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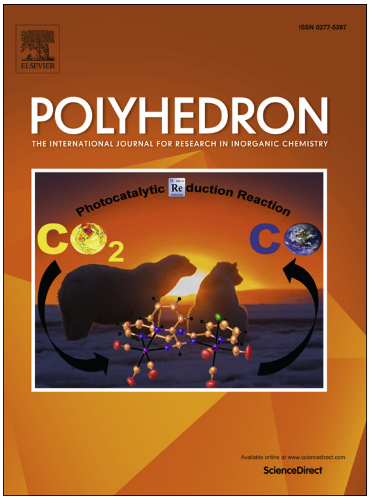

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Oxidative coupling of 2-naphthol catalyzed by a new methoxido bridged dinuclear oxidovanadium(V) complex

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Abstract

A new dinuclear oxidovanadium(V) complex, $[(VO)_2(\mu\text{-L-}\kappa^4 O,N,N,O)(\mu\text{-}OCH_3)_2(OMe)_2]\cdot CH_3OH$ (**1**), is synthesized by the reaction of V_2O_5 with 1,1'-((1*E*,1'*E*)-hydrazine-1,2-diylidenebis(methanylylidene))bis(naphthalen-2-ol) (**H_2L**) in methanol. **H_2L** is synthesized by two different methods: i) from the reaction of hydrazine hydrate with 2-hydroxy-1-naphthaldehyde ii) from the reaction of hydrazine hydrate with 2-naphthol in the presence of formaldehyde (Mannich condensation). The ligand and its vanadium complex are characterized by elemental analysis, spectroscopic methods (FT-IR, NMR and UV-Vis) and their structures are determined by single crystal X-ray analysis. X-ray studies show that **1** is a neutral dinuclear complex of oxidovanadium(V) in which two vanadium(V) ions are connected by two methoxido bridging groups. The Schiff base ligand is coordinated to both vanadium centers by two NO-donor sets. Complex **1** is employed as initiator for oxidative coupling of 2-naphthol to produce BINOL. The effect of temperature, reaction atmosphere and solvent in catalytic reaction is studied. According to the obtained results, a mechanism is proposed for catalytic oxidative coupling reaction in the presence of complex **1**.

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Keywords: Dinuclear oxidovanadium(V), Schiff base ligand, Oxidative coupling, BINOL synthesis, Catalytic coupling

Introduction

The C-C coupling reactions are one of the most important reactions in organic chemistry [1]. Therefore, developing catalytic coupling reactions which generate new C-C bonds have continued to attract the attention of many researchers during last several decades [2]. 1,1'-bi-2-naphthol (BINOL) and its derivatives are a class of important bis(phenol) compounds because they are used as ligands for synthesis of several transition metal complexes [3]. BINOL complexes are used as efficient catalysts for a wide range of organic functional transformations [4]. The oxidative coupling of 2-naphthols is a useful method for synthesis of BINOL derivatives. In this context, many reagents and a variety of methods have been reported for 2-naphthols coupling. Catalytic oxidation coupling of 2-naphthols using transition metal complexes such as Cu [5], Fe [6], Ru [7], V [8,4b], etc. is one of the most important reported methods for this reaction. Many transition metal complexes catalytically couple 2-naphthol derivatives to BINOLs, vanadium compounds are particularly useful for this process [9]. Vanadium-mediated couplings occur via a favorable one-electron phenolic oxidation in mild reaction conditions with the further advantage that only water is formed as side product [10]. Although several catalytic systems have been reported for preparing BINOLs from 2-naphthols, development of new catalysts and methods are gaining much attention [11].

Vanadium plays a vital role in biological systems since the active sites of some enzymes such as haloperoxidases consist of vanadate moieties [12]. Vanadium participates in many important catalytic redox processes. The utility of vanadium complexes in oxidation reactions like epoxidation of olefins [13], oxidation of sulfides [14] and oxidation of alcohols [15] is well documented. Nevertheless, the reports on oxidative coupling reactions catalyzed by mononuclear [16] and dinuclear vanadium complexes [17] are relatively low (in comparison with mentioned oxidation reactions). According to the reported studies in the literature, the dinuclear vanadium complexes have higher reactivity in comparison with mononuclear ones [18,11b]. This is mainly attributed to the mechanism of 2-naphthol coupling in which the α-positions of two 2-naphtholic groups approach to each other by coordinating to the two adjacent vanadium cores [19].

