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Original Scientific Paper

Hydrogen Bonded Dimer *N*-(2-hydroxyethyl)-2-oxy-1-naphthaldimine and Its Oxo-vanadium(V) Complex*

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N-(2-hydroxyethyl)-2-oxy-1-naphthaldimine is a potential tridentate ligand prepared in a condensation reaction from 2-hydroxy-1-naphthaldehyde and 2-aminoethanol using catalytic amounts of triethylamine. Its vanadium(V) coordination compound was obtained by a template reaction from the methanol solution upon oxidation of $VO^{2+} \rightarrow VO^{3+}$ in air. Physico-chemical properties of both compounds were examined by thermogravimetric analysis, differential scanning calorimetry and FT IR spectroscopy. These results supplied some elements of structural information. Nevertheless, the entire stereochemistry of both the non-coordinated ligand and metal complex was elucidated by the X-ray structural determination. The ligand forms molecular complex by dimerization *via* intermolecular O–H$\cdots$O hydrogen bonding. In the metal complex, four square pyramid basal plane coodination places are occupied by dinegative tridentate ligand ONO donor atoms and a methoxy group. All V–O bond distances are significantly different, depending on the nature of the functional group to wich oxygen atoms belong. The vanadium complex is an example of a fairly rare pentacoordinated square pyramidal V^V species.

Key words: tridentate naphthaldimine, oxo-vanadium(V) complex, dimerization by hydrogen bonding, X-ray diffraction, thermal analysis, FT IR spectroscopy.

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* Dedicated to Professor Boris Kamenar on the occasion of his 70th birthday.

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INTRODUCTION

Oxovanadium(V) complexes containing ligands with mixed ON donor atoms are considered model compounds for the active centre in vanadate-dependent bromoperoxidases from seaweeds that catalyze the halogenation of organic substrates with the help of hydrogen peroxide. While land-living organisms like fungi or lichen feature mainly chlorinating and iodinating enzymes, the bromination to yield bromoform, for example, plays an important role for marine organisms. The exact function of vanadium in the rather acidic bromoperoxidase enzymes is still unclear.[1–4] Solutions containing VO^{2+} and dinegative tridentate ligands of the $^{-}O–N–O^{-}$ type are easily oxidized to the corresponding V^{V} complexes and V^{IV} complexes are possibly stable only if insoluble.[5] In order to understand how vanadium might function in a complex biomolecule, it is first necessary to define its basic coordination chemistry with biologically relevant ligands.

EXPERIMENTAL

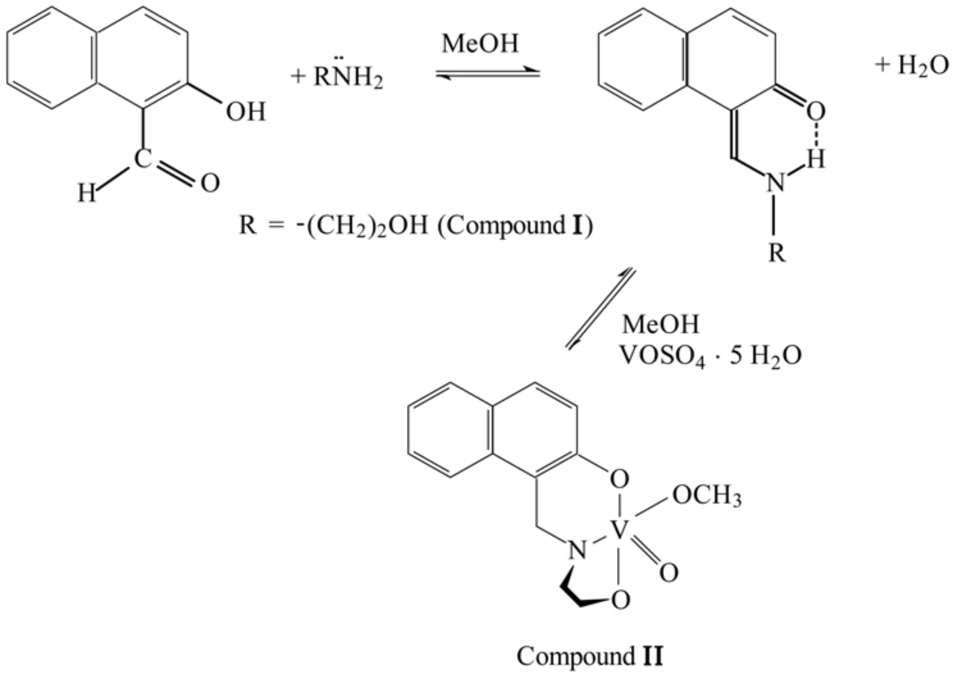
Synthesis

N*-(2-hydroxyethyl)-2-oxy-1-naphthaldimine, Compound **I** {Systematic Name: 1-(2-Hydroxyethyl)aminomethylene-2-naphthalenone}*

Methanol solutions of 2-hydroxy-1-naphthaldehyde (1.72 g; 10 mmol) and 2-aminoethanol (0.66 mL; 10 mmol) were mixed at room temperature in a 1:1 molar ratio using triethylamine as catalytic agent. The yellow crystalline product was obtained from the deep-yellow coloured solution by standing for a few hours. The precipitate was filtered off and washed out with cold methanol (yield 59%, Scheme I). The compound is soluble in dichlormethane, chloroform, methanol, ethanol and dioxane. Single crystals of good diffraction quality were obtained by the evaporation method from chloroform solution.

*Methoxy[*N*-(2-hydroxyethyl)-2-oxo-1-naphthaldiminato]oxovanadium(V), Compound **II** {Systematic Name: Methoxy[(2-hydroxyethyliminomethyl)-2-naphtholato-*N,O*]-oxovanadium(V)}*

From the mixture of methanol solutions of Compound **I** (0.430 g; 2 mmol) and vanadium salt $VOSO_4 \cdot 5\ H_2O$ (0.253 g; 1 mmol) in the molar ratio 2 : 1, orange-red crystals appeared immediately at room temperature. The change of color in aerobic solution from green to reddish-brown indicates a rapid oxidation to a V^{V} complex in the presence of dinegative tridentate Schiff base anion. After a few hours standing, transparent red crystals were separated by vacuum filtration from the mother liquor (yield 48%, Scheme I). The complex is readily soluble in dichlormethane, chloroform, acetone, moderately soluble in methanol, ethanol and diethylether and insoluble in benzene, carbon tetrachloride and *n*-hexane.



Scheme I.

TGA, DCS and FT IR Experiment

The compounds were examined by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and FT IR spectroscopy. The DSC measurements were performed with a Mettler DSC 30 calorimeter with inert gas-flow (200 cm^3/min. of Ar) over the samples using aluminum crucibles. The temperature gradient was 10 °C/min. The TGA measurements were performed on a Mettler TG 50 thermobalance under the same conditions as applied to the DSC experiment. The results were developed by applying the GrafVare 2.1 program under UNIX operating system. IR spectra were recorded using KBr discs for both Compounds **I** and **II** on a Perkin-Elmer FT IR 1600 spectrophotometer in the region 4000–400 cm^{-1}.

X-ray Experiment

The X-ray diffraction experiment was carried out on an automatic four-circle Philips PW1100 diffractometer (upgraded by STOE, Germany) using graphite monochromated Mo-Kα radiation (λ = 0.7107 Å) at room temperature. The cell parameters were determined by fitting 30 (Compound **I**) and 32 (Compound **II**) strong, general reflections in the range of $22° \le 2\theta \le 31°$ and $20 \le 2\theta \le 35°$, respectively. The reflections were collected by the ω-scan technique for a 2θ range 4 to 54°. The structure of Compound **I** was solved by direct methods, while the structure of Compound **II**

TABLE I

General and crystal data and a summary of intensity data collection and structure refinement

	Compound **I**	Compound **II**
General and crystal data		
Empirical formula	$C_{13}H_{13}NO_2$	$C_{14}H_{14}NO_4V$
Formula weight	215.25	311.21
Color and shape	Pale yellow; prism	Orange; prism
Crystal system and space group	Monoclinic, $C2/c$	Monoclinic, $P2_1/c$
Crystal dimensions / mm	0.62 × 0.51 × 0.47	0.77 × 0.47 × 0.13
a / Å	16.0574(11)	12.280(3)
b / Å	4.9839(3)	8.0067(14)
c / Å	28.5710(18)	13.6339(18)
β / °	107.944(5)	92.973(15)
Cell volume / Å^3	2175.26(15)	1338.7(4)
Formula units per unit cell	8	4
D_{calc} / g cm^{-3}	1.315	1.544
F(000)	912	640
Absorption coefficient, μ / mm^{-1}	0.08	0.73
Intensity data collection (at 293 K)		
Diffractometer	Philips PW1100; STOE upgraded	
Graphite monochromated radiation / Å	λ(Mo-Kα) = 0.7107	
Scan mode and 2θ data collection range / °	ω; 4–54	
Range of h, k, l	–20 to 19; 0 to 6; 0 to 36	–15 to 15; 0 to 10; 0 to 17
Reflections measured	2435	5854
Independent reflections	2382 (R_{int} = 0.016)	2927 (R_{int} = 0.040)
Observed reflections with [$I_{\text{net}} \geq 2\sigma (I_{\text{net}})$]	1276	1867
Refinement		
No. of parameters varied	145	181
Data to parameter ratio	8.8	10.3
$(\Delta/\sigma)_{\text{max}}$	0.001	0.001
k in $w^{-1} = [\sigma^2 F_o + kF_o^2]$	0.003	0.004
Final residuals: R; wR; GoF	0.037; 0.060; 1.06	0.036; 0.068; 1.02
Largest ΔF peak and hole / e Å^{-3}	0.15; –0.15	0.28; –0.26
Computer programs	STADI4, X-RED, NRCVAX94, ORTEPIII	

was solved by the heavy-atom method to reveal the position of vanadium. All other non-hydrogen atoms were located from subsequent 3D difference Fourier maps. Both structures were refined by full-matrix least-squares methods based on *F.* The fractional coordinates of hydrogen atoms with unambiguous positions in the structures were calculated according to the relevant carbon stereochemistry, and with C–H bond distances normalized to 0.95 Å. Isotropic temperature factors for H were calculated using $U_{iso}(H) = 1.2\ U_{eq}(C)$. The positions of two hydrogen atoms involved in N–H···O *intra-* and O–H···O *inter*-molecular hydrogen bonds in Compound **I** were located from a difference Fourier map calculated at the final stages of refinement. Both were found as small positive electron densitiy peaks (aprox. 0.7 e Å^{-3}) 0.814 Å from the N1 imino nitrogen and 0.797 Å from the O2 hydroxyl oxygen atom. Computer programs used: STADI4,[6] X-RED[7] (cell refinement, data collection procedure, Lp and ψ-scan absorption corrections performed for Compound **II**); NRCVAX94[8] (solving and refining the structures, and preparing the tables for publication); ORTEPIII[9] (molecular graphics).

RESULTS AND DISCUSSION

Thermal Analyses

The purity of the compounds was confirmed and the melting point enthalpies were established by the DSC measurements. Melting points were 154.4 °C (Compound **I**) and 363.9 °C (Compound **II**) and the corresponding melting enthalpies were 31.19 kJ mol^{-1} and 18.24 kJ mol^{-1}, respectively. The high melting point as well as the melting point enthalpy of Compound **I** is a consequence of the crystal structure, proved by the X-ray experiment, which shows the dimerization of molecules *via inter*molecular hydrogen bonds involving the potent proton donor hydroxyl group. On the other hand, the vanadium complex, though showing a relatively large melting point (due to its molar mass), exists in the crystal as discrete molecules. The content of vanadium in Compound **II** was determined by the thermogravimetric analysis as V_2O_5 (V_{calc} = 16.37%; V_{found} = 15.51%).

Infrared Spectroscopy

Most of the oxovanadium (IV) complexes exhibit an intense band near 1000 cm^{-1}, which has been assigned to the V=O stretching frequency. In contrast, in some oxovanadium complexes this stretch appears at wave numbers below 900 cm^{-1}. The shift to lower energy has been explained in terms of polymerization, which occurs by interaction of terminal oxygen with the vanadium atom from an adjacent molecule.[5] The V=O double bond stretching in Compound **II** is observed as a strong and sharp band at 989 cm^{-1}. No appearance of any other frequency indicating polymerization of the complex

TABLE II

Fractional atomic coordinates and equivalent isotropic thermal parameters $U_{\rm eq}$ / Å^2 for Compounds **I** and **II**

Atom	x	y	z	$U_{\rm eq}$
		Compound **I**		
O1	0.30968(9)	0.2939(3)	0.08585(5)	0.0589(6)
O2	0.07200(9)	0.4443(3)	–0.04947(5)	0.0522(6)
N1	0.16701(10)	0.5630(3)	0.05345(6)	0.0465(6)
C1	0.18861(11)	0.2273(4)	0.11610(6)	0.0389(6)
C2	0.27558(12)	0.1698(4)	0.11496(7)	0.0450(7)
C3	0.32400(13)	–0.0353(5)	0.14706(8)	0.0534(8)
C4	0.28902(14)	–0.1771(5)	0.17682(7)	0.0531(7)
C5	0.20165(13)	–0.1288(4)	0.17801(7)	0.0444(7)
C6	0.16636(16)	–0.2818(5)	0.20862(8)	0.0582(9)
C7	0.08371(18)	–0.2332(6)	0.21057(9)	0.0692(11)
C8	0.03410(15)	–0.0336(6)	0.18167(10)	0.0691(10)
C9	0.06614(13)	0.1180(5)	0.15105(8)	0.0539(8)
C10	0.15126(11)	0.0753(4)	0.14806(6)	0.0411(6)
C11	0.13873(12)	0.4245(4)	0.08407(6)	0.0411(6)
C12	0.11552(13)	0.7565(4)	0.01840(7)	0.0493(7)
C13	0.11494(13)	0.6896(4)	–0.03322(7)	0.0501(8)
		Compound **II**		
V	0.16335(4)	0.23883(7)	0.11424(4)	0.0401(2)
O1	0.2854(2)	0.1122(3)	0.1619(2)	0.0493(8)
O2	0.0624(2)	0.2590(3)	0.0118(2)	0.0466(7)
O3	0.0767(2)	0.1259(3)	0.1909(2)	0.0512(8)
O4	0.1764(2)	0.4198(3)	0.1601(2)	0.0552(8)
N1	0.2621(2)	0.2725(3)	–0.0056(2)	0.0399(8)
C1	0.4370(3)	0.1946(4)	0.0707(2)	0.0386(9)
C2	0.3920(3)	0.1176(4)	0.1508(2)	0.0414(9)
C3	0.4603(3)	0.0383(4)	0.2242(2)	0.0498(12)
C4	0.5704(3)	0.0437(4)	0.2190(2)	0.0511(12)
C5	0.6212(3)	0.1248(4)	0.1403(2)	0.0440(9)
C6	0.7362(3)	0.1297(5)	0.1365(3)	0.0530(12)
C7	0.7833(3)	0.2002(5)	0.0587(3)	0.0604(14)
C8	0.7191(3)	0.2726(5)	–0.0169(3)	0.0609(14)
C9	0.6073(3)	0.2728(4)	–0.0145(3)	0.0508(11)
C10	0.5543(2)	0.1999(4)	0.0642(2)	0.0391(9)
C11	0.3661(3)	0.2542(4)	–0.0089(2)	0.0404(9)
C12	0.1995(3)	0.3194(5)	–0.0966(2)	0.0512(11)
C13	0.0893(3)	0.3711(5)	–0.0646(2)	0.0490(10)
C14	0.0552(4)	–0.0457(6)	0.1829(3)	0.0756(16)

$U_{\rm eq}$ is defined as one-third of the trace of the orthogonalized U tensor.

via V=O···V has been observed. The monomeric nature of the complex has also been confirmed by the X-ray analysis. The coordination of the ligand through nitrogen in Compound **II** is clearly indicated by the ν(C=N) band at 1630 cm^{-1} by comparison with the ν(C=N) band at 1545 cm^{-1} in Compound **I**, suggesting that the Schiff base ligand in the solid state exists exclusively as ketoamino tautomer. A reverse situation is noticed for salicylaldimine Schiff bases since they are dominated by the enolimino tautomer in the crystalline state. The ν(Csp^2–O) (naphthaldiminato oxygen) band at 1642 cm^{-1} in Compound **I** is, as expected, shifted towards a lower frequency in the complex (1540 cm^{-1}), indicating the coordination of oxygen to the vanadium atom.[10–18] The metal complex spectrum bands at 593 cm^{-1}, 564 cm^{-1}, 502 cm^{-1} and 420 cm^{-1} can be assigned to the vanadium-to-oxygen bond stretching frequencies in the order: V–O3, V–O2, V–O1, and V–N1, respectively.[15] The band at 3159 cm^{-1} associated with the O–H bond frequency in the spectrum of the ligand did not appear in the spectrum of the complex suggesting (i) deprotonation of N-substituent hydroxyl group, and (ii) the nature of the Schiff base as tridentate ligand. Spectral data did not reveal the presence of methanol in the form of coordinated methoxy monoanion in **II**. The bond distance values between vanadium and O_4N donor set atoms revealed by the X-ray analysis corroborate the above mentioned spectroscopic structural assignments.

Structure Description

Table I summarizes the general and crystal data and intensity data collection and the refinement procedure for both Compounds **I** and **II**. Table II lists the free ligand and oxovanadium(V) complex final fractional atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms. A complete list of bond lengths and bond angles values is presented in Table III.

*Compound **I***

The conformation of the ligand molecule in the crystalline state is largely caused by the O–H···O *inter*molecular hydrogen bonding (Figure 1). Namely, two molecules link together forming dimers through hydrogen bond formation between the *N*-alkyl hydroxyl group substituent acting as proton donor and the oxygen of the aldehyde aryl core [O2···O1^i 2.7048(18) Å; (i): 0.5–*x*, 0.5–*y*, –*z*]. The latter oxygen atom is simultaneously included as proton acceptor in the formation of an N–H···O *intra*molecular hydrogen bond with the imino nitrogen atom [N1···O1 2.5685(21) Å].

By dimerization *via inter*molecular hydrogen bonding a 10-membered non-H atom ring (14-membered if hydrogens are included) is formed around

TABLE III

Interatomic bond distances / Å and valence bond angles / ° for Compounds **I** and **II**

Compound **I**		Compound **II**	
Bond distances / Å			
		V–O1	1.896(2)
		V–O2	1.826(2)
		V–O3	1.776(2)
		V–O4	1.583(2)
		V–N1	2.102(3)
O1–C2	1.286(2)	O1–C2	1.326(4)
O2–C13	1.410(3)	O2–C13	1.426(4)
		O3–C14	1.402(5)
N1–C11	1.301(2)	N1–C11	1.288(4)
N1–C12	1.451(3)	N1–C12	1.474(4)
C1–C2	1.436(3)	C1–C2	1.393(4)
C1–C10	1.451(3)	C1–C10	1.449(4)
C1–C11	1.412(3)	C1–C11	1.437(4)
C2–C3	1.432(3)	C2–C3	1.422(5)
C3–C4	1.354(3)	C3–C4	1.358(5)
C4–C5	1.434(3)	C4–C5	1.426(5)
C5–C6	1.404(3)	C5–C6	1.416(5)
C5–C10	1.413(3)	C5–C10	1.422(4)
C6–C7	1.367(4)	C6–C7	1.357(5)
C7–C8	1.378(4)	C7–C8	1.392(6)
C8–C9	1.370(3)	C8–C9	1.375(6)
C9–C10	1.412(3)	C9–C10	1.409(5)
C12–C13	1.509(3)	C12–C13	1.502(5)
O1···H1N1	1.887		
O1···H1O2$^{\mathrm{i}}$	1.886		
N1–H1N1	0.829		
Bond angles / °			
		O1–V–O2	143.4(1)
		O1–V–O3	90.8(1)
		O1–V–O4	107.0(1)
		O1–V–N1	81.77(9)
		O2–V–O3	95.3(1)
		O2–V–O4	105.8(1)
		O2–V–N1	77.9(1)
		O3–V–O4	106.6(1)
		O3–V–N1	155.5(1)
		O4–V–N1	98.0(1)
		V–O1–C2	135.3(2)
		V–O2–C13	116.2(2)
		V–O3–C14	124.7(2)
		V–N1–C11	128.7(2)
		V–N1–C12	113.0(2)

TABLE III (cont.)

C11–N1–C12	125.0(2)	C11–N1–C12	118.3(3)
C2–C1–C10	120.3(2)	C2–C1–C10	119.8(3)
C2–C1–C11	119.1(2)	C2–C1–C11	119.3(3)
C10–C1–C11	120.6(2)	C10–C1–C11	120.6(3)
O1–C2–C1	122.0(2)	O1–C2–C1	122.5(3)
O1–C2–C3	120.1(2)	O1–C2–C3	117.1(3)
C1–C2–C3	117.9(2)	C1–C2–C3	120.4(3)
C2–C3–C4	121.8(2)	C2–C3–C4	120.1(3)
C3–C4–C5	121.7(2)	C3–C4–C5	121.9(3)
C4–C5–C6	120.6(2)	C4–C5–C6	121.0(3)
C4–C5–C10	119.2(2)	C4–C5–C10	118.9(3)
C6–C5–C10	120.2(2)	C6–C5–C10	120.1(3)
C5–C6–C7	120.8(2)	C5–C6–C7	120.4(3)
C6–C7–C8	119.5(2)	C6–C7–C8	120.3(3)
C7–C8–C9	121.3(2)	C7–C8–C9	120.7(4)
C8–C9–C10	121.1(2)	C8–C9–C10	121.3(3)
C1–C10–C5	119.1(2)	C1–C10–C5	118.8(3)
C1–C10–C9	123.7(2)	C1–C10–C9	124.0(3)
C5–C10–C9	117.2(2)	C5–C10–C9	117.3(3)
N1–C11–C1	124.0(2)	N1–C11–C1	125.1(3)
N1–C12–C13	111.0(2)	N1–C12–C13	105.3(3)
O2–C13–C12	111.6(2)	O2–C13–C12	106.6(3)
O1$\cdots$H1O2^{i}–O2^{i}	166.6		
O1$\cdots$H1N1–N1	138.8		

Symmetry code (i): 0.5–*x*, 0.5–*y*, –*z*.

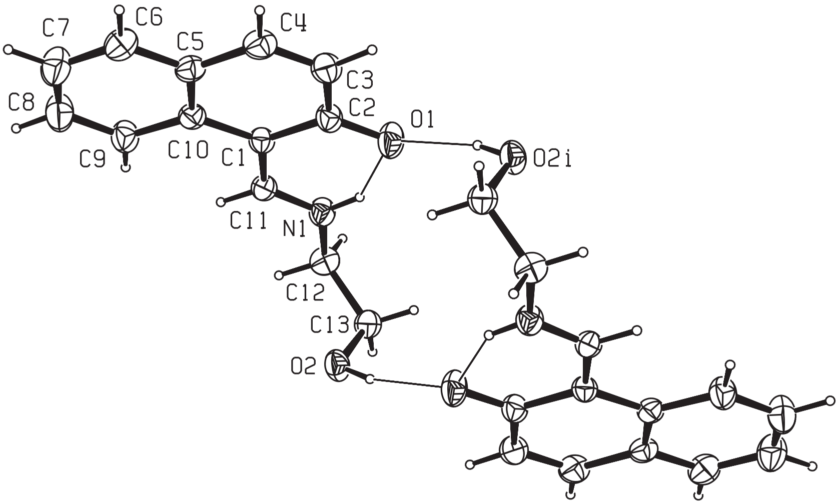


Figure 1. An ORTEPIII picture of Compound **I**. Non-hydrogen atom thermal ellipsoids are drawn at 30% probability level. Thin solid lines represent *intra*molecular N–H···O and *inter*molecular O–H···O hydrogen bonds, respectively.

the inversion centre at the 4(*c*) crystallographic position of the space group. At the same time, the *intra*molecular hydrogen bond forms a six membered »pseudo-chelate« ring indicating, particularly by the hydrogen atom position, the presence of the ketoamino tautomer only. The quinoid effect observed in the naphthaldimines derived from 2-hydroxy-1-naphthaldehyde {short C3–C4 [1.354(3) Å], long C2–C3 [1.432(3) Å] bond length, with oxygen in position 2 of the naphthalene ring with very short O1–C2 [1.2862(24) Å]} is the consequence of peculiar D_{2h} crystallographic symmetry of the fused ring.[19] Although the position of H in the *intra*molecular N–H···O hydrogen bond was clearly determined, the O1–C2 and N1–C11 [1.3012(24) Å] bond length values indicate considerable π-electron delocalization in the chelate ring. Namely, from the accepted standard values for single and double C–O bonds [1.362 (in phenols), and 1.222 Å (in benzoquinones), respectively] and C–N bonds in C–C=N–C fragments [1.353, and 1.279 Å, respectively], the bond orders for the corresponding bond lengths found in Compound **I** could be estimated to be between 1 and 2.[19] Bond distances in the peripheral aliphatic part are within the expected values with O2–C13 1.410(3) Å in agreement with the standard Osp^3–Csp^3 bond length value.[19] The dihedral angle between planes calculated through the naphthalene and non-hydrogen chelate ring atoms is 2.50(7)°, indicating overall planarity of the aromatic part of the molecule. Imino hydrogen H1N1 found from the difference Fourier map deviates by only 0.0508(15) Å from the chelate plane. The spatial orientation of *N*-substituent in relation to almost planar naphthaldimine moiety is defined by the C11–N1–C12–C13 torsion angle amounting to 55.2(2)°. The twisting around the N1–C12 single bond is for sure strongly determined by the participation of hydroxyl O2 atom in the formation of the *inter*molecular hydrogen bridge.

*Compound **II***

The complex (Figure 2) represents an example of a very rare mononuclear oxovanadium species with a VO^{3+} core. The central metal atom has a heavily distorted square pyramidal coordination having an oxygen atom (O4) from VO^{3+} moiety in the apical position. The four basal plane coordination sites are occupied by the Schiff base ligand $^{-}ONO^{-}$ donor set (doubly deprotonated Compound **I**) and monodentate CH_3O^- ligand from the methanol medium with methoxy O3 oxygen atom coordinated opposite to the imino nitrogen. The tridentate ligand coordinates vanadium with the ONO donor set forming a fused ring system of one five- and one six-membered ring, with the imino N1 common to both chelate rings. The V=O4 bond distance of 1.5832(24) Å is in the range 1.55–1.66 Å for the corresponding double bond lengths in vanadium complexes containing VO^{2+} and VO^{3+} species showing no significant vanadium oxidation state dependence.[2,15,20] The discrepancy between bond lengths V–O1 [1.8961(23) Å] and V–O2 [1.8256(23) Å] results from (1) the size of the chelate ring (six- *versus* five-membered ring), (2) of the rings electronic features (pseudo aromatic aldiminic six-membered and saturated 2-imino alkoxidic five-membered ring, respectively), and (3) the difference between the functional groups to which atoms O1 and O2 belong. All V–O bond lengths are significantly shorter than the V–N1 [2.102(3) Å] distance, indicating relatively low affinity of oxovanadium species for imino nitrogen.[16,21] The position of the methoxy O3 *trans* to the coordination polyhedron longest bond length (*trans* to N1) and not to the shortest V=O4 is believed to reflect the order of O→V donation and is valid if the oxygen function is monoanionic.[15] The V–O3 [1.7763(22) Å] bond distance is intermediate between the values for V–O1,O2 and V–O4, and this is due to the strong donor effect of monodentate alkoxidic CH_3O^- oxygen.[15]

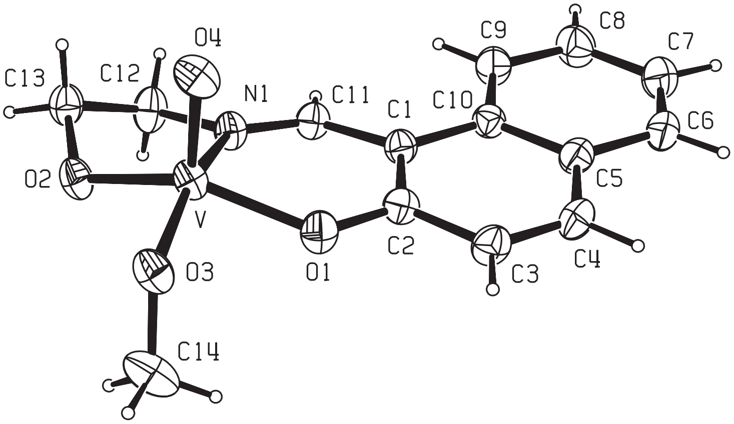


Figure 2. An ORTEPIII drawing of the vanadium complex molecule with thermal ellipsoids at 30% probability level.

The deformation of the coordination polyhedron is quantified by its valence angles ranging from 77.89(10)° [O2–V–N1] to 95.26(10)° [O2–V–O3]. Two of them are less than 90° [O2–V–N1, 77.89(10)° and O1–V–N1, 81.77(9)°] due to the rigidity of the chelate rings, *i.e.* the restrictions imposed by relativly inflexible 'bite' distances N1···O1 and N1···O2 [2.622(3) Å and 2.478(4) Å, respectively]. The bond angles involving oxygen donor atoms in the pyramid base plane, vanadium and terminal oxygen O4 atom are generally greater than 90° having values from 97.98(11)° [O4–V–N1] to 106.99(12)° [O1–V–O4]. This is in agreement with the short V=O4 double bond.[20–22] The O1–V–O2 [143.36(11)°] and O3–V–N1 [155.45(11)°] bond angles deviate significantly from linearity due to the displacement of the vanadium atom out of the base plane. The vanadium atom is displaced by 0.4793(14) Å out of the least-squares plane calculated through O1, O2, O3 and N1 towards the terminal oxygen atom O4.

Substitution of the N1-imino proton by vanadium leads to dramatic changes in the distribution of π-electron density, particularly in the area of both chelate rings. Slight lengthening of the N1$\cdots$O1 bite distance in the complex is observed [2.622(3) in contrast to 2.5685(21) Å in free ligand].[16] The bond distances involving O1, O2 and N1 with other light ligand atoms are remarkably different in Compounds **I** and **II**. The longer O1–C2 [1.326(4) Å, (**II**); 1.2862(24) Å, (**I**)] and shorter N1–C11 [1.288(4) Å, (**II**); 1.3012(24) Å, (**I**)] bond lengths are present in the chelate complex while the dimensions of the corresponding ones in Compound **I** are determined by the dominant keto resonance form of the ligand itself.[16] The above mentioned changes in the bond length values generate a corresponding shortening of C1–C2 and lengthening of C1–C11 bond distances in Compound **II** (*cf*. Table III). According to the previously mentioned electron redistribution, both hetero-to-carbon atom bond lengths in the five membered chelate ring are elongated upon coordination.

The conformational change within the tridentate ligand occurs upon the introduction of the metal centre due to the electronic (bond order changing, new bond formation, and $V^{IV} \rightarrow V^{V}$ oxidation) and steric reasons (change in the chelate rings geometry as a consequence of the size difference between H and V). According to the crystallographic 3σ criterion for equality of geometric parameters, there is no difference in dihedral angle between naphthalene and O1, N1, C1, C2, C11 chelate atoms plane in Compound **I** [2.50(7)°] and Compound **II** [2.29(9)°], respectively, with V atom deviation from the chelate plane by 0.523(4) Å. The conformation of the five-membered chelate ring is in the form of an open envelope according to the C13 atom shifting out [0.659(5) Å] of the calculated best plane defined by V, N1, C12 and O2 atoms.

According to the Cambridge Structural Database (version April, 1998),[19] only seven vanadium structures have been described so far which contain a tridentate Schiff base ligand with ONO donor set forming a system of fused five- and six-membered chelate rings with N common to both rings.[12,15,16,23–25] One of them is mononuclear with pentacoordinated vanadium(V).[23] The others are either polynuclear with vanadium atoms that can have mixed valence IV and V, or hexacoordinated. The structure of a dimer of the general formula $(LV^{V}O)_2O$ (L = doubly deprotonated Compound **I**) built up of two Compound **II** molecules, having replaced two methoxides with a bridging oxygen, is determined.[25] The most interesting part of the dimer is $[O_3NV–O–VO_4N]$ central moiety. One vanadium is coordinated in the form of a tetragonally distorted square pyramid. The other vanadium atom enlarges its sphere to a severely distorted octahedral by coordination of one square pyramid oxygen atom at a very long bond distance of 2.459 Å. This oxygen approaches the metal atom *trans* to V=O double bond and interchanges the lengthening of the remaining two V–O bond distances in the pyramid basal plane. The position of the bridging oxygen atom is crucial because it is placed *trans* to the imino nitrogen atoms regardless of the vanadium coordination sphere. There are some discrepancies in bond angle values but no difference in the bond lengths, except for those V–O interchanged and the very long one, in monomer and dimer molecules.[25]

Compound **II** exists as discrete molecules in the solid state. The crystal structure is dominated by the electrostatic interactions of van der Waals type not shorter than 3.5 Å.

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Supplementary Materials. – Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK and can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 103124 (Compound **I**) and 103125 (Compound **II**), respectively.

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SAŽETAK

Vodikovom vezom dimeriziran *N*-(2-hidroksietil)-2-oksi-1-naftaldimin i njegov oksovanadijev(V) kompleks

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Schiffova baza *N*-(2-hidroksietil)-2-oksi-1-naftaldimin potencijalni je tridentatni ligand nastao kondenzacijom 2-hidroksi-1-naftaldehida i 2-aminoetanola uz trietilamin kao katalizator. Koordinacijski spoj vanadija(V) s tim ligandom dobiven je, nakon oksidacije VO^{2+} u VO^{3+} kisikom iz zraka, u templatnoj reakciji iz metanolne otopine. Fizikalno-kemijska svojstva spojeva ispitivana su termogravimetrijskom analizom, diferencijalnom pretražnom kalorimetrijom i FT IR spektroskopijom. Osnovni zaključci o građi obadva spoja, izvedeni na temelju rezultata ovih istraživanja, potvrđeni su određivanjem kristalne i molekulske strukture difrakcijom rentgenskih zraka. Ligand stvara molekulski kompleks dimerizacijom putem međumolekulskog O–H···O vodikova vezivanja. U kompleksu metala četiri koordinacijska mjesta osnovice kvadratne piramide zauzeta su donornim atomima ONO tridentatnog liganda i metoksidnim kisikom. Sve vezne udaljenosti V–O znatno se razlikuju u duljini ovisno o prirodi funkcionalne skupine kojoj kisikov atom pripada. Kompleks vanadija primjer je izuzetno rijetkog pentakoordiniranog kvadratno-piramidnog spoja peterovalentnog vanadija.