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Oxidovanadium(V) complexes containing hydrazone based *O*,*N*,*O*-donor ligands: Synthesis, structure, catalytic properties and theoretical calculations

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ABSTRACT

Two new mono oxidovanadium(V) complexes, $[VOL^1(OEt)]$ (1) and $[VOL^2(OMe)]$ (2), of the tridentate Schiff base hydrazone-type *O*,*N*,*O*-donor ligands H₂L¹ and H₂L², obtained by monocondensation of 3hydroxy-2-naphthohydrazide with 5-bromo-2-hydroxybenzaldehyde and benzoylacetone, respectively, have been synthesized starting from VO(acac)₂ $[H_2L^1 = (E)-N^r-(5-bromo-2-hydroxybenzylidene)-3$ $hydroxy-2-naphthohydrazide; <math>H_2L^2 = (E)-3-hydroxy-N^r-((Z)-4-hydroxy-4-phenylbut-3-en-2-ylidene)-2$ naphthohydrazide]. Single-crystal X-ray structure analysis revealed for both complexes a slightly distorted square-based pyramidal NO₄ coordination environment around the metal centre, with the aroylhydrazone Schiff bases acting as *O*,*N*,*O*-tridentate, dinegative ligands. The complexes were also characterized by spectroscopic methods in the solid state (IR) and in solution (UV-Vis, ¹H NMR) and by cyclic voltammetric experiments in DMSO, and their properties were interpreted by means of DFT theoretical calculations.

The catalytic potential of these complexes has been tested for the oxidation of thioanisol using H_2O_2 as the terminal oxidant. The effects of various parameters, including the molar ratio of oxidant to substrate, the temperature and the solvent, have been studied. Both complexes showed superabundant catalytic activity in the oxidation of thioanisol at room temperature with excellent conversions.

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1. Introduction

There is continuous interest in the chemistry of vanadium(IV/V) complexes due to their biological relevance and catalytic properties [1,2]. In most cases, the active site contains either VO³⁺ or VO²⁺ coordinated by *O*,*N*-donor ligands. The discoveries of several medicinal properties of vanadium(IV/V) complexes, *i.e.* their insulin-mimetic [3–5], anticancer [6], antitumour [7] and antibacterial activities [8], have further stimulated research in this area. In particular, the presence of vanadium in the prosthetic group of certain nitrogen fixing nitrogenases and haloperoxidases involved in the insertion of halogens into organic substrates has also been reported. Vanadium haloperoxidases are enzymes that catalyze different oxidation reactions [9,10]. The active site structure of the vanadium-dependent haloperoxidases contains vanadate covalently bound by histidine and stabilized by an H-bonding network, with vanadium in a trigonal bipyramidal coordination environment [11-14]. Some VO³⁺ complexes are being considered as potential functional models of vanadium-dependent haloperoxidases.

Schiff bases are widely employed as ligands in coordination chemistry. These ligands are readily available, versatile and, depending on the nature of the starting materials employed for their preparation, can exhibit various denticities and functionalities. [15,16]. Hydrazones are a special group of compounds in the Schiff base family. They are characterized by the presence of the RR'C=N-NH–C(=O)R^{''} moiety, where R, R['] and R^{<math>''} can be H, alkyl or aroyl</sup> groups. These ligands, due to their facile keto-enol tautomerization and the availability of several potential donor sites depending on the nature of the substituents attached to the hydrazone unit, represent good polydentate chelating agents with interesting modes of ligation for a variety of metal ions [17-20]. Aroylhydrazone complexes, on the other hand, are good candidates for catalytic oxidation studies because of their ability to resist oxidation. Keto-enol tautomerism occurs readily in hydrazones and has an important role in determining the overall charge on the ligands coordinating





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the metal ions. The =N-NH-C(=O)R moiety in hydrazone based ligands can lose its amidic hydrogen and coordinate in the enol form to metal ions as a mono-negative ligand [21]. In addition, this moiety in its keto form can coordinate to metal centres as a neutral ligand [22]. The lengths of the NC and C=O bonds are very important indicators of the type of coordination. When hydrazone based ligands coordinate to metal ions in the keto form, the lengths of the HN-C and C=O bonds are around 1.34 and 1.27 Å, respectively [23], while their bond lengths in the enol form are about 1.28 and 1.34 Å, respectively [24]. From a spectroscopic point of view, FT-IR is very suitable for detecting the keto/enol form of coordinated ligands. There is a strong band between 1630 and 1670 cm^{-1} in the FT-IR spectra of complexes containing the hydrazone ligand coordinated in the keto form, which is attributed to the C=O moiety [25], while this band is not observed for complexes having ligands coordinated in the enol form [26]. However, keto-enol tautomerism in hydrazones depends on other parameters, such as pH, the nature of the metal, etc. In different types of compounds, hydrogen bonding plays a crucial role in the keto-enol tautomerism and it can shift the keto-enol equilibrium in one of the two directions [27]. It was recently observed in hydrazone ligands based on 3-hydroxy-2-naphthoic acid hydrazide that intramolecular hydrogen bonding affects the keto-enol tautomerism and despite the elimination of the NH hydrogen, it prevents tautomerism and the ligand coordinates in the keto form [28]. To continue exploring the structural and electronic effects of the ortho and para substituents in the aryloxy ring of hydrazone ligands on vanadium in [V^VO(ONO)(O)] complexes applied to oxidation catalysis [29], we report herein the synthesis, spectroscopic characterization and catalytic reactivity of two new oxidovanadium complexes with hydrazone ligands based on 3-hydroxy-2-naphthoic acid hydrazide (Scheme 1). In addition, with the aim of explaining the origin of the properties of the complexes and to understand the details of intramolecular hydrogen bonding effects on the keto-enol tautomerism, we carried out geometry optimizations, electronic and vibrational spectra calculations along with density functional theory (DFT) [30] for both the ligands and their complexes. The prepared complexes were successfully used as catalysts in the oxidation of thioanisol using H_2O_2 as the terminal oxidant.

2. Experimental details

2.1. Materials and instrumentation

Vanadyl(IV) bis(acetylacetonate), VO(acac)₂, 3-hydroxy-2naphthoic acid hydrazide, 5-bromo-2-hydroxybenzaldehyde, benzoylacetone and methyl phenyl sulfide (thioanisol) were purchased from Merck and used as received. (*E*)-*N*'-(5-bromo-2hydroxybenzylidene)-3-hydroxy-2-naphthohydrazide (H_2L^1) was synthesized according to the literature [29]. Solvents of the highest grade commercially available (Merck) were used without further purification. IR spectra were recorded as KBr discs using a Bruker FT-IR spectrophotometer. UV–Vis solution spectra were recorded using a thermo-spectronic Helios Alpha spectrometer. ¹H and ¹³C NMR spectra of the ligands and complexes in DMSO-d₆ solution were recorded on a Bruker 250 MHz spectrometer and chemical shifts were indicated in ppm relative to tetramethylsilane. Cyclovoltammetric experiments were performed using a Metrohm computrace voltammetric analyzer model 757 VA.

The reaction products of the oxidation were determined and analyzed using an HP Agilent 6890 gas chromatograph equipped with an HP-5 capillary column (phenyl methyl siloxane $30 \ \mu m \times 320 \ \mu m \times 0.25 \ \mu m$) and gas chromatograph-mass spectrometry (Hewlett–Packard 5973 Series MS-HP gas chromatograph with a mass-selective detector). The elemental analyses (carbon, hydrogen and nitrogen) of the compounds were obtained from a Carlo ERBA Model EA 1108 analyzer. The vanadium content of the complexes was measured by atomic absorption on a Varian AAS-110 spectrometer.

