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Theoretical Studies on Oxovanadium(IV) Complexes with Sterically Crowded Schiff Base Ligands

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Abstract. Electronic structures of five oxovanadium(IV) complexes with sterically crowded Schiff base ligands are optimized by using density functional theory (DFT/B3LYP) method with LANL2DZ basis set. The studied complexes are [N,N'-ethylenebis(o-(tert-butyl-p-methylsalicylaldiminato)] oxovanadium (IV) (1), [N,N'-propanediylbis(o-(tert-butyl-p-methylsalicylaldiminato)] oxovanadium (IV) (2), bis(N-methylsalicylaldiminato) oxovanadium (IV) (3), bis (N-isopropyl-o-methylsalicylaldiminato) oxovanadium (IV) (4) and bis(N-methyl-o-(tert-butyl-p-methylsalicylaldiminato) oxovanadium (IV) (5). The structural parameters and stretching frequencies were obtained for five oxovanadium(IV) complexes. The calculated structural parameters show that the vanadium(IV) center is distorted square pyramidal (dsp) for complexes (1), (2) and distorted trigonal bipyramidal (dtbp) for complexes (3), (4) and (5). The excitation energies of complexes were obtained by using time-dependent density functional theory (TD-DFT/B3LYP) method with LANL2DZ basis set in dichloromethane solvent. The calculated excitation energies are in a good agreement with experimental datum for oxovanadium(IV) complexes. Frontier orbital energies (E_{LUMO} and E_{HOMO}), global hardness (η), softness (σ) and LUMO-HOMO energy gap (ΔE) were calculated to predict the antidiabetic effects of complexes. According to these quantum chemical parameters, antidiabetic effect ranking of the complexes were predicted as (1) > (2) > (5) > (3) > (4).

Keywords: Density functional calculations, oxovanadium(IV) complexes, Schiff base ligands, Quantum chemical parameters

Sterik Olarak Kalabalık Olan Schiff Baz Ligandlı Oxovanadyum(IV) Kompleksleri Üzerine Teorik Çalışmalar

Özet. Sterik olarak kalabalık olan Schiff baz ligandlı 5 oxovanadyum(IV) kompleksinin elektronik yapısı LANL2DZ temel setli yoğunluk fonsiyonel teori (DFT/B3LYP) kullanılarak optimize edildi. Çalışılan kompleksler [N,N'-etilenbis(o-(ter-butil-p-metilsalisilaldiminato)] oxovanadyum(IV) (1), [N,N'-propanedilbis(o-(ter-butil-p-metilsalisilaldiminato)] oxovanadyum(IV) (2), bis(N- metilsalisilaldiminato) oxovanadyum(IV) (3), bis(N-isopropil-o- metilsalisilaldiminato) oxovanadyum(IV) (4) ve bis(N-metil-o-(ter-butil-p- metilsalisilaldiminato) oxovanadyum(IV) (5) dir.5 oxovanadyum(IV) kompleksleri için yapısal parametreler ve gerilme frekansları elde edildi. Hesaplanmış yapısal parametreler vanadyum(IV) merkezinin kompleks (1) ve (2) de bozulmuş kare düzlem ve kompleks (3), (4) ve (5) te bozulmuş üçgen bipiramidal olduğunu gösterdi. Komplekslerin uyarılma enerjileri diklorometan çözücüsünde LANL2DZ temel setli zaman-bağımlı yoğunluk fonsiyonel teori kullanılarak elde edildi. Hesaplanan uyarılma enerjileri deneysel veriler ile iyi bir uyum içindedir. Öncü orbital enerjileri (E_{LUMO} ve E_{HOMO}), sertlik (η), yumuşaklık (σ) ve LUMO-HOMO enerji boşluğu (ΔE) komplekslerin antidiyabetik etkisinin öngörülmesi için hesaplandı. Bu kuantum kimyasal parametrelere göre komplekslerin antidiyabetik etki sıralaması (1) > (2) > (5) > (3) > (4) olarak öngörüldü.