By taking the advantage of vanadium complexes toward oxidation reactions, we tried to prepare a dinuclear vanadium complex in the aerobic oxidative coupling of 2-naphthol. We focused on prepare a new vanadyl complex containing two vanadium ions connected by rigid bridging groups together with monodentate ligands susceptible to replacing by 2-naphtholate anion. In the present work, we report the synthesis, characterization, crystal structure and catalytic reactivity of a new methoxido bridged dinuclear oxidovanadium(V) complex bearing a tetradentate Schiff base ONNO-type ligand.

2. Experimental

2.1. Materials and instrumentations

Vanadium(V) oxide, V_2O_5, hydrazine hydrate, 2-hydroxy-1-naphthaldehyde, 2-naphthol and formaldehyde were purchased from Merck and used as received. Solvents of the highest grade commercially available (Merck) were used without further purification. ^1H and ^{13}C NMR spectra of the ligand and complex **1** in $CDCl_3$ solution were measured on a Bruker 250 and 62.9 MHz spectrometer, respectively.

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FT-IR spectra were recorded as KBr disks with a Bruker FT–IR spectrophotometer. The vanadium content of the complex was measured by atomic absorption analysis using Varian Spectra AA-220 equipment.

Scheme 1.

2.2. Synthesis of 1,1'-((1E,1'E)-hydrazine-1,2-diylidenebis(methanylylidene))bis(naphthalen-2-ol) (**H_2L**)

Method A) A methanol solution (10 mL) of hydrazine hydrate (0.22 mL, 4.5 mmol) was added to a methanolic solution of 2-hydroxy-1-naphthaldehyde (1.81 g, 9 mmol). The solution was refluxed for 3 h at the 70 ˚C. The obtained yellow solid was separated, filtered and washed with cold methanol and finally recrystallized from ethanol. Yield 91%. *Method B*) Methanolic solution of formaldehyde (37%) (0.8 mL, 10 mmol) was added to methanolic solution of 2-naphthol (1.44 g. 10 mmol) and the rapidly stirred solution was cooled to 0 °C. The mixture was stirred for 10 min, then hydrazine hydrate (0.24 mL, 5 mmol) was added and the mixture was refluxed for 12 h. The resultant solution was evaporated on a steam bath to 5 mL and cooled to room temperature. The resulting precipitate was separated and filtered off, washed with 20 mL of cooled methanol and re-crystallized from ethanol. Yield 85%. M.p. 316-318 ˚C. *Anal.* Calc. for $C_{22}H_{16}N_2O_2$ (MW = 340.37): C, 77.63; H, 4.74; N, 8.23. Found: C, 77.71; H, 4.70; N, 8.29%. FT-IR (KBr, cm^{-1}): 3454 (w, br), 3057 (w), 2920 (w), 1621 (vs), 1604 (s), 1580 (s), 1508 (w), 1467 (s), 1417 (m), 1385 (w), 1321 (s), 1282 (m), 1242 (m), 1214 (w), 1185 (m), 1167 (m), 1142 (w), 1084 (w), 1030 (w), 962 (w), 965 (w), 871 (m), 833 (s), 797 (m), 787 (s), 754 (s), 721 (w), 680 (w), 658 (w), 527 (w), 509 (w), 440(w). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C, TMS): 10.14 (s, 1H, phenolic OH); 8.18 (s, 2H, C*H*=N); 7.75-7.57 ppm (m, 12H, aromatic). ^{13}C NMR (62.90 MHz, $CDCl_3$): = 162.09 (C-OH), 151.7 (C=N), 134.2, 128.9, 128.5, 127.9, 125.9, 124.2,

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122.6, 119.8, 118.5 ppm. UV-Vis (in CH_3OH, c = 2.5×10^{-5} M, $_{max}$ [nm] with [M^{-1} cm^{-1}]): 226 (48400), 279 (4760), 333 (3500).

2.3. Synthesis of the complex $[(VO)_2(\mu\text{-}L\text{-}\kappa^4 O,N,N,O)(\mu\text{-}OCH_3)_2(OMe)_2]\cdot CH_3OH$ *(**1**)*