2.2. Synthesis of (E)-3-hydroxy-N'-((Z)-4-hydroxy-4-phenylbut-3-en-2-ylidene)-2-naphthohydrazide (H_2L^2)

This ligand was synthesized by refluxing a mixture of 3-hydroxy-2-naphthoic acid hydrazide (1.5 mmol, 303 mg) and benzoylacetone (1.5 mmol, 243 mg) in 20 mL methanol for 5 h. The solution volume was decreased to 5 mL by removing the solvent under reduced pressure and then cooled to room temperature. The obtained solids were separated and filtered off, washed with cooled methanol and then dried in air. Yield 92% (480 mg). Anal. Calc. for C₂₁H₁₈N₂O₃ (MW = 346.38): C, 72.82; H, 5.24; N, 8.09. Found: C, 72.57; H, 5.21; N, 8.16%. FT-IR (KBr, cm⁻¹): 3473 (w, br), 3270 (m), 1644 (vs), 1620 (vs), 1557 (s), 1537 (s), 1492 (m), 1361 (m), 1295 (m), 1224 (m), 1208 (m), 1082 (s), 1026 (m), 920 (s), 877 (s), 850 (s), 787 (S), 752 (vs), 730 (s), 686 (w), 666 (s), 612 (s), 481 (m), 443 (m). ¹H NMR (250.13 MHz, DMSO-d₆, 25 °C, TMS, ppm) *δ*: 12.58 (s, 1H, N-H), 11.10 (s, 2H, O-H), 8.4 (s, 1H, $C-H_{azomethine}$), 8.02 (d, J = 7.25 Hz, 1H), 7.75 (d, J = 8.25 Hz, 2H), 7.46 (m, 4H), 7.31 (m, 3H), 6.01 (s, 1H), 2.15 (s, 3H). ¹H NMR (250.13 MHz, DMSO-d₆ + D₂O 25 °C, TMS, ppm) δ: 8.37 (s, 1H, C-Hazomethine), 7.17-7.95 (m, 11H, aromatic), 5.96 (s, 1H), 2.10 (s, 3H). ¹³C NMR (62.90 MHz, DMSO-d₆, ppm) δ: 185.0, 165.9, 164.6,



Scheme 1. Ligands discussed in this paper in their neutral and dianionic forms present in the corresponding VO³⁺ isolated complexes.

153.9, 139.2, 136.32, 135.0, 131.4, 131.2, 129.2, 128.9, 128.7, 127.2, 126.3, 124.3, 120.5, 111.0, 92.3, 18.5. UV/Vis (CH₃OH): λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 237 (41700), 410 (32600).

2.3. Synthesis of the complex $[VO(L^1)(OEt)]$ (1)

Single crystals of $[VO(L^1)(OCH_2CH_3)]$ (1) were obtained by the thermal gradient method. $VO(acac)_2$ (1.0 mmol, 265 mg) and H_2L^1 (1.0 mmol, 385 mg) were placed in the main arm of a branched tube. Ethanol was carefully added to fill the arms, the tube was sealed and the reagents containing arm was immersed in an oil bath at 60 °C while the other arm was kept at ambient temperature. After 3 days, crystals were deposited in the cooler arm, which were filtered off and air dried. Yield 76% (375 mg). Anal. Calc. for C₂₀H₁₆BrN₂O₅V (MW = 495.20): C, 48.51; H, 3.26; N. 5.66: V. 10.29. Found: C. 48.59: H. 3.22: N. 5.72: V. 10.36%. FT-IR (KBr, cm⁻¹): 3460 (vs, br), 2927 (m), 2865 (m), 1637 (vs), 1615 (vs), 1584 (m), 1541 (m), 1520 (s), 1464 (s), 1444 (m), 1384 (s), 1374 (m), 1339 (m), 1299 (m), 1269 (m), 1240 (m), 1218 (m), 1199 (m), 1171 (m), 1148 (m), 1124 (m), 1087 (s), 1032 (s), 1001 (s), 964 (s), 905 (m), 876 (m), 829 (m), 818 (w), 798 (m), 761 (m), 746 (m), 700 (m), 670 (s), 634 (s), 580 (s), 528 (m), 506 (m), 481 (m), 471 (m), 468 (w), 435 (w), 402 (m). ¹H NMR (250.13 MHz, DMSO-d₆, 25 °C, TMS, ppm) δ: 11.45 (s, 1H, $O-H_{naphthol}$), 9.05 (s, 1H, CH = N), 6.88–8.61 (m, 9H, aromatic), 3.42 (q, J = 6.75 Hz, 2 H, OCH₂), 1.036 (t, J = 6.75 Hz, 3H, CH₃). ¹³C NMR (62.90 MHz, DMSO-d₆, ppm) δ: 18.8 (CH3), 84.67 (OCH₂), 110.9, 111.2, 119.4, 122.3, 124.1, 126.4, 126.6, 127.3, 128.9, 129.3, 131.2, 135.1, 136.8, 137.1, 152.7 (C-O_{phenol}), 154.8 (C-O_{naph-} thol), 162.5 (C=N), 170.8 (N=C-O_{amide}). UV/Vis (CH₃CH₂OH) λ_{max}, nm (ɛ, M⁻¹ cm⁻¹): 229 (26800), 263 (20180), 326 (14460), 408 (6220).

2.4. Synthesis of the complex $[VO(L^2)(OMe)]$ (2)

Single crystals of $[VO(L^2)(OCH_3)]$ (2) were obtained following the same procedure as for complex **1**, using $VO(acac)_2$ (1.0 mmol. 265 mg) with H₂L² (1.0 mmol. 346 mg) in the branched tube and methanol as the solvent. After 2 days, the obtained dark brown crystals were filtered off and air dried. Yield 85% (376 mg). Anal. Calc. for C₂₂H₁₉N₂O₅V (MW = 442.34): C, 59.74; H, 4.33; N, 6.33; V, 11.52. Found: C, 59.68; H, 4.36; N, 6.29; V, 11.67%. FT-IR (KBr, cm⁻¹): 3430 (m), 1639 (s), 1588 (s), 1572 (s), 1540 (vs), 1518 (s), 1485 (s), 1466 (vs), 1427 (s), 1385 (s), 1366 (s), 1305 (s), 1214 (m), 1099 (m), 1068 (m), 1046 (m), 992 (vs), 875 (m), 767 (s), 752 (s), 745 (s), 702 (vs), 687 (s), 632 (vs), 524 (m), 469 (m). ¹H NMR (250.13 MHz, DMSO-d₆, 25 °C, TMS, ppm) δ: 11.41 (s, 1H, O-H_{naphthol}), 8.85 (s, 1H, CH=N), 7.40-8.53 (m, 11H, aromatic), 6.09 (s, 1H), 3.46 (s, 3H, OCH₃), 2.39 (s, 3H, CH₃). ¹³C NMR (62.90 MHz, DMSO-d₆, ppm) *δ*: 18.6 (CH3), 43.1 (OCH₃), 65.9, 111.3, 119.5, 123.6, 124.7, 126.4, 127.2, 128.6, 129.1, 131.8, 134.1, 136.3, 137.5, 139.9, 154.9 (C-O_{naphthol}), 164.5 (C=N), 167.8 (N=CO), 183.2 (C-O_{enol}). UV/Vis (CH₃CH₂OH) λ_{max} , (ϵ , M⁻¹ cm⁻¹): 234 (32000), 265 (27300), 370 (11600), 410^{sh} (8900).

2.5. Cyclic voltammetry

For the cyclic voltammetry studies, a conventional three-electrode system was used with a polished glassy carbon electrode (area 3.14 mm²) as the working electrode and a platinum wire counter electrode. The reference electrode was an aqueous Ag/AgCl saturated electrode, separated from the bulk of the solution by a bridge with solvent and a supporting electrolyte. The electrolytic medium consisted of 0.1 mol/L tetrabutylammonium perchlorate (TBAP) in dimethyl sulfoxide; experiments were carried out at room temperature. The solutions were freshly prepared before use and purged with N_2 for ca. 15 min prior to taking measurements in order to remove dissolved O_2 . The voltammograms were recorded under various scan rates in the range -0.5-1.0 V versus Ag/AgCl.