Anahtar kelimeler: Yoğunluk Fonksiyon Hesaplamaları, Oxovanadyum(IV) kompleksleri, Schiff baz ligandları, Kuantum kimyasal parametreler

1. INTRODUCTION

Several metal ions and their complexes exhibit antidiabetic effects. Elemental vanadium plays an important role in many environmental and biological processes [1]. Coordination chemistry of vanadium has become of great interest due to the presence of vanadium in enzymatic systems[2, 3]. Elemental vanadium and oxovanadium(IV) complexes have interesting pharmacological properties which make

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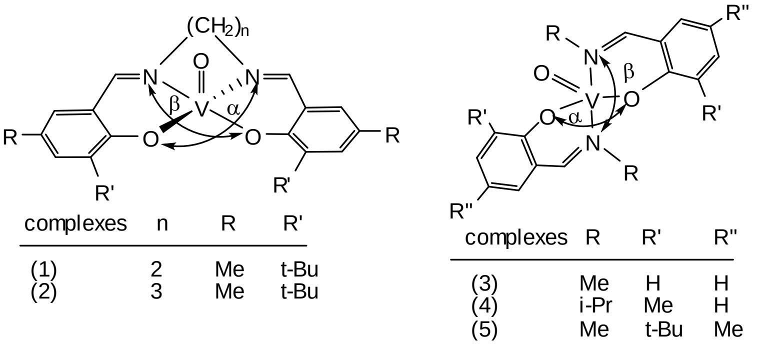
them promising agents in the treatment of diabetes mellitus [4]. Efficiency of the vanadium complexes with organic ligand as drug is more than its inorganic salts [5]. Some pharmacological properties of oxovanadium(IV) complexes are high-hypoglycemic efficacy and non-toxic nature. These properties of oxovanadium(IV) complexes make promising as insulin enhancing agents [6-8].

Sakurai et al. suggested that bis(picolinato)oxovanadium(IV), [VO(pic)$_2$], has a strong insulin-mimetic effect in an in vitro system. This complex was effective in normalizing the blood glucose of STZ-rats when given by daily i.p. injections or oral administration [9]. Bis(3-mehylpicalinato)oxovanadium(IV), [VO(3mpa)$_2$], and bis(6-methylpicolinato) oxovanadium(IV), [VO(6mpa)$_2$], were synthesized by Sakurai et al. and insulin-mimetic activities of these complexes was obtained in the order VO(6mpa)$_2$>VO(pic)$_2$>VO(3mpa)$_2$ [10-12].

The stereochemistry of vanadium complexes have been studied by Carrano et al. depending on the metal environment. According to Carrano proposal, provided that no significant steric constraints, five-coordinate vanadium(V) complexes have square pyramidal geometries [13-17] and six-coordinate vanadium(V) complexes constitute octahedral geometries [18-21]. Five-coordinate oxovanadium(IV) complexes containing sterically crowded Schiff base ligands were synthesized by Cornman et al. in 1997. Electronic structures, V=O stretching frequencies and electronic spectra were determined for mentioned complexes [22]. Schematic structure of mentioned complexes are given in Fig.1.



complexes	n	R	R'
(1)	2	Me	t-Bu
(2)	3	Me	t-Bu

complexes	R	R'	R"
(3)	Me	H	H
(4)	i-Pr	Me	H
(5)	Me	t-Bu	Me

Fig. 1. The schematic structures of oxovanadium(IV) complexes and the defining of α and β angles

Antidiabetic effects of many oxovanadium(IV) complex have been previously studied [23-28]. The purpose of this theoretical study is to determine the optimized complex structures, to calculate the vibrational and electronic spectra and to discuss the antidiabetic effects of complexes by using the quantum chemical parameters such as the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), the energy gap ($\Delta E_{LUMO-HOMO}$), hardness (η) and softness (σ).

2. CALCULATION METHOD

The input files of the oxovanadium(IV) complexes were prepared with GaussView 5.0.8 [29]. All calculations were made by using Gaussian 09 Revision-A.02 [30]. All complexes were fully optimized by using DFT/B3LYP method with LANL2DZ [31] basis sets in gas phase. B3LYP combination of exchange and correlation functional [32, 33] in DFT is applied to all the electronic structure calculations. LANL2DZ basis set is used for post-third-row atoms. It uses effective core potentials (ECP) in calculations [34]. The vibrational frequency analyses indicate that optimized structures of all complexes are at stationary points corresponding to local minima without imaginary frequencies. Single point energy calculations were performed to calculate quantum chemical parameters at B3LYP/cc-pVTZ level.

In the second step, electronic excitation energies were calculated for the optimized complexes by using TD-DFT/B3LYP method with LANL2DZ basis set in CH_2Cl_2 solvent. The interactions of solute-solvent were taken into account by the conductor-like polarizable continuum model (CPCM). According to this model, the solute molecule is placed into a cavity surrounded by the solvent considered as a continuum medium of a certain dielectric constant. The charge distribution of the solute polarizes the dielectric continuum, which creates an electrostatic field that in turn polarizes the solute [35]. The TD-DFT approach had been demonstrated to be reliable for calculating spectra properties of many transition metal complexes [36-38].