The ligand H_2L (0.344 g, 1 mmol) and V_2O_5 (0.182 g, 1 mmol) were placed in the main arm of branched tube. Methanol was carefully added to fill the arms the tube was sealed and the reagents containing arm immersed in an oil bath at 60 ˚C while the other arm was kept at ambient temperature. After a week, black crystals were appeared in the cooler arm, which were separated and washed by methanol. Yield 69%. *Anal.* Calc. for $C_{27}H_{30}N_2O_9V_2$ (MW = 628.41): C, 51.60; H, 4.81; N, 4.46; V, 16.21. Found: C, 51.48; H, 4.74; N, 4.43; V, 16.34%. FT-IR (KBr, cm^{-1}): 3440 (m, br), 2923 (w), 2848 (w), 1618 (s), 1598 (vs),1545 (s), 1455 (w), 1408 (w), 1384 (m), 1335 (m), 1288 (w), 1247 (w), 1225 (w), 1198 (w), 1180 (w), 1167 (w), 1043 (w), 1010 (w), 1043 (m), 955 (m), 951 (w), 927 (m), 903 (m), 874 (w), 824 (w), 749 (m), 713 (w), 633 (w), 596 (w), 561 (w), 510 (w), 484 (w), 462 (w). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C, TMS): 9.28 (s, 2H, CH=N); 8.58-7.09 (m, 12H, aromatic); 5.29 (s, 1H, $OH_{methanol}$), 3.14 (m, 9H, OCH_3), 3.24 (s, 6H, OCH_3) ppm. UV-Vis (in CH_3OH, c = 2.5×10^{-5} M, $_{max}$ [nm] with [M^{-1} cm^{-1}]): 220 (70800), 327 (19700), 428 nm (7440).

*2.4. Representative procedure for oxidative coupling of 2-naphthol catalyzed by complex **1***

Liquid phase catalytic coupling of 2-naphthol was carried out in a 25 mL round bottom flask equipped with a magnetic stirrer. In a typical experiment, catalyst (63 mg, 0.01 mmol) was added to a flask containing the anhydrous solvent (5 mL). The solution was stirred for 10 minutes under desired atmosphere and then treated with a solution of 2-naphthol (2-naphthol was dissolved in the same solvent used in the

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reaction). Temperature was kept stable during the reaction and controlled by a thermometer and the course of the reaction was monitored by TLC (24 hours). After checking by TLC, the reaction mixture was concentrated under reduced pressure and the product was isolated by column chromatography (ethyl acetate: petroleum ether = 1 : 3) to give the coupling product, BINOL. M.p. 205-207 °C. *Anal.* Calc. for $C_{20}H_{14}O_2$ (MW = 286.33): C, 83.90; H, 4.39%. Found: C, 83.88; H, 4.36%. FT-IR (KBr, cm^{-1}): 34.85 (m), 34.03 (m), 3051 (w), 2923 (w), 2851 (w), 1617 (s), 1590 (s), 1508 (m), 1470 (m), 1461 (m), 1435 (w), 1404 (w), 1382 (vs), 1347 (w), 1322 (m), 1273 (m), 1252 (m), 1217 (s), 1175 (s), 1146 (s), 1125 (m), 1023 (w), 979 (w), 960 (w), 930 (w), 864 (w), 826 (vs), 784 (w), 774 (w), 751 (vs), 723 (w), 675 (w), 665 (w), 624 (w), 585 (w), 573 (m), 533 (w), 489 (w). ^{1}H NMR (250.13 MHz, $CDCl_3$, 25 °C, TMS): = 7.97 (d, *J*=9.0 Hz, 2H), 7.53 (d, *J*=7.75 Hz, 2H), 7.40-7.25 (m, 6H), 7.15 (d, *J*=8 Hz, 2H), 5.03 ppm (s, 2H, OH). ^{13}C NMR (62.90 MHz, $CDCl_3$): = 152.73 (C-OH), 133.4, 131.4, 129.44, 128.4, 127.5, 124.2, 124.0, 117.7, 110.8 ppm. UV-Vis (in CH_3OH, c = 2.5×10^{-5} M, $_{max}$ [nm] with [M^{-1} cm^{-1}]): 228 (51300), 278 (4440), 335 (3400).

2.4. X-ray crystallography

A summary of the crystal data and refinement details for complex **1** is given in Table 1. Single crystal data collection for **1** were performed on Xcalibure PX diffractometer with Onyx CCD detector, equipped with an Oxford Cryosystems open-flow nitrogen cryostat, using ω-scan and a graphite-monochromated Mo Kα (λ= 0.71073 Å) radiation at 100 K. The structure was solved by direct methods with SHELXS-97 [20], and refined with full-matrix least-squares techniques on F^2 with SHELXL-97 [21]. The C-bonded hydrogen atoms were calculated in idealized geometry riding on their parent atoms. The molecular structure plot was prepared

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using Diamond [22]. The X-ray data of pure ligand gave same results as earlier reported [23].

Table 1.

