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New oxidovanadium(V) complexes of the cation [VO]³⁺: Synthesis, structural characterization and DFT studies

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ABSTRACT

5-Tert-butyl-(3-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-ylimino)methyl)-2-hydroxybenzaldehyde (L₁), (4-tert-butyl-2-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-ylimino)methyl)-6-(dimethoxymethyl) phenol (L₂) and (2-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-ylimino)methyl)-6-methoxyphenol (L₃), react with vanadyl acetylacetonate to give the vanadium(V) complexes $[VO(L_1-3H^+)]_2$ -dmso, $[VO(L_2-3H^+)]_2$ and $[VO(L_3-3H^+)]_2$ -dmso. All complexes present the vanadium(V) center as the less common $[VO]^{3+}$ cation. The structural features of the title compounds, specially the occurrence of supramolecular assemblies supported by bifurcated and trifurcated hydrogen bonding are discussed, as well as DFT studies and HOMO–LUMO energy gaps. Calculated spatial maps of the Fukui functions, $f^+(r)$ and $f^-(r)$, are also presented and discussed.

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1. Introduction

Vanadium(IV) occurs as the highly stable vanadyl dication $[VO]^{2+}$ or as vanadium dioxide, VO_2 . While vanadium(V) is well known as $[VO_2]^+$, the existence of $[VO]^{3+}$ has been reported many times [1–6]. Oxidovanadium compounds with unlike oxidation states have been extensively studied in different fields of bioinor-ganic chemistry: the intriguing discovery that some nitrogenases display a cofactor in which molybdenum is replaced by vanadium or iron has stimulated widespread research into nitrogenase [7,8]; vanadium plays also an important role in the halogenation of organic substrates [9], and in the natural occurring Amavadin (shown in Fig. 1), a vanadium-containing anion found in three species of poisonous *Amanita* mushrooms: *A. muscaria, A. regalis* and *A. velatipes*, first extracted in 1972 [10]. The tunichromes, in turn, constitute a series of vanadium compounds isolated from the blood cells of the ascidians, marine invertebrates [11].

Vanadium-containing compounds have also revealed a great potential as inhibitors of chemically-induced tumors in test animals and cell cultures *in vitro*, being efficient, for example, in the treatment of leukemia, breast adenocarcinoma and Ehrlich tumors in murines, as well as in human lung, breast, ovarian, testicular, renal, gastrointestinal, nasopharyngeal and HEp-2 carcinomas [13– 17]. Mimetic complexes of dioxidovanadium(V), VO₂⁺ have been reported in the understanding of the rules of vanadium-bromoperoxidase [18], in the molecular mechanism of vanadium transport in ascidians [19] and, more recently, as highly efficient and reusable catalyst [20].

Schiff bases, in the other hand, have been used extensively as ligands in the coordination chemistry [21,22]. These compounds can show a highly suitable applicability regarding antitumor activities [23], photochromism [24] and thermochomism [25] by proton displacement between the hydroxyl O atom and the imine N atom. Specifically 2-hydroxy Schiff base ligands are of interest, mainly due to the existence of $O-H\cdots N$ and $N-H\cdots O$ hydrogen bonds as models for the study of keto–enol tautomerism [26–28]. Structurally, Schiff bases derived from salicylaldehyde generally exist in the phenol-imine form [29,30], and sometimes enamine or keto tautomer, and a zwitterionic structure with a longer N⁺–H bond [31]. Tris(hydroximethyl)amino methane (TRIS) has been widely used in biochemistry and molecular biology as a component of buffer solutions [32]. More recently, TRIS has been used also in medicine against metabolic acidosis in acute lung injury [32].

Therefore, we have focused our attention in studies on the coordination chemistry of vanadium(V) with such ligands. The present work describes a new synthetic route for the preparation of three new complexes of vanadium(V), as well as their structural characterization, spectroscopy, and treatment in the view of the density functional theory (DFT). The title compounds of this work are not unusual because of their syntheses or even due to structural specifities. They flee from known standards with respect to oxidovanadium compounds, since, as we will see, vanadium(V) appears in form

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Fig. 1. Structure of Amavadin, reported by Garner et al. [12].

of the uncommon cation $[VO]^{3+}$, instead of the more frequent dioxidovanadium species $[VO_2]^+$.

2. Experimental

2.1. X- ray crystallography

Data were collected with a Bruker APEX II CCD area-detector diffractometer and graphite-monochromatized Mo K α radiation. The structures of **1**, **2** and **3** were solved by direct methods using SHELXS-97 [33]. Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinements were carried out with the SHELXL-97 package [34]. All refinements were made by full-matrix least-squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were included in the refinement in calculated positions. Drawings were made with the DIAMOND for Windows [35]. Crystal data and more details of the data collections and refinements are contained in Table 1.