3. RESULT and DISCUSSION

3.1 Molecular Structures

Fig. 2. Shows the optimized molecular structures and atomic numbering scheme for complex (1) and (2).

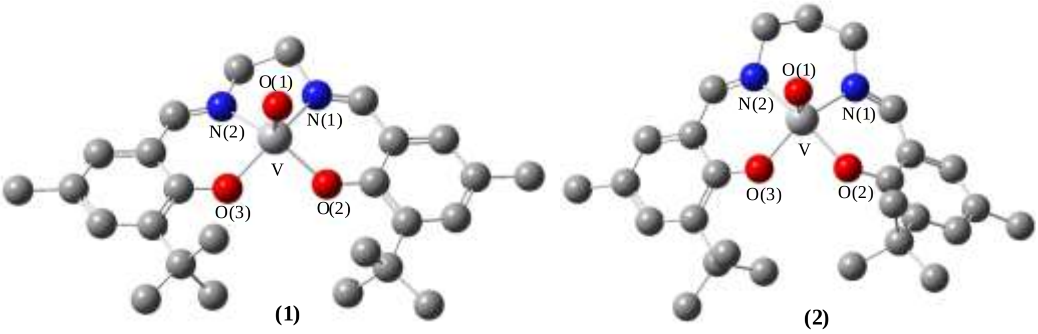


Fig. 2. Optimized molecular structures and atomic numbering scheme for complex **(1)** and **(2)**. Hydrogen atoms were omitted for clarity.

Fig. 2 represents the vanadium(IV) ion with N2O3 coordination environment for complex **(1)** and **(2)**. In these structures the donor atoms (two nitrogen and two oxygen) of two bidentate Schiff base ligands coordinate with vanadium(IV) on equatorial plane and the last oxygen atom, which is oxo ligand, coordinates with vanadium(IV) on axial position. Nitrogen atoms on the equatorial plane are almost trans to oxygen atoms. The selected optimized geometric parameters were listed in Table 1.

Table 1. The calculated and experimental parameters for complex (1) and (2).

	Complex **(1)**		Complex **(2)**	
Bond Length (Å)	Calc.	Exp^a.	Calc.	Exp^a.
V - N(1)	2.0608	2.0589	2.0782	2.095
V - N(2)	2.0648	2.0710	2.0996	2.100
V - O(1)	1.6048	1.5913	1.6038	1.581
V - O(2)	1.9247	1.9226	1.9592	1.937
V - O(3)	1.9393	1.9351	1.9287	1.954
Bond Angle (˚)				
N(1) - V - O(1)	101.02	103.01	106.83	106.45

N(1) - V - O(2)	85.35	86.06	85.23	85.45
N(1) - V - O(3)	152.05	150.65	133.51	140.49
N(1) - V - N(2)	78.91	77.72	88.88	89.21
N(2) - V - O(1)	107.56	111.08	95.14	97.97
N(2) - V - O(2)	138.71	135.21	161.12	158.26
N(2) - V - O(3)	85.68	86.18	84.49	86.90
O(1) - V - O(2)	112.84	113.18	103.73	103.65
O(1) - V - O(3)	105.83	105.65	119.56	113.06
O(2) - V - O(3)	91.24	88.44	86.61	84.03

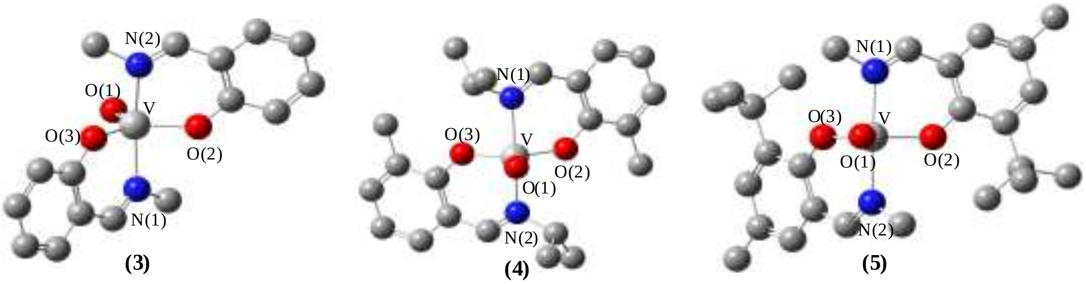
[a]*Experimental values are taken from Ref. 22*