2.6. X-ray diffraction data collection and refinement

A summary of the crystal data and refinement details for the compounds discussed in this paper are given in Table 1. Only special features of the analyses are mentioned here. Single crystal data collection for $[VO(L^1)(OEt)]$ (1) and $[VO(L^2)(OMe)]$ (2) was performed on a Bruker SMART APEX CCD area detector and a Stoe IPDS II diffractometer, respectively, equipped with an Oxford Cryosystems open-flow nitrogen cryostat, using ω scans and graphitemonochromated Mo K α (λ = 0.71073 Å) radiation. All data sets were corrected for Lorentz, polarization and absorption effects (semi-empirical based on multi-scan methods). The structures were solved by direct methods using SHELXS97 [31] and SIR92 [32] for 1 and 2, respectively, completed with difference Fourier synthesis and refined with full-matrix least-square procedures based on F^2 using shelxL97. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in idealized positions and constrained to ride on their parent atoms.

2.7. Computational methods

The ground state geometries in the gas phase of the ligands H_2L^1 and H_2L^2 and of the complexes [VO(L¹)(OEt)] (1) and [VO(L²)(-OMe)] (2) were fully optimized using the restricted HF/6-31G, B3LYP/6-31G and B3LYP/6-31G(dp) methods, starting from the crystallographic structural models [33,34]. The functional B3LYP, used throughout this study, consisted of a hybrid exchange functional as defined by Beckes's three parameter equation and the non-local Lee–Yang–Parr correlation functional. The electronic spectra of the compounds were calculated using the time dependent density functional theory (TDDFT) method [35] in a methanolic solution environment employing the Polarizable Continuum Model (PCM). The vibrational frequencies were obtained at the

Table 1 Crystal data for $[VO(L^1)(OEt)]$ (1) and $[VO(L^2)(OMe)]$ (2).

	$[VO(L^{1})(OEt)](1)$	$[VO(L^2)(OMe)]$ (2)
Empirical formula	C ₂₀ H ₁₆ BrN ₂ O ₅ V	C ₂₂ H ₁₉ N ₂ O ₅ V
T(V)	150 (2)	202 (2)
(K)	triclinic	z95 (z) triclinic
Crystal system		unchinic D4
space group	P1	PI
Crystal size (mm)	$0.08 \times 0.03 \times 0.02$	$0.3 \times 0.3 \times 0.3$
a (A)	6.8538(12)	9.9860(6)
b (Å)	11.386(2)	14.1137(8)
<i>c</i> (Å)	12.460(2)	16.1355(8)
α(°)	89.067(3)	109.075(5)
β (°)	82.650(3)	99.902(5)
γ (°)	79.057 (3)	103.126(5)
V (Å ³)	946.8 (3)	2016.84(22)
Ζ	2	4
$D_{\text{calc}}(\text{g cm}^{-3})$	1.737	1.457
$\mu ({\rm mm}^{-1})$	2.670	0.529
θ (°)	2.45-27.22	3.21-26.37
Reflections collected	8225	16280
Unique reflections (R_{int})	4169, 0.015	8242, 0.027
Observed reflections $[I > 2\sigma(I)]$	3514	6349
Goodness-of-fit (GOF)	1.04	1.055
Absorp. Correction	multi-scan	multi-scan
Tmin. Tmax	0.654, 0.746	0.757. 1.000
Final R_1 w R_2 [$I > 2\sigma(1)$]	0.0292 0.0757	0.0551 0.1434
Largest diff neak and hole (e Å ⁻³)	0.36 0.55	0.930 0.789
Largest and peak and note (CA)	0.50, 0.55	0.550, 0.785

B3LYP/6-31G level for the validation of the optimized geometries. All of the calculations were performed with the GAUSSIAN-03 program [36]. Topological analyses were carried out on 1 and 2 to calculate the charge density (ρ) and its second derivative Laplacian $(\nabla^2 \rho)$ at the bond critical points (BCP) using Bader's Atoms in Molecules (AIM) theory with the program AIM2000 [37]. According to QTAIM, any bonded atoms are connected by a single line, "bond path", of locally maximum electron density, $\rho(r)$, that originates a bond critical point (BCP), which represents a minimum of $\rho(r)$ along the bond path. The sign of the Laplacian, $\nabla^2 \rho$, of the electron density at a BCP indicates two limit situations; (1) a negative value of $\nabla^2 \rho$ indicates a local charge concentration, which means that the interaction is a covalent bond; (2) a positive value of $\nabla^2 \rho$ indicates charge depletion, which means a closed-shell interaction, as found in ionic bonds. It is also possible to find positive $\nabla^2 \rho$ and relative high $\rho(r)$ at the BCP, which indicates a covalent polar bond. The absolute value of the Laplacian and the bond critical point value for $\rho(r)$ relate to the bond order between two neighboring nuclei.

2.8. Catalytic procedure

Liquid phase catalytic oxidations of thionaisol were carried out under air (atmospheric pressure) in a 25 mL round bottom flask equipped with a magnetic stirrer. In a typical experiment, H_2O_2 was added to a flask containing the catalyst (2×10^{-3} mmol) and thioanisol (1.0 mmol) in a solvent (3 mL). The course of the reaction was monitored using a gas chromatograph equipped with a capillary column and a flame ionization detector. The oxidation products were identified by comparing their retention times with those of authentic samples or alternatively by ¹H NMR and GC– Mass analyses. Control reactions were carried out in the absence of catalyst, but otherwise under the same conditions as the catalytic runs.

3. Results and discussion

3.1. Synthesis of the ligands and complexes, and spectroscopic characterization

 H_2L^2 was synthesized by the reaction of 3-hydroxy-2-naphthohydrazide with 2-benzoyilacetone in methanol to afford the desired dissymmetric tridentate *O*,*N*,*O*-donor Schiff base ligand in excellent yield and purity. The oxidovanadium(V) complexes [VO(L¹)(OEt)] (**1**) and [VO(L²)(OMe)] (**2**) were prepared in high yields by treating an ethanol or methanol solution of the appropriate ligand with an equimolar amount of VO(acac)₂. During the synthesis, V(IV) is oxidized to V(V) by aerial oxygen (dissolved in the solvent) according to Eq (1).

$$\begin{split} & 2H_2L^{1-2} + 2V^{IV}O(acac)_2 + 2ROH + \frac{1}{2}O_2 \\ & \rightarrow 2[V^VO(L^{1-2})(OR)] + 4Hacac + H_2O \end{split} \tag{1}$$

Selected IR spectroscopic data are presented in Table 2. A comparison of the spectra of the complexes with those of the ligands (Fig. S2) provides evidence for the coordination mode adopted by the ligands in **1** and **2**. There is a band at 3189 and 3270 cm⁻¹ in the IR spectra of H_2L^1 and H_2L^2 , respectively, which is due to the N–H stretching vibration. In IR spectra of the ligands a very strong band also appears at 1647 (in H_2L^1) and 1644 cm⁻¹ (in H_2L^2) due to the C=O stretching vibration. The absence of the band due to the NH stretching in the IR spectra of the complexes indicates enolization/deprotonation of the amide functionality upon coordination to the metal centre. However, the presence of a strong band at 1638 (in **1**) and 1639 cm⁻¹ (in **2**) in the IR spectra of the complexes, which can be assigned to the C=O stretching vibration, indicates that keto–enol tautomerism has not occurred and the deprotonated ligands coordinate in the keto form.

The amide deprotonation without enolization is in contrast with reported studies of arovlhydrazones complexes, but is in good agreement with our previous observation in copper(II) and manganese complexes using the 2-hydroxy-3-naphthohydrazone based ligand. The infrared spectra of 1 and 2 also display a band at 1584 and 1588 cm^{-1} , respectively, which can be assigned to the C=N stretching frequency of the coordinated hydrazone ligand and this band is red shifted with respect to the free ligand. Therefore, the absence of an NH stretching band and the red shift in the azomethine (C=N) stretching band [38] indicate a tridentate coordination of the dianionic ligands (Scheme 1). Furthermore, in the IR spectra of the two complexes a very broad band at around 3460 cm⁻¹ is observed, which can be assigned to the stretching vibration of the naphtholic -OH group involved in intramolecular hydrogen bonding. The strong band at 987 and 992 cm⁻¹ in the IR spectra of **1** and **2**, respectively, can be assigned to v(V=0)stretching.