2.2. Physical measurements

IR spectra were measured as KBr pellets on a Shimadzu FTIRspectrometer in the 4000–400 cm⁻¹ region. ¹H NMR spectra for the ligands 1 and 2 were acquired on a Bruker DPX 400 (¹H at 400.13 MHz) in DMSO-*d*₆/TMS (DMSO, dimethyl sulfoxide; TMS, tetramethylsilane) solutions at 298 K. Abbreviations used for the reported ¹H NMR spectra are as follows: s, singlet; d, doublet and br, broad.

2.3. Computational details

First principles calculations based on the density functional theory (DFT) have been performed using the GAUSSIAN 09 package [36]. The hybrid B3LYP functional was employed to the exchange and correlation functional [37], and the molecular orbitals were described using the 6-31+G(d,p) basis set [38]. Infrared vibrational frequency calculations have been performed for the isolated molecules forming the molecular crystals at the geometries directly taken from the crystallographic X-ray data. These non-optimized geometries are determined not to be true local minima. Geometry optimizations were then performed and the obtained geometries were verified to exhibit only real infrared frequencies. The HOMO and LUMO orbitals of each studied molecule at the equilibrium geometries are then visualized using the GaussView 5 package [39].

2.4. Synthesis of 5-tert-butyl-3-(1,3-dihydroxy-2-(hydroxymethyl) propan-2-ylimino)methyl)-2-hydroxybenzaldehyde (L₁)

TRIS (0.121 g, 1 mmol), dissolved in 10 ml of anhydrous methanol, was mixed with 0.206 g (1 mmol) of 5-(1,1-dimethylethyl)-2hydroxy-1,3-benzenedicarboxaldehyde. The yellow solution was stirred by 1 h under Ar atmosphere. The yellow precipitate was removed by filtration. The slow evaporation of the mother solution yielded yellow crystals. Yield: 84%.

Properties: yellow crystals. Melting point: $182-184 \,^{\circ}$ C. *Anal.* Calc. C, 65.36; H, 5.83; N, 16.34. Found: C, 65.02; H, 5.39; N, 16.46%. IR (KBr, cm⁻¹): 3440 [shoulder, v(O-H)]; 2959 [weak, v(C-H)]; 1680 [strong, v(C=O)]; 1638 [strong, v(C=N)]; 1237 [middle, v(C-N)]; 1051 [strong, $v(C-O)_{alkoh}$].

¹H NMR (400 MHz, DMSO-*d*₆): δ 10.37 (s, 1H, CHO); 8.61 (s, 1H, CHN); 7.78 (d, 1H, ${}^{1}J_{HH}$ = 3 Hz, ar); 7.73 (d, 1H, ${}^{1}J_{HH}$ = 3 Hz, ar); 4.97 (br, 3H, OH); 3.68 (s, 6H, CH₂); 1.27 (s, 9H, CH₃).

2.5. Synthesis of 4-tert-butyl-2-(1,3-dihydroxy-2-(hydroxymethyl) propan-2-ylimino)methyl)-6-(dimethoxymethyl) phenol (L_2)

TRIS (0.121 g, 1 mmol), dissolved in 10 ml of anhydrous methanol, was mixed with 0.103 g (0.5 mmol) of 5-(1,1-dimethylethyl)-2-hydroxy-1,3-benzenedicarboxaldehyde. The bright yellow solution was stirred by 1 h under Ar atmosphere. After evaporation of the solvent the oily product was recrystallized in a mixture of methanol with 5% DMSO, resulting a yellow solid. Yield: 78%.

Properties: oily, yellow-orange substance. *Anal.* Calc. C, 65.36; H, 5.83; N, 16.34. Found: C, 65.02; H, 5.39; N, 16.46%. IR (KBr, cm⁻¹): 3396 [sh, v(O–H)]; 2956 [w, v(NC–H)]; 1634 [s, v(C=N)]; 1236 [m, v(C–N)]; 1049 [s, v(C–O)_{alkoh}]. ¹H NMR (400 MHz, DMSO-*d*₆): *δ* 8.56 (s, 1H, CHN); 7.50 (s, 1H, ar); 7.33 (s, 1H, ar); 5.58 (s, 1H, CH); 4.59 (br, 3H, OH); 3.64 (s, 12H, CH₂ + OCH₃); 1.27 (s, 9H, CH₃).

2.6. Synthesis of (2-(1,3-dihydroxy-2-(hydroxymethyl))propan-2-ylimino)methyl)-6-methoxyphenol (L_3)

 L_3 was prepared starting from *o*-vanillin, with basis on literature methods [3]. TRIS (0.121 g, 1 mmol), dissolved in 10 ml of anhydrous methanol, was mixed with 0.150 g (1 mmol) of *o*-vanillin. The bright yellow solution was stirred by 1 h under Ar atmosphere. The slow evaporation of the solvent led to the formation of a crystalline yellow solid. Yield: 93%.