As can be seen from Table 1, the calculated bond lengths and bond angles are in a good agreement with experimental values. Approximately V-O(1) bond distances are 1.60 Å in both complexes. V-O(2) and V-O(3) bond lengths are about 1.93 Å for each two complexes. The average of V-N(1), V-N(2) bond distances is 2.07 Å in both complexes. The biggest difference between experimental and theoretical bond lengths for complex (1) arises at V-O(1) (0.0135 Å) and for complex (2) at V-O(3) (0.0253 Å). The biggest difference between experimental and theoretical bond angle for complex (1) appears at N(2)-V-O(1) (3.52˚) and for complex (2) at N(1)-V-O(3) (6.98˚). Molecular geometries of complexes are predicted by calculating τ values from Eq. 1 [22].

$$\tau = \frac{\beta - \alpha}{60} \qquad (1)$$

where α and β are bond angles defined in Fig 1. τ value must be equal to 1 for ideal trigonal bipyramidal and must be equal to 0 for ideal square pyramidal. For the complexes under study, we described the geometry with $0<\tau<0.5$ as dsp, while the geometry with $0.5<\tau<1$ as dtbp. τ value is obtained as 0.22 theoretically from α[N(2)-V-O(2)]=138.71 and β[(N(1)-V-O(3)]=152.05^0 angles for complex (1). In the same way τ value is obtained as 0.46 for complex (2). The calculated τ values are found between 0.5 and zero. Therefore, we will describe the geometry as dsp for complex (1) and (2).

The optimized molecular structures and atomic numbering scheme for complexes (3), (4) and (5) were given in Fig. 3.



(3) **(4)** **(5)**

Fig. 3 Optimized molecular structures and atomic numbering scheme for complex **(3)**, **(4)** and **(5)**. Hydrogen atoms were omitted for clarity.

Figure 3 represents the vanadium(IV) ion with a N2O3 coordination environment. Nitrogen atoms coordinate with vanadium(IV) from axial position. The two imine nitrogens are almost in trans position in these structures. Oxygen atoms of two bidentate Schiff base ligands and oxo ligand constitute equatorial plane together with vanadium(IV) ion.

The calculated and experimental structural parameters were listed in Table 2. If the calculated structural parameters in Table 2 are compared with experimental values, it can be seen that the theoretical bond lengths are in a good agreement with experimental values. For complex (3), (4) and (5), V-O(1) bond distances are almost 1.60 Å; V-O(2), V-O(3) bond distances are 1.90 Å approximately and the average of V-N(1), V-N(2) bond distances are 2.10 Å. The biggest difference between experimental and theoretical bond length arises at V-O(1) (0.016 Å) for complex (3), V-O(1) (0.011 Å) for complex (4) and V-N(2) (0.021 Å) for complex (5).

As for evaluating bond angles, the calculated bond angles are compatible with the experimental bond angles. The biggest difference between experimental and theoretical bond angle appears at N(1)-V-N(2) (3.11˚) for complex (3), O(1)-V-O(2) (2.41˚) for complex (4) and N(1)-V-N(2) (3.49^0) for complex (5). τ value is obtained as 0.66 theoretically from α[N(1)-V-N(2)]=126.59 and β[(O(2)-V-O(3)]=165.91^0 angles for complex (3). In the same way τ values are obtained as 0.65 and 0.79 for complex (4) and (5), respectively. Since the calculated τ values are found between 0.5 and 1.0, we will describe the geometry as dtbp for complex (3), (4) and (5). The calculated geometries for relevant complexes are compatible with experimental structures.

Table 2. The calculated and experimental parameters for complexes **(3)**, **(4)** and **(5).**

