International Journal of Progressive Sciences and Technologies (IJPSAT)
ISSN: 2509-0119.

http://ijpsat.ijsht-journals.org
Vol. 24 No. 1 December 2020, pp. 645-661

Coordination Chemistry of Vanadium Aquo Complex Ions in Oxidation States +II, +III, +IV, and +V: A Hybrid-Functional DFT Study

Anant Babu Marahatta[1, 2]

[1]Department of Chemistry, Amrit Science Campus, Tribhuvan University, Kathmandu, Nepal
[2]Chemistry Subject Committee, Kathford International College of Engineering and Management (Affiliated to Tribhuvan University), Kathmandu, Nepal

Abstract – The vanadium aquo complexes: $[V(H_2O)_6]^{2+}$, $[V(H_2O)_6]^{3+}$, $[VO(H_2O)_5]^{2+}$, and $[VO_2(H_2O)_3]^{+}$. H_2O containing V^{n+}: *n* = +II, +III, +IV, and +V ion respectively with only H_2O as ligands are the most prevailing ionic species in their aqueous type medicinal and biological fluid matrices, and all-vanadium redox flow battery (VRFB) systems. Since, they tend to display particular configurations with distinctive electronic stabilities, understanding how each adjacent vanadium ion stabilizes itself with specific hydration number and acquires unique equilibrium structure is very indispensable. With this as a major objective, the coordination chemistry of all these four hydrated vanadium complexes are studied here thoroughly by applying a hybrid-functional DFT method. It is found that all the theoretically derived bond lengths (*Th.*) of each optimized complex ion agree reasonably with the experimental values (*Exp.*): (a) $[V(H_2O)_6]^{2+}$: V−OH_2 *Th.* 2.0 Å, *Exp.* 2.1 Å; (b) $[V(H_2O)_6]^{3+}$: V−OH_2 *Th.* 1.98 Å, *Exp.* 1.99 Å; (c) $[VO(H_2O)_5]^{2+}$: equatorial V−OH_2 *Th.* 2.03 Å, *Exp.* 2.03 Å, *trans* V−OH_2 *Th.* 2.17 Å, *Exp.* 2.20 Å, and V=O *Th.* 1.57 Å, *Exp.* 1.59 Å; (d) $[VO_2(H_2O)_3]^{+}$. H_2O: V=O *Th.* 1.6 Å, *Exp.* 1.6 Å, and V−OH_2 *Th.* 2.0 Å, *Exp.* 2.0 Å. Similarly, the bonding patterns and a closed 3D coordination geometry of each complex ion revealed through the theoretically generated electron density map (mapped with the total density) are also very reliable. The importance and originality of this study lies in deriving all the structural data sets and characteristic coordination geometry of each hydrated vanadium complex ion theoretically as they are very essential while modelling VRFB simulator.

Keywords – Adjacent vanadium ions, Vanadium hydrated complexes, Coordination chemistry, and Electron density map.

I. INTRODUCTION

In the history of chemistry, the periodic table of elements has become an integral tool more especially for describing the elemental/atomic properties in a comprehensive and concise way. For example, knowing the electronic configurations of the tabulated elements not only gives us a better way for deducing their bonding abilities, and other physical and chemical properties but also reasons with the division of the periodic table into *s*−, *p*−, *d*−, and *f*− blocks. The *d*−block elements are more particularly important as they exhibit transitional behavior between the *s*−, and *p*− blocks, and are arranged in 3*d*, 4*d*, 5*d*, or 6*d* series, among which the 3*d* series are mostly fascinated with their typical characteristics such as metallic property, ionic and atomic radii, variable oxidation states, wide-ranging complex and color giving tendencies, intense hydration/solvation reactions, unique coordination chemistry etc. [1]. As a rule, all the 3*d* metal ions (M^{n+}) in their aqueous solution stabilize themselves by associating with distinct number of water molecules that are either bonded feebly or firmly as a monodentate ligand to the central metal atom/ion through