Methanol solutions of the complexes are of a brown-yellow colour and have been used to record their electronic spectra. The hydrazone ligands show the most intense band at around 230 nm and other less intense bands in the range 300–400 nm (Fig. S3). These bands may be assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. All the bands shift in the complexes, indicating the coordination of the ligands to the metal ion [39]. The oxidovanadium complexes also show a band at around 265 nm, which corresponds to the $O \rightarrow V$ ligand to metal charge transfer (LMCT) transition of the V=O moiety, which it is seen at 274 nm for [VO(acac)₂]. The lowest energy transition at about 410 nm for the two complexes corresponds to L $\rightarrow V$ LMCT transitions [40–42].

3.2. Description of the structures

In order to define conclusively the coordination sphere of the metal centre in **1** and **2**, a single-crystal X-ray diffraction study was undertaken. X-ray analysis indicates both **1** and **2** are neutral mononuclear complexes of V(V). The vanadium centre in both complexes has a square pyramidal coordinated geometry in an NO₄ donor environment with one nitrogen and two oxygen donor

Га	bl	le	2	

Selected IR bands (cm^{-1}) of the ligands H_2L^1 [29] and H_2L^2 , and the complexes $[VO(L^1)(OEt)]$ (1) and $[VO(L^2)(OMe)]$ (2)^a.

	$\tilde{v}(C=N)^{b} + \delta(NH)$	$\tilde{v}(C=0)$	ν̃(NH)	ν̃(OH)	$\tilde{v}(V=0)$	$\tilde{v}(V-O)$	$\tilde{v}(V-N)$
H _a I ¹	1625(m) 1552(s)	1647(vs)	3189(s)	3662(w. hr)	((* 0))	((* 0)	
H_2L^2	1620(vs), 1537(s)	1644(vs)	3270(m)	3473(w, br)			
1	1584(m)	1638(vs)	-	3460	987(vs)	634(s)	471(m)
2	1588(s)	1639(s)	-	3430(m)	992(vs)	632(vs)	469(m)

^a Scaled IR spectra for **1** and **2** were also calculated at the DFT/B3LYP level (see Experimental) and assignments of the vibration modes were made with a very good correlation coefficient between the experimental and calculated values (see Tables S1 and S2, and Fig. S1).

^b The bands assigned to the $\bar{v}(C=N)$ (azomethyne stretching vibration) are not pure as they contain significant contributions from the aromatic $\bar{v}(C=C)$ stretching bands.

atoms provided by the Schiff base ligands, an oxygen atom from a coordinated alkoxy group (ethoxy in complex **1** and methoxy in complex **2**) and an oxido ligand (see Figs. 1 and 2, and Table 3 for selected interatomic distances). The terminal oxido ligand occupies the axial position at a distance of 1.5775(16) (**1**) and 1.588(2)/1.569(3) Å (**2**) (Table 3).

In both complexes, the vanadium to oxygen bond lengths follow the order $V=O_{oxido} < V-O_{alkoxo} < V-O_{phenolate} < V-O_{hydrazone}$. The metal centre is displaced by 0.457 (1) and 0.474/0.491 Å (2) from the mean plane defined by the donor atoms N2, O2, O3 and O5 towards the V=O moiety. The tridentate *O*,*N*,*O* donor ligands form one six-membered and one five-membered chelate ring with bite angles of about 83° (O3–V1–N2) and 75° (N2–V1–O2) (Table 3). The structures of the complex units are stabilized by an intramolecular OH···N hydrogen bond, with the nitrogen atom of the amide group (-N=C–O) acting as the hydrogen bond acceptor (see Figs. 1 and 2).

The crystal packing of complex **1** is mainly determined by four π - π stacking interactions [43]; two of them are shown in Fig. 3a. One of these interactions is between the naphthalene and salicylidene rings (centroid–centroid distance = 3.743 Å) and the other interaction is between the second naphthalene ring and the six membered chelate ring (centroid–centroid distance = 3.565 Å). These two interactions cause the pairing of two [VO(L¹)(OEt)] complex units (Fig. 3a). The remaining two π - π stacking interactions are between two naphthalene moities belonging to symmetry related dimeric associations of [VO(L¹)(OEt)] complex units, as described above, with a centroid–centroid distance of 3.725 Å (Fig. S5), which create a lamellar stacking of complex units in the crystal lattice (Fig. 3b).

Dimeric associations, similar to those observed between the complex units in **1**, are also formed in **2** between pairs of $[VO(L^2)(-OMe)]$ molecules (**2A** or **2B**, see note a in Table 3); these interact



Fig. 1. View of the asymmetric unit in $[VO(L^1)(OEt)]$ (1) with the atom numbering scheme adopted. Displacement ellipsoids are drawn at the 30% probability level. H1…N1 1.91, O1…N1 2.632(6) Å; <O1-H1…N1 143.10°.



Fig. 2. View of one of the two asymmetric units (**2A**) in [VO(L²)(OMe)] (**2**) with the atom numbering scheme adopted. Displacement ellipsoids are drawn at the 30% probability level. H1A···N1A 1.91, O1A···N1A 2.632(6) Å; <O1A–H1A···N1A 146°.

Table 3

Selected bond lengths (Å) and angles (°) in the crystal structure of complexes 1 and 2.^a

	1	2a	2b
V1-N2	2.1318(18)	2.067(2)	2.079 (3)
V1-02	1.9152(16)	1.9126(18)	2.079 (3)
V1-03	1.8245(15)	1.8501(18)	1.842 (2)
V1-04	1.5775(16)	1.588(2)	1.569 (3)
V1-05	1.7558(16)	1.768(2)	1.742 (3)
C11-O2	1.312(3)	1.321(3)	1.324 (4)
C11-N1	1.305(3)	1.293(4)	1.295 (4)
C12-N2	1.289(3)	1.324(3)	1.309 (4)
N1-N2	1.390(2)	1.391(3)	1.394 (4)
04-V1-05	106.42(8)	105.88(11)	109.7 (2)
04-V1-03	107.65(8)	104.75(10)	104.52 (13)
05-V1-03	98.95(7)	97.11(9)	97.43 (14)
04-V1-02	104.56(8)	107.23(10)	104.00 (13)
05-V1-02	91.09(7)	89.65(9)	88.39 (11)
03-V1-02	141.77(7)	144.04(9)	146.91 (10)
04-V1-N2	95.77(8)	99.85(10)	101.21 (16)
05-V1-N2	155.96(7)	153.16(10)	147.71 (15)
03-V1-N2	82.58(7)	83.41(8)	83.21 (10)
02-V1-N2	74.16(6)	75.36(8)	75.11 (10)

^a In the crystal structure of **2**, two crystallographically independent molecules of $[VO(L^2)(OMe)]$ (described as **2a** and **2b**) are present in the asymmetric unit (see Fig. S4).

with each other *via* an extensive network of hydrogen bonds (Fig. S6).

3.3. Geometry optimization, charge distribution and electronic structure

The geometries of the ligands and oxidovanadium complexes 1 and **2** were optimized in the singlet state by means of the HF and DFT/B3LYP methods using the 6-31G and 6-31G(dp) basis sets. In general, the predicted bond lengths and angles are in good agreement with the values based upon X-ray crystal structural data, with a maximum difference in bond length of about 3% at the B3LYP/6-31G level. Therefore, the B3LYP/6-31G basis set was used for all further calculations. Selected optimized and experimental values of geometrical parameters for complexes 1 and 2 are listed in Tables S3 and S4, respectively. The slight differences between the theoretical and experimental values may be related to the fact that the experimental data belong to the solid state, while the calculated values refer to a single molecule in the gas phase. The general trends observed in the experimental data are well reproduced in the calculated ones. In Table 4, the changes observed upon coordination in some selected bond distances and angles of the two ligands are compared. The experimental differences and calculated ones at the DFT level are similar for each selected geometrical parameter. The maximum variation is observed/computed for the C-O_{hydrazone} bond length, with a lengthening upon coordination to the vanadium centre.