Properties: yellow crystalline substance. *Anal.* Calc. C, 56.47; H, 6.66; N, 5.49. Found: C, 56.42; H, 6.69; N, 5.46%. IR (KBr, cm⁻¹): 3375 [sh, v(O–H)]; 2959 [w, v(C–H)]; 1638 [s, v(C=N)]; 1237 [m, v(C–N)]; 1051 [s, v(C–O)_{alkoh}].

2.7. Synthesis of $[VO(L_1-3H^+)]_2 \cdot dmso(1)$

 L_1 (0.2 mmol, 61.8 mg) was dissolved in 8 ml of methanol and mixed with 0.1 mmol (27.9 mg) of 95% vanadyl acetylacetonate. The mixture was stirred for 1.5 h at 100 °C. The precipitate was removed by filtration and after few days the solvent evaporation yielded orange crystals. Yield: 45%.

Properties: deep yellow, irregular crystals. Melting point: 182–184 °C. *Anal.* Calc. for $C_{18}H_{26}NO_7SV$ (451.40): C, 65.36; H, 5.83; N, 16.34. Found: C, 65.02; H, 5.39; N, 16.46%. IR (KBr, cm⁻¹): 3431 [sh, v(O-H)]; 2924 [w, v(C-H)]; 1678 [s, v(C=O)]; 1630 [s, v(C=N)]; 1243 [m, v(C-N)]; 1045 [m, $\delta(S=O)_{dmso}$]; 1018 [s, $v(C-O)_{alkoh}$]; 955 [m, $v(V=O)_{alkoh}$]; 750 [w, $v(V=O_2)_{ass}$]; 560 [m, $v(C=O_2)_{sym}$].

2.8. Synthesis of $[VO(L_2-3H^+)]_2$ (2)

 L_2 (0.1 mmol, 40 mg) was dissolved in 8 ml of methanol and mixed with 0.1 mmol (27.9 mg) of 95% vanadyl acetylacetonate. The mixture was stirred for 2 h at 100 °C. The precipitate was removed by filtration and after 45 days the solvent evaporation yielded orange crystals. Yield: 20%.

Properties: orange, blade-forming crystals. Melting point: 182– 184 °C. Anal. Calc. for $C_{18}H_{26}NO_7V$ (419.34): C, 65.36; H, 5.83; N, Table 1

Crystal data and structure refinement for **1**, **2** and **3**.

Complex	1	2	3
Empirical formula	C ₁₈ H ₂₆ NO ₇ SV	C ₁₈ H ₂₆ NO ₇ V	C14H20NO7SV
Formula weight	451.40	419.34	397.31
<i>T</i> (K)	293(2)	293(2)	293(2)
Radiation, λ (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic
Space group	ΡĪ	$P2_1/c$	$P2_1/c$
Unit cell dimensions			
a (Å)	10.2553(11)	15.9166(9)	11.9998(2)
b (Å)	11.3306(11)	10.7581(6)	11.6888(2)
c (Å)	11.4504(12)	11.8319(6)	12.4056(2)
α (°)	65.105(6)		
β (°)	67.165(6)	98.348(4)	110.4500(10)
γ (°)	64.966(6)		
$V(Å^3)$	1057.25(19)	2004.54(19)	1630.39(5)
Z, calculated density (g cm $^{-3}$)	2, 1.418	4, 1.390	4, 1.619
Absorption coefficient (mm ⁻¹)	0.606	0.533	0.773
F(000)	472	880	824
Crystal size (mm)	$0.278\times0.160\times0.127$	$0.256\times0.193\times0.088$	$0.164 \times 0.133 \times 0.075$
θ range (°)	2.63-27.16	2.57-25.76	1.81-27.13
Index ranges	$12 \leqslant h \leqslant 13$	$19 \leqslant h \leqslant 19$	$15 \leqslant h \leqslant 15$
	$14 \leqslant k \leqslant 14$	$13 \leq k \leq 12$	$14 \leqslant k \leqslant 14$
	$14 \leqslant l \leqslant 14$	$14 \leqslant l \leqslant 14$	15 <i>≤ l ≤</i> 15
Reflections collected	18244	15323	14943
Reflections unique	4647 $[R_{int} = 0.0426]$	$3797 [R_{int} = 0.0974]$	$3594 [R_{int} = 0.0714]$
Completeness to theta max.	98.9%	98.9%	99.9%
Absorption correction			
Maximum and minimum transmission	0.9652 and 0.9359	0.9325 and 0.8643	0.9608 and 0.8639
Refinement method	full-matrix	full-matrix	full-matrix
	least-squares on F ²	least-squares on F ²	least-squares on F ²
Data/restraints/parameters	4647/0/262	3797/18/280	3594/0/225
Goodness-of-fit (GOF) on F^2	1.080	1.002	1.056
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0661, wR_2 = 0.1741$	$R_1 = 0.0591, wR_2 = 0.1205$	$R_1 = 0.0458, wR_2 = 0.1130$
R indices (all data)	$R_1 = 0.0914, wR_2 = 0.1915$	$R_1 = 0.1313, wR_2 = 0.1481$	$R_1 = 0.0803, wR_2 = 0.1408$
Largest difference peak and hole (e $Å^{-3}$)	0.635 and 0.827	0.298 and 0.250	0.547 and -0.482

