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Synthesis, Crystal Structure, and Catalytic Property of Oxovanadium(V) Complex Derived from *N*'-(2-Hydroxynaphthylidene)-4-Chlorobenzohydrazide and 1,10-Phenanthroline[1]

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Abstract—A new oxovanadium(V) complex, [VO(L)(Phen)], where L is the dianionic form of *N*'-(2-hydroxynaphthylidene)-4-chlorobenzohydrazide, Phen is 1,10-phenanthroline, has been synthesized and characterized by elemental analysis, FT-IR spectra, and single crystal X-ray determination. The crystal of the complex is monoclinic: space group $P2_1/c$, $a = 11.2376(8)$, $b = 13.3068(10)$, $c = 17.5593(11)$ Å, $\beta = 106.806(2)°$, $V = 2513.6(3)$ Å^3, $Z = 4$. The V atom in the complex is in octahedral coordination, with the phenolate O, imine N, and enolate O atoms of L and one N atom of Phen define the equatorial plane, and with the other N atom of Phen and one oxo O atom located at the axial positions. The complex is a good catalyst for the oxidation of thioanisole to the corresponding sulfoxide by cumene hydroperoxide.

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INTRODUCTION

The coordination chemistry of oxovanadium complexes with multi-dentate ligands has received considerable attention in recent years for their biological and medicinal applications [1–4], as well as catalytic capabilities [5–7]. Among the multi-dentate ligands, benzohydrazones are considered as a very important class of organic compounds which have wide applications in many biological aspects. The remarkable biological activity of benzohydrazones, R–CO–NH–N=CH–R', and the dependence of their mode of chelation with transition metal ions present in the living system have been of significant interest. The complexes of benzohydrazones have been known for their pharmacological applications [8–10]. Benzohydrazones usually act as tridentate ligands. These ligands due to their facile keto-enol tautomerization and the availability of several potential donor sites can coordinate to various metals. These ligands have a tendency to stabilize the vanadium in its highest oxidation state. Vanadium complexes derived from benzohydrazones seem to be a good candidate for various catalytic procedures [11, 12]. Recently, it has been established that vanadium peroxidases are able to catalyse the oxidation of organic sulfides to the corresponding sulfoxides in the presence of hydrogen peroxide [13]. In the present paper, we descibe the synthesis, characterization, and catalytic property of a new oxovanadium(V) complex, [VO(L)(Phen)], where L is the dianionic form of *N*'-(2-hydroxynaphthylidene)-4-chlorobenzohydrazide (H_2L), Phen is 1,10-phenanthroline.

EXPERIMENTAL

Materials and methods. 2-Hydroxy-1-naphthyaldehyde, 4-chlorobenzohydrazide, and 1,10-phenanthroline were purchased from Fluka. Other reagents and solvents were analytical grade and used without further purification. Elemental (C, H, and N) analyses were made on a Perkin-Elmer Model 240B automatic analyzer. The vanadium content was determined as V_2O_5. IR spectra were recorded on an IR-408 Shimadzu 568 spectrophotometer. Thermogravimetric analysis (TGA) experiments were carried out with a Dupont thermal analyzer from room temperature to 1000°C under nitrogen at a heating rate of 10°C min^{-1}.

Synthesis of H_2L. 2-Hydroxy-1-naphthyaldehyde (1.72 g, 0.01 mmol) and 4-chlorobenzohydrazide (1.71 g, 0.01 mol) were mixed in methanol (60 mL). The mixture was stirred at reflux for 30 min and three quarter of the solvent was evaporated, to give colorless solid product of H_2L, which was collected by filtration

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[1] The article is published in the original.

Table 1. Crystallographic data and structure refinement summary for the complex

Parameter	Value
Habit, colour	Block, deep brown
Formula weight	569.9
Temperature, K	298(2)
Crystal size, mm	0.30 × 0.30 × 0.27
Radiation (λ, Å)	MoK_α (0.71073)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions:	
a, Å	11.2376(8)
b, Å	13.3068(10)
c, Å	17.5593(11)
β, deg	106.806(2)
V, Å^3	2513.6(3)
Z	4
ρ_{calcd}, mg cm^{-3}	1.506
F(000)	1164
Absorption coefficient, mm^{-1}	0.543
θ Range for data collection, deg	2.42–25.50
Index ranges	$-11 \le h \le 13$, $-16 \le k \le 16$, $-21 \le l \le 21$
Reflections collected	24186
Independent reflections	4676
Reflections with ($I > 2\sigma(I)$)	3325/
Parameters	352
Restraints	0
Final R indices ($I > 2\sigma(I)$)	0.0440
R indices (all data)	0.0981
Goodness-of-fit	1.035
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	0.323, –0.192