3. Results and discussion

3.1. Syntheses and spectroscopy

The reaction of hydrazine hydrate with 2-hydroxy-1-naphtaldehyde gave the desired ligand in high yield and purity. The reaction of 2-naphthol with hydrazine hydrate in the presence of formaldehyde in methanol also produced the same compound (Scheme 1). Spectroscopic data, elemental analysis and single crystal X-ray studies [23] confirmed the formation of the same ligand in both methods. In the ^{1}H-NMR spectrum of H_2L, the presence of a broad singlet signal at δ 10.14 ppm was assigned to the naphtholic O-H groups. The singlet peak at δ 8.18 ppm is assigned to the hydrogen atom of azomethine (-CH=N-) group and confirms that the Schiff base ligand is formed. The FT-IR spectrum of the H_2L shows an absorption band at 1621 cm^{-1} which can be assigned to the imine C=N stretching frequency [24].

Complex $[V_2O_2(L)(\mu\text{-}OCH_3)_2(OCH_3)_2]{\cdot}CH_3OH$ (**1**) was synthesized by the reaction of H_2L and V_2O_5 with molar ratio 1 : 1 in methanol. Slow change in the color of the reaction mixture from yellowish-brown to dark brown was the first evidence for the complexation of ligand to the vanadium core. Single crystals of complex **1** were obtained by thermal gradient method during one week. Comparison of the FT-IR spectrum of complex **1** with the FT-IR spectrum of free ligand shows evidences for the coordination of Schiff base ligand to the vanadium ion. The infrared spectrum of **1** displays a band at 1618 cm^{-1} which can be assigned to the C=N stretching frequency of the coordinated Schiff base ligand and is red shifted with respect to the free ligand

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(1621 cm^{-1}) [24]. Furthermore, in the FT-IR spectrum of complex **1** the band observed at 955 cm^{-1} is assigned to the V=O stretching vibration [13a,14,15d]. Very broad band around 3440 cm^{-1} expresses the presence of methanolic –OH group which involved in hydrogen bonding interaction [25].

3.2. Description of structure

The molecular structure of complex **1** is shown in Fig. 1 and selected bond distances and angles are summarized in Table 2. Single crystal X-ray analysis indicates that **1** is a neutral dinuclear complex of oxidovanadium(V) with a methanol molecule of solvation. Two vanadium atoms are doubly bridged by two methoxido bridging groups. The Schiff base ligand acts as a tetradentate dianionic compartmental donor, with two NO-donor cavities. Both vanadium centers have similar coordination environments, VNO_5, and the coordination geometry around them can be described as distorted octahedral. One oxygen atom and one nitrogen atom of the Schiff base ligand occupy two coordination sites of each vanadium core and the remaining four sites are occupied by the two oxygen atoms provided by two methoxido bridging groups, the oxygen atom of terminal methoxido ligand and the oxygen atom of oxido group. The azomethine nitrogen atom, naphtholate oxygen and the oxygen atom of methoxido ligand together with oxygen atom of bridging methoxido group form the equatorial plan. The $V–O_{methoxido}$ bonds *trans* to the oxido ligands are longer than $V–O_{methoxido}$ bonds in *cis* position, which can be attributed to the *trans* influence of V=O. The V atoms are displaced by 0.275(2) Å (V1) and 0.307(2) Å (V2) from the plane defined by the equatorial donor atoms towards the V=O. The V1···V2 distance is 3.264(1) Å and is close to the ethoxido bridged dinuclear vanadium complexes [26]. The dihedral angle between the V1,O1M,O2M and V2,O1M,O2M planes is 20.4(1)°.

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The V1−O1M−V2 and V1−O2M−V2 angles are 105.9(2)°. The crystal packing of complex **1** is stabilized by several C−H···O and C−H···π interactions. Furthermore, an uncoordinated methanol molecule is connected to complex molecule by O−H···O and C−H···O hydrogen bonding interactions (Fig. 2).

Fig. 1.

Fig. 2.

Table 2.

*3.3. Oxidative coupling of 2-naphthol catalyzed by complex **1***

Considering the catalytic reactivity of oxidovanadium complexes in preparing BINOLs, we were interested to employee complex **1** as catalyst in the oxidative coupling of 2-naphthol. For this purpose, 2-naphthol was added to the reaction flask containing complex **1** in a solvent and the reaction progress was monitored by TLC. The reaction did not take place in the absence of molecular oxygen or catalyst. In the presence of oxygen and complex **1**, the oxidative coupling of 2-naphthol took place and BINOL was obtained as sole product. Several parameters effects on the reaction speed. Reaction atmosphere (O_2, N_2 and air), temperature and solvent are the important parameters in this reaction because they can effect on this catalytic reaction. Firstly, the effect of solvent was studied in the coupling reaction. CCl_4, CH_2Cl_2, $CHCl_3$, CH_3CN, toluene, THF, DMSO and CH_3OH were examined as solvent at room temperature. These reactions were done at aerial atmosphere. Among the used solvents, CCl_4 was found to be the most suitable solvent since in this solvent the reaction was completed in a shorter time. It was observed that the catalytic activity of the catalyst decreased with respect to CCl_4 (donor number [27] DN = 0) > dichloromethane (DN = 0) > chloroform (DN = 0) > acetonitrile (DN = 14.1) > toluene (DN = 0) > THF (DN = 20) > CH_3OH (DN = 19) ≈ DMSO (DN = 29.8).