The Mulliken atomic charges for both complexes are summarized in Table 5. The calculated Mulliken charges on the vanadium atom in both complexes are considerably lower than the formal charge of 5+, confirming a significant charge donation from the ligands. The charges on the terminal oxido oxygen, alkoxo oxygen and oxygen atoms from the Schiff base ligands are significantly smaller than -2 and -1, respectively. The terminal oxido oxygen atoms are less negative in comparison with the oxygen atoms from the Schiff-base ligands. This indicates a higher electron density delocalization from the terminal oxido ligands towards the vanadium centers and agrees with the observed differences in bond lengths: V=O4_{oxido} < V-O5_{alkoxo} < V-O3_{phenolate} < V-O2_{hydrazone}.

Interestingly, while the hydrogen atom of the naphthol group (OH) in the free ligands is oriented towards the outer part of the molecules and takes part in intermolecular hydrogen bonding



Fig. 3. (a) The π - π stacking interactions between two symmetry-related [VO(L¹)(OEt)] (1) complex units involving the naphthalene, salicylidene and six membered chelate rings; (b) partial view of the lamellar stacking of [VO(L¹)(OEt)] (1) complex units.

Table	4
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Selected optimized geometrical parameters (bond lengths, Å; bond angles, °) for the ligands H₂L¹ and H₂L², and their changes upon metal coordination.

	B3LYP/6-31G		B3LYP/6-31G		$\Delta_{\text{Complex-Ligand}}$ [DFT (Experimental)]	
	H_2L^1	H_2L^2	Complex 1	Complex 2	Complex 1	Complex 2
C11-02	1.2492	1.2521	1.3123	1.3156	0.0631 (0.077)	0.0635 (0.087)
C11-C10	1.4992	1.5020	1.4657	1.4654	-0.0335 (-0.029)	-0.0366 (-0.025)
C11-N1	1.3835	1.3763	1.3188	1.3129	-0.0647 (-0.033)	-0.0634(-0.045)
N2-N1	1.3672	1.3762	1.3728	1.3762	0.0056 (0.012)	0 (0.013)
N2-C12	1.3010	1.3195	1.2999	1.3222	-0.0011 (0.005)	0.0027 (0.042)
N1-C11-C10	116.778	116.708	120.313	120.552	3.535 (4.04)	3.844 (4.30)
N1-C11-O2	121.899	122.315	120.398	120.044	-1.501 (-1.16)	-2.271 (-1.94)
C11-N1-N2	118.917	118.932	109.581	109.815	-9.336 (-12.58)	-9.117 (-12.06)
C12-N2-N1	120.249	120.249	117.271	117.220	-2.978 (2.95)	-3.029 (2.83)

Experimental data for the ligands are taken from Ref. [44].

[44,45], in both complexes it prefers an *endo* orientation and participates in intramolecular hydrogen bonding (see Scheme 1, Figs. 1 and 2). This different behavior can be attributed to the presence of the NH group of the hydrazone moiety in the free ligands, which is eliminated upon complexation and thus provides enough space for the rotation of atom of the naphthol group towards the inner part of the ligand molecules. The intramolecular hydrogen

bonding established by the naphtholic OH group of both ligands facilitates their keto-enol tautomerisation upon coordination and stabilizes the keto-form while the amidic hydrogen atom is eliminated. In Fig. 4, the bond lengths and the Mulliken charges calculated for the hydrazone part of complexes 1 and 2 are compared with those calculated for model complexes featuring a naphthalene moiety instead of the naphtholic group.

Table 5

Selected calculated atomic	charges for	complexes 1	1 and 2	e.
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Atom	Mulliken charge			
	Complex 1	Complex 2		
V1	+1.238	+1.665		
02	-0.615	-0.653		
03	-0.666	-0.692		
04	-0.371	-0.451		
05	-0.564	-0.655		
N2	-0.426	-0.585		

Clearly, the presence of intramolecular hydrogen bonding between the naphtholic –OH group and the deprotonated amidic nitrogen atom stabilizes the keto form of the coordinated ligands and the increased amount of negative charge on the amidic nitrogen.

A molecular electrostatic potential (MESP) map was also computed for the two ligands and the two complexes to better identify the most probable nucleophilic and electrophilic regions on the molecules [46–48], as shown in Fig. 5. Blue colors indicate positive MESP regions and red colors indicate negative MESP regions. The MESP maps show that for the free ligands the negative regions are mainly located on the benzene ring, phenolic oxygens and the carbonyl group of the hydrazone moiety. The oxygen of the naphthol group in the free ligands is included in a positive region. After complexation, a decrease of the electron density is observed on the benzene rings, phenolic oxygens and carbonyl moieties of the ligands, in keeping with metal coordination of the oxygen atoms and, therefore, with a charge transfer from the O donors towards the vanadium(V) metal centre. Interestingly, the naphtholic –OH group, upon coordination, passes to a negative MESP region of the complex molecule. The O4 oxygen atom of the V=O moiety is located in a more negative region than those of the other oxygen atoms in the complexes.

Figs. 6 and 7 show some calculated frontier molecular orbitals (Kohn–Sham MOs) and the corresponding energies in eV for complexes **1** and **2**, respectively. Frontier Kohn–Sham MOs for H_2L^1 and H_2L^2 are represented in Figs. S7 and S8, respectively.

In both complexes, the HOMO is mainly localized on the naphtholic oxygen atom and on the naphthalene ring of the Schiff base ligands. The five d-type orbitals of the vanadium centre mainly contribute to unoccupied MOs, in agreement with a d⁰ configuration for the metal centre in these complexes. On the other hand, the LUMO to LUMO+2 MOs in both complexes are mainly localized on the vanadium center and coordinated atoms from the ligands. The HOMO–LUMO gap for complexes **1** and **2** equals 2.595 and 2.558 eV, respectively. This value of this gap for H_2L^1 and H_2L^2 is 3.701 and 3.401 eV, respectively.

TDDFT/B3LYP-6-31G calculations using the PCM model (methanol was selected as the solvent) were performed for both ligands and complexes. Selected calculated states, together with their



Fig. 4. Bond lengths and the Mulliken charges calculated for the hydrazone part of complexes 1 (top left) and 2 (bottom left) and for the analogous model complexes (right) featuring a naphthalene moiety instead of the naphtholic moiety.



Fig. 5. B3LYP/6-31G calculated 3D molecular electrostatic potential (MESP) maps of the complexes (above) and ligands (below) in various orientations. The considered charge range for the ligands is the same as that for the corresponding complexes.



Fig. 6. Frontier molecular orbitals of complex 1 with the energy eigenvalues in eV.



Fig. 7. Frontier molecular orbitals of complex 2 with the energy eigenvalues in eV.

vertical excitation wavelengths, scaled by 0.7 for the complexes and 0.95 for the ligands [49], and oscillator strengths are displayed in Table 6. For both complexes, the lowest energy band (408 nm in 1) corresponds to the HOMO \rightarrow LUMO monoelectronic excitation, which results from a LMCT (ligand to metal charge transfer) from the Schiff base ligand to the vanadium(V) metal centre. The broad absorption band observed at 326 nm for **1** falls in the same region where $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ ligand transitions are present (Table S5). This band arises from the overlap of several bands originating from various transitions, all LMCT in nature. In complex **1**, the highest energy band observed at 263 nm is assigned to a HOMO \rightarrow LUMO+1 monoelectronic transition which is LMCT in

Table 6	
Calculated and observed λ_{max} values for the principal singlet electronic transitions of complexes 1 and	2.

