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Electronic Structure of Vanadium Tetrachloride Di-Hydroxyl Metal Complex

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Abstract: Electronic structure of vanadium tetrachloride di-hydroxyl metal complex is relax by using SDD-B3LYP/DFT method. The structural parameters and stretching frequencies were calculated for the complex. The excitation energy of the complex was obtained by using the TD-DFT/B3LYP method with SDD basis sets. Frontier orbitals (E_{HOMO} and E_{LUMO}), LUMO-HOMO energy gap, global hardness and softness were calculated to predict the activity of the complex. From the calculations of the quantum chemical parameters, vanadium tetrachloride di-hydroxyl metal complex has small energy gap with high activity to interact with enzymes.

Key words: Vanadium metal complex, B3LYP, SDD basis set, quantum chemical parameters, tetrachloride, parameters

INTRODUCTION

Elemental vanadium plays an important role in many environmental and biological processes (Biernacki *et al*., 2011). Coordination chemistry of vanadium has become of great interest due to the presence of vanadium in enzymatic systems (Chasteen, 1990; Sigel and Sigel, 1995). Elemental vanadium and oxovanadium (IV) complexes have interesting pharmacological properties which make them promising agents in the treatment of diabetes mellitus (Yeh *et al*., 2003). According to Carrano proposal, provided that no significant steric constraints, 5 coordinate Vanadium (V) complexes have square pyramidal geometries (Mokry and Carrano, 1993; Rath *et al*., 1997; Diamantis *et al*., 1986; Liu *et al*., 1994; Ludwig *et al*., 1995) and six-coordinate Vanadium (V) complexes constitute octahedral geometries (Chakravarty *et al*., 1994; Liu and Gao, 1998a, b).

Vanadium is a trace element which may be beneficial and possibly essential in humans (Nielsen and Uthus, 1990) but certainly essential for some living organisms (Kustin *et al*., 1983, 1990; Michibata and Sakurai, 1990; Smith *et al*., 1995; Wever and Kustin, 1990; Slebodnick *et al*., 1997; Taylor *et al*., 1997; Faeq and Abbood, 2017; Michibata *et al*., 2002, 2003). Metal ions and thus vanadium ions can play a role in biology as counter ions for protein, DNA, RNA and in various biological organelles. The structural role is often manifested by the maintenance of various biological structures whereas a functional role is to bring key reactivity to a reaction center for a protein. Vanadium ions have many structural roles reflected by its structural and electronic analogy to phosphorus (Faeq and Abbood, 2017; Chasteen, 1983; Gresser *et al*., 1987; Gresser and Tracey, 1990; Chasteen, 1990; Rehder, 1991; Crans, 1994; Rehder *et al*., 1995; Crans *et al*., 1996; Tracey and Crans, 1998). In addition, the vanadium ion is an enzyme cofactor (Slebodnick *et al*., 1997; Faeq and Abbood, 2017; Pee *et al*., 2000; Butler, 1998, 1999; Wever *et al*., 1997; Vilter, 1995; Butler and Walker, 1993; Eady, 2003; Rehder *et al*., 2000; Rehder and Jantzen, 1996; Rehder *et al*., 2003) and is found in certain tunicates (Smith *et al*., 1995; Wever and Kustin, 1990; Slebodnick *et al*., 1997; Taylor *et al*., 1997; Faeq and Abbood, 2018; Michibata *et al*., 2003) and possibly mammals (Nielsen and Uthus, 1990). Reviews on how vanadium can act and function in the biosphere include investigations into the fundamental coordination and redox chemistry of the element (Faeq and Abbood, 2018; Michibata *et al*., 2002; Rehder and Jantzen, 1996; Baes and Mesmer, 1976; Chasteen, 1981; Boas, and Pessoa, 1987; Butler and Carrano, 1991; Crans, 1995) as well as structural and functional aspects of biological systems and/or metabolites (Rehder *et al*., 2003; Chasteen, 1995). Modeling biological activities of various types have long been of interest to chemists with this discipline focusing on the structural modeling until about a decade ago when the focus shifted to functional modeling. Clearly modeling that includes both aspects will be most informative and the ultimate goals for model chemists. Although, the latter in general may be of greater interest at the present time, the structural aspects of the various oxidation states are defining its effects in many biological systems.

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MATERIALS AND METHODS

Computational details: GaussView 5.0.8 program (Gauss, 2009) was used to draw the initial structure of the complex and provide the data base for it is input file. The calculations were carried out by using Gaussian 09 package of programs (Frisch *et al*., 2009a, b). Vanadium tetrachloride di-hydroxyl metal complex was fully relax by employing B3LYP-SDD/DFT (Hay and Wadt, 1985) in gas phase. B3LYP combination of exchange and correlation functional (Becke, 1993; Lee *et al*., 1988) in DFT is applied to all calculations of electronic structure. The electronic excitation energy was calculated for the relax metal complex by employing TD-DFT/B3LYP method with SDD basis sets. TD-DFT method has been verified to be reliable for calculating spectra properties of many transition metal complexes (Liu *et al*., 2007; Zhou *et al*., 2005ab).

RESULTS AND DISCUSSION

The relax structure of vanadium tetrachloride di-hydroxyl metal complex in Fig. 1 was optimized at the minima by employing the hybrid functional B3LYP-DFT with SDD basis sets. The calculated values of the optimize parameters for the complex were listed in Table 1 and the standard orientation for the coordination for each atom in the complex was listed in Table 2. The results of the relax structure showed the virial ratio (-V/T = 2.0056) without any imaginary frequency in which refers to a suitable SDD basis sets used in the relaxation of such complex (Hasan and Abbood, 2016; Mazhir *et al*., 2016; Ghalib *et al*., 2014).

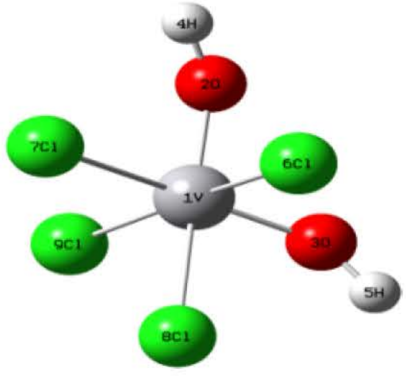

Fig. 1: The relax structure of vanadium tetrachloride di-hydroxyl metal complex

Table 1: The optimize parameters for the complex

Bond	Value (A$^?$)	Angle	Value (deg.)
Cl-V	2.20222-2.58365	Cl-V-Cl	74.91591-163.90473
O-V	1.71233-2.05040	O-V-Cl	86.20706-161.89511
H-O	0.97881	H-O-V	138.87745

Table 3 shows the calculated values of ground state total energy E_T, frontier orbitals (α-HOMO and β-LUMO), energy gap E_{gap} and quantum chemical parameters (Hardness H and Softness S). As known, the frontier orbitals have a significant role in chemical reactions and electronic spectra of the complexes, E_{HOMO} is a quantum chemical descriptor associated with electron donating ability of the complex and E_{LUMO} is a descriptor associated with electron acceptor. In our complex, there are α and β frontier orbitals containing unpaired electrons. Figure 2 shows the surfaces of the frontier orbitals for the complex and Fig. 3 illustrates the density of states DOS diagram of the complex involves all the occupied and the virtual orbitals. From Table 3, the complex under study has a small LUMO-HOMO energy gap, E_{gap} of the complex is 2.19 eV, the smaller E_g is a sign of the biological reactivity of the complex.

The hardness and softness are quantum chemical parameters to clarify the activity of the complex. The coordination tendency of the complexes towards the enzymes can be discussed with the global hardness and softness. Soft complex has small energy gap and can

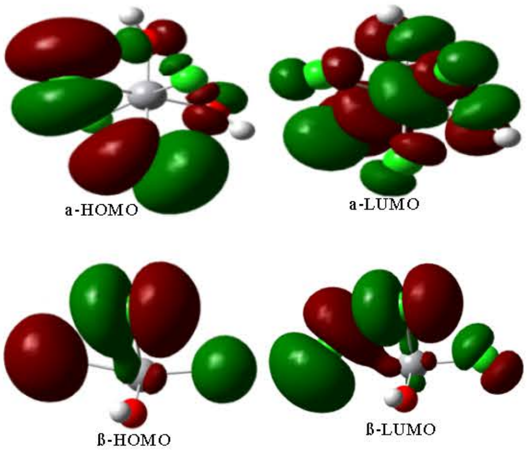

Fig. 2: Frontier orbital surfaces for tetrachloride di-hydroxyl metal complex

Table 2: The optimize parameters for the complex

Atom	X	Y	Z
V	0.185716	-0.487393	0.000000
O	-0.081848	-1.547522	1.317805
O	-0.081848	-1.547522	-1.317805
H	-0.406644	-1.509691	2.240383
H	-0.406644	-1.509691	-2.240383
Cl	-2.344177	0.036896	0.000000
Cl	-0.081848	1.287777	1.579257
Cl	-0.081848	1.287777	-1.579257
Cl	2.381483	-0.318933	0.000000

Table 3: Some quantum chemical parameters for the complex

E_T (a.u.)	α-E_{HOMO} (eV)	α-E_{LUMO} (eV)	E_{gap} (eV)	S(eV)$^{-1}$	H (eV)
-2064.219	-8.111055	-5.917304	2.193751	0.4558	1.0969

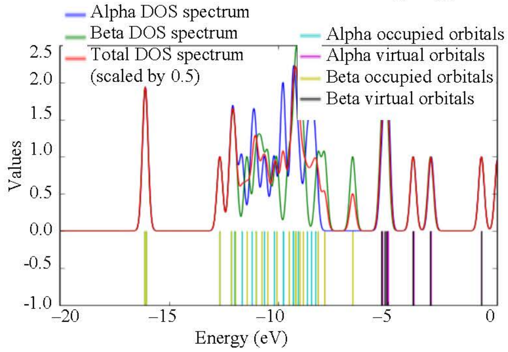

Fig. 3: The DOS for the tetrachloride di-hydroxyl metal complex

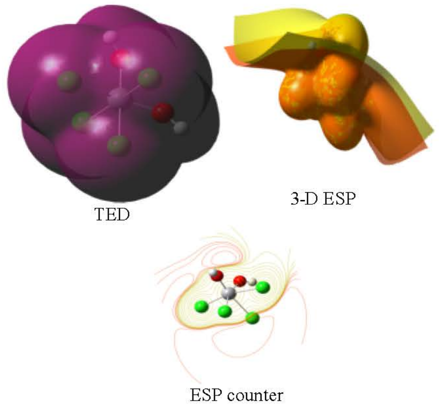

Fig. 4: TED and ESP surfaces of the complex

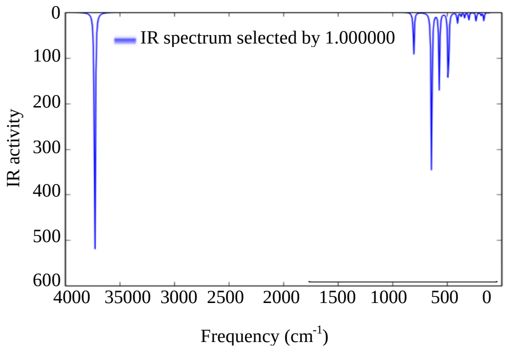

Fig. 5: IR-Spectrum for tetrachloride di-hydroxyl metal complex

easily interact with enzyme because the enzymes are big and soft molecules according to the coordination tendency of the complex with the surrounding species (Faeq and Abbood, 2017). Soft complex has a small energy gap and hard complex has a large energy gap.

Figure 4 illustrates the total electron density TED and electrostatic potential ESP surfaces of the vanadium tetrachloride di-hydroxyl metal complex (Fig. 5). As shown, the TED surface was distributed according to the coordination of the complex due to difference of the atomic number of oxygen and chlorine atoms. The ESP surface was dragged towards the chlorine atoms of the higher electronegativity, this leads to high ability to replacing the ligands in the complex by others to construct new vanadium metal complexes.

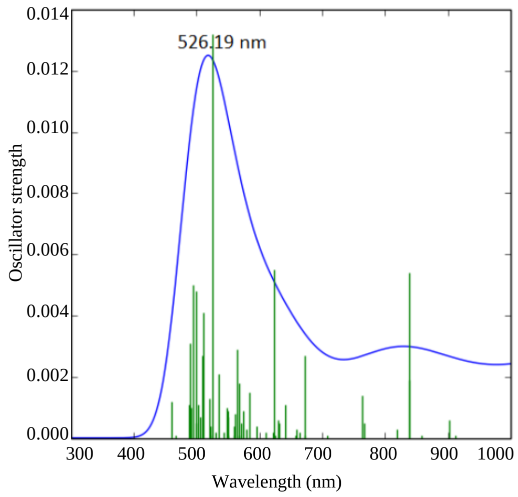

Fig. 6: UV-Vis spectrum of vanadium tetrachloride di-hydroxyl metal complex

Figure 5 illustrates the infrared IR spectrum of vanadium tetrachloride di-hydroxyl metal complex from the B3LYP-SDD/DFT. The results showed the stretching O-H bonds was observed at 3728.27 and 3733.7 cm^{-1} corresponding to intensities equal to 477 and 139.5 km/mol, respectively, the bending O-H bonds lies at 402.5 and 485.7 cm^{-1} corresponding to 25.7 and 199.6 km/mol, respectively. High frequencies were observed for stretching V-OH, the first lies at 803.4 cm^{-1} corresponds to 103.2 km/mol and the second lies at and 822.8cm^{-1} corresponds to low intensity 2.48 km/mol while the bending V-OH bonds was observed at 298.2 cm^{-1} corresponds to 18.0 km/mol. The four V-Cl bonds appear bending vibration in the range (143.1-255.6) cm^{-1} with low intensities (0.06-0.7) km/mol (Fig. 6).

The excitation energy of tetrachloride di-hydroxyl metal complex was calculated by using the B3LYP-TD-SCF-SDD level of theory. The excitation energy of the main band, the oscillator strength, wave length, electronic transitions (HOMO→LUMO) and the transition characters were calculated and listed in Table 4. The excitation energy for the main band of the complex under study appears at 2.356 eV. The electronic transitions in this band were observed between the molecular orbitals: 46α→51α, 49α→52α, 50α→51α 50α→53α, 40β→50β, 45β→53β, 46β→53β, 48β→51β and 49β→52β. The transitions 50α→51α, 46α→51α, 49α→52α and 46β→53β provide the

Table 4: The excitation energy, oscillator strength, wavelength, the main

transitions and the transition character for the main band of tetrachloride di-hydroxyl metal complex from the B3LYP-TD-SCF-SDD/DFT

Excitation energy (eV)	Oscillator strength	Wavelength (nm)	Transitions HOMO→LUMO	Transition Character (TC%)
2.356	0.0132	526.19	46 α→51α	18.2
			49 α→52α	17.7
			50 α→51α	22
			50 α→53α	2.3
			40 β→50β	5.3
			45 β→53β	2.9
			46 β→53β	11.9
			48 β→51β	9.6
			49 β→52β	10.1

largest contribution to the formation of the band. These transitions can be careful as π→π* transitions. Figure 6 shows the UV-Vis spectrum of the complex drawn at the Gauss Sum program.

CONCLUSION

B3LYP density functional theory was used together with SDD basis sets to study of the electronic structure of vanadium tetrachloride di-hydroxyl metal complex. The structural parameters and stretching frequencies were calculated for the complex. TD-DFT/B3LYP method with SDD basis sets was used to obtain the excitation energy of the complex. Frontier orbitals (E_{HOMO} and E_{LUMO}), LUMO-HOMO energy gap, global hardness and softness were calculated to predict the activity of the complex. The results of the quantum chemical parameters showed the vanadium tetrachloride di-hydroxyl metal complex has small energy gap with high activity to interact with enzymes. The transition characters from the transitions HOMO→LUMO can be careful as π→π* transitions.

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