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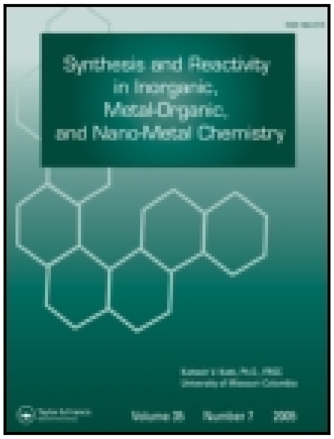

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Synthesis and Crystal Structure of a μ $_2$-Oxo Bridged Dinuclear Oxovanadium(V) Complex Derived From N′-(2-Hydroxy-4-diethylaminobenzylidene)-3-methylbenzohydrazide

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Synthesis and Crystal Structure of a μ_2-Oxo Bridged Dinuclear Oxovanadium(V) Complex Derived From *N′*-(2-Hydroxy-4-diethylaminobenzylidene)-3-methylbenzohydrazide

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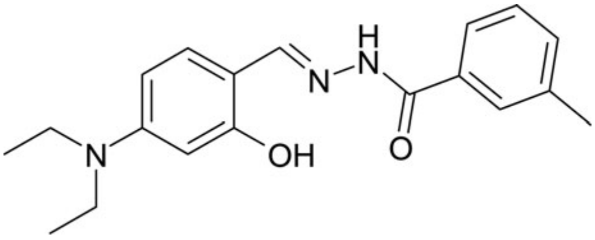
A tridentate hydrazone ligand *N′*-(2-hydroxy-4-diethylamino benzylidene)-3-methylbenzohydrazide (H_2L), reacts with vanadyl sulfate in methanol to give a novel μ_2-oxo bridged dinuclear oxovanadium(V) complex, $[V_2O_2(\mu_2\text{-}O)L_2]$. The complex was characterized by physicochemical and spectroscopic methods. The crystal of the complex is triclinic with space group *P*–1, $a = 11.349(2)$, $b = 13.385(3)$, $c = 13.644(2)$ Å, $\alpha = 90.377(2)°$, $\beta = 93.772(2)°$, $\gamma = 109.239(2)°$, $V = 1951.8(6)$ Å^3, $Z = 2$. X-ray crystallography indicates that each V atom is in a distorted square pyramidal coordination. The two V atoms are bridged by one O atom, with a distance of 3.010(1) Å.

Keywords crystal structure, dinuclear complex, hydrazone, oxovanadium complex, synthesis


SCH. 1. The new ligand H_2L.

INTRODUCTION

Metal complexes containing Schiff bases and hydrazone ligands containing the −C=N- functional groups have been widely investigated due to their versatile structures and widely applications.[1–4] The vanadium complexes with Schiff bases or hydrazone ligands have been received much attention for their interesting structures and biological properties. During the search of literature, we have found that most of the polynuclear vanadium complexes derived from hydrazone ligands are bridged by deprotonated solvent molecules, such as methoxy and ethoxy,[5–8] and others derived from Schiff base ligands are bridged by double oxo O atoms.[9–12] The dinuclear oxovanadium complexes derived from hydrazone ligands with single oxo O atom as bridging group are very rare.[13–16] In this study, a novel single μ_2-oxo bridged dinuclear oxovanadium(V) complex, $[V_2O_2(\mu_2\text{-}O)L_2]$, derived from the new hydrazone ligand *N′*-(2-hydroxy-4-diethylaminobenzylidene)-3-methylbenzohydrazide (abbr. as H_2L in Scheme 1), was prepared and characterized.

EXPERIMENTAL

Materials and Measurements

All chemicals were obtained from commercial sources and were used as received without further purification. Infrared spectrum was recorded in KBr pellets using a Nicolet 520 FT–IR spectrophotometer. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240C elemental analyzer.

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TABLE 1
Crystallographic data for the complex

Formula	$C_{38}H_{42}N_6O_7V_2$
FW	796.7
Crystal shape, color	Block, brown
Crystal size, mm	0.20 × 0.17 × 0.16
Crystal system	triclinic
Space group	P–1
a, Å	11.349(2)
b, Å	13.385(3)
c, Å	13.644(2)
α, °	90.377(2)
β, °	93.772(2)
γ, °	109.239(2)
V, Å^3	1951.8(6)
Z	2
λ (Mo$K\alpha$), Å	0.71073
T, K	298(2)
μ, mm^{-1} (Mo$K\alpha$)	0.534
$T_{\min}$	0.9008
$T_{\max}$	0.9195
No. of measured reflections	13582
No. of unique reflections and R_{int}	7079 and 0.0314
No. of observed reflections	4677
Data/restraints/parameters	7079/51/483
F(000)	828
Goodness of fit on F^2	1.046
R_1, wR_2 [$I \geq 2\sigma(I)$]	0.0693, 0.1933
R_1, wR_2 (all data)	0.1033, 0.2273

Synthesis of H_2L

A mixture of 4-diethylaminosalicylaldehyde (0.193 g, 1.0 mmol) and 3-methylbenzohydrazide (0.150 g, 1.0 mmol) in 50 mL methanol was stirred at room temperature for 1 h to give a clear colorless solution. The solution was evaporated by distillation and cooled to room temperature, yielding colorless solid product, which was recrystallized from methanol. Yield: 87%. Anal. Calcd. for $C_{19}H_{23}N_3O_2$: C, 70.1; H, 7.1; N, 12.9%. Found: C, 70.3; H, 7.2; N, 12.8%.