16.34. Found: C, 65.02; H, 5.39; N, 16.46%. IR (KBr, cm⁻¹): 3440 [sh, v(O-H)]; 2957 [w, v(NC-H)]; 1625 [s, v(C=N)]; 1292 [m, $v(C-N)^{-1}$]; 1108 [s, $v(C-O)_{hemiacetal}$]; 1054 [s, $v(C-O)_{alkoh}$]; 964 [m, $v(V=O)_{alkoh}$]; 670 [w, $v(V=O_{2})_{ass}$]; 567 [m, $v(C=O_{2})_{sym}$].

2.9. Synthesis of $[VO(L_3-3H^+)]_2 \cdot dmso(3)$

Complex **3** was prepared with basis on literature methods [9]. L_3 (0.1 mmol, 40 mg) was dissolved in 10 ml of methanol together with 0.1 mmol (27.9 mg) of 95% vanadyl acetylacetonate. The mixture was stirred for 1 h at 80 °C. The precipitate was removed by filtration and after 20 days the solvent evaporation yielded darkbrown crystals. Yield: 35%.

Properties: dark-brown crystalline substance. Melting point: 179–181 °C. *Anal.* Calc. for C₁₄H₂₀NO₇SV (397.31): C, 43.57; H, 4.74; N, 3.91. Found: C, 44.02; H, 4.39; N, 3.69%. IR (KBr, cm⁻¹): 3431 [sh, v(O-H)]; 2924 [w, v(C-H)]; 1630 [s, v(C=N)]; 1296 [m, v(C-N)]; 1052 [m, δ (S=O)_{dmso}]; 1018 [s, $v(C-O)_{alkoh}$]; 955 [m, $v(V=O)_{alkoh}$]; 750 [w, $v(V=O_{2})_{ass}$].

3. Results and discussion

3.1. Structure

Fig. 2 exhibits the dimeric arrangement with an inversion center of the binuclear complex $[VO(L_1-3H^*)]_2 \cdot dmso$ (1). Each polydentate ligand L_1 contributes with five coordination sites: two oxygen atoms – one of them with a bridge function – from the twofold deprotonated molecule of TRIS, a nitrogen (imine) bond and a deprotonated phenolic oxygen atom, as can be seen in Fig. 2. Thus, the two metal centers have a coordination number



Fig. 2. Molecular structure of complex **1** with 50% thermal (by DIAMOND [35]) ellipsoids. Symmetry operations used to generate equivalent atoms: (#) 1 - x, 1 - y, -z. For clarity, the hydrogen atoms are omitted.

six, giving a distorted octahedral geometry. This fact can be confirmed from the analysis of the angles formed between the atoms O4-V-O2, O5-V-N1 and O1-V-O4#, which are, respectively, $170.83(15)^{\circ}$, $167.38(11)^{\circ}$ and $153.02(11)^{\circ}$.

The distances of the V–O bonds around the atoms of vanadium (O2, O1, O4, O5 and O#4) range from 1.601(5) (the double bond character of the vanadyl oxygen) to 2.276(6) Å. On the other hand, the distance of the V–N1 bond is 2.130(9) Å. The values found are

Table 2	
Selected bond lengths (Å) and angles (°) for the compounds $\textbf{1},\textbf{2}$ and	3.