	Complex 3		Complex 4		Complex 5	
Bond Length(Å)	Calc.	Exp[a].	Calc.	Exp[a].	Calc.	Exp[a].
V - N(1)	2.1029	-	2.1052	2.098	2.097	2.089
V - N(2)	2.1029	2.097	2.1052	2.096	2.097	2.076
V - O(1)	1.6066	1.590	1.6097	1.5988	1.610	1.601
V - O(2)	1.9084	1.893	1.9090	1.9149	1.909	1.9027
V - O(3)	1.9085	-	1.9090	1.9117	1.909	1.9005
Bond Angle(˚)						
N(1) - V - O(2)	86.80	-	86.87	87.56	86.32	86.19
N(1) - V - N(2)	165.91	162.8	166.14	164.17	169.26	165.77
N(1) - V - O(3)	86.88	87.5	86.95	86.21	88.45	87.34
N(2) - V - O(3)	86.80	85.2	86.87	86.84	86.32	87.11
O(1) - V - N(1)	97.04	-	96.93	98.07	95.36	97.32
O(1) - V - N(2)	97.05	98.6	96.93	97.77	95.37	96.86
O(1) - V - O(2)	116.72	-	116.53	114.12	119.12	118.36
O(1) - V - O(3)	116.68	115.2	116.53	116.56	119.15	117.66
O(2) - V - N(2)	86.88	-	86.95	85.87	86.46	86.07
O(2) - V - O(3)	126.59	129.6	126.94	129.31	121.73	123.99

[a]*Experimental values are taken from Ref. 22*

3.2 Vibrational Spectra

Several oxo metal(IV) complexes have been studied experimentally. (M=O) stretching frequencies have been determined and some (M=O) frequencies were given in Table 3.

Table 3. Some experimental (M=O) stretching frequencies.

Complex	$\nu_{M=O}$ (cm^{-1})	References
$[NBu^n_4][MoO(mnt)(SPh)(bipy)].CH_2Cl_2$	921	39
$[NBu^n_4][MoO(mnt)(SPh)(phen)]$	928	39
$[Mo_2O_3(mnt)_2(phen)_2].CH_2Cl_2$	974	39
$[VO(EPA)_2]$	983	40
$[VO(DMMM)_2]$	966	40
$[VO(BDEM)_2]$	1027	40
$[VO(OOCC_{13}H_{27})(SB\text{-}2)]$	967	41
$[VO(acac)_2]$	997	42
$[VO(maltol)_2]$	993	42
$[VO(mpp)_2]$	983	42

The vibrational spectra of the five oxovanadium complexes were calculated by using B3LYP/LANL2DZ level in gas phase and scaled by 0.9257 [43]. Some calculated frequencies, assignments and band intensities were given in Table 4 for the complex (1) and (2). The experimental V-O(1) stretching frequencies were given as 988 and 984 cm^{-1} for complex (1) and (2), respectively [22]. These frequencies were calculated as 983.3 and 981.4 cm^{-1} in the optimized geometries. V-O(2) and V-O(3) stretching frequencies have been obtained as 529 cm^{-1} by Xie *et al*. for similar salicylaldiminato oxovanadium(IV) complex [24]. This stretching frequency was calculated as 509.6 and 516.0 cm^{-1} for complex (1) and (2), respectively. These results show that there is an agreement between the experimental and theoretical vibrational frequencies. The calculated stretching frequencies for V-N(1) and V-N(2) are lower than V-O(2) and V-O(3). The lower frequency indicates that V-N coordinations are weaker than V-O coordination.

Table 4. Selected vibrational frequencies for the complex **(1)** and **(2).**

Assignments	Complex **(1)**		Complex **(2)**	
	Freq.[a]	Intens.[b]	Freq.[a]	Intens.[b]
V-N(1), V-N(2) asym stretch	422.8	17.3	416.8	31.0
V-O(2), V-O(3) asym stretch	509.6	144.0	516.0	101.9
V-O(1) stretch	983.3	70.2	981.4	167.9
C-O stretch + ring C-H bend	1209.7	94.5	1212.3	100.0
C-C stretch	1466.2	282.5	1465.0	239.0
C-C stretch	1469.6	145.1	1475.2	174.4
C=N stretch	1520.6	591.5	1508.9	377.2
C=N stretch	1537.3	201.0	1531.4	229.6
C=C stretch	1544.1	87.4	1544.1	81.9
C=C stretch	1547.0	126.9	1547.1	143.1
C-H(methyl connected to ring) sym	2805.2	72.1	2803.9	71.9
C-H(t-but) asym	2894.1	111.9	2894.0	99.3

[a] *Scaled frequencies are in unit* cm^{-1}, [b]*Intensities are in unit km/mol*

Some calculated stretching frequencies, assignments and band intensities were given in Table 5 for the complex (3), (4) and (5). The experimental V=O(1) stretching frequencies were obtained as 980, 976 and 968 cm^{-1} for complex (3), (4) and (5) respectively[22]. These frequencies were calculated as 979.8, 970.6 and 970.1 cm^{-1} in optimized geometries, respectivelly. These results are in a good agreement with experimental datum. In addition, calculated frequencies are close to experimental M=O frequencies in Table 3.