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Overall, solvents with high donor ability decrease the reactivity of the catalyst, and the lowest conversion in DMSO or CH_3OH is due to the highest coordinating ability of these solvents. Having higher conversion in aprotic solvents is in agreement with the previous reports for vanadium catalyzed oxidative coupling reaction of 2-naphthols [4b,8a,18b].

2-Naphthol oxidative coupling is quite sensitive towards the reaction atmosphere. Therefore, the reaction was studied at nitrogen, oxygen and aerial atmospheres. The results are shown in Table 3. In oxygen atmosphere, the reaction was completed faster than in aerial atmosphere and the product was not observed in the nitrogen atmosphere. These results show that the presence of molecular oxygen as an oxidant is essential parameter in the oxidation coupling of 2-naphthol. The coupling reaction was studied at 0 °C, room temperature and 40 °C. Increase the reaction temperature from 0 to 40 °C causes increase the catalytic activity of complex **1** since the reaction is completed in a shorter time.

Table 3.

3.4. Mechanism

Till now, several studies have been done and reported to understand the possible mechanism pathways of the vanadium catalyzed oxidative couplings of 2-naphthols. It was observed that the dinuclear vanadium complexes generate an intermediate with two naphthoxy groups connected to the two adjacent vanadium centers [10b,18a]. Several experimental studies have been reported that this intermediate probably is the most important and capable intermediate in the oxidation coupling of 2-naphthol by oxidovanadium complexes. The coupling occurs by intramolecular manner when the conformations of 2-naphtholates change and their alpha carbons locate near to each other. This suggestion is also supported by the fact that the

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mononuclear vanadium complexes are much less catalytically active than the dinuclear ones [28].

Although the mechanism of this reaction was not studied here, on the basis of the reported mechanisms for oxidative coupling of 2-naphthols catalyzed by dinuclear vanadium complexes, it is predicted that the key step in this process is the replacing of two monodentate terminal methoxido ligands by 2-naphthoxy groups. The proposed catalytic pathway is shown in Scheme 2. Dinuclear vanadium(V) complex reacts with two molecules of 2-naphthol and compound X1 is formed by replacing two methoxido ligands. Two methanol molecules forms in this step. Consequently, the oxidation state of vanadium core doesn't change by replacing two methoxido groups with two naphtholate groups. In the next step, the alpha positions of the 2-naphthol molecules approach each other yielding X2, which is then intramolecularly coupled by a manner similar to the reported mechanism by Gong *et. al.* [29,4b,17,18a]. In the next step, one water molecule is formed by oxidation reaction and the BINOL product is generated (X3). The oxidation by molecular oxygen is supported by the fact that the reaction is faster in the oxygen atmosphere. The obtained BINOL molecule releases by coordinating of two next 2-naphthol molecules to the catalytically active species and this cycle occurs several times.

4. Conclusion

In summary, a new methoxido bridged dinuclear complex of oxidovanadium(V) was synthesized and characterized by spectroscopic methods and single crystal X-ray analyses. The catalytic ability of this complex was investigated in the oxidation coupling of 2-naphthol. The effects of temperature, solvent and reaction atmosphere

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(O_2, N_2, air) have been studied. The results showed that complex **1** promotes the preparation of BINOL from 2-naphthol in the presence of O2

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Appendix A. Supplementary data

CCDC 1448933 contains the supplementary crystallographic data for complex **1**. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2016.???.???.

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Tables/Schemes/Figures caption

Table 1. Crystallographic data of **1**

Table 2. Selected geometrical parameters (Å, °) for complex **1**

Table 3. Comparison the catalytic activities of complex **1** in the oxidative coupling of 2-naphthol in different conditions

Scheme 1. The synthesis of H_2L

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Scheme 2. Proposed mechanism for the oxidative coupling of 2-naphthol catalyzed by complex **1**

Fig. 1. Molecular structure of complex $[V_2O_2(L)(\mu\text{-}OCH_3)_2(OCH_3)_2]\cdot CH_3OH$ (**1**)

Fig. 2. O–H•••O and C–H•••O hydrogen bonding interactions in the crystal of complex **1**

Table 1. Crystallographic data of **1**

	Complex **1**
net formula	$C_{26}H_{26}N_2O_8V_2\cdot CH_4O$
M_r/g mol^{-1}	628.41
crystal size/mm	0.16 × 0.11 × 0.04
T/K	100
Radiation	MoK
Diffractometer	Xcalibur PX
crystal system	Orthorhombic
Crystal shape, color	Plate, brown
space group	$Pca2_1$
a/Å	12.892(4)
b/Å	12.717(4)
c/Å	16.350(6)
V/Å^3	2680.5(15)
Z	4
calc. density/g cm^{-3}	1.557
μ/mm^{-1}	0.76
F(000)	1296
range	2.6–29.6
h,k,l	−17•8,−17•17, −10•21
R_{int}	0.088
$R(F_{obs})$	0.055
$R_w(F^2)$	0.119
S	1.02
Absorption correction	Analytical
measured reflections	9857
independent reflections	4769
reflections with $I > 2\sigma(I)$	2369
Parameters	350
Restraints	1
Max electron density/e Å^{-3}	0.86
Min electron density/e Å^{-3}	−0.71

Table 2. Selected geometrical parameters (Å, °) for complex **1**

Bond	**Angle/deg**	**Bond**	**Distance/Å**

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O3M—V1—O2M	91.0(3)	V1—O3	1.578(6)
O1M—V1—O2M	72.3(2)	V1—O3M	1.796(6)
O1—V1—O2M	89.1(2)	V1—O1M	1.884(5)
O3—V1—N1	95.6(3)	V1—O1	1.908(5)
O3M—V1—N1	163.1(3)	V1—O2M	2.171(5)
O1M—V1—N1	82.2(2)	V1—N1	2.194(7)
O1—V1—N1	80.2(2)	V2—O4	1.589(5)
O2M—V1—N1	73.2(2)	V2—O4M	1.788(6)
O4—V2—O4M	102.5(3)	V2—O2	1.900(6)
O4—V2—O2	99.4(3)	V2—O2M	1.916(5)
O4M—V2—O2	95.1(3)	V2—O1M	2.198(6)
O4—V2—O2M	98.2(2)	V2—N2	2.218(8)
O4M—V2—O2M	97.4(3)		
O2—V2—O2M	155.7(3)	**Bond**	**Angle/deg**
O4—V2—O1M	164.8(2)	V1—O1M—V2	105.9(2)
O4M—V2—O1M	89.8(3)	V1—O2M—V2	105.9(2)
O2—V2—O1M	88.2(2)	O3—V1—O3M	100.9(3)
O2M—V2—O1M	71.0(2)	O3—V1—O1M	97.5(2)
O4—V2—N2	95.6(3)	O3M—V1—O1M	99.3(3)
O4M—V2—N2	161.7(3)	O3—V1—O1	98.2(3)
O2—V2—N2	79.5(2)	O3M—V1—O1	93.6(3)
O2M—V2—N2	82.2(2)	O1M—V1—O1	157.4(2)
O1M—V2—N2	72.7(2)	O3—V1—O2M	165.5(2)

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Table 3. Comparison the catalytic activities of complex **1** in the oxidative coupling of 2-naphthol in different conditions

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Entry	Solvent	Atmosphere	T/˚C	Yield (%)[a]					
				1day	**2day**	**3day**	**4day**	**5day**	**6day**
1	CCl_4	N_2	RT	0	0	0	0	0	0
2	CH_2Cl_2	Air	RT	-	23	-	45	-	73
3	$CHCl_3$	Air	RT	-	16	-	33	-	64
4	Toluene	Air	RT	0	-	-	18	-	32
5	THF	Air	RT	0	0	-	10	-	15
6	CH_3OH	Air	RT	0	0	0	0	0	0
7	DMSO	Air	RT	0	0	0	0	0	0
8	CCl_4	Air	0	0	-	15	-	31	48
9	CCl_4	Air	RT	-	-	42	-	78	98
10	CCl_4	Air	40	-	80	98<[b]			
11	CCl_4	O_2	40	70	98<[b]				
12	CH_3CN	O_2	0	0	-	-	13	-	36
13	CH_3CN	Air	RT	0	-	-	18	-	54
14	CH_3CN	Air	40	-	30	-	60	-	98<[b]

[a] Isolated yield except *b* cases

[b] TLC showed no signs of 2-naphthol.