Electronic transition	Calculated λ (nm) ^a	f^{b}	Observed λ (nm)	Character
Complex 1 1:				
HOMO → LUMO HOMO-1 → LUMO 2.	378.5	0.0043	408	$L \rightarrow V (LMCT)$
$HOMO-2 \rightarrow LUMO$ $HOMO-1 \rightarrow LUMO$ 3.	366.5	0.0211	326	$\begin{array}{l} L \rightarrow V \ (LMCT), \ n \rightarrow \pi^*(L) \\ L \rightarrow V \ (LMCT), \ \pi \rightarrow \pi^*(L) \end{array}$
HOMO \rightarrow LUMO+1 Complex 2	317.4	0.0074	263	$L \to V \text{ (LMCT), } \pi \to \pi^*(L)$
HOMO \rightarrow LUMO	430.7	0.0227	418	$L \rightarrow V (LMCT)$
HOMO \rightarrow LUMO HOMO-1 \rightarrow LUMO	372.2	0.0006	370	$\begin{array}{l} L \rightarrow V \mbox{ (LMCT)} \\ L \rightarrow V \mbox{ (LMCT)}, n \rightarrow \pi^* \mbox{ (L)}, \pi \rightarrow \pi^* \mbox{ (L)} \end{array}$
HOMO-1 \rightarrow LUMO+1 HOMO-1 \rightarrow LUMO+3	318.4	0.3103	234, 265	$\begin{array}{l} L \rightarrow V \ (LMCT), \ \pi \rightarrow \pi^*(L) \\ L \rightarrow V \ (LMCT), \ \pi \rightarrow \pi^*(L) \end{array}$

^a Scaling factor: 0.7.

^b Oscillator strength.

nature. Also in this case intra-ligand $\pi \to \pi^*$ transitions can contribute to the absorption band. For complex **2** the highest energy is assigned to the HOMO-1 \to LUMO+1 monoelectronic transition, which is LMCT in nature.

3.4. Atoms in molecules theory (QTAIM)

The quantum theory of atom in molecules (QTAIM) has been shown to provide valuable information about many different bonding chemical systems by an analysis of the molecular electron density distribution. Several excellent reviews [50-52] have been published on this theory developed by Bader. The values computed for $\nabla^2 \rho$ and $\rho(r)$ at the bond critical points (BCP) of some selected bonds in 1 and 2 are collected in Table 7. The bond critical points (BCP) and ring critical points (RCP) of complexes 1 and 2 were schematized with a small red symbol for BCPs and a yellow symbol for RCPs (Figs. S9 and S10, respectively). These figures show the positions of the maxima in electron density (nuclei) and bond paths connecting the nuclei, as well as the positions of the BCPs and RCPs. With regard to the Laplacian of density ($\nabla^2 \rho$) values, the bonds between the vanadium and the coordinated donor atoms can be classified as ionic or highly polar covalent because $\nabla^2 \rho$ for these bonds has a positive value ($\nabla^2 \rho > 0$). The electron charge density at the BCP of the V-O4 bond is the highest (0.255 and 0.263 au for 1 and 2, respectively) and that at the BCP of the

Table 7

	Complex 1			Complex 2		
	ho (r) [au]	$ abla^2 ho$ [au]	Ellipticity	ho (r) [au]	$ abla^2 ho$ [au]	Ellipticity
V1-04	0.255	1.035	0.0041	0.263	0.968	0.0031
V1-05	0.153	0.883	0.1109	0.155	0.759	0.1049
V1-03	0.119	0.692	0.0774	0.118	0.568	0.0617
V1-02	0.099	0.545	0.0827	0.105	0.465	0.0807
V1-N2	0.066	0.292	0.0565	0.075	0.261	0.0807
C1-01	0.269	-0.504	0.0080	0.267	-0.494	0.0057
01-H1	0.305	-1.389	0.0171	0.312	-1.768	0.01841
N1-H1	0.042	0.1454	0.0258	0.049	0.138	0.02817
RCP1	0.019	0.151	-1.1742	0.019	0.152	-1.1829
RCP2	0.018	0.147	-1.1836	0.019	0.149	-1.1905
RCP3	0.015	0.097	-1.2299	0.016	0.097	-1.2441
RCP4	0.030	0.174	-1.6678	0.031	0.177	-1.6859
RCP5	0.015	0.091	-1.2807	0.016	0.098	-1.2773
RCP6	0.019	0.155	-1.1754	0.020	0.160	-1.1854

V–N2 bond is the lowest (0.066 and 0.075 au for **1** and **2**, respectively). The order of bond lengths on the basis of the $\rho(r)$ values at the BCPs, V–O4_{oxido} < V–O5_{alkoxo} < V–O3_{phenolate} < V–O2_{hydrazone}, is in good agreement with the experimental findings. Interestingly, the low values calculated for the ellipticity, ε , at the BCP of these bonds (Table 7) indicates an axial symmetry for them. The parameters calculated at the O1–H1 and N1–H1 BCPs (Table 7) agree with the formation of an intramolecular O1–H1…N1 hydrogen bond.

A comparison of the electron density at the RCPs shows that the electron density at the RCP of the chelating ring containing the vanadium metal centre (RCP5) is of the same magnitude of that at the RCPs of the aromatic rings, thereby confirming the π - π stacking interactions observed in the crystal packing of complexes **1** and **2**.

3.5. Electrochemical studies

Electrochemical cyclic voltammetry measurements were carried out to probe the redox properties of the complexes in solution [53]. The cyclic voltammograms of the complexes in dimethylsulf-oxide (DMSO) displayed a quasi-reversible redox peak due to the VO³⁺–VO²⁺ couple. Cyclic voltammetry data are collected in Table 8 and Fig. 8 displays the cyclic voltammograms of the complexes at different scan rates, from 10 to 700 mVs⁻¹. The $\Delta Ep = (Epa - Epc)$ value is 458 mV for complex 1 and 0.571 mV for complex 2. $I_{p,a}/I_{p,c}$ is 0.715 and 0.744 for complexes 1 and 2, respectively. There is a linear relationship between the cathodic and anodic peak currents and the square root of the scan rate ($v^{1/2}$) in the range 10–700 mVs⁻¹ (Fig. 9). This behavior is diagnostic of a diffusion controlled electron transfer process.

3.6. Catalytic reactivity of the complexes

Since oxidovanadium complexes are active catalysts for the oxidation of sulfides [54] and hydrocarbons [55], the catalytic oxidation of thioanisol (Scheme 2) as a representative substrate with

Table 8	
Electrochemical data of the complexes	1 and 2 in DMSO solution at 298 K.

	$E_{p.a}(V)$	I _{p.a}	$E_{\rm p.c.}(V)$	I _{p.c}	$\Delta E_{\rm P}({\rm V})$	$I_{\rm p.a}/I_{\rm p.c}$
Complex 1 Complex 2	0.545 0.587	$\begin{array}{c} 6.07\times 10^{-7} \\ 5.15\times 10^{-7} \end{array}$	0.087 0.0154	$\begin{array}{c} -8.49\times 10^{-7} \\ -6.65\times 10^{-7} \end{array}$	0.458 0.571	0.715 0.744



Fig. 8. Cyclic voltammograms of complexes **1** and **2** (10³ mol L⁻¹) in DMSO and with TBAP as the supporting electrolyte (0.1 mol L⁻¹); scan rate 10, 20, 30, 40, 60, 80, 100, 150, 200, 300, 350, 400, 450, 500, 600 and 700 mV s⁻¹.



Fig. 9. Plot of the cathodic and anodic currents versus the square root of sweep rate ($v^{1/2}$) for the complexes 1 and 2.



Scheme 2. Catalytic oxidation of thioanisol in the presence of the oxidovanadium complexes 1 or 2.

hydrogen peroxide was studied in the presence of complexes **1** and **2**. The results of control experiments revealed that the presence of the catalyst and oxidant (H_2O_2) is essential for the oxidation. The results of the studies are summarized in Table 9. Thioanisol was converted to the corresponding sulfoxide with 100% selectivity by both complexes at room temperature, the activity of **1** being a little higher than that of **2**. Other reaction conditions which can be manipulated to achieve the maximum oxidation of thioanisol, such as the oxidant concentration (moles of oxidant per moles of thioanisol), solvent and temperature of the reaction were investigated. The effects of oxidant concentration on the oxidation of thi-

Table 9
Comparison of the catalytic activities of 1 and 2 in the oxidation of thioanisol with
hydrogen peroxide in different solvents.