the coordinate covalent bonds ($H_2O \rightarrow M^{n+}$), owing to form the specific type hydrated complex ions/ compounds possessing unique coordination geometry [1], [2]. Being vanadium (Z = 23) a third 3*d* series element, it obviously shows a variable oxidation states but more typical as V^{n+}; *n* = +II, +III, +IV, and +V having recognizably different stabilities and more unique and contrasting color giving tendencies in their aqueous solutions (V^{n+} hydrated complexes are lilac, green, blue, and yellow in color respectively) [2], [3], [4], [5]. Such distinctive V^{n+} aquo complexes are produced in the aqueous type solutions as a result of a close association of the discrete number of water molecules around the central V^{n+} ions. This hydration reaction of the V^{n+} ions is usually facilitated by their incredibly small ionic size and higher ionic charge density.

As vanadium is one of the most omnipresent elements available in the Earth's crust, and hydrospheric and atmospheric regions, it's essentiality in most living beings and vital roles in many biological systems are widely recognized [2], [6], [7]. More particularly in the oceanic life (ocean algae), it is used as an active enzymatic center; and in the blood cells (vanadocytes) of some marine invertebrates (subphylum *Tunicata*), it's +III, +IV or +V oxidation states serve as a defense mechanism [7]. In other biological systems, its role is both structural by activating numerous signaling pathways (due to the structural similarity between vanadate (VO_4^{3-}) and phosphate (PO_4^{3-})), and functional by functionalizing the active centers of some significant biomolecules such as enzymes, proteins, and coenzymes [2], [6], [8], [9]. This is why, it is regarded as a dietary micronutrient and biologically significant element, sometime given to people suffering from vanadium deficiency as a dietary supplement. Though there are insufficient evidences to claim, if the vanadium is taken orally and appropriately, some deadliest diseases such as cancer, anemia, tuberculosis, heart diseases etc. are thought to be averted [8], [9], [10]. Similarly, high doses of vanadyl sulfate ($VOSO_4$) are believed to lower blood sugar level and improve insulin using capability of those adult humans who are suffering from type 2 diabetes [10]. Additionally, several therapeutic drugs based on the vanadium and its compounds in the organic derivatives are already proposed to treat many parasitic human diseases [8], [9]. Despite being such extremely essential bioelement and precursor element for synthesizing vanadium based drugs, inappropriate oral doses of vanadium are usually considered as toxic causing serious side effects such as stomach discomfort, diarrhea, nausea, greenish tongue, loss of energy, kidney damage etc. [10].

From the above wide-ranging abundancies and availabilities of vanadium element/ions/ compounds in various medicinal drugs and living beings, it can be depicted that the vanadium element and its variable oxidation states V^{n+} remain suspended predominantly in the aqueous type medicinal as well as biological fluid matrices. And, in such aqueous media, the V^{n+} ions most preferentially undergo hydration reactions by displaying a variety of hydrated structures and configurations with distinctive electronic stabilities and coordination chemistry [2], [3]. Beyond this, such hydrated vanadium complex compounds with variable oxidation states are most frequently confronted while implementing several industrial aqueous type chemical reactions in a number of potential applications such as: V_2O_5 is used as a catalyst for manufacturing sulfuric acid through contact process; "all vanadium" redox couples are used as electrolyte solution in vanadium redox flow battery (hereafter, VRFB) etc. [4], [5]. Understanding the unique coordination chemistry and the electronic stabilities of the hydrated V^{n+} complexes is more crucial for the VRFB technology as it is highly suffered from the excessive and unwanted collection of water in the positive half-cell (flooding of the electrodes). According to extended X− ray absorption fine structure and large-angle X− ray scattering studies on vanadium complexation in oxygen-donor solvent such as water [2], [3], and many other previously reviewed publications [11], [12], [13], the four adjacent oxidation states of vanadium (V^{n+}; *n* = +II, +III, +IV, and +V) stabilize themselves in their aqueous type solutions by forming $[V(H_2O)_6]^{2+}$, $[V(H_2O)_6]^{3+}$, $[VO(H_2O)_5]^{2+}$, and $[VO_2(H_2O)_4]^{+}$ hydrated complexes respectively. However, the preexisting controversial and more contrasting opinions about the instability of the last ion $[VO_2(H_2O)_4]^{+}$ are already clarified by the same author elsewhere [14], where the most energetically and structurally stable form of this V(V) ion is reported as $[VO_2(H_2O)_3]^{+}.H_2O$. Up to the knowledge of this author, there is no article concentrating on the detailed structural consequences of all these four hydrated complexes of V, and explaining fully about their coordination chemistry in the aqueous type solutions theoretically. Thus, being the computational/theoretical techniques (geometry optimizations and frequency calculations) quite reliable and powerful mean to deal with them, present insight is mainly aimed at revealing their ground state electronic structures and concerned coordination chemistry and 3D geometries theoretically. Since, the former computational technique always locates low energy electronic structure from the given trial molecular model, and the latter computes concerned frequencies at a nuclear Cartesian coordinates of that specific structure (stationary point), their outcomes greatly ease us to analyze the 3D molecular structures/ geometries, and hence to interpret the experimentally observed evidences quantitatively. Therefore, such computational skills would be definitely applicable to probe energetically low hydrated structures of the V^{n+}, and to generate their specific structural parameters which in turn offers quantitative aspects for predicting accurate geometrical patterns.