Complex 1		Complex 2	
Bond lengths and	l angles		
V-02	1.601(3)	V-01	1.590(3)
V=03 V=01	1.769(2)	V=03 V=02	1.781(3) 1.851(3)
V-04	1.894(2)	V-04	1.899(3)
V-N	2.131(3)	V-N	2.118(3)
V-04#1	2.276(2)	V-04#1	2.386(3)
05-C25	1.408(4)	04–C24 04 V#1	1.430(4)
04–C24 04–V#1	2.276(2)	04 - 04 = 04	1.323(5)
03–C23	1.406(5)	03–C23	1.417(4)
01-C1	1.323(4)	03-H3	0.8200
06–C61	1.194(5)	06–C61	1.411(5)
N = C21 N = C22	1.285(4)	N-C21 N-C22	1.286(5) 1 486(5)
07–S	1.521(3)	07-C61	1.382(5)
C18-S	1.766(5)		
C17–S	1.789(6)		
02-V-05	99.96(12)	01-V-05	101.83(14)
02-V-01	101.25(12)	01-V-02	104.04(15)
05 - V - 01	96.01(11) 98.05(12)	05 - V - 02	97.05(12) 99.58(13)
02-V-04 05-V-04	99.00(11)	01-V-04 05-V-04	94.91(12)
01-V-04	153.04(11)	02-V-04	150.63(12)
02-V-N	92.30(12)	01-V-N	90.41(13)
05–V–N	167.39(11)	05-V-N	166.52(14)
01-V-N 04-V-N	84.39(11) 76.16(10)	02-v-N 04-V-N	85.26(12) 77 30(12)
02-V-04#1	170.84(11)	01-V-04#1	170.96(12)
05-V-04#1	86.72(10)	05-V-04#1	85.23(11)
01-V-04#1	84.14(10)	04-V-04#1	73.95(11)
04-V-04#1 N_V_04#1	74.55(10) 80.78(10)	02-V-04#1 N_V_04#1	80.42(11) 82.06(11)
V-04-V#1	105.45(10)	V-04-V#1	106.05(11)
C21-N-C22	118.0(3)	C21-N-C22	119.4(3)
C21-N-V	128.2(2)	C21-N-V	126.3(3)
C22–N–V	113.6(2)	C1-02-V	137.3(3)
Complex 3			
Bond lengths and	l angles		1 603(2)
V-04			1.783(2)
V-02			1.871(2)
V-05			1.914(2)
V-N V 05#1			2.128(3)
S-07			1.504(3)
S-C13			1.776(4)
N-C8			1.294(4)
01-V-04			100.20(12)
01-V-02			102.14(12)
04 - v - 02 01 - v - 05			97.99(10) 97.61(11)
04-V-05			97.40(10)
02-V-05			152.31(10)
01-V-N			90.78(12)
04 - v - N 02 - V - N			107.89(11) 84.54(10)
05–V–N			75.91(10)
01-V-05#1			169.73(11)
04-V-05#1			85.98(9)
02-V-05#1 05-V-05#1			84.96(9) 73 31(9)
N–V–05#1			82.44(9)
V-05-V#1			106.69(9)
C8-N-V			127.6(2)

within the range of bond lengths of V–N and V–O expected, according to data of the literature [9]. Some selected bond lengths and angles of **1**, **2** and **3** are resumed in Table 2.

The molecule has numerous hydrogen interactions, some of them being associated with the solvate molecule of dimethylsulf-



Fig. 3. Section of the extended one-dimensional chain of the complex **1**. Symmetry operations used to generate equivalent atoms: (#) 2 - x, 1 - y, -z. For clarity, the hydrogen atoms not involved in secondary bonds (dashed lines) are omitted.

Secondary interactions: lengths (Å) and angles (°) for complex 1		Table 3
becondary interactions, lengths (1) and angles () for complex i	ions: lengths (Å) and angles (°) for complex 1.	Secondary interactions:

$\begin{array}{ccccccc} 02 \cdots H18c-C18 & 0.960(7) & 2.451(9) & 2.342(14) & 154.40(34) \\ 02\# \cdots H18b-C18 & 0.960(6) & 2.484(11) & 3.432(16) & 169.21(33) \\ H25b\# \cdots 06=C51 & 0.914(4) & 2.607(4) & 3.347(15) & 152.99(43) \\ H24a\# \cdots 06=C51 & 0.970(5) & 2.685(13) & 3.507(17) & 142.99(24) \\ \end{array}$	$(D-H\cdot\cdot\cdot A)^a$	D–H (Å)	H···A (Å)	$D \cdots A(Å)$	D−H···A (°)
	02…H18c-C18	0.960(7)	2.451(9)	2.342(14)	154.40(34)
	02#…H18b-C18	0.960(6)	2.484(11)	3.432(16)	169.21(33)
	H25b#…06=C51	0.914(4)	2.607(4)	3.347(15)	152.99(43)
	H24a#…06=C51	0.970(5)	2.685(13)	3.507(17)	142.99(24)

^a D, donor; A, acceptor.

oxide molecule. Fig. 3 allows the visualization of intermolecular $O2\cdots H-C$ secondary interactions in the *ab* plane, between the atoms $O2\cdots H18c-C18$ and $C18-H18b\cdots O2\#$. The $O2(\#)\cdots H-C$ angles and distances confirm that these intermolecular bonds support the growth of a supramolecular assembly of complex **1** along the crystallographic *a* axis (see Fig. 3, symmetry transformations used to generate equivalent atoms: (#) 2 - x, 1 - y, -z). The comparison of hydrogen secondary bonds for compound **1** is shown in Table 3.

In addition to these intermolecular interactions involving the solvate molecules, it is noteworthy that also along the *a* axis there is an expressive number of further bifurcated hydrogen bonding, as shown in Fig. 4 [40–44]. These secondary bonds are of electrostatic nature, but sometimes their nature can undergo variations. According to Desiraju and Steiner [44], for supramolecular organizations the directionality of the connection depends on the donor and the receiver, as is shown in Scheme 1.

The supramolecular organization depicted in Fig. 4 exemplifies the parameters shown in Scheme 1: for strong hydrogen bonds, the directionality of the receiver matches the geometry of the product obtained by the covalent bond of a hypothetical proton transfer reaction [45,46].