Table 5. Selected vibrational frequencies for the complex **(3)**, **(4)** and **(5).**

Assignments	Complex **(3)**		Complex **(4)**		Complex **(5)**	
	Freq.^{a}	Intens.^{b}	Freq.^{a}	Intens.^{b}	Freq.^{a}	Intens.^{b}
V-N(1), V-N(2) asym stretch	432.9	94.9	512.3	85.5	394.7	69.1
V-O(2), V-O(3) asym stretch	598.8	134.5	607.7	66.3	534.1	184.8
V-O(1) stretch	979.8	207.1	970.6	181.3	970.1	218.1
C-O stretch + ring C-H bend	1188.8	78.2	1175.8	125.1	1177.5	207.8
C-O stretch + ring C-H bend	1222.5	435.7	1214.6	302.1	1206.6	171.7
C=C stretch	1471.5	136.7	1488.0	182.9	1479.0	165.5
C=C stretch	1527.0	100.9	1521.8	71.2	-	-
C=N stretch	1547.2	675.3	1539.9	523.8	1548.5	512.1
C=N stretch	1552.3	97.2	1544.7	87.8	1552.6	134.5
C-H(methyl) stretch	2808.5	112.9	2913.9	80.1	1842.8	83.2
C-H(t-but) stretch	-	-	-	-	2813.2	160.1
C-H(CN) stretch asym	2863.8	75.8	-	-	2861.1	71.5
C-H(t-but) stretch	-	-	-	-	2892.7	167.6

^{a} *Scaled frequencies are in unit cm^{-1}*, ^{b}*Intensities are in unit km/mol*

3.3 Electronic Spectra

Frontier orbitals, HOMO and LUMO, have an important role in electronic spectra and chemical reactions [44]. There are α and β frontier orbitals in the complexes containing unpaired electrons. Due to the similarity of geometric structures, frontier orbitals of complex (1) are similar to complex (2) and frontier orbitals of complex (3) are similar to complex (4) and (5). Therefore, frontier orbital surfaces and energies for complex (1) and (3) were given in Fig. 4.

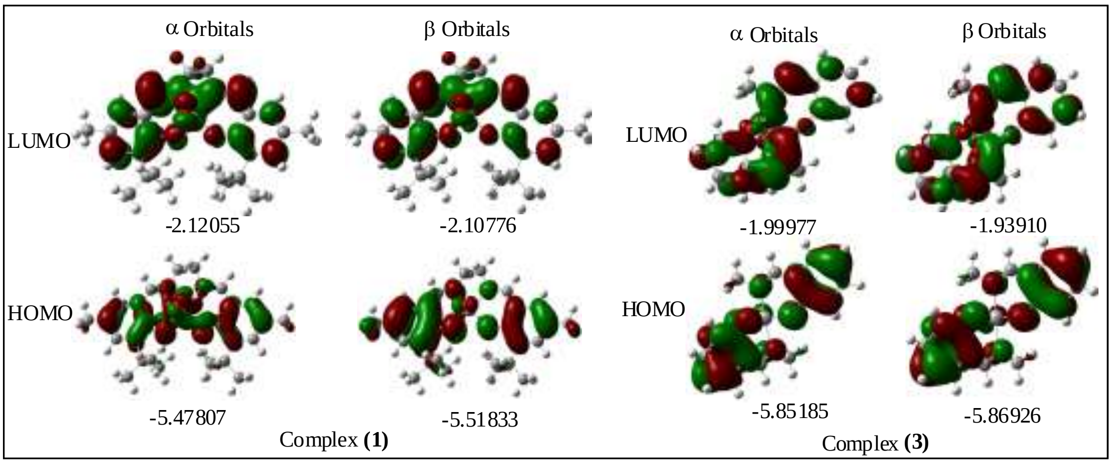


Fig. 4. Frontier orbital surfaces and energies (eV) for complex **(1)** and **(3).**

As can be seen from Fig. 4, the energy gap is between 3.0-4.0 eV approximately. This energy range corresponds to the near UV region. Excitation energies of complexes were calculated by using B3LYP/LANL2DZ level in CH_2Cl_2 solvent for the assignment of the band. The excitation energies of the main band, electronic transitions, transition characters and orbital characters were determined and given in Table 6. As can be seen from Table 6, the calculated excitation energy of main band for each complex is consistent with experimental values. The transition characters (TC%) can be calculated from the wave function coefficients for each excitation. TC% were calculated from wave function coefficients which are greater than +0.15 and smaller than -0.15 by using Eq. (2) [45, 46].

$$\%TC=\frac{t^2}{\Sigma t^2}x100 \tag{2}$$

where t is the coefficient of the wave function for each excitation and Σt^2 is the sum of the squares of all coefficient of the wave function for each excitation in a specific band. Molecular orbital characters can be calculated from coefficients of atomic orbitals which contribute to a specific molecular orbital. % orbital characters (OC%) were calculated from atomic orbital coefficients which are greater than +0.1 and smaller than -0.1 by using Eq. (3) [47, 48].

$$\%OC=\frac{n^2}{\Sigma n^2}x100 \tag{3}$$

where n is the atomic orbital coefficient and Σn^2 is the sum of the squares of all atomic orbital coefficients in a specific molecular orbital.

Table 6. The calculated excitation energies (nm), oscillator strengths, transitions, % transition characters (%TC) and HOMO-LUMO characters (%OC) for five oxovanadium(IV) complexes.

Excitation Energy (nm)[a]	Oscillator Strengths	Transitions HOMO→LUMO	%TC	%OC (HOMO)			%OC (LUMO)		
				V	L	O	V	L	O
Complex **(1)** (α_{HOMO}=121, β_{HOMO}=120)									
389.8 (388.1)	0.0581	119α→122α	50.4	0.4	97.4	2.2	3.8	91.2	5.0
		120α→122α	7.1	35.3	62.8	1.9	3.8	91.2	5.0
		120α→126α	6.9	35.3	62.8	1.9	38.0	50.5	11.5
		119β→121β	31.7	0.4	99.1	0.4	2.4	94.3	3.3
		120β→122β	3.9	0.4	97.5	2.1	1.6	98.1	0.2
Complex **(2)** (α_{HOMO}=125, β_{HOMO}=124)									
377.2 (387.0)	0.0426	123α→126α	7.1	47.3	52.3	0.4	9.4	84.3	6.3
		124α→127α	19.9	17.8	81.8	0.4	1.8	97.8	0.3
		125α→127α	28.1	22.4	75.1	2.5	1.8	97.8	0.3
		123β→125β	5.0	0.5	99.0	0.5	4.2	93.7	2.1
		123β→126β	9.4	0.5	99.0	0.5	0.3	99.4	0.3
		124β→126β	30.4	0.5	96.8	2.7	0.3	99.4	0.3
Complex **(3)** (α_{HOMO}=82, β_{HOMO}=81)									
341.4 (348.0)	0.0631	82α→84α	40.8	0.4	95.7	3.7	1.3	98.5	0.3
		80β→82β	59.2	0.5	96.4	3.0	6.7	88.4	4.9
Complex **(4)** (α_{HOMO}=106, β_{HOMO}=105)									
349.0 (354.0)	0.075	106α→108α	55.9	0.4	82.5	17.1	1.3	98.5	0.3
		104β→106β	44.1	0.5	87.0	12.6	7.1	92.6	0.3
Complex **(5)** (α_{HOMO}=122, β_{HOMO}=121)									
357.6 (363.0)	0.073	122α→124α	73.4	0.4	96.1	3.5	1.1	98.6	2.5
		120β→122β	21.5	0.5	97.2	2.3	7.7	87.3	5.0
		121β→123β	5.1	0.4	96.9	2.3	7.5	92.2	0.3

[a]*Experimental values in bracket are taken from Ref. 22, L shows the Schiff base ligand*

The main band for complex **(1)** appears at 389.8 nm. This band consists of electronic transitions between the following orbitals: 119α→122α, 120α→122α, 120α→126α, 119β→121β 120β→122β. Where 120β and 121α orbitals are HOMO, 121β and 122α orbitals are LUMO for complex **(1)**. The largest contribution to the formation of this band is provided from the transitions 119α→122α and 119β→121β. 119α, 122α, 119β and 121β orbitals have L ligand character. Therefore, these transitions can be considered as intraligand (IL) or $\pi\rightarrow\pi^*$ transitions. However, the transitions 120α→122α and 120α→126α with the lower transition character indicate that there are ligand to metal charge transfer (LMCT) transitions in complex **(1)**. Similar comments can be made for other complexes. The other bands in electronic spectra of complexes have small extinction coefficient. The bands with small extinction coefficient were not obtained theoretically for the oxovanadium(IV) complexes. The calculated excitation energies for $\pi\rightarrow\pi^*$ or LMCT transitions are in a good agreement with experimental energies.