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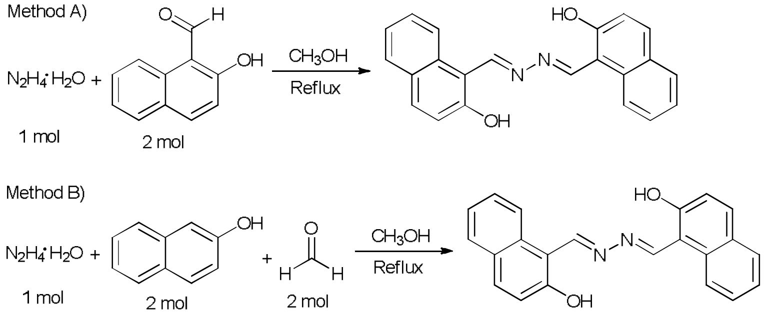

Scheme 1. The synthesis of H_2L

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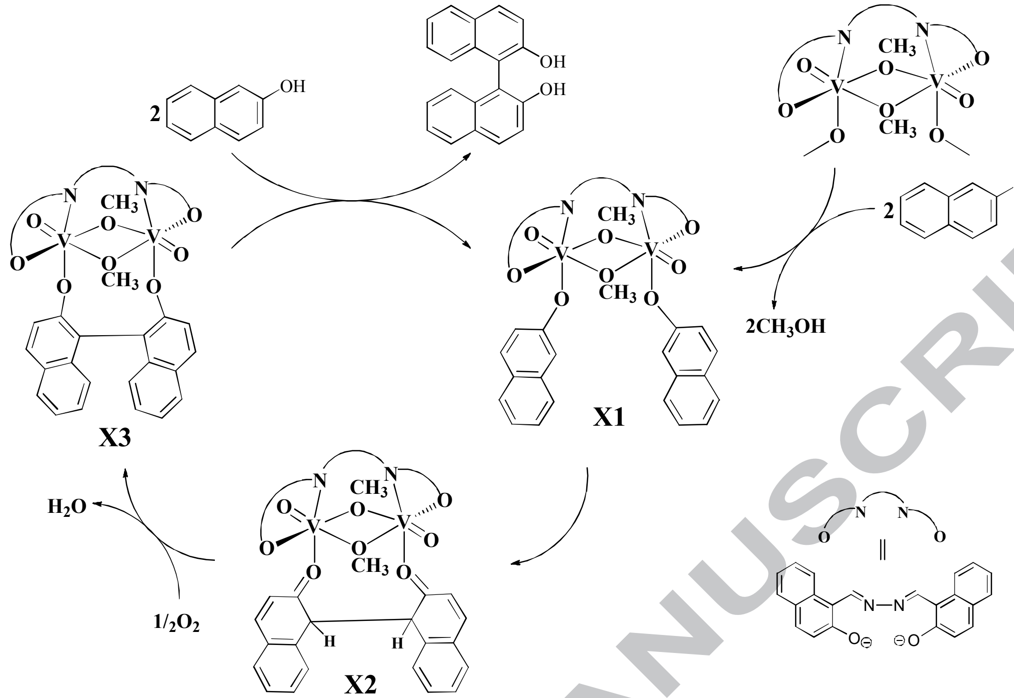

Scheme 2. Proposed mechanism for the oxidative coupling of 2-naphthol catalyzed by complex **1**

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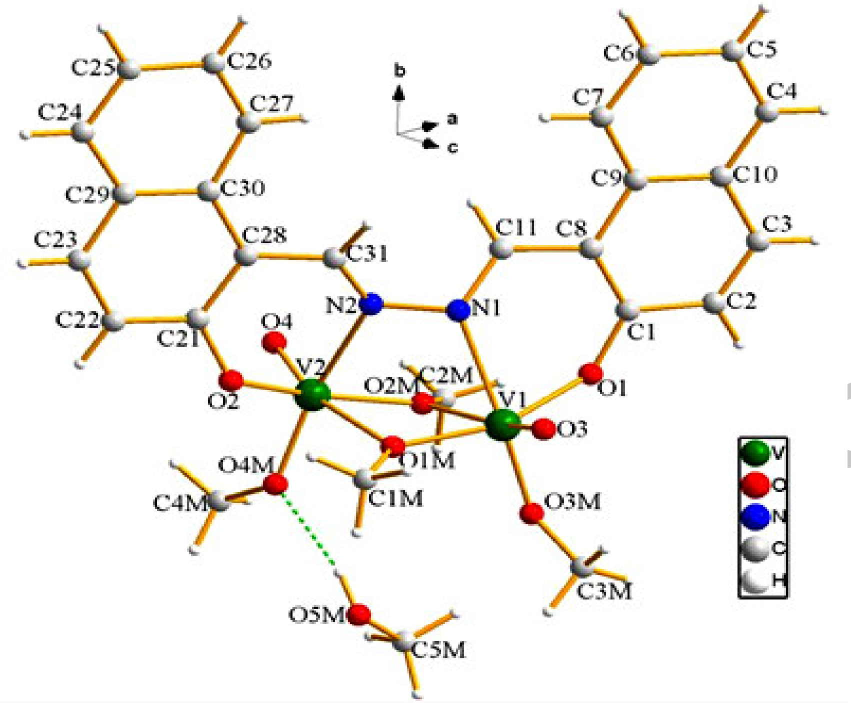

