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# Synthesis, Characterization, Structures, and Catalytic Property of Oxovanadium(V) Complexes with Hydrazone Ligands[1]

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**Abstract**—The reaction of [VO(Acac)$_2$] with 4-methyl-N'-[(2-hydroxy-1-naphthyl)methylidene]benzohydrazide (H$_2$L$^1$) and 4-methyl-N'-[1-(2-hydroxynaphthyl)ethyiidene]benzohydrazide (H$_2$L$^2$), respectively, in methanol, affords two new oxovanadium(V) complexes [VO(OMe)L$^1$]$_2$ (**I**) and [VO(OMe)L$^2$] (**II**). Both complexes have been characterized by elemental analysis, IR, and single crystal X-ray diffraction methods. Complex **I** is a methoxide-bridged dinuclear oxovanadium(V) compound, while complex **II** is a mononuclear oxovanadium(V) compound. The dinegative hydrazone ligands coordinate to the metal atoms through phenolate, imine, and deprotonated amide donor atoms. The geometry around vanadium atom in **I** is a distorted VNO$_5$ octahedron, while that in **II** is a VNO$_4$ square pyramid. Both complexes have effective catalytic property for the sulfoxidation reaction.

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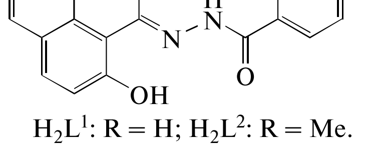
## INTRODUCTION

Oxovanadium(V) complexes with N- and O-containing ligands have been extensively investigated in recent years with respect to their remarkable efficiency as insulin mimetic compounds [1–3]. The interaction of simple vanadium species with ligands having pharmacological activity is of particular interest. Hydrazone compounds have been widely used as versatile ligands in coordination chemistry [4–6], and they have shown interesting biological properties, such as antibacterial, antitumor, and antifungi activities [7–9] as well as catalytic properties [10–12]. Recently, we have reported a few vanadium complexes [13]. As an extension of the work on such complexes, in the present paper, we describe the synthesis, spectroscopic characterization, crystal structure determination, and catalytic property of two new oxovanadium(V) complexes with similar tridentate hydrazone ligands 4-methyl-N'-(2-hydroxy-1-naphthyl)methylidene]benzohydrazide (H$_2$L$^1$) and 4-methyl-N'-[1-(2-hydroxynaphthyl)ethylidene]benzohydrazide (H$_2$L$^2$).



H$_2$L$^1$: R = H; H$_2$L$^2$: R = Me.

## EXPERIMENTAL

**Materials and methods.** 2-Acetyl-1-naphthol, 2-hydroxy-1-naphthaldehyde, and 4-methylbenzhydrazide were purchased from Aldrich Chemical Co. All other reagent-grade chemicals and reagents were purchased commercially and used without further purification. Elemental analyses (C, H, N) were obtained with a PerkinElmer model 240C instrument. IR spectra were recorded in KBr discs on a Nicolet 170SX spectrophotometer. The $^1$H NMR spectra with tetramethylsilane (TMS) as an internal standard were obtained using a Bruker Avance III 400MHz spectrophotometer.

**Synthesis of H$_2$L$^1$.** A mixture of 2-hydroxy-1-naphthaldehyde (1.72 g, 10 mmol) and 4-methylbenzhydrazide (1.50 g, 10 mmol) in 100 mL of methanol was refhrxed for 1 h. After reducing the solvent to 20 mL by distillation and cooling to room temperature, the precipitated white solid was filtered off, washed with methanol and dried in air. Recrystallization from methanol yielded pure product of H$_2$L$^1$. The yield was 2.32 g (76%).

For $C_{19}H_{16}N_2O_2$

| | | | |
|---|---|---|---|
| anal. caicd., %: | C, 74.98; | H, 5.30; | N, 9.20. |
| Found, %: | C, 74.73; | H, 5.41; | N, 9.15. |

IR (KBr; ν, cm$^{-1}$): 3217 w, 1645 s, 1627 m, 1601 w, 1582 m, 1558 w, 1472 m, 1415 w, 1397 w, 1355 w, 1335 m, 1297 s, 1237 w, 1215 m, 1189 m, 1138 w, 1113 w, 1026 w, 960 m, 855 w, 823 m, 799 m, 745 s, 692 w, 673 w, 551 w.