Entry	Catalyst	H_2O_2 (mmol)	Solvent	Temp. (°C)	Yield (%) ^a
1	1	2.5	CH₃CN	25	98
2	1	2.5	CH₃OH	25	95
3	1	2.5	CH ₃ CH ₂ OH	25	85
4	1	2.5	CHCl ₃	25	93
5	1	2.5	CH_2Cl_2	25	61
6	1	2.5	petroleum ether	25	45
7	1	2.5	DMF	25	24
8	1	2.5	DMSO	25	19
1	2	2.5	CH_3CN	25	97
2	2	2.5	CH ₃ OH	25	92
3	2	2.5	CH ₃ CH ₂ OH	25	87
4	2	2.5	CHCl ₃	25	90
5	2	2.5	CH_2Cl_2	25	55
6	2	2.5	petroleum ether	25	48
7	2	2.5	DMF	25	27
8	2	2.5	DMSO	25	16

Reaction conditions: catalyst, 2 $\mu mol;$ thio anisol, 1 mmol; solvent, 3 mL; time, 15 min.

^a Yields are based on the starting thioanisol.



Fig. 10. Time dependence of thioanisole conversion to the corresponding sulfoxide in the presence of $[VO(L^1)(OEt)]$ (1) (2 µmol), CH₃CN (3 mL), thioanisol (1 mmol), at T = 25 °C.



Fig. 11. Time dependence of thioanisole conversion to the corresponding sulfoxide in the presence of $[VO(L^2)(OMe)]$ (2), (2 µmol), CH₃CN (3 mL), thioanisol (1 mmol), at T = 25 °C.

oanisol by these complexes are illustrated in Figs. 10 and 11. Different oxidant/thioanisol molar ratios (1:1, 2:1, 2.5:1 and 3:1) were considered, while the ratio of thioanisol (1.0 mmol) to catalyst (2 µmol) in 3 mL of acetonitrile at room temperature was kept constant. The conversion of thioanisol increased with increasing amounts of hydrogen peroxide in the reaction mixture. When the H₂O₂/substrate mole ratio was 2.5/1, a maximum conversion of 98% was achieved. Aqueous hydrogen peroxide was selected by considering its high selectivity, atom economy and environmentally friendly properties. Table 9 illustrates the influence of the solvent nature in the catalytic oxidation of thioanisol by these complexes. Methanol, ethanol, dichloromethane, chloroform, petroleum ether, DMF, DMSO and acetonitrile were used as solvents, and acetonitrile was found to be the most suitable solvent for this reaction. The highest conversion of 98% was obtained in acetonitrile after 15 min. It was observed that the catalytic activity

of the catalysts decreased in the order acetonitrile > methanol > chloroform > ethanol > dichloromethane > petroleum ether > DMF > DMSO. Overall, the reactivity of these catalysts in other solvents was very much lower than acetonitrile. From Table 9, one could see that solvents with moderate donation ability and high polarities seemed to favor the oxidation reaction. Solvents with a high coordinating property, such as DMF and DMSO, inhibited the reaction. The selectivity of sulfoxide decreased when the reaction was carried out at high temperatures (40 and 60 $^{\circ}$ C) (Table 10). At high temperatures methylsulfonylbenzene (sulfone) was obtained by further oxidation of methylsulfinylbenzene (sulfoxide). The mechanism of the oxidation reactions by oxidovanadium complexes of naphthohydrazone ligands have been studied in detail and it is predicted that the active site in this catalytic reaction is a peroxo-vanadium-hydrazone Schiff base species, formed in the reaction mixture in the presence of hydrogen peroxide [29].

Table 10
The effect of temperature on the catalytic oxidation of thioanisol by complexes 1 and
2.

Entry	Catalyst	Temp. (°C)	Conversion (%) ^a	Sulfoxide	Sulfone
1	1	60	100	61	39
2	2	40	100	83	17
3	2	60	100	52	48

Reaction conditions: catalyst, 2 µmol; thioanisol, 1 mmol; CH₃CN, 3 mL; H₂O₂, 2.5 mmol.

Yields are based on the starting thioanisol.

4. Conclusions

In this work two new mono oxidovanadium(V) complexes of tridentate Schiff base hydrazone-type O,N,O-donor ligands, H₂L¹ and H_2L^2 , were fully synthesized and characterized by spectroscopic and single crystal X-ray analyses, as well as DFT calculations. Electrochemical studies by the cyclic voltammetry technique indicated that these complexes behave as quasi-reversible electroactive species. Both complexes were successfully applied as catalysts in the oxidation of thioanisol to the corresponding sulfoxide in acetonitrile and in the presence of H_2O_2 .

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Appendix A. Supplementary data

CCDC 813641 and 898183 contains the supplementary crystallographic data for 1 and 2. These 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.2013.11.020.

References

- [1] M.V. Kirillova, M.L. Kuznetsov, J.A.L. da Silva, M.F.C.G. da Silva, J.J.R.F. da Silva, A.J.L. Pombeiro, Chem. Eur. J. 14 (2008) 1828.
- [2] P. Noblio, M. Vieites, B.S. Prarajòn-Costa, E.J. Baran, H. Cerecetto, P. Draper, M. Gonzåles, O. Piro, E.E. Castellano, A. Azqueta, L. de Ceráin, A. Monge-Vega, D. Gambino, J. Inorg. Biochem. 99 (2005) 443.
- [3] D. Rehder, J.C. Pessoa, C.F. Geraldes, J. Biol. Inorg. Chem. 7 (2002) 675.
- [4] S.A. Dikanov, B.D. Liboiron, C. Orvig, J. Am. Chem. Soc. 124 (2002) 2969.
- [5] J.H. McNeill, V.G. Yuen, H.R. Hoveyda, C. Orvig, J. Med. Chem. 35 (1992) 1489. [6] R. Liasko, T.A. Kabanos, S. Karkabounus, M. Malamas, J.A. Tasiopoulos, D.
- Stefanou, P. Collery, A. Evangelou, Anticancer Res. 18 (1998) 3609. [7] A. Butler, J.V. Walker, Chem. Rev. 93 (1993) 1937.
- M.J.M. Campbell, Coord. Chem. Rev. 15 (1975) 279.
- [9] R. Wever, H. Hemrika, in: J.O. Nriagu (Ed.), Vanadium in the Environment. Part 1. Chemistry and Biochemistry, Wiley, New York, 1997, p. 309.
- [10] A. Pohlmann, S. Nica, T.K.K. Luong, W. Plass, Inorg. Chem. Commun. (2005) 289
- [11] M. Schulz, R. Debel, H. Gorls, W. Plass, M. Westerhausen, Inorg. Chim. Acta 365 (2011) 349.
- [12] M. Weyand, H.J. Hecht, M. Kieb, M.F. Liand, H. Vilter, D. Schomburg, J. Mol. Biol. 293 (1999) 595.
- [13] S. Macedo-Ribeiro, W. Hemrika, R. Renirie, R. Wever, A. Messerschmidt, J. Biol. Inorg. Chem. 4 (1999) 209.
- [14] C. Wikete, P. Wu, G. Zampella, L.D. Gioia, G. Licini, D. Rehder, Inorg. Chem. 46 2007) 196
- [15] Hernández-Molina, A. Mederos, in: J.A. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II, vol. 1, Elsevier, Amsterdam, 2004, p. 411.
- [16] M. Andruh, F. Tuna, in: M. A. Cato (Ed.), Focus on Organometallic Chemistry Research, Nova Publishers, Hauppauge, 2005, p. 144.
- [17] W. Plass, Coord. Chem. Rev. 237 (2003) 205.