3.4 Antidiabetic effects

Biological activity is expressed as a function of the quantum chemical parameters [49]. There are experimental/theoretical studies about the relationship between quantum chemical parameters and biological activity [50-52]. Antidiabetic effects of complexes can be discussed by using quantum chemical parameters. LUMO-HOMO energy gap (ΔE), global hardness (η) and softness (σ) were calculated from the frontier orbital energies by using Eq. (4), (5) and (6). These quantum chemical parameters were given in Table 7.

$$\Delta E = E_{LUMO} - E_{HOMO} \tag{4}$$

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} \tag{5}$$

$$\sigma = \frac{1}{\eta} \tag{6}$$

Table 7. Some quantum chemical parameters of oxovanadium(IV) complexes.

Parameter	Complex **(1)**	Complex **(2)**	Complex **(3)**	Complex **(4)**	Complex **(5)**
α-E_{LUMO} (eV)	-2.232	-2.143	-2.076	-1.986	-2.000
α-E_{HOMO} (eV)	-5.407	-5.391	-5.769	-5.708	-5.648
Energy gap (ΔE)	3.174	3.249	3.694	3.722	3.648
Hardness (η)	1.587	1.624	1.847	1.861	1.824
Softness (σ)	0.630	0.616	0.541	0.537	0.548

As can be seen from Table 7, the trend of quantum chemical parameters depend on the molecular geometries of complexes. Energy gap and hardness of dtbp complexes decrease in the order (4)>(3)>(5). Energy gaps of dtbp complexes are greater than dsp. This result indicates that global hardness of dtbp complexes are greater than dsp. Global hardness of complex (2) is greater than complex (1).

E_{HOMO} is a quantum chemical descriptor and usually associated with electron donating ability of molecule. High value of E_{HOMO} indicates the tendency of electron transfer to low empty molecular orbital of appropriate acceptor molecule. If the energy of HOMO is decisive for the antidiabetic effect, the ranking of the complexes should be:

(2) > (1) > (5) > (4) > (3)

The low E_{LUMO} value indicates the ability of the complex to accept electrons [53]. The interaction ability of complex with enzyme increases with increasing of the HOMO and decreasing of the LUMO of complexes. If the energy of LUMO is decisive for the antidiabetic effect, the ranking of the complexes should be:

(1) > (2) > (3) > (5) > (4)

The LUMO-HOMO energy gap (ΔE) is an important parameter as a function of reactivity of complexes towards diabetes mellitus. The smaller value of ΔE means the more reactivity [54]. According to the ΔE values, the ranking of complexes should be:

(1) > (2) > (5) > (3) > (4)

The other important parameters are hardness and softness to explain the activity of complexes. The coordination tendencies of complexes towards the enzymes can be discussed with the HSAB (hard-soft-acid-base) approximation [55]. The rule is that hard acids prefer to coordinate to hard bases and soft acids to soft bases. Hard molecules have a big ΔE and soft molecules have small ΔE [55]. Soft complexes can interact easily with enzyme. Because enzymes are big and soft molecules. The softness of mentioned complexes ranking should be:

(1) > (2) > (5) > (3) > (4)

Given the above description, the activity ranking of complexes toward diabetes mellitus should be as following:

(1) > (2) > (5) > (3) > (4)

4. CONCLUSIONS

The elctronic structure for five oxovanadium(IV) complexes with sterically crowded schiff base ligands were optimized by using DFT/B3LYP method with LANL2DZ basis set. The optimization results were indicated that the calculated structural parameters are in a good agreement with experimental values. The molecular geometries were predicted from calculated τ values. It was found that the structures of comlexes (1) and (2) are distorted square pyramidal and complexes (3), (4) and (5) are distorted trigonal bipyramidal. Vibrational spectra of oxovanadium(IV) compelxes were evaluated. Some calculated frequencies were confirmed with experimental frequencies. Electronic spectra were calculated by using TD-DFT/B3LYP method with LANL2DZ basis set in CH_2Cl_2 solvent. It was found that $\pi \rightarrow \pi^*$ or LMCT transitions had large oscillator strength. Theoretical excitation energies of transitions with large oscillator strength are in a good agreement with experimental values. Quantum chemical parameters were calculated to predict the antidiabetic effect of complexes and the activity ranking of mentioned complexes was found as (1) > (2) > (5) > (3) > (4).

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