Synthesis of the Complex

A methanol solution (10 mL) of vanadyl sulfate (0.082 g, 0.5 mmol) was added dropwise to the methanol solution (20 mL) of H_2L (0.163 g, 0.5 mmol) with stirring. The mixture was stirred at reflux for 30 min and then cooled to room temperature. Brown block-shaped single crystals were formed after slow evaporation of the solution in air for a few days. Crystals were filtered out and air-dried. Yield: 45%. Anal. Calcd. for $C_{38}H_{42}N_6O_7V_2$: C, 57.3; H, 5.3; N, 10.5%. Found: C, 57.2; H, 5.4; N, 10.7%.

X-Ray Structure Determination

A high-quality crystal of the complex was selected and mounted on the top of a glass fiber. The data was collected on a Bruker SMART 1000 CCD area diffractometer at 298(2) K. Graphite-monochromatized Mo K_α radiation ($\lambda = 0.71073$ Å) and the ω scan technique was used to collect the data sets. Absorption corrections were applied using SADABS.[17] The crystal structure was solved with direct method and refined with a full-matrix least-squares technique using SHELXTL.[18] Anisotropic thermal parameters were applied to all non-hydrogen atoms. Hydrogen atoms were generated geometrically. The crystallographic data as well as details of the data collection and refinement for the complex are listed in Table 1. Selected bond lengths and angles are given in Table 2.

RESULTS AND DISCUSSION

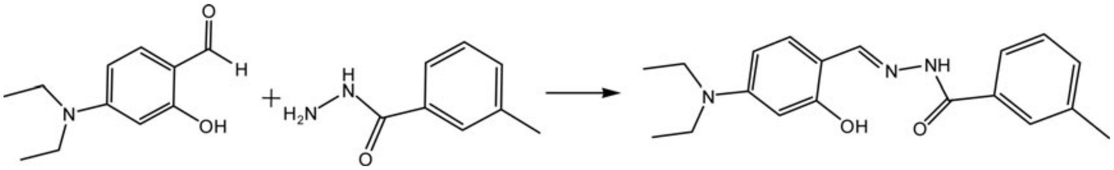
The hydrazone ligand H_2L was readily prepared by the reaction of 4-diethylaminosalicylaldehyde and 3-methylbenzohydrazide in methanol (Scheme 2). The dinuclear oxovanadium(V) complex was prepared by the reaction of the hydrazone ligand and vanadyl sulfate in methanol. The hydrazone ligand transferred to its deprotonated and enolic form during coordination (Scheme 3).

IR Spectrum

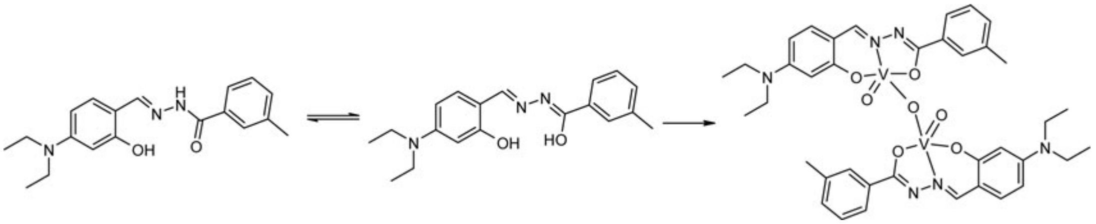
In the IR spectrum of the complex, the shifting of $\nu_{C=N}$ of H_2L to lower wavenumber in the complex (1610 cm^{-1}) indicates the coordination of the azomethine N atom to the V atom.[19,20] A new band appearing at 1243 cm^{-1} in the complex