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**Table 1.** Crystallographic data and structure refinement for complexes **I** and **II**

| Parameter | Value | |
|---|---|---|
| | **I** | **II** |
| Formula | $C_{40}H_{34}N_4O_8V_2$ | $C_{21}H_{19}N_2O_4V$ |
| $M$ | 800.6 | 414.3 |
| Crystal size, mm | 0.27 × 0.25 × 0.23 | 0.32 × 0.30 × 0.27 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ |
| $a$, Å | 9.105(2) | 9.898(1) |
| $b$, Å | 20.085(2) | 14.634(2) |
| $c$, Å | 9.931(2) | 13.213(2) |
| β, deg | 98.849(2) | 91.842(2) |
| $V$, Å | 1794.5(5) | 1913.0(5) |
| $Z$ | 2 | 4 |
| $\rho_{calcd}$, g/cm$^3$ | 1.482 | 1.439 |
| μ, mm$^{-1}$ | 0.582 | 0.548 |
| $F$(000) | 824 | 856 |
| Temperature, K | 298(2) | 298(2) |
| $T_{min}/T_{max}$ | 0.8587/0.8778 | 0.8441/0.8661 |
| Reflections measured | 10176 | 10942 |
| Independent reflections, $R_{int}$ | 3900 | 4133 |
| Observed reflections | 2860 | 2658 |
| Goodness of fit on $F^2$ | 1.031 | 1.024 |
| Final $R$ indices, $I \geq 2\sigma(I)$* | $R_1 = 0.0392$<br>$wR_2 = 0.0960$ | $R_1 = 0.0444$<br>$wR_2 = 0.1058$ |
| $R$ indices, all data* | $R_1 = 0.0591$<br>$wR_2 = 0.1074$ | $R_1 = 0.0785$<br>$wR_2 = 0.1222$ |

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

**Synthesis of $H_2L^2$.** This compound was prepared by following the same procedure outlined for $H_2L^1$, but with 2-hydroxy-1-naphthaldehyde replaced by 2-acetyl-1-naphthol (1.86 g, 10 mmol). The pure product was obtained as a white solid. The yield was 2.70 g (85%).

For $C_{20}H_{18}N_2O_2$

anal. calcd., %: C, 75.45; H, 5.70; N, 8.80.
Found, %: C, 75.21; H, 5.78; N, 8.92.

IR (KBr; ν, cm$^{-1}$): 3225 w, 1640 s, 1612 m, 1605 w, 1583 m, 1560 w, 1470 m, 1414 w, 1395 w, 1360 w, 1333 m, 1293 s, 1238 w, 1213 m, 1182 m, 1146 w, 965 m, 841 w, 833 m, 787 m, 745 s, 670 w, 653 w.

**Synthesis of [VO(OMe)L$^1$]$_2$ (I).** [VO(Acac)$_2$] (0.263 g, 1.0 mmol) dissolved in 20 mL methanol was added dropwise to a methanol solution (10 mL) of $H_2L^1$ (0.304 g, 1.0 mmol) with stirring, and then the mixture was heated at reflux with stirring for 1 h and cooled to room temperature. When the solution was allowed to stand at room temperature for a few days to slow evaporation of the solvent, X-ray quality brown block-shaped single crystals were collected by filtration. The crystals were washed with methanol and dried in air. The yield was 0.230 g (58%).

For $C_{40}H_{34}N_4O_8V_2$

anal. calcd. %: C, 60.01; H, 4.28; N, 7.00.
Found, %: C, 59.80; H, 4.37; N, 7.12.

IR (KBr; cm$^{-1}$): 1659 m, 1604 s, 1549 m, 1501 w, 1453 m, 1404 s, 1328 w, 1280 w, 1183 w, 1017 m, 983 s, 817 w, 742 w, 603 m, 534 w, 466 w.

**Synthesis of [VO(OMe)L$^2$] (II).** This complex was prepared by following the same procedure outlined for **I**, but with $H_2L^1$ replaced by $H_2L^2$ (0.318 g, 1.0 mmol). The X-ray quality brown block-shaped single crystals were obtained. The yield was 0.203 g (49%).

For $C_{21}H_{19}N_2O_4V$

anal. calcd., %: C, 60.88; H, 4.62; N, 6.76.
Found, %: C, 60.97; H, 4.55; N, 6.85.

IR (KBr; ν, cm$^{-1}$): 1657 m, 1601 s, 1546 m, 1508 s, 1455 m, 1417 m, 1382 m, 1366 w, 1321 m, 1282 m, 1217w, 1199 w, 1156 w, 1078 w, 1045 s, 1016 m, 972 s, 865 m, 828 m, 751 s, 723 m, 630 m, 583 s, 523 w, 436 w.

