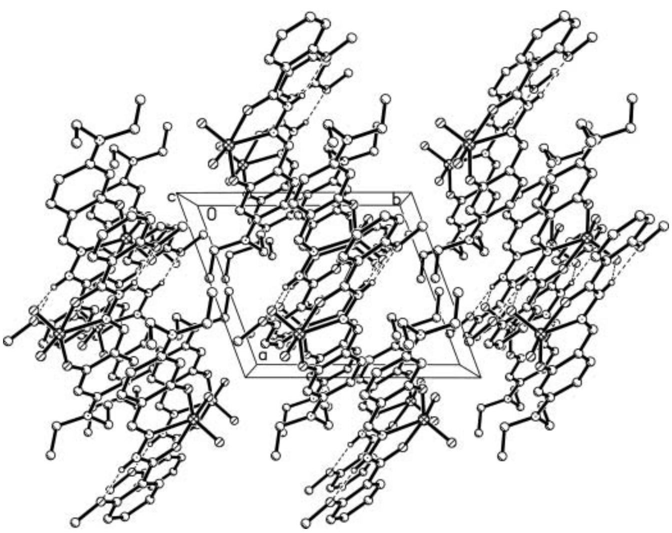


FIG. 4. Molecular packing diagram for (**2**), viewed along the *c* axis.

TABLE 4
X–H···*Cg* interactions for (**1**)

X–H···*Cg*(J)[a]	H···*Cg* (Å)	X–H···*Cg* (°)	X···*Cg* (Å)
C(13)–H(13)···*Cg*(2)$^{\#7}$	2.79	138	3.540
C(15)–H(15A)···*Cg*(2)$^{\#8}$	2.91	142	3.721
C(16)–H(16C)···*Cg*(3)$^{\#2}$	2.89	126	3.538

[a] *Cg*(2) and *Cg*(3) are the centroids of the C(1)-C(2)-C(3)-C(4)-C(5)-C(6) and C(9)-C(10)-C(11)-C(12)-C(13)-C(14) of (**1**). Symmetry codes: #2, 1 – *x*, – *y*, 1 – *z*; #7, *x*, *y*, 1 + *z*; #8, *x*, 1/2 – *y*, –1/2 + *z*.

trigonal-bipyramidal geometry τ is 1. The V–O and V–N bond lengths in the complex are comparable with the bond lengths in (**1**), and also comparable to those reported for dioxovanadium(V) complexes with similar ligands.[16–18]

In the crystal structure of the complex (Figure 4), the molecules are stacked together by weak $\pi \cdots \pi$ interactions among the molecules (Tables 3 and 4).

It is notable that the distance between atoms C8 and N2 in (**1**) is shorter than that in (**2**), and the distance between atoms C8 and O2 in (**1**) is longer than that in (**2**), indicating the enolization of the N2–C8–O2 group in (**1**). The nitro group of (**1**) located at the same site of the V coordination, while the methoxy group of (**2**) located at the opposite site of the V coordination, which is caused by the intramolecular N–H···O hydrogen bond in (2) (Table 5), and no such linkage in (**1**).

IR Spectra

The weak and broad bands in the region 3340–3360 cm^{-1} of the Schiff bases are assigned to the ν(O–H) vibrations. The ν(C = O) vibration at 1655 cm^{-1} and the sharp ν(NH) vibration of 3227 cm^{-1} for H$_2$BN are absent in the complex (**1**), indicating the enolization of the amide functionality and subsequent proton replacement by the vanadium atom, which is accord with the results analyzed by the x-ray determination. The sharp band at 3184 cm^{-1} in the spectrum of complex (**2**) indicates that the H atom is attached to the N atom of the amide group. The ν(C-O) (enolic) mode of (**1**) appears at 1338 cm^{-1}, and the ν(C = O) mode of (**2**) appears at 1422 cm^{-1}. The strong bands at 1608 cm^{-1} in (**1**) and 1606 cm^{-1} in (**2**) are assigned to the azomethine groups. The bands observed in the range 924–973 cm^{-1} for both complexes are assigned to the V = O stretches.

TABLE 5
Hydrogen bonding for (**2**)

D–H···*A*[a]	*d*(*D*–H) (Å)	*d*(H···*A*) (Å)	*d*(*D*···*A*) (Å)	Angle(*D*–H···*A*) (°)
N2–H2···O5^{i}	0.900(10)	2.25(2)	3.044(3)	148(3)
N2–H2···O3	0.900(10)	2.06(3)	2.615(2)	119(3)

[a] Symmetry code: (i) 1 – *x*, 1 – *y*, – *z*.

The bands indicative of the V–O and V–N bands are in the range 404–495 cm^{-1}. The asymmetric and symmetric vibrations of the nitro groups in complex (**1**) are at 1504 and 1352 cm^{-1}.

CONCLUSION

Using the similar tridentate Schiff bases prepared from 4-diethylaminosalicylaldehyde with 2-nitrobenzohydrazide and 2-methoxybenzohydrazide, respectively, two new oxovanadium(V) complexes have been synthesized and characterized for their structures. The dianionic BN ligand and the deprotonated BM ligand coordinate to the V atom through the phenolate-O, the imine-N, and the enolic or carbonylO atoms.

SUPPLEMENTARY MATERIAL

CCDC 806701 and 806702 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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