Table 2. Coordinate bond distances (Å) and angles (deg) for the complex

Bond	d, Å	Bond	d, Å
V(1)–O(1)	1.935(2)	V(1)–O(2)	1.996(2)
V(1)–O(3)	1.592(2)	V(1)–N(1)	2.047(2)
V(1)–N(3)	2.312(2)	V(1)–N(4)	2.138(2)
Angle	ω, deg	Angle	ω, deg
O(3)V(1)O(1)	102.88(9)	O(3)V(1)O(2)	100.66(9)
O(1)V(1)O(2)	153.08(8)	O(3)V(1)N(1)	104.22(9)
O(1)V(1)N(1)	85.16(7)	O(2)V(1)N(1)	76.53(7)
O(3)V(1)N(4)	91.76(9)	O(1)V(1)N(4)	89.51(7)
O(2)V(1)N(4)	102.68(7)	N(1)V(1)N(4)	163.91(8)
O(3)V(1)N(3)	164.33(9)	O(1)V(1)N(3)	80.22(8)
O(2)V(1)N(3)	80.64(7)	N(1)V(1)N(3)	91.30(8)
N(4)V(1)N(3)	72.82(7)		

and dried in vacuum containing anhydrous $CaCl_2$. The yield was 2.63 g (81%).

For $C_{18}H_{13}ClN_2O_2$			
anal. calcd., %:	C, 66.57;	H, 4.03;	N, 8.63.
Found, %:	C, 66.36;	H, 4.12;	N, 8.71.

Synthesis of the complex. H_2L (0.5 mmol, 0.16 g) and Phen (0.5 mmol, 0.09 g) in methanol (20 mL) were added with stirring to $VO(Acac)_2$ (0.5 mmol, 0.13 mg) in methanol (10 mL). The mixture was stirred at refluxed for 30 min to give a brown solution. The solution was left still at room temperature in air to give deep brown block-shaped single crystals, which were collected by filtration and dried in vacuum containing anhydrous $CaCl_2$. The yield was 0.12 g (42%).

For $C_{30}H_{19}N_4O_3ClV$				
anal. calcd., %:	C, 63.23;	H, 3.36;	N, 9.83;	V, 8.94.
Found, %:	C, 63.02;	H, 3.50;	N, 9.71;	V, 9.05.

X-ray crystal determination. Data were collected from a selected crystal mounted on a glass fiber. The data for the complex were processed with SAINT [14] and corrected for absorption using SADABS [15]. Semi-empirical absorption corrections were applied with ψ scans [16]. The structure was solved by direct method using the SHELXS-97 program and refined by full-matrix least-squares techniques on F^2 using anisotropic displacement parameters [17]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at the calculated positions. The crystallographic data for the complex are listed in Table 1. Selected bond lengths and angles are given in Table 2. Supplementary materials have been deposited with the Cambridge Crystallographic Data Centre (no. 955618); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Catalytic oxidation of sulfides. A DMSO solution of the complex (4×10^{-5} mol) was stirred with cumene hydroperoxide (4×10^{-3} mol) in DMSO (10 mL) for 5 h at 20°C. To the resulting yellow solution heated to 50°C the methyl phenyl sulfide (4×10^{-4} mol) dissolved in DMSO was added. The mixture was kept at 50°C. The rate of the oxidation reaction was studied with the help of high performance liquid chromatography. Samples of the reaction mixture were withdrawn at intervals and then chromatographed with a Kromasil-100 C-8 column and acetonitrile-water (4 : 6 v/v) as an eluent. Chromatography was carried