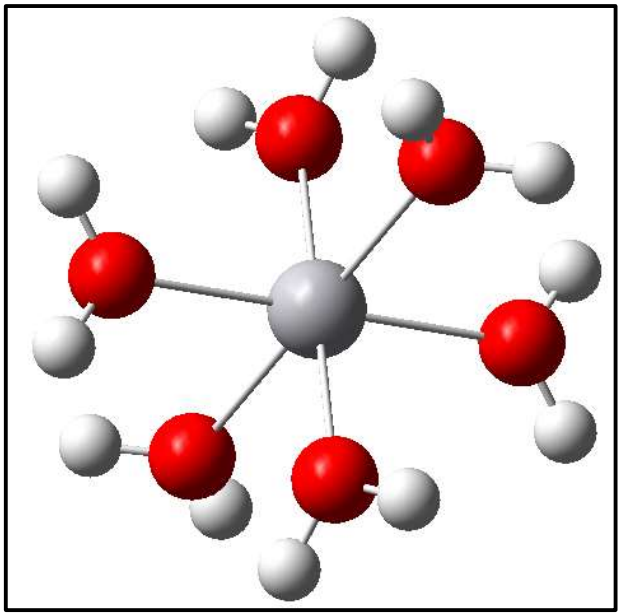
Several previously published research articles [14], [15], [16], [17], [18] have centralized their contents for seeking most suitable quantum mechanical model applicable to derive ground state electronic structures of the transition metal complexes. Michael *et al*. [15] have applied almost all DFT functionals including B3LYP to thirty two halide complexes of the 3*d* row transition metals by utilizing experimentally produced geometries as trial structures. They reported that all the DFT functionals are equally appropriate to reproduce the metal−halide bond lengths (experimentally observed) with very reasonable accuracy in spite of the flexible type metal−ligand coordination. Bonnie [16] has reported an excellent performance of the DFT model while applying to transition metal−siderophores complexes, Christopher *et al.* [17] and Athanassios [18] have thoroughly reviewed the most recent progresses of the DFT model in terms of its potentiality to reveal the coordination chemistry of the transition metal complexes and stressed its success. As a whole, all these evidences are found to stand on the support of the DFT model, implying this model could be an appropriate computational/theoretical mean to disclose the coordination chemistry of the hydrated V^{n+} complex ions: $V(H_2O)_6]^{2+}$, $[V(H_2O)_6]^{3+}$, $[VO(H_2O)_5]^{2+}$, and $[VO_2(H_2O)_3]^{+}.H_2O$. Most importantly, a very recent achievement of the same author while addressing the controversial perceptions given to describe the stability of the V(V) complexes by applying the DFT (B3LYP) model [14] would be a more trustworthy evidence behind the selection of this theoretical method here as well.

The structure of this paper is organized as follows: the theoretical approaches and computational details are outlined in section 2, the results and discussