Simulation Study of Structural and Electronic Properties for Adducts complexes of Bis(Acetylacetonato)oxoVandium (IV) with 4-(Para-substituted phenyl)-1,2,3-Selenadiazole

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Abstract. A series of 4-(para-substituted phenyl)-1,2,3-selenadiazole adducts of [VO(acac)₂] were studied by density functional theory (DFT) calculations. The 4-(para-substituted phenyl)-1,2,3-selenadiazole molecules have been selected to be bound with vanadium atom in [VO(acac)₂] through Se, N₂ and N₃. The resulting adducts have been investigated in two geometries (cis and trans) in order to show the effect of such structural change on the electronic properties of the studied adducts. The optimized geometries, (binding and reorganization) energies and the spatial distribution of the highest molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the adducts are presented and discussed.

1. Introduction

Coordination complexes are of great significance in different fields due to their presence in many shapes and structures. There are numerous examples of coordination complexes in biochemistry field. For example, the iron, magnesium, cobalt and copper coordination complexes are demonstrated by hemoglobin, chlorophyll, Vitamin B₁₂ and hemocyanin respectively [1-4].

The Vanadyl moiety in coordination complexes has been extensively studied. Bis(acetylacetonato)oxidovanadium (IV), or [VO(acac)₂], is one of the most important vanadium complexes [5]. X-ray diffraction studies on the [VO(acac)₂] complex clearly show the existence and stability of VO²⁺ entity in the solid state. The geometry of complex demonstrates as an almost square pyramidal geometry [6]. Many applications have been demonstrated for the [VO(acac)₂] complex. It has been used as the vanadium precursor for the preparation of different vanadium compounds [7-9] and also it has been used as a catalyst precursor in organic reactions [10-12]. Furthermore, Vanadium complexes show a wide variety of biological applications, and numerous complexes have been investigated as anti-parasitic, spermicidal, antiviral, anti-HIV, anti-tuberculosis, and antitumor agents [13].

Organo heterocyclic compounds of selenium which containing nitrogen such as selenirenines, selenophenes, selenadiazoles, selenatriazoles and benzoselenazolones can have many biological effects. Among such features they are active immunostimulants, inhibitors of enzymes, antioxidants, anti-inflammatory, antitumor, antiviral and antimicrobial agents [14].

Bis(acetylacetonato)oxidovanadium(IV), or [VO(acac)₂] is known to interact with various ligand containing donor atoms like N, P, O, S and Se to form adduct compounds. Although some vanadium-chalcogene complexes have been synthesized and characterized, only very few examples with analogous organo selenium derivatives as ligands have been described [15-18].
In this work, a series of 4-(para-substituted phenyl)-1,2,3-selenadiazole adducts of [VO(acac)₂] have been investigated theoretically in order to show the effect of such structural change on the structural and electronic properties of the adducts.

2. Computational Methods
The calculations presented in this paper have been carried out by using hyperchem program 7.5 [19]. The geometry of the 4-(para-substituted phenyl)-1,2,3-selenadiazole ligands were optimized by carrying out the semiempirical molecular orbital theory at the PM3 level [20], using the restricted Hartree–Fock (RHF) procedure [21]. The Polak–Ribier algorithm [22] was used for the optimization, with the termination condition being a root mean square (RMS) of <0.001 kcal/mol. Further, Geometry optimization was done by performing the B3LYP/3-21G theory method [23-25]. Concerning the adduct molecules, the initial geometry optimization carried out with the molecular mechanics (MMC) force field [26-27], where the lowest energy conformations are obtained. Further, Geometry optimization was done was done by performing the B3LYP/STOG and B3LYP/3-21G theory methods. All calculations have been done on Pc, Intel(R) Core(TM) i3-3220 CPU @ 3.30GHz. Due to computational limitations and the large size of the studied adduct molecules, we were unable to achieve higher level optimizations on the adducts molecules.

3. Result and discussion
Scheme 1 shows the 4-(para-substituted phenyl)-1,2,3-Selenadiazole ligands. These ligands have been investigated theoretically to study their structural and electronic properties. Table 1 shows the calculated proton affinities of the substituted ligands according to semiemperical PM3 and BLYP/3-21G levels, the highest occupied and the lowest unoccupied molecular orbital energies (HOMO and LUMO respectively), their calculated hardness (1/2 the HOMO-LUMO gap). The values of hardness can give an information about the molecules if they are soft or hard, where the molecules which have a large HOMO-LUMO gap are hard while the molecules which have a small HOMO-LUMO gap are soft [28]. It can be seen clearly that electron-donating and electron-releasing groups have small effects on the hardness values for the calculations methods. For the PM3 calculation the trend of hardness of the substituted 1,2,3-selenadiazole ligands decrease in the order CF₃>H>Br>F>CN>CH₃>Cl>OCH₃>Ph>NH₂; while for BLYP/3-21G the hardness decrease in the order H>CF₃>CN>F>CH₃>Cl>Br>OCH₃>Ph>NH₂.

![Scheme 1](image)

X= H, CH₃, Ph, NH₂, OCH₃, F, Cl, Br, CF₃, CN

Scheme 1. The general structure of 4-(para-substituted phenyl)-1,2,3-selenadiazole molecules (left) and optimized molecular structure of 4- phenyl-1,2,3-selenadiazole molecules (right)

The values of partial charges of selenium and nitrogen atoms are also given in Table 1. For both type of calculations, selenium atom indicates a positive charge. The Positive charge on the selenium atom should considerably decrease their base strengths electrostatically. Nitrogen is a better donor atom than Se. N2 atom possess negative charge vary from -0.092 to -0.085 and from -0.302 to -0.297 according to PM3 and BLYP/3-21G calculations respectively. N3 atom possess positive charge vary from 0.097 to 0.092 and negative charge vary from -0.294 to -0.272 according to PM3 and BLYP/3-21G calculations respectively.
Table 1. Selected calculated energy, hardness and parial charges of the 4-(para-substituted phenyl)-1,2,3-selenadiazole ligands according to semiempirical PM3 and BLYP/3-21G calculation.

| X      | Methods | $E_{\text{HOMO}}$ eV | $E_{\text{LUMO}}$ eV | Hardness eV | Mulliken charge | PA$^a$ (kcal/mol) |
|--------|---------|----------------------|----------------------|-------------|-----------------|------------------|
|        |         |                      |                      |             | Se   | N2   | N3   | N2   | N3   | Se   | N2   | N3   |
| H      | PM3     | -9.357               | -1.280               | 4.039       | 0.158 | -0.090 | 0.097 | 172.90 | 178.20 |
|        | 3-21G   | -6.222               | -1.455               | 2.384       | 0.671 | -0.296 | -0.271 | 197.92 | 215.29 |
| CH$_3$ | PM3     | -9.198               | -1.251               | 3.974       | 0.156 | -0.090 | 0.097 | 173.82 | 179.24 |
|        | 3-21G   | -6.009               | -1.379               | 2.315       | 0.667 | -0.297 | -0.273 | 199.88 | 217.47 |
| Ph     | PM3     | -8.921               | -1.347               | 3.787       | 0.158 | -0.090 | 0.096 | 174.21 | 181.78 |
|        | 3-21G   | -5.802               | -1.750               | 2.026       | 0.652 | -0.297 | -0.289 | 201.11 | 220.32 |
| NH$_2$ | PM3     | -8.226               | -1.038               | 3.594       | 0.146 | -0.092 | 0.092 | 178.57 | 185.30 |
|        | 3-21G   | -4.990               | -1.327               | 1.832       | 0.630 | -0.302 | -0.294 | 194.33 | 209.03 |
| OCH$_3$| PM3     | -9.00                | -1.221               | 3.890       | 0.155 | -0.090 | 0.095 | 174.63 | 180.08 |
|        | 3-21G   | -5.655               | -1.316               | 2.170       | 0.664 | -0.297 | -0.274 | 194.19 | 211.77 |
| F      | PM3     | -9.444               | -1.433               | 4.006       | 0.165 | -0.087 | 0.095 | 170.76 | 175.57 |
|        | 3-21G   | -6.166               | -1.529               | 2.319       | 0.675 | -0.296 | -0.273 | 195.86 | 212.71 |
| Cl     | PM3     | -9.250               | -1.395               | 3.928       | 0.163 | -0.088 | 0.096 | 171.95 | 177.07 |
|        | 3-21G   | -6.253               | -1.638               | 2.308       | 0.679 | -0.294 | -0.272 | 198.64 | 215.42 |
| Br     | PM3     | -9.470               | -1.433               | 4.019       | 0.165 | -0.088 | 0.097 | 171.09 | 176.15 |
|        | 3-21G   | -6.141               | -1.595               | 2.273       | 0.679 | -0.295 | -0.273 | 197.83 | 214.86 |
| CF$_3$ | PM3     | -9.810               | -1.674               | 4.068       | 0.175 | -0.085 | 0.098 | 167.68 | 172.28 |
|        | 3-21G   | -6.608               | -1.884               | 2.362       | 0.690 | -0.293 | -0.269 | 195.46 | 212.17 |
| CN     | PM3     | -9.654               | -1.656               | 3.999       | 0.173 | -0.086 | 0.097 | 168.50 | 173.19 |
|        | 3-21G   | -6.668               | -2.031               | 2.319       | 0.710 | -0.305 | -0.282 | 190.62 | 207.06 |

$^a$PA are the values of $\Delta H$ and $\Delta E$ for PM3 and 3-21G calculations respectively for the reaction: 

\[
\text{BH}^+ \rightarrow \text{B} + \text{H}^+ (\text{B selenadiazole})
\]

The electron-releasing and electron-withdrawing effects of substituted groups are not reflected very well on the charges of both nitrogen and selenium atoms. The values of calculated proton affinity for N2 and N3 atoms are listed in Table 1. According to the PM3 and BLYP/3-21G calculations, N3 atom indicated the greatest values of proton affinity which means that N3 is more basicity than N2.

A few studies have been achieved to study the coordination chemistry of 1,2,3-selenadiazole ligands [29]. These studies indicated that the coordination between metal and 1,2,3-selenadiazole ring might be through N2 in 4-methyl-1,2,3-selenadiazole [30-32] or through N3 in 4-(2-pyridyl)-1,2,3-selenadiazole [33]. Connecting this N3 atom into coordination becomes more likely because of the metal chelation with the pyridinyl nitrogen and the nearby selenadiazole-N3.

In an attempt to detect the donor atom on 1,2,3-selenadiazole ring which is coordinating with [VO(acac)$_2$], various 4-(para-substituted phenyl)1,2,3-selenadiazole molecules have been selected to be bound with vanadium atom in [VO(acac)$_2$] through Se, N2 and N3. The resulting molecules have been selected to adopt cis or trans isomer.

Scheme 2 denotes the structures formula of cis and trans [VO(acac)$_2$L] adducts. The donor atom (Se, N2 and N3) of 4-(para-substituted phenyl)-1,2,3-selenadiazole may be coordinate cis or trans to the O-oxido. The studied molecules have been optimized by performing the molecular mechanics force field, where the lowest energy conformations are obtained.

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Scheme 2. Structures formula of cis and trans $[\text{VO(acac)}_2L]$ adducts, the donor atoms (Se, N2, N3) in 4-(para-substituted phenyl)-1,2,3-Selenadiazole may coordinate cis or trans to the O-oxido.

Figure 1. Optimized structures formula of cis and trans-$[\text{VO(acac)}_2L]$ adducts isomers, the donor atoms (Se, N2, N3) in 4-(para-substituted phenyl)-1,2,3-selenadiazole may coordinate cis or trans to the O-oxido.

Figure 1 presents the optimized structures formula of cis and trans $[\text{VO(acac)}_2L]$ adduct. L is 4-phenyl-1,2,3-selenadiazole.
Table 2. Total energy of conformations (in kcal/mol) of cis and trans [VO(acac)₂L] adducts, the donor atom (Se, N2 or N3) of 4-(para-substituted phenyl)-1,2,3-selenadiazole may coordinate cis or trans to the O-oxido.

| X     | trans-isomer | cis-isomer  |
|-------|--------------|-------------|
|       | Se-V | N2-V | N3-V | Se-V | N2-V | N3-V |
| H     | 50.377 | 47.993 | 50.862 | 51.046 | 23.988 | 39.657 |
| CH₃   | 52.283 | 49.719 | 52.020 | 50.777 | 22.3659 | 39.122 |
| Ph    | 60.881 | 58.343 | 60.010 | 49.901 | 23.306 | 37.867 |
| NH₂   | 51.365 | 48.871 | 50.953 | 55.923 | 28.912 | 45.028 |
| OCH₃  | 52.640 | 50.188 | 52.170 | 55.062 | 28.398 | 43.160 |
| F     | 50.286 | 47.791 | 49.988 | 50.988 | 23.978 | 39.934 |
| Cl    | 50.257 | 47.784 | 50.139 | 51.379 | 24.363 | 40.198 |
| Br    | 50.050 | 47.549 | 49.512 | 51.512 | 24.480 | 40.237 |
| CF₃   | 52.701 | 50.153 | 52.338 | 55.711 | 28.618 | 43.479 |
| CN    | 53.185 | 49.524 | 51.415 | 51.566 | 24.286 | 39.468 |

Figure 2. Optimized structures formula of cis-[VO(acac)₂L] adduct. L is 4-(para-substituted phenyl)-1,2,3-selenadiazole.

Table 2 listed the total energy of cis and trans [VO(acac)₂L] adducts conformations. The results of the computed adducts revealed that all isomers of cis and trans adopted distorted octahedral. It can be
seen clearly form Table 2 that the cis-adduct isomers have the lowest total energy in comparison with trans-adduct isomers. It's means that these molecules may be more stable compared with other studied molecules. Furthermore, the cis-adducts isomers with N2-V binding have the lowest energy in comparison with the other cis-adducts isomer with Se-V or N3-V binding. Thus, the coordination of [VO(acac)2] with 4-(para-substituted phenyl)1,2,3-selenadiazole molecules is more likely to be through N2 atom on the selenadiazole ring.

Table 3. Selected geometrical parameters of cis-[VO(acac)2L] adducts, L is 4-(para-substituted phenyl)-1,2,3-selenadiazole calculated using BLYP/3-21G calculation. N2 atom is coordinated cis to the O-oxido.

| Bond distance (Å) | X | H | CH3 | Ph | NH2 | OCH3 | F | Cl | Br | CF3 | CN |
|------------------|---|---|-----|----|-----|------|---|----|-----|------|-----|
| V=O (oxo) | 1.789 | 1.789 | 1.789 | 1.789 | 1.789 | 1.789 | 1.789 | 1.789 | 1.789 | 1.789 | 1.789 | 1.789 | 1.789 |
| V-O * (ketonic) | 1.854 | 1.854 | 1.854 | 1.855 | 1.854 | 1.854 | 1.854 | 1.854 | 1.854 | 1.854 | 1.854 | 1.854 | 1.854 |
| V-O b (enolic) | 1.850 | 1.850 | 1.854 | 1.850 | 1.851 | 1.850 | 1.850 | 1.850 | 1.850 | 1.850 | 1.850 | 1.850 |
| V-N2 | 1.917 | 1.917 | 1.920 | 1.917 | 1.917 | 1.917 | 1.917 | 1.917 | 1.917 | 1.918 | 1.919 | 1.919 |
| Se-N2 | 1.834 | 1.834 | 1.835 | 1.833 | 1.834 | 1.834 | 1.834 | 1.834 | 1.834 | 1.834 | 1.834 |
| N2=N3 | 1.252 | 1.253 | 1.253 | 1.252 | 1.252 | 1.252 | 1.252 | 1.252 | 1.252 | 1.252 | 1.252 | 1.252 |
| N3-C4 | 1.267 | 1.267 | 1.267 | 1.267 | 1.267 | 1.267 | 1.267 | 1.267 | 1.267 | 1.267 | 1.267 |
| C4=C5 | 1.342 | 1.342 | 1.342 | 1.342 | 1.342 | 1.342 | 1.342 | 1.342 | 1.342 | 1.342 | 1.342 | 1.342 |
| C5-Se | 1.879 | 1.879 | 1.879 | 1.880 | 1.879 | 1.880 | 1.880 | 1.880 | 1.879 | 1.879 | 1.879 |

| Bond angle (°) | X | H | CH3 | Ph | NH2 | OCH3 | F | Cl | Br | CF3 | CN |
|----------------|---|---|-----|----|-----|------|---|----|-----|------|-----|
| O=V-O | 170.08 | 169.85 | 177.90 | 170.00 | 169.95 | 170.28 | 170.19 | 170.83 | 176.09 | 169.72 |
| O-V-O | 96.09 | 96.09 | 80.23 | 95.97 | 96.03 | 95.98 | 95.91 | 95.81 | 95.78 | 90.03 |
| O=V-N2 | 98.20 | 98.28 | 91.25 | 98.26 | 98.46 | 98.10 | 98.16 | 91.27 | 90.69 | 98.34 |
| V-N2-Se | 121.85 | 121.71 | 122.43 | 121.89 | 121.89 | 121.86 | 121.88 | 122.35 | 122.53 | 121.89 |
| V-N2=N3 | 120.12 | 120.25 | 119.98 | 120.10 | 120.08 | 120.13 | 120.10 | 119.76 | 119.77 | 120.07 |
| Se-N2=N3 | 118.03 | 118.04 | 117.59 | 118.01 | 118.04 | 120.13 | 118.01 | 117.89 | 117.71 | 118.03 |
| N2-Se-C5 | 78.88 | 78.89 | 79.13 | 78.88 | 78.89 | 78.89 | 78.87 | 78.96 | 70.07 | 78.89 |
| Se-C5=C4 | 113.34 | 113.34 | 113.19 | 113.36 | 113.31 | 113.34 | 113.37 | 113.32 | 113.23 | 113.32 |
| C5=C4-N3 | 113.95 | 113.97 | 113.96 | 113.91 | 114.00 | 113.94 | 113.91 | 113.93 | 113.96 | 113.98 |

| Bond dihedral (°) | X | H | CH3 | Ph | NH2 | OCH3 | F | Cl | Br | CF3 | CN |
|------------------|---|---|-----|----|-----|------|---|----|-----|------|-----|
| N3-C4'-C1'-C2' | -0.17 | -0.36 | 0.10 | -0.16 | 0.15 | -0.09 | -0.10 | -0.07 | 0.48 | -0.30 |
| C5-C4-C1'-C6' | -0.13 | -0.21 | 0.00 | -0.05 | 0.00 | -0.05 | -0.05 | 0.03 | -0.23 | -0.21 |

Further geometry optimization has been carried out for the cis-[VO(acac)2L] adducts at the B3LYP/STOG and B3LYP/3-21G levels of theory in order to study the structural and electronic properties of resulting adducts. Figure 2 presents the optimized structures formula of cis-[VO(acac)2L] adduct. Table 3 shows the selected geometrical parameters of cis-[VO(acac)2L] adducts, calculated using BLYP/3-21G method. The experimental data of crystallography of [VO(acac)2] and 4-(4-Chlorophenyl)-1,2,3-selenadiazole moieties have reported [34,35]. It is very useful to compare these data with the theoretical data that calculated by B3LYP/3-21G method.

The optimized structures of the studied molecules indicate to have a distorted octahedral geometry. The bonds angle of O=V-O and O-V-O gave values in the range of 169.72-177.9 and 80.23-96.09
respectively. As shown in Table 3, the length of V=O (oxo) bond was 1.789 Å compared with 1.586 Å in free [VO(acac)_2] [25]. The calculated bond length of V-O (ketonic) and V-O (enolic) bonds in the adducts vary from 1.850 to 1.855 Å compared with 1.973 Å and 1.967 Å respectively in the free [VO(acac)_2]. Concerning 1,2,3-selenadiazole ring, the experimental bonds length of Se-N2, N2=N3, N3-C4, C4=C5 and C5-Se were 1.857, 1.265, 1.381 and 1.353 Å respectively in 4-(4-Chlorophenyl)-1,2,3-selenadiazole [26]. On the other hand, the experimental bonds angle of Se-N2=N3, N2-Se-C5, Se-C5=C4 and C5=C4-N3 were 111, 86.42, 111.9, and 113.1 (°) respectively in 4-(4-Chlorophenyl)-1,2,3-selenadiazole [26]. All these values are in good agreement with the calculated values, see Table 3. Finally, there is no clear trend for the variation of electronic donating or withdrawing groups on the structural properties of the studied adducts.

Some of the calculated energies of cis-[VO(acac)_2]L adducts using BLYP/STOG and BLYP/3-21G calculations are given in Table 4. The Binding energy of adducts formation and the reorganization energy of 4-(para-substituted phenyl)-1,2,3-Selenadiazole and [vo(acac)_2] in the adducts using BLYP/3-21G calculation are given in Table 5.

Table 4. Some of the calculated energies of cis-[VO(acac)_2]L adducts, L is 4-(para-substituted phenyl)-1,2,3-selenadiazole calculated using BLYP/STOG and BLYP/3-21G calculations. N2 atom is coordinated cis to the O-oxido.

| X   | Methods | Binding energy kcal/mol | E_HOMO eV | E_LUMO eV |
|-----|---------|-------------------------|-----------|-----------|
| H   | STOG    | -2736528.57             | -5.661    | -3.884    |
|     | 3-21G   | -2506056.73             | -9.762    | -7.882    |
| CH₃ | STOG    | -2760219.78             | -5.444    | -3.642    |
|     | 3-21G   | -2061255.01             | -9.545    | -7.578    |
| Ph  | STOG    | -2372471.90             | -5.345    | -3.467    |
|     | 3-21G   | -2484322.38             | -9.657    | -7.802    |
| NH₂ | STOG    | -2769768.20             | -5.469    | -3.6      |
|     | 3-21G   | -2098283.03             | -9.834    | -7.732    |
| OCH₃| STOG    | -2777009.67             | -5.499    | -3.622    |
|     | 3-21G   | -2151226.07             | -9.945    | -7.711    |
| F   | STOG    | -2796070.93             | -5.696    | -3.679    |
|     | 3-21G   | -2148539.39             | -9.563    | -7.43     |
| Cl  | STOG    | -2976746.76             | -5.36     | -3.34     |
|     | 3-21G   | -2244784.61             | -9.472    | -7.23     |
| Br  | STOG    | -4295115.76             | -5.803    | -3.742    |
|     | 3-21G   | -4105436.87             | -9.603    | -7.216    |
| CF₃ | STOG    | -2616844.67             | -5.106    | -3.121    |
|     | 3-21G   | -1971597.43             | -9.754    | -7.301    |
| CN  | STOG    | -2515070.12             | -5.14     | -3.162    |
|     | 3-21G   | -1957462.17             | -9.876    | -7.233    |

The binding energy of adduct formation reactions has been calculated by the difference between the binding energy of cis-[VO(acac)_2]L adduct and that of individual [VO(acac)_2] and 4-(para-substituted phenyl)-1,2,3-selenadiazole ligand. Also, the reorganization energy of ligands and [VO(acac)_2] that is needed to change the geometry of them into that present in the final [VO(acac)_2]L adduct has been calculated [36-37].

Table 5.
As shown in Table 5, the values of binding energy are somewhat large values (vary from 1066083.30 to 321355.55 kcal/mol) these may be due to needing to overcome steric interactions of [VO(acac)$_2$] and 4-(para-substituted phenyl)-1,2,3-selenadiazole ligands.

The organization energy of [VO(acac)$_2$] represents the required energy to convert the geometry of vanadyl complex from a square pyramidal to distorted octahedral, while the organization energy of ligands represents the required energy to change the bonds lengths and angles of free ligand into that present in adduct. It can be seen clearly form Table 5 that the required energy to convert the geometry of vanadyl complex from a square pyramidal to distorted octahedral is almost similar (vary from 29.94-30.66 kcal/mol). On the other hand, the organization energy of ligand was different values for each ligand (vary form 20.44-23.90 kcal/mol).

Figure 3 shows the spatial distribution of the highest molecular orbital (HOMO) and lowest unoccupied molecular orbital of selected adducts. The negative region is showed with violet color, while the positive region is showed with green color. In general, HOMOs orbitals are located mainly on the nitrogen atom in diazole ring and on [VO(acac)$_2$] moiety. In contrast, LUMOs orbitals are located mainly on[VO(acac)$_2$] moiety and on different atoms (Se, N and C) in selenadiazole moiety. In other words, from the diagrams of HOMO and LUMO, it can be concluding existence two types of interaction between nitrogen and vanadium atoms in the adducts. First type of interaction is πr-dπ, where the nitrogen atom donates pairs of electrons to vanadium atom to form σ covalent bond. The second type of interaction is dr-pπ, where the vanadium atom donates single electron to nitrogen atom to form π bond. These two types of interactions are illustrated in Figure 4.

| X     | $\Delta E^a$ kcal/mol | $E_{\text{reorg}}$ of L$^b$ kcal/mol | $E_{\text{reorg}}$ of [vo(acac)$_2$]$^c$ kcal/mol |
|-------|-----------------------|------------------------------------|-----------------------------------------------|
| H     | 321355.55             | 23.50                              | 30.14                                         |
| CH$_3$| 790676.75             | 23.17                              | 30.45                                         |
| Ph    | 487183.07             | 20.89                              | 29.94                                         |
| NH$_2$| 763650.40             | 22.36                              | 30.05                                         |
| OCH$_3$| 747617.61            | 23.72                              | 30.43                                         |
| F     | 740787.81             | 23.90                              | 30.55                                         |
| Cl    | 869602.35             | 20.44                              | 30.12                                         |
| Br    | 329069.26             | 21.23                              | 30.66                                         |
| CF$_3$| 1066083.36            | 20.69                              | 30.01                                         |
| CN    | 927484.28             | 29.85                              | 30.00                                         |

$^a$ The binding energy of adduct formation which is calculated by the difference between the energy of the adduct and that of the individual 4-(para-substituted phenyl)-1,2,3-selenadiazole and [vo(acac)$_2$] moieties.

$^b$ Reorganization energy of 4-(para-substituted phenyl)-1,2,3-selenadiazole.

$^c$ Reorganization energy of [vo(acac)$_2$].

4. Conclusions

In the present investigation we have investigated the adducts formed between [Vo(acac)$_2$] and 4-(para-substituted phenyl)-1,2,3-selenadiazole ligands. The studied ligands have more than one donor atoms (Se, N2 and N3) that may coordinate with
Figure 3. Molecular orbital spatial distribution for the HOMO and LUMO of \textit{cis}-[VO(acac)$_2$L] adduct. L is 4-(\textit{para}-substituted phenyl)-1,2,3-Selenadiazole.

\textbf{σ-type orbital interaction} \hspace{1cm} \textbf{π-type orbital interaction}

\[ d_{x^2-y^2} \hspace{1cm} d_{xy} \]

Figure 4: interaction types of selenadiazole ring with d orbitals of vanadium atom

vanadium atom on the [VO(acac)$_2$]. In an attempt to detect the donor atom on 1,2,3-selenadiazole ring which is coordinating with [VO(acac)$_2$], the 4-(\textit{para}-substituted phenyl)1,2,3-selenadiazole molecules have been selected to be bound with vanadium atom in [VO(acac)$_2$] through Se, N2 and N3. The resulting adducts have been investigated in two geometries (\textit{cis} and \textit{trans}) in order to show the effect of such structural change on the electronic properties of the studied adducts. Based on the electron
density of nitrogen atoms, calculations of basicity of nitrogen atom and calculations of lowest energy conformation, the suggested structures of adducts of [VO(acac)₂] with 4-(para-substituted phenyl)1,2,3-selenadiazole molecules have been detected.

The resulting structure of adduct have been studied at two levels of DFT theory to investigated their structural and electronic properties. The structural properties (i.e. bond lengths and angles) of the studied [VO(acac)₂] and 4-(para-substituted phenyl)1,2,3-selenadiazole moieties indicated a good agreement with experimental data of free molecules.

The organization energy of both [VO(acac)₂] and 4-(para-substituted phenyl)1,2,3-selenadiazole moieties into that present in adducts have been calculated, where the required energy to convert the geometry of vanadyl complex from a square pyramidal to distorted octahedral was almost 30 kcal/mol. The HOM and LUMO spatial distribution indicated interesting interactions between nitrogen and vanadium atoms.

The variation of electronic donating or withdrawing groups on the structural properties of the studied adducts have no interesting effects on the structural and electronic properties of the studied adducts. Finally, the new adducts species have interesting properties and deserve to be investigated experimentally.

References

[1] Buchler, J. W. (1978) hemoglobin—an inspiration for research in coordination chemistry. Angew. Chem. In. Ed. Engl. 17:407–423.
[2] Senge, M. O., Ryan, A. A., Letchford K. A., MacGowan S. A. and Mielke, T. (2014) chlorophylls, symmetry, chirality, and photosynthesis. Symmetry. 6: 781–843.
[3] Randaccio, L. Geremia, S. Demiti N. and J. Wuerges (2010) vitamin B12: unique metalorganic compounds and the most complex vitamins. Molecules.15: 3228–3259.
[4] Van Holde, K. E., Miller K. I. and H. Decker (2001) hemocyanins and invertebrate evolution. J. Biol. Chem. 276:15563–15566.
[5] Dodge, R. P., Zalkin, A., and Templeton, D. H. (1961) crystal structure of vanadyl bisacetylacetonate. geometry of vanadium in fivefold coordination. J. Chem. Phys.35:55-67.
[6] Fedorova, E. V., Rybakov, V. B., Senyavin, V. M., Anisimov, A. V. and Aslanov , L. A. (2005) synthesis and structure of oxovanadium(IV) complexes [VO(Acac)2] and [VO(Sal: L-alanine)(H2O)]. Crystallogogr. Rep., 50:224–229.
[7] Maurya, M. R., Uprety B., Avecilla, F. and Adão, P. (2015) vanadium(v) complexes of a tripodal ligand, their characterisation and biological implications. J. C. Pessoa, Dalton Trans. 44:17736-17755.
[8] Maurya, M. R., Chaudhary, N., Avecilla, F., Adão, P. (2015) oxidovanadium(IV) and dioxidovalanadium(v) complexes of hydrazones of 2-benzoylpyridine and their catalytic applications. J. C. Pessoa, Dalton Trans.44:1211-1232.
[9] Maurya, M. R. (2003) Development of the coordination chemistry of vanadium through bis(acetylacetonato)oxovanadium(IV): synthesis, reactivity and structural aspects. Coord. Chem. Rev. 237:163-181.
[10] Liu, H. B., Wang, M., Wang, Y., Sun, H., and Sun, L. C. (2009) asymmetric oxidation of sulfides with hydrogen peroxide catalyzed by a vanadium complex of a new chiral NOO-ligand. Catal. Commun.11:294–297.
[11] Hirao, T. (1997) vanadium in modern organic synthesis. Chem. Rev.97:2707-2724.
[12] Pereira, C., Silva, J. F., Pereira, A. M., Araujo, J. P., Blanco, G., Pintado, J. M., and Freire, C. (2011) [VO(acac)₂] hybrid catalyst: from complex immobilization onto silicnanoparticles to catalytic application in the epoxidation of geraniol. Catal. Sc. Techn. 1:784-793.
[13] Pessoa, J. C., and Tomaz, I. (2010) transport of therapeutic vanadium and ruthenium complexes by blood plasma components. Curr. Med. Chem.17:3701–3738.
[14] Jain, V. K., Priyadarsini K. I. Organoselenium Compounds in Biology and Medicine: Synthesis, Biological and Therapeutic Treatments. 2017.
[15] Tetteh, S., and Zugle, R. (2017) theoretical study of terminal vanadium(v) chalcogenido complexes bearing chlorido and methoxido ligands. J. Chem. 2017:1-8.
[16] Molter, A., Bill, E., and Mohr, F. (2012) synthesis, structures and reactivity of two oxidovanadium(IV) and dioxidovanadium(V) selenosemicarbazonato complexes. Inorg. Chem. Comm. 17:124–127.
[17] Ying Luo, H., Zhou J. and Zou, H. (2019) a series of new vanadium(iii) chalcogenido-antimonates: an unusual seven-coordinate nitro-selenidovanadium(iii) complex Dalton Trans. 48: 3090-3097.
[18] Pisk, J., Daran, J.-C., Poli, R. and Agustin, D. (2015) Pyridoxal based ONS and ONO vanadium(V) complexes: Structural analysis and catalytic application in organic solvent free epoxidation. J. of Mol. Cata. A-Chemical. 403:52–63.
[19] HyperchemTM Release 7.52, Windows Molecular Modeling System, hypercube, Inc. 2002.
[20] Stewart, J.J.P. (1989) Optimization of parameters for semiempirical methods II. Applications. J. Comput. Chem. 10:221-261.
[21] Roothaan, C.C. (1951) New Developments in Molecular Orbital Theory. J. Rev. Mod. Phys. 23:69-89.
[22] Gill, P.E., Murray, W., Wright, M.H. Practical Optimization. Academic Press, New York, 1981.
[23] Lee, C., Yang, W., and Parr, R.G. (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Rev. B 37: 785-789.
[24] Becke, A.D. (1993) density-functional thermochemistry. III. The role of exact exchange J. Chem. Phys. 98:5648-5652.
[25] Keith, T.A., and Bader, R.F.W. (1992) calculation of magnetic response properties using atoms in molecules Chem. Phys. Lett. 194:1-8.
[26] Burkert, U., and Allinger, N.L. Molecular Mechanics ACS Monograph, American Chemical Society, Washington, DC, 1982, p. 177.
[27] Li, J.-H., Gallion, S. Bender, C., Wikström, H., Allinger, N.L., Flurchiek, K.M., and Teeter M.M. (1989) molecular mechanics (MM2) calculations on peptides and on the protein crombin using the CYBER 205. J. Comput. Chem. 10:503-513.
[28] Pearson, R. G. (1988) absolute electronegativity and hardness: application to inorganic chemistry. Inorg. Chem. 27:734–740.
[29] Arsenyan, P., Rubina, K., Shestakova, I. and Domracheva, I. (2007b) 4-Methyl-1,2,3-selenadiazole-5-carboxylic acid amides: Antitumor action and cytotoxic effect correlation. Eur. J. Med. Chem. 42:635-640.
[30] Todres, Z. V. Chalcogenadiazoles: Chemistry and Applications. CRC Press, 2011.
[31] Baetzel, V. and Boese, R. (1981) synthese und struktur von 1,2,3-Thiadiazol- und 1,2,3-Selenadiazol-Pentacarbonyl-Komplexen der Elemente Chrom und Wolfram / synthesis and structure of 1,2,3-thiadiazol- and 1,2,3-selenadiazol-pentacarbonyl-complexes of the elements chromium and tungsten. Zeitschr. Naturforsch. 36B:172-179.
[32] Richardson, Ch. and Steel, P.J. (2002) metal complexes of 2-[1,2,3-thiaand selena]diazol-4-y]pyridine and an unusual silver-induced selenadiazole rearrangement. Austral. J. Chem. 55:783-788.
[33] Pannell, K. H., Mayr, A. J., Hoggard, R., McKennis, J.S., and Dawson, J.C. (1983) (cycloalkenono-1,2,3-selenadiazol- und -thiadiazol)carbonyl-(6b)-metall-komplexe. Chem. Ber. 116: 230-237.
[34] Ravichandran, K., Ranjith, S., Sankari, S., Beemaraao M. and Ponnuswamy M. N. (2018) 4-(4-Chloro-phen-yl)-1,2,3-selena-diazole. IUCrData.3: 80462-80465.
[35] Oshi, R., Abdalla, S., and Springborg, M. (2017) study of the influence of functionalization on the reorganization energy of naphthalene using DFT. Comput. Theoret. Chem. 1099 209-215.
[36] D. F. Shrifier, P. Atkins, Inorganic Chemistry, 5th ed.; Freeman: New York, 2010.
[37] B. E. Douglas, McDaniel, D. H.; Alexander, J. J. Concepts and Models of Inorganic Chemistry, 3rd ed.; Wiley: New York, 1994.