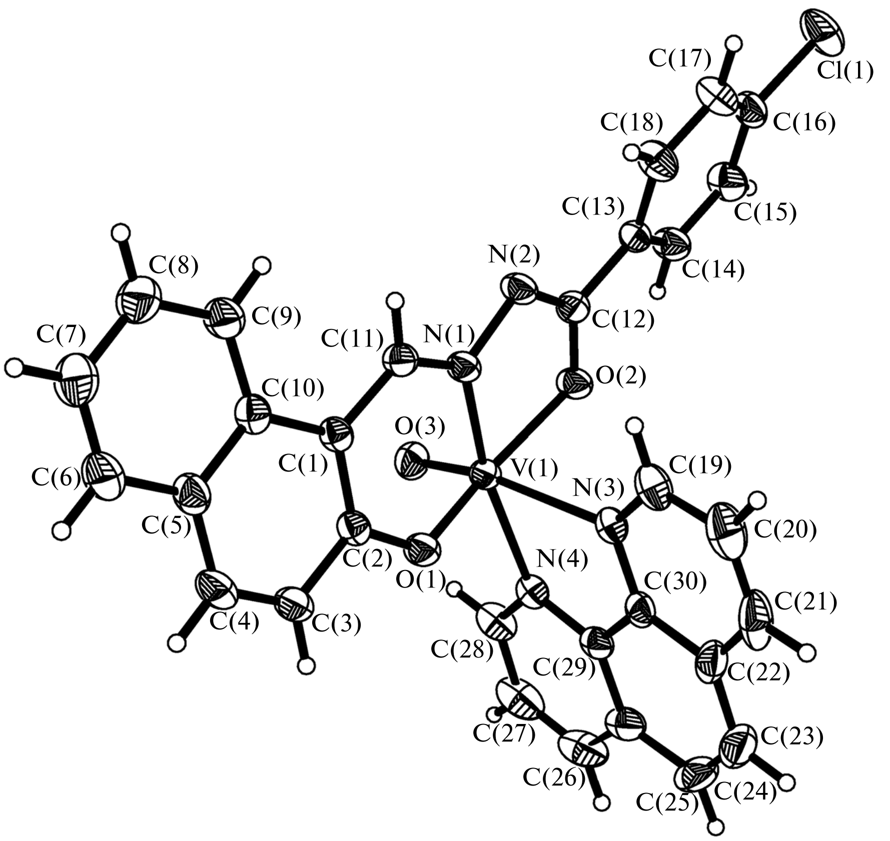
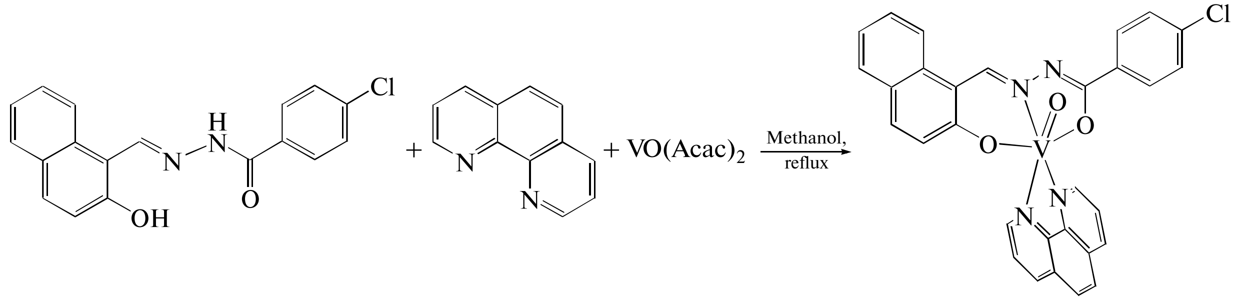


Fig. 1. Molecular structure of the complex at 30% probability displacement.

out with a flow rate of 1 mL min^{-1} and components were detected with spectrophotometric detector at 260 nm.

RESULTS AND DISCUSSION

The synthesis of the complex is shown below:



The molecular structure of the complex is shown in Fig. 1. The V atom in the complex is in an octahedral coordination, with the phenolate O, imine N, and enolate O atoms of the benzohyrazone ligand, and N(4) atom of Phen defining the equatorial plane, and with N(3) atom of Phen and the oxo O atom located at the axial positions. The V atom deviates from the least-squares plane defined by the four equatorial donor atoms of 0.332(1) Å. The V–O and V–N coordinate bond lengths in the complex are comparable to the corresponding values observed in other similar oxovanadium(V) complexes with benzohydrazone ligands [18, 19]. The two ligands, L and Phen, form a dihedral angle of 94.2(3)°. The naphthyl ring and the benzene ring in L form a dihedral angle of 34.0(3)°.

Infrared spectrum of the complex in KBr disk do not display any band assignable to the O–H and N–H stretches observed for the free benzohydrazone ligand. Thus, both phenolic and the amino protons are dissociated and the dianionic ligand binds the metal centre via the phenolate-O, the imine-N, and the enolate-O in the complex. This type of coordination mode of L has been confirmed by X-structure determination. The strong band observed at 1611 cm^{-1} is attributed to the conjugate C=N–N=C moiety of the ligand L [19]. The V=O stretch appears as a medium band at 960 cm^{-1} [20].

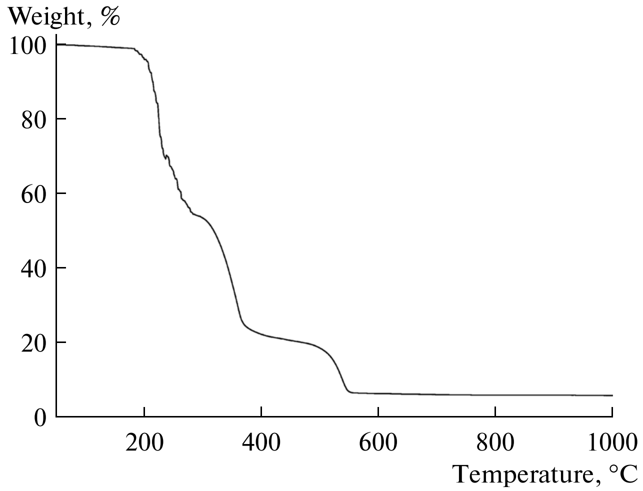


Fig. 2. TG curve of the complex.

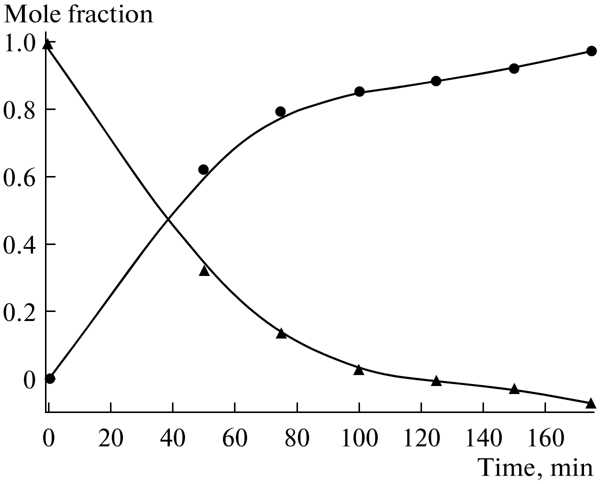


Fig. 3. Oxidation of methyl phenyl sulfide by cumene hydroperoxide with the complex as catalyst in DMSO at 50°C: ▲—sulfide, ●—sulfoxide.

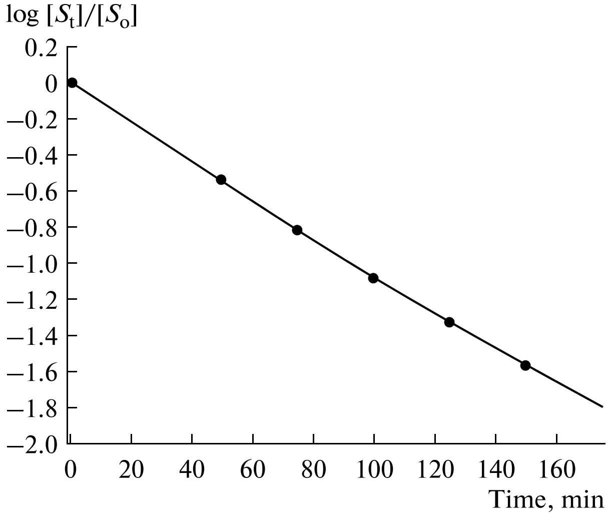


Fig. 4. Plot of log[S_t]/[S_o] versus reaction time. [S] = c_{sulfide}.

Figure 2 is the TG curve of the complex. The complex undergoes three-stage decomposition. The first weight loss 45.7% (calcd. 46.5%) was observed in the temperature range 183–293°C and corresponds to the loss of the benzohydrazone ligand except for the two O atoms. The second stage of decomposition started at about 295°C and completed at 360°C corresponding to the loss of the Phen ligand. The third stage of decomposition occurred in the range 500–550°C, which can be due to the loss of the remaining part of the residue and leaving V_2O_5 as a final product.

Figure 3 shows the time dependence of the decrease in methyl phenyl sulfide and of the increase of methyl phenyl sulfoxide concentrations during the oxidation of the former compound by cumene hydroperoxide in the presence of catalytic amount of the complex. With the cumene hydroperoxide in larger excess the oxidation of the sulfide proceed as the reaction of first order. The plots of log([S_t]/[S_o]) versus time gave a straight line in the range of three half-lives shown in Fig. 4, where the [S] denote concentration of the sulfide at the subscripted time.

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