- [18] M.R. Maurva, S. Khurana, C. Schulzke, D. Rehder, Eur. J. Inorg, Chem. (2001) 779
- [19] W. Plass, A. Pohlmann, H.P. Yozgatli, J. Inorg. Biochem. 80 (2000) 181.
- [20] S. Nica, A. Pohlmann, W. Plass, Eur. J. Inorg. Chem. (2005) 2032.
- [21] M.U. Anwar, K.V. Shuvaev, L.N. Dawe, L.K. Thompson, Inorg. Chem. 50 (2011) 12141.
- [22] X.-S. Gao, J.-T. Wang, Inorg. Chim. Acta 386 (2012) 1.
- [23] (a) C. He, X. Wu, J. Kong, T. Liu, X. Zhang, C. Duan, Chem. Commun. 48 (2012) à290;
 - (b) Z. He, C. He, E.-Q. Gao, Z.-M. Wang, X.-F. Yang, C.-S. Liao, C.-H. Yan, Inorg. Chem. 42 (2003) 2206;
 - (c) H. Hosseini-Monfared, M. Vahedpour, M.M. Yeganeh, M. Ghorbanloo, P. Mayer, C. Janiak, Dalton Trans. 40 (2011) 1286;
 - (d) C.-Y. Niu, B.-L. Wu, X.-S. Wan, H.-Y. Zhang, H.-Q. Zhang, Mol. Struct. 973 (2010) 194;
- (e) D.S. Raja, N.S.P. Bhuvanesh, K. Natarajan, Eur. J. Med. Chem. 47 (2012) 73. [24] (a) L.K. Thompson, T.L. Kelly, L.N. Dawe, H. Grove, Inorg. Chem. 43 (2004) 7605
 - (b) L. Zhao, C.J. Matthews, L.K. Thompson, S.L. Heath, Chem. Commun. (2000) 265;
 - (c) Y. Chen, J. Dou, D. Li, S. Wang, Inorg. Chem. Commun. 13 (2010) 167;
 - (d) Hung Huy Nguyen, Polyhedron 28 (2009) 3945.
- [25] (a) D. Senthil Raja, N.S.P. Bhuvanesh, K. Natarajan, Eur. J. Med. Chem. 47 (2012) 73;
- (b) P. Singh, A.K. Singh, V.P. Singh, Polyhedron 65 (2013) 73. [26] (a) R. Bikas, H. Hosseini-Monfared, T. Lis, M. Siczek, Inorg. Chem. Commun. 15 (2012) 151;
 - (b) H. Hosseini-Monfared, R. Bikas, M. Siczek, T. Lis, R. Szymczak, P. Aleshkevych, Inorg. Chem. Commun. 35 (2013) 172;
 - (c) R. Bikas, H. Hosseini-Monfared, G. Zoppellaro, R. Herchel, J. Tucek, A.M. Owczarzak, M. Kubicki, R. Zboril, Dalton Trans. 42 (2013) 2803;
 - (d) H. Hosseini-Monfared, R. Bikas, R. Szymczak, P. Aleshkevych, A.M. Owczarzak, M. Kubicki, Polyhedron 63 (2013) 74;
 - (e) R. Bikas, H. Hosseini-Monfared, M. Siczek, A. Gutierrez, M.S. Krawczyk, T. Lis, Polyhedron 67 (2014) 396.
- [27] (a) L.-J. Yu, R. Pang, S. Tao, H.-T. Yang, D.-Y. Wu, Z.-Q. Tian, J. Phys. Chem. A 117 (2013) 4286:
- (b) A.S. Ozen, P. Doruker, V. Aviyente, J. Phys. Chem. A 111 (2007) 13506. [28] (a) H. Hosseini-Monfared, H. Falakian, R. Bikas, P. Mayer, Inorg. Chim. Acta 394
- (2013) 526; (b) H. Hosseini-Monfared, R. Bikas, J. Sanchiz, T. Lis, M. Siczek, J. Tucek, R.
- Zboril, P. Mayer, Polyhedron 61 (2013) 45.
- [29] H. Hosseini-Monfared, R. Bikas, P. Mayer, Inorg. Chim. Acta 363 (2010) 2574. [30] J.M. Seminario (Ed.), Density Functional Theory, Adv. Quantum Chem, vol. 33, Academic, San Diego, 1998.
- [31] G.M. Sheldrick, Acta Crystallogr., Sect A 64 (2008) 112.
- [32] A. Altomare, G. Cascarano, C. Giacovazzo, J. Appl. Crystallogr. 26 (1993) 343.
- [33] C.J. Christopher, Essentials of Computational Chemistry, Chichester, John Wiley & Sons Ltd., 2002. p. 153.
- [34] A. Szabo, N. Ostlund, Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory, McGraw-Hill Inc., New York, 1989.
- [35] M.E. Casida, Recent developments and applications in modern density functional theory, in: J.M. Seminario (Ed.), Theor. Comput. Chem., vol. 4, Elsevier, Amsterdam, 1996.
- [36] GAUSSIAN 03, Revision B.03, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, T. Vreven, Jr., K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. K. AyalaMorokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, D.R.L. Martin, J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, GAUSSIAN Inc., Pittsburgh, PA, 2003.
- [37] F. Biegler-Konig, J. Schoenbohm, AIM2000, 2.0 ed, Buro fur Innovative Software, Bielefeld, Germany, 2002.
- [38] R.T. Conley, Infrared Spectroscopy, Allyn & Bacon, Boston, 1966.
- [39] A.B.P. Lever, Inorganic Electronic Spectroscopy, second ed., Elsevier, Amsterdam, 1984.
- [40] S. Mondal, S. Dutta, A. Chakravorty, J. Chem. Soc., Dalton Trans. (1995) 1115.
- [41] J. Chakravarty, S. Dutta, A. Dey, A. Chakravorty, J. Chem. Soc., Dalton Trans.
- 1994) 557.
- [42] F.A. Walker, R.L. Carlin, P.H. Rieger, J. Chem. Phys. 45 (1966) 4181.
- [43] C. Janiak, J. Chem. Soc., Dalton Trans. (2000) 3885. [44] J.T. Lei, Y.X. Jiang, L.Y. Tao, S.S. Huang, H.L. Zhang, Acta Crystallogr., Sect. E 64 (2008) 0909
- [45] W.Y. Liu, Y.Z. Li, Acta Crystallogr., Sect. E 60 (2004) o694.
- [46] J.A. Fernández, P. Miró, J. Bonet-Ávalos, C. Bo, J.M. Poblet, Inorg. Chim. Acta 363 (2010) 4368
- [47] P. Politzer, D.G. Truhlar (Eds.), Chemical Application of Atomic and Molecular Electrostatic Potentials, Plenum, New York, 1981.
- [48] J.A. Fernandez, X. Lopez, J.M. Poblet, J. Mol. Catal. A: Chem. 262 (2007).

- [49] A. Lahiri, J. Ulicny, A. Laaksonen, Int. J. Mol. Sci. 5 (2004) 75.
 [50] R.F.W. Bader, Chem. Rev. 91 (1991) 893.
 [51] P.L.A. Popelier, Atoms in Molecules: An Introduction, Pearson Education, Harlow, 2000.
- [52] R.F.W. Bader, J. Phys. Chem. A 102 (1998) 7314.
- [53] H. Hosseini-Monfared, Z. Kalantari, M.A. Kamyabi, C. Janiak, Z. Anorg. Allg. Chem. 633 (2007) 1945.
- [54] (a) G. Romanowski, J. Kira, M. Wera, Polyhedron 67 (2014) 529;
 (b) G. Romanowski, T. Lis, Inorg. Chim. Acta 394 (2013) 627;

- (c) S.M. Islam, A.S. Roy, P. Mondal, J. Mol. Catal. A: Chem. 358 (2012) 38;
 (d) G. Romanowski, J. Kira, Polyhedron 53 (2013) 172.
 [55] (a) N. Asghari Lalami, H. Hosseini-Monfared, H. Noei, P. Mayer, Transition Met.
 - (b) H. Hosseini-Monfared, N. Asghari-Lalami, A. Pazio, K. Wozniak, C. Janiak, Inorg. Chim. Acta 406 (2013) 241;
 (c) H. Hosseini-Monfared, S. Alavi, A. Farrokhi, M. Vahedpour, P. Mayer,
 - Polyhedron 30 (2011) 1842.