The adequate knowledge of the nature of hydrogen bonds and of the acceptor–receiver concept can provide a good basis for the



Fig. 4. Bifurcated hydrogen interactions in complex 1. Symmetry operations used to generate equivalent atoms: (#) 1 + x, -1 + y, z. For clarity, the hydrogen atoms not involved in secondary bonds (dashed lines) are omitted.



Scheme 1. Supramolecular arrangements and the geometric parameters for the hydrogen bond according to Desiraju and Steiner [44] (D, donor; R, receiver).

understanding of supramolecular assemblies and the crystal engineering of this kind of compound. Specifically, supramolecular synthons [47] based upon bifurcated and trifurcated hydrogen bonds involving these acceptor groups have been successfully described.

The dimeric structure of $[VO(L_2-3H^+)]_2$ (2), shown in Fig. 5, is similar to that of compound 1. The coordination of L_2 with VO³⁺ occurs through the deprotonated oxygen atoms O2, O5, μ -O4 and μ -O4#, as well as the nitrogen of the neutral imino ligand. The same inversion center of complex **1** was observed. The double, covalent V–O1 bond presents shorter distance (1.590(2) Å) than the coordinative ones V–O5 (1.781(1)), V–O2 (1.851(4)), V–O4 (1.899(1)), V–O4# (2.386(3)) and V–N (2.118(1) Å). This causes a distortion of the octahedral geometry of the vanadium(V) ion. The axial angle N–V–O5 measures 166.52°, thus, the binuclear complex **2** presents the same geometry of complex **1**, a distorted octahedral configuration. In the case of complex **2**, an interesting difference was observed in the substituted aldehyde (O6, see Fig. 2), with the formation of an *acetal* (C61, see Fig. 5).

The formation of an acetal group from the reaction between the aldehyde and methanol was confirmed by the ¹H NMR experiments. By comparing the ¹H NMR spectra of complexes **1** and **2** it is possible to observe in the spectrum of **2** the vanishing of the signal at 10.37 ppm for the aldehyde (present in the spectrum of **1**), and the appearance of a signal at 5.58 ppm for the CH group of the acetal. Furthermore, it has been also recorded an intensive signal at 3.64 ppm, corresponding to 12H, regarding the two methoxyl signals (6H) of each ligand.



Fig. 5. A representation of the molecular structure of complex **2**, generated by reflection of the asymmetric unit. Symmetry transformations used to generate equivalent atoms: # 1 - x, 2 - y, 1 - z. For clarity, the hydrogen atoms are omitted.



Scheme 2. Proposed mechanism for the formation of the acetal group in complex 2.

Hemiacetals result from addition of an alcohol's hydroxyl group to the carbon in the C=O bond. This kind of organic substituent represents an example of the dynamic covalent chemistry (DCC) and results from the introduction into molecules of bonds formed through reversible chemical reactions. To expand the possibilities of DCC it is necessary to explore other reversible reactions with controllable formation efficiency and exchange kinetics [48]. The hemiacetal groups are important species because they are efficient organic ligands for the achievement of a wide variety of 3d-metal clusters of high nuclearity with interesting optical and magnetic properties, as well as for the synthesis of actinide complexes. We propose the mechanism described further in Scheme 2 for the obtainment of this organic functions in complex **2** [49,50].

In $[VO(L_3-3H^+)]_2$ ·dmso (**3**), whose structure is depicted in Fig. 6, the V–O and V–N distances are not in disagreement with these distances in other analogue compounds: the V–O distances are 1.603(2) {V–O1}, 1.871(2) {V–O2}, 1.784(2) {V–O4}, 1.914(2) {V- μ -O5} and 2.270(2) Å {V- μ -O5#}, while the V–N distance is 2.129(5) Å (symmetry transformations used to generate equivalent atoms: # -x, -y, 2 - z). Complex **3** exhibits also a dinuclear (dimeric) oxidovanadium(V) structure, having an inversion center. Both vanadium atoms are in the center of distorted octahedral environments. From the three CH₂OH groups, one is free and the other two are bound to the metal center after deprotonation.

The single structure illustrated in Fig. 6 seems to be very similar to the other examples discussed in this work, but if we compare the hydrogen interactions between the V–O1 fragment and the neighboring molecules, it becomes clear that, unlike the first example, we have now the contribution of hydrogen bonds not only from the DMSO solvate, but also from C–H units, yielding a typical example of *trifurcated* hydrogen interactions [40,41], as shown in



Fig. 6. Molecular structure of the complex **3**. For clarity, the DMSO molecule is not displayed. Symmetry transformations used to generate equivalent atoms: # -x, -y, 2 - z. For clarity, the hydrogen atoms are omitted.



Fig. 7. DIAMOND plot of complex **3** with the atom numbering. The thermal ellipsoids are drawn at 50% probability level. Symmetry code for the generated atoms: # x, 0.5 - y, -0.5 + z; # 2 - x, 0.5 + y, 1.5 - z. For clarity, the hydrogen atoms not involved in secondary bonds (dashed lines) are omitted.

Fig. 7. Table 4 resumes the intermolecular secondary interactions of **3**.

3.2. DFT calculations

Fig. 8 shows the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals of the complexes **1**, **2** and **3**. It can be clearly seen that, independently of the substituent at the ortho position of the benzene ring (aldehyde, hemiacetal, and *o*vanillin), the frontier orbitals present similar character. The *Ci* point group symmetry of these molecules is also reflected at these (frontier) orbitals. The HOMO levels show greater contributions of π -like orbitals at the benzene rings at both sides of the molecule centers, with smaller contributions from *p*-orbitals at the N and O atoms close to the benzene rings. On the other hand, the LUMO

 Table 4

 Secondary interactions: lengths (Å) and angles (°) for complex 3.

$(D-H\cdots A)$	D-H (Å)	H···A (Å)	$D{\cdots}A~(\text{\AA})$	$D-H\cdots A$ (°)
O1…H13b#–C13#	0.960(5)	2.574(2)	3.418(5)	146.77(28)
O1…H8#–C8#	0.929(4)	2.476(3)	3.228(5)	138,24(23)
O1…H12b#2 –C12#2	0.991(3)	2.540(3)	3.524(4)	172.24(28)

orbitals are concentrated in the center of the molecules. The greater contributions of the LUMO orbitals come from *d*-orbitals of the vanadium atoms, with further significant contributions from the *p*-like orbitals of the O atoms around the V atoms. Such frontier orbitals characterize a ligand-metal CT transition for these kinds of compounds.

The calculated HOMO-LUMO energy gaps are: 3.43 eV (361.88 nm), 3.45 eV (359.78 nm), and 3.26 eV (380.75 nm), for the molecules containing aldehyde (1), hemiacetal (2), and methoxyl (of o-vanillin) (3) as substituents at the benzene rings, respectively. The closeness of the calculated gaps for the three molecules, all in the UV region, is related to the character of the frontier orbitals, which do not depend directly of the substituents.

The local version of the Hard and Soft Acids and Bases principle [51] has been used to investigate the nucleophilic and electrophilic centers of the three studied complex molecules. According to the conceptual density functional theory [52], the regioselective reactivity of a chemical system can be given by the local softness, S(r), which can be defined as [53]

$$S(r) = \left(\frac{\partial \rho(r)}{\partial \mu}\right)_{\nu(r)} = \left(\frac{\partial N}{\partial \mu}\right)_{\nu(r)} f(r) = \frac{f(r)}{\eta} = Sf(r),$$

where $\rho(r)$ represents the electronic density, μ is the chemical potential v(r) is the external potential, N is the total number of

electrons, f(r) is the Fukui function, with η and S being the global hardness an global softness of the system. From the equation above, one can see that the Fukui function is given as the derivative of the electronic density with respect to the total number of electrons for a fixed external potential

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})},$$

while the global hardness (the negative electronegativity) is defined by

$$\eta = \left(\frac{\partial N}{\partial \mu}\right)_{\nu(r)} = -\chi,$$

where γ is the electronegativity.

For chemical reactions in which the system exchanges an electron, the derivatives defining f(r) and η can be calculated by finite differences as

$$f^{+}(r) = \rho_{\nu,N+1}(r) - \rho_{\nu,N}(r)$$

$$f^{-}(r) = \rho_{\nu,N}(r) - \rho_{\nu,N-1}(r)$$

$$\eta = \frac{I - A}{2}$$

with *I* and *A* being the vertical ionization potential and electron affinity, respectively.

The Fukui functions $f^*(r)$ and $f^-(r)$ will give the regions at which the molecular system is most able to accommodate the addition and removal of an electron, respectively. Hence, large values of $f^*(r)$ will indicate the molecular regions most susceptible to nucleophilic attacks, while large $f^-(r)$ values will be associated with regions susceptible to electrophilic attacks.

We have performed total energy calculations for the three studied molecules at three different charge states, i.e., neutral, singly positively and negatively charged. All these calculations were



Fig. 8. Highest occupied (HOMO) in left column and the lowest unoccupied molecular orbitals (LUMO) in right column of the molecules, respectively, for compounds 1, 2 and 3.



Fig. 9. The calculated maps of the Fukui functions, $f^*(r)$ and $f^-(r)$. The highest values at the $f^*(r)$ maps, at the left column show the most reactive sites for nucleophilic attacks, i.e., the electrophilic centers of these molecules, whereas the highest values at the $f^-(r)$ maps, at the right column, show the nucleophilic centers of these molecules.

performed at the equilibrium geometries of the neutral charge state of the molecules. From these calculations we determined *I* and *A*, and consequently η , as well as spatial maps of the Fukui functions $f^{\pm}(r)$ (that are similar to the $s^{\pm}(r)$ maps).