**X-ray structure determination I and II.** The crystal and instrumental parameters used in the unit cell determination and data collection are summarized in Table 1. Diffraction measurements were made at room temperature on a Bruker SMART APEX II X-ray diffractometer using graphite-monochromated Mo$K_\alpha$ radiation and co scan mode. Unit-cell dimensions were determined and refined in the range 2.03°–27.00° for **I** and 2.08°–26.99° for **II**. Both structures were solved by the direct methods using SHELXS-97 and refined by full-matrix least-squares techniques on $F^2$ with SHELXL-97 [14]. The empirical absorption corrections were applied by the multi-scan method [15]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in their idealized positions and refined isotropically. Selected bond distances and angles for the complexes **I** and **II** are listed in Table 2.

Supplementary material for structures **I** and **II** has been deposited with the Cambridge Crystallographic Data Centre (nos. 917365 (**I**) and 858860 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

## RESULTS AND DISCUSSION

The hydrazone compounds were prepared by the condensation of similar carbonyl-containing compounds with 4-methylbenzhydrazide in methanol. Each of them has two dissociable protons at the phenolic-OH and the amide functionality. The reaction of bis(acetylacetonato)oxovanadium(IV) with stoichiometric amounts of the hydrazone ligands in methanol in air afforded the two vanadium(V) complexes as brown crystalline solids. It should be pointed out that the vanadium in the starting materials is in V(IV) oxidation state, but it appears to be V(V) in both complexes, indicating that it was oxidized by air during the reaction procedures. Elemental analyses of the complexes are satisfactory with the empirical formulae.

The IR spectra of the ligands exhibit two bands in the regions 3215–3230 and 1640–1645 $cm^{-1}$ due to the ν(N–H) and ν(C=O) stretches [16]. The absence of these bands in the spectra of the complexes is consistent with the enolisation of the amide functionality and subsequent proton replacement by the vanadium atom. The bands appearing at about 1280 $cm^{-1}$ range are assigned to the ν(C–O)(enolic) mode. The strong bands at 1604 and 1601 $cm^{-1}$ in **I** and **II**, respectively, with shoulders are assigned to the conjugate C=N–N=C moieties [17]. The bands observed at 983 and 972 $cm^{-1}$ for **I** and **II**, respectively, are assigned to the V=O stretching [16, 18].

The molecular structure of **I** is shown in Fig. 1. The complex is a bis-methoxide oxygen-bridged centrosymmetric dinuclear vanadium(V) compound. The V···V distance is 3.393(2) Å. The dianionic tridentate hydrazone ligand binds the metal atom through the phenolate–O, imine–N and deprotonated amide–O atoms, forming a six- and a fivemembered chelate rings, which are inclined to each other by 11.5(3)°. Each V atom is in a distorted $NO_5$ octahedral coordination with the three donor atoms of the hydrazone ligand and one methoxide O atom defining the equatorial plane, and with one oxo O and one symmetry-related methoxide O atom occupying the axial positions. The mean deviation of the four equatorial donor atoms from the least-squares plane is 0.008(3) Å. The displacement of the V atom towards the oxo group from the plane is 0.348(2) Å. The distances of V=O and other coordination bonds in complex **I** are within the range of similar vanadium(V) complexes [19, 20].

The molecular structure of **II** is shown in Fig. 2. The methoxide ligand lies *trans* to the imine-N atom. The dianionic tridentate hydrazone ligand binds the metal atom through the phenolate–O, imine–N and deprotonated amide–O atoms, forming a six- and a fivemembered chelate rings, which are inclined to each other by 18.3(3)°. The V atom is in a distorted $NO_4$ square pyramidal coordination, with the three donor atoms of the hydrazone ligand, and the methoxide O atom defining the basal plane, and with the oxo O atom occupying the apical position. The mean deviation of the four equatorial donor atoms from the least-squares plane is 0.133(3) Å. The displacement of the V atom towards the oxo group from the plane is 0.501(2) Å. The τ value for complexes **II** is 0.42, indicating the coordination is a distorted square pyramid instead of trigonal bipyramid [21]. The distances of V=O and other coordination bonds in complex **II** are within the range of similar vanadium(V) complexes [22–24].

**Table 2.** Selected bond lengths (Å) and bond angles (deg) for complex **I** and **II***

| Bond | *d*, Å | Bond | *d*, Å |
|---|---|---|---|
| | **I** | | |
| V(1)–O(1) | 1.836(2) | V(1)–O(2) | 1.922(2) |
| V(1)–O(3) | 1.580(2) | V(1)–O(4) | 1.823(2) |
| V(1)–N(1) | 2.094(2) | V(1)–O(4*A*) | 2.409(2) |
| | **II** | | |
| V(1)–O(1) | 1.825(2) | V(1)–O(2) | 1.899(2) |
| V(1)–O(3) | 1.756(2) | V(1)–O(4) | 1.576(2) |
| V(1)–N(1) | 2.086(2) | | |
| Angle | ω, deg | Angle | ω, deg |
| | **I** | | |
| O(3)V(1)O(4) | 103.4(1) | O(3)V(1)O(1) | 100.4(1) |
| O(4)V(1)O(1) | 105.7(1) | O(3)V(1)O(2) | 100.5(1) |
| O(4)V(1)O(2) | 89.4(1) | O(1)V(1)O(2) | 150.5(1) |
| O(3)V(1)N(1) | 96.8(1) | O(4)V(1)N(1) | 156.3(1) |
| O(1)V(1)N(1) | 82.5(1) | O(2)V(1)N(1) | 74.6(1) |
| O(3)V(1)O(4*A*) | 177.5(1) | O(4)V(1)O(4*A*) | 74.2(1) |
| O(1)V(1)O(4*A*) | 80.8(1) | O(2)V(1)O(4*A*) | 79.1(1) |
| N(1)V(1)O(4*A*) | 85.5(1) | | |
| | **II** | | |
| O(4)V(1)O(3) | 105.7(1) | O(4)V(1)O(1) | 107.4(1) |
| O(3)V(1)O(1) | 100.4(1) | O(4)V(1)O(2) | 111.4(1) |
| O(3)V(1)O(2) | 87.1(1) | O(1)V(1)O(2) | 136.7(1) |
| O(4)V(1)N(1) | 97.0(1) | O(3)V(1)N(1) | 154.9(1) |
| O(1)V(1)N(1) | 82.5(1) | O(2)V(1)N(1) | 74.6(1) |

* Symmetry code for *A*: 2 – *x*, –*y*, 1 – *z*.

In both complexes, the N–C and C–O bond lengths in the fivemembered chelate rings are consistent with the enolate form of the amide functionality. The corresponding bond values are comparable to each other. The difference in the molecular structures of the two complexes in solid state may arise due to the crystal packing forces or bulk solid state effects mediated by the differing substitute groups.

The complexes were tested for their ability to catalyze the oxidation of prochiral sulfides, using methyl phenyl sulfide PhSMe (thioanisol) and benzyl phenyl sulfide PhSBz as model substrates [25].

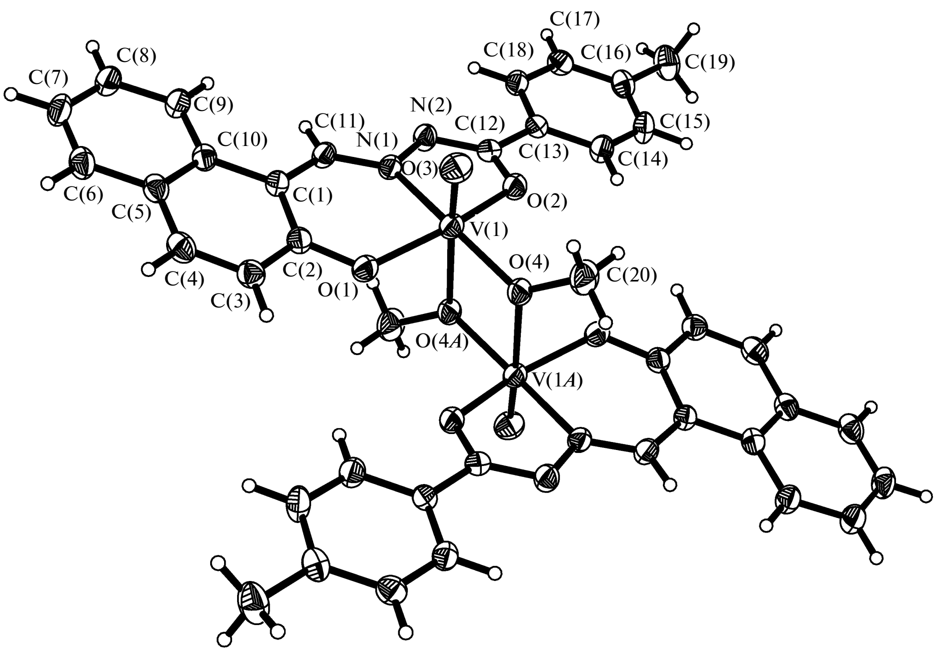


**Fig. 1.** Molecular structure of **I** with 30% thermal ellipsoids. Unlabelled atoms are related to the symmetry operation $2 - x$, $-y$, $1 - z$.

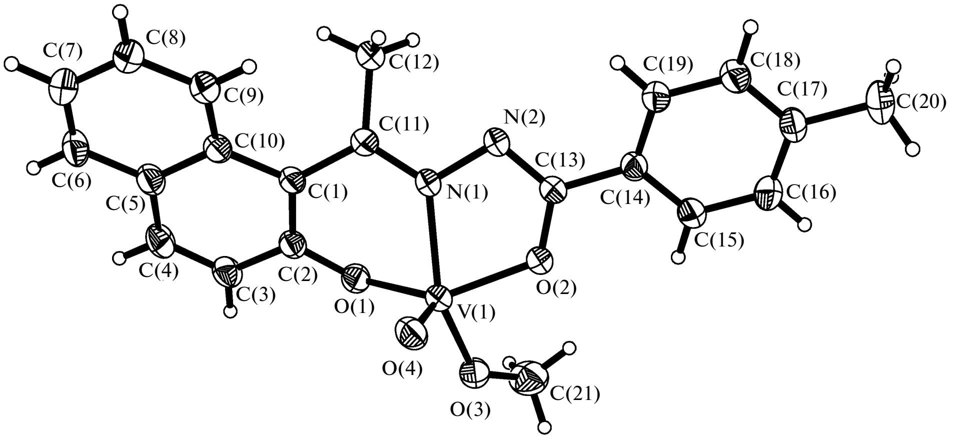
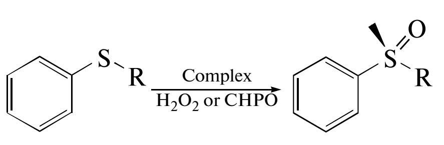


**Fig. 2.** Molecular structure of **II** with 30% thermal ellipsoids.



The results are summarized in Table 3. A 1.25-fold excess, based on the sulfide substrate, of $H_2O_2$ or cumene hydroperoxide (CHPO) as oxidants was used. For all the reactions performed, no sulfone formation as a side product was observed. The best results have been obtained for **II** as a catalyst in the oxidation of methyl phenyl sulfide with $H_2O_2$ as the oxidant. In this case an overall yield of 91% within 24 h reaction time and a 15% *ee* of the S-configured sulfoxide were obtained. For the same time of reaction, catalyst and sulfide, but with CHPO as the oxidant, a lower yield (85%) and 9% *ee* of the S-configured sulfoxide were observed. When benzyl phenyl sulfide was used as the substrate with a more bulky substituent, an increase of reaction time to 48 h is noticed. Moreover, the yields of conversion are much smaller and the enantioselectivity decreases to value of 5 and 2% with $H_2O_2$ and CHPO as oxidants, respectively. As for **I**, reduced catalytic activity on comparison to **II** is observed. With $H_2O_2$ as the oxidant in the sulfoxidation reaction, for methyl phenyl sulfide 87% was converted within 24 h and with 11% *ee* of the S-configured sulfoxide, whereas with CHPO as the oxidant, 82% conversion was observed with 7% *ee* of the S-configured sulfoxide.

**Table 3.** Catalytic results of complexes **I** and **II**

| Complex | Substrate | Oxidant | Yield, % | Time, h | *ee*, % |
|---|---|---|---|---|---|
| **I** | PhSMe | $H_2O_2$ | 87 | 24 | 11 (S) |
| | PhSMe | CHPO | 82 | 24 | 7 (S) |
| | PhSBz | $H_2O_2$ | 75 | 48 | 3 |
| | PhSBz | CHPO | 70 | 48 | 2 |
| **II** | PhSMe | $H_2O_2$ | 91 | 24 | 15 (S) |
| | PhSMe | CHPO | 85 | 24 | 9 (S) |
| | PhSBz | $H_2O_2$ | 82 | 48 | 5 (S) |
| | PhSBz | CHPO | 73 | 48 | 2 (S) |

In the case of benzyl phenyl sulfide, after a 48 h reaction time, with $H_2O_2$ and CHPO as oxidants, overall yields of 75 and 70% were obtained, respectively.

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