TABLE 2
Coordinate bond lengths (Å) and angles (°) for the complex

Bond distances			
V1–O1	1.814(3)	V1–O2	1.946(3)
V1–O5	1.801(3)	V1–O6	1.579(4)
V1–N1	2.058(4)	V1–V2	3.0097(12)
V2–O3	1.825(3)	V2–O4	1.935(3)
V2–O5	1.797(3)	V2–O7	1.582(4)
V2–N3	2.069(4)		
Bond angles			
O6–V1–O5	107.77(18)	O6–V1–O1	104.25(18)
O5–V1–O1	101.40(15)	O6–V1–O2	103.84(17)
O5–V1–O2	85.92(13)	O1–V1–O2	147.10(15)
O6–V1–N1	100.04(19)	O5–V1–N1	149.16(15)
O1–V1–N1	84.01(15)	O2–V1–N1	74.52(14)
O7–V2–O5	107.43(19)	O7–V2–O3	104.16(18)
O5–V2–O3	100.92(14)	O7–V2–O4	103.00(17)
O5–V2–O4	87.34(13)	O3–V2–O4	147.62(15)
O7–V2–N3	99.9(2)	O5–V2–N3	150.04(15)
O3–V2–N3	83.66(14)	O4–V2–N3	74.57(14)



SCH. 2. The synthesis of the ligand H_2L.



SCH. 3. The synthesis of the oxovanadium(V) complex.

is attributed to the $\nu_{\text{C–O(enolic)}}$ mode. The weak bands in the region 400–650 cm^{-1} can be attributed to the stretching vibrations of the V–O and V–N coordinate bonds. The weak and broad band (3435 cm^{-1}) indicative of the O–H vibration is absent in the complex, indicating the deprotonation of the phenol group when complexation. The spectrum of the complex exhibits a typical band at 993 cm^{-1}, which can be assigned to the V=O stretching.[21,22]

Structure Description of the Complex

The complex is a μ_2-oxo bridged dinuclear oxovanadium(V) compound, as shown in Figure 1. The distance between the two V atoms is 3.010(1) Å. The complex crystallizes in the triclinic crystal system with space group *P*–1. Each V atom in the complex is five-coordinated in a distorted square pyramidal geometry, in which the basal plane is defined by the phenolate O, azomethine N, and enolic O atoms of the hydrazone ligand, and the μ_2-oxo O atom; the apical position is occupied by one terminal oxo O atom. The V—O and V—N bond lengths are agree well with the corresponding values reported in similar oxovanadium(V) complexes.[13–16,23] The V1 and V2 atoms are displaced 0.465(2) and 0.455(2) Å, respectively, from the least-squares planes defined by the corresponding four basal donor atoms, toward the apical positions. The obvious distortion from an ideal square pyramidal geometry for the V atoms could be a result of the five-membered chelate rings V1—N1—N2—C8—O2 and V2—N3—N4—C27—O4. The greatest distortion of the coordination from the ideal square pyramidal geometry can be observed from the coordinate bond angles. The angles in the basal planes of the square pyramidal geometries are in the range 74.5(1)–149.2(2)° for V1 and 74.6(1)–150.0(2)° for V2. The angles among the apical and the basal donor atoms are in the range 100.0(2)–107.8(2)° for V1 and 99.9(2)–107.4(2)° for V2. The relatively short C8—N2 and C27—N4 bond lengths of 1.289(6) and 1.295(6) Å, and the relatively long N1—N2 and N3—N4 bond lengths of 1.393(5) and 1.399(5) Å, indicate that there are conjugation effects along the backbones of the hydrazone ligands.

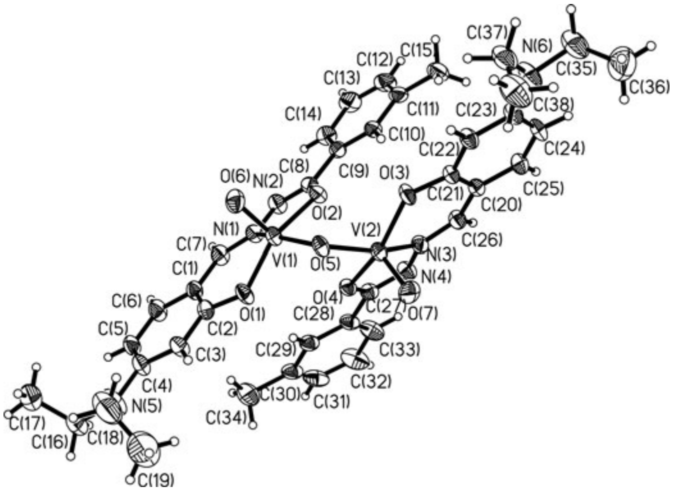


FIG. 1. The structure of the complex with 30% probability level.

In the crystal structure of the complex, molecules are stacked along the *a* axis with weak $\pi\cdots\pi$ stacking interactions.

CONCLUSIONS

We have successfully synthesized the novel μ_2-oxo bridged dinuclear oxovanadium(V) complex with the tridentate hydrazone ligand *N*′-(2-hydroxy-4-diethylaminobenzylidene)-3-methylbenzohydrazide. The elemental analyses, IR spectra, and single-crystal X-ray diffraction support the dinuclear structure of the complex.

SUPPLEMENTARY MATERIALS

CCDC-856606 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdccam.ac.uk/const/retrieving.html or from the

Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

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