The calculated values for the vertical ionization potentials/electronic affinities are 7.58/2.04, 6.92/1.37 and 6.79/1.29 eV, resulting also very similar global hardness values: 2.77, 2.78 and 2.75 eV for the molecules containing aldehyde, hemiacetal and methoxyl (ovanillin), respectively (complexes **1**, **2** and **3**). These global hardness values suggest that these three molecules will act similarly against electrophilic, nucleophilic or radical attacks.

The calculated maps of the Fukui functions, $f^{+}(r)$ and $f^{-}(r)$, are shown in Fig. 9. The highest values at the $f^{+}(r)$ maps, at the left column of Fig. 9, show the most reactive sites for nucleophilic attacks, i.e., the electrophilic centers of these molecules, whereas the highest values at the $f^{-}(r)$ maps, at the right column of Fig. 9, show the nucleophilic centers of these molecules.

The $f^*(r)$ maps show that the spatial localization of active electrophilic centers of these molecules resemble the respective LUMO orbitals, i.e., these molecules tend to receive electrons mainly through the V atoms, with smaller contributions from the O atoms close to the V atoms at the molecules. The nucleophilic centers of these molecules shown at the $f^-(r)$ maps, on the other hand, do not have the same information as the respective HOMO orbitals. Contrarily to the HOMO orbitals, which have great contributions from the benzene rings, the nucleophilic centers are located at the O atoms that connect the V atoms and the benzene rings. There

are other nucleophilic centers located at the C atoms near the butyl groups for the molecules containing the aldehyde and hemiacetal groups, and at the O atoms close to the o-vanillin group for the molecule containing this specific chemical group. It must be pointed out that comparison between experimentally determined and theoretically predicted quantities like IP (ionization potential) and EA (electronic affinity) would give a better account of the degree of accuracy of the used theoretical approach. However, we would like to stress that the experimental samples are crystals, not isolated molecules, and although they are molecular crystals, the crystalline environment will certainly influence the experimental values for work functions and electron affinities. It means that IPs and EAs obtained from calculations for isolated molecules would be of low predictive value in our case. Actually, one possible theoretical approach capable to take into account the influence of crystal fields on the properties of molecules in molecular crystals would be the use of polarizable continuum models (PCM) [54]. It would require the determination of the PCM parameters for each of the crystalline environments involving each molecular unit in the molecular crystals (which would be seen as continuum media). This, however, would be out of the scope of this paper. Furthermore, even if we decided to show the calculated vertical IP and EA values for each isolated molecule (which is an easy task once the equilibrium structures are already determined), we would need to compare them with results from direct and inverse photoemission spectroscopy measurements. Unfortunately, these techniques are not available in our laboratory nowadays.

We have described the synthesis and the structural characterization, together with DFT studies, of the three new oxidovanadium(V) complexes of the cation $[VO]^{3+}$, $[VO(L_1-3H^+)]_2 \cdot dmso$ (1), $[VO(L_2 (3H^+)_2$ (2) and $[VO(L_3-3H^+)_2]_2$ dmso (3), where L are different Schiff bases ligands (see Section 2). The reactions reported in this work corroborate also earlier literature statistics [55,56], that dibasic tridentate ligands prefer dimeric vanadium complexes. The oxidation of the starting reagent [VO]²⁺ from IV to V, assuming the chelated form [VO]³⁺, can be explained also with basis in results obtained by Rao [9], according to which the final presence of VO_2^+ or VO^{3+} dinuclear complexes depends upon the reaction conditions: vanadium exists in acidic solutions as VO₂⁺, and in highly alkaline medium as tetrahedral VO_4^{3-} [57]. It has been reported the formation of VO³⁺ and VO₂⁺ using the same ligand, under different experimental conditions, but without any X-ray structure [58]. Reactions performed [9] in neutral medium between $VO(acac)_2$ and H_3L^y (L = Schiff base ligand holding alkoxo group(s); $L^y = L^2$, L^7 , L^8) gave as products [VOL^y]₂, also, dimers of the core VO³⁺. The synthesis of a large variety of alkoxo-bound oxidovanadium(V) complexes using Schiff bases as ligands resulted in VO³⁺ and VO₂⁺ complexes, and the studies on their interconversions have shown that the addition of small amounts of acid converts VO₂⁺ to VO³⁺, but the reverse does not happen in the presence of base [9].

The results of DFT calculations show that the distribution of the electron density in the title complexes is very similar, also if compared with other molecules already synthesized by us. Such equalitarian distribution of electron density may reveal, among other consequences, a tendency for inhibition of the biological activity of certain enzymes, such as acetylcholine. This performance, however, deserves further systematic studies, before one can make any statements about it.

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Appendix A. Supplementary data

CCDC 856023, 856024, 856025 contain the supplementary crystallographic data for this paper. 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.

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