Fig. 1. Molecular structure of complex $[V_2O_2(L)(\mu\text{-}OCH_3)_2(OCH_3)_2]\cdot CH_3OH$ (**1**)

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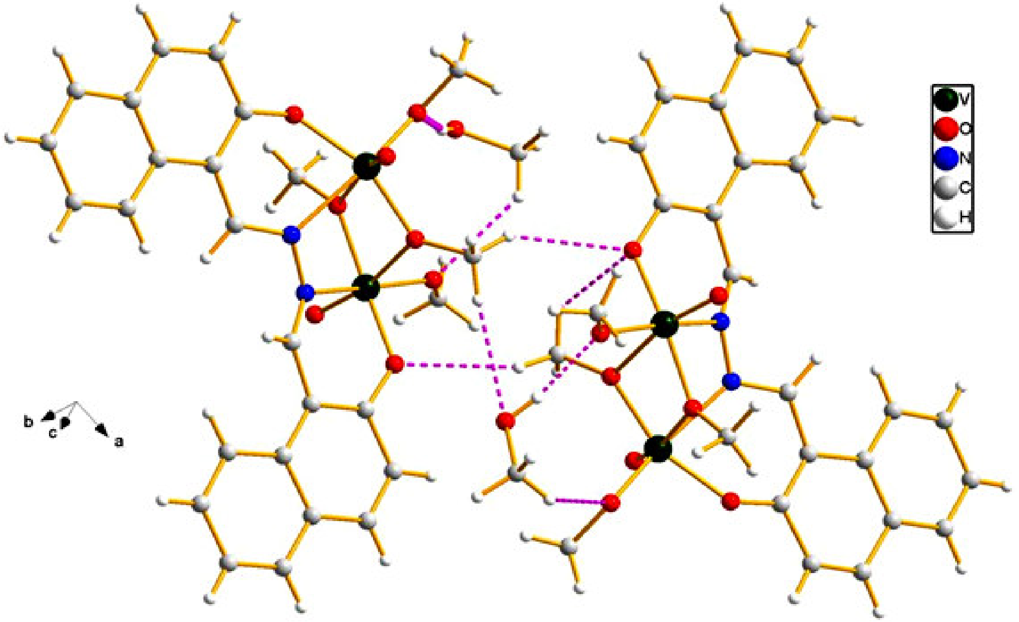

Fig. 2. O-H•••O and C-H•••O hydrogen bonding interactions in the crystal of complex **1**

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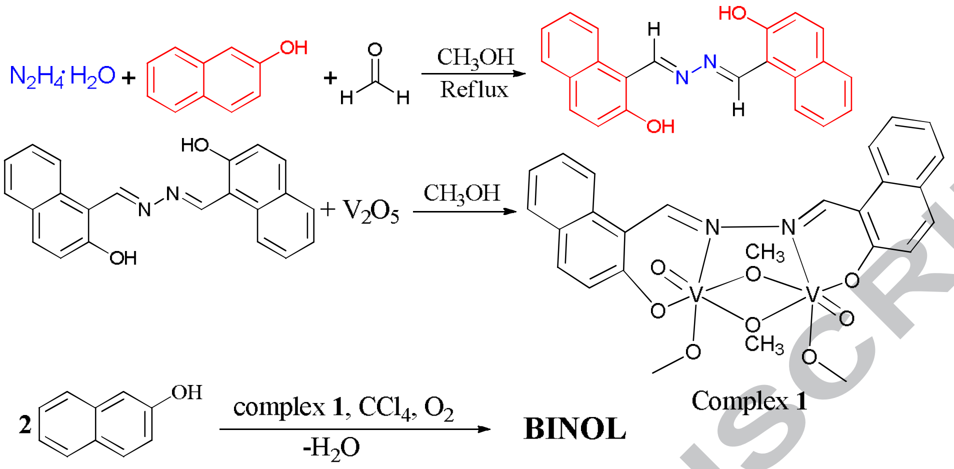
Graphical Abstract



Graphical abstract

- Synthesis and structure of a new dinuclear oxidovanadium(V) complex with an N_2O_2-donor ligand
- Catalytic behavior of the V(V) complex for the oxidative coupling of 2-naphthol to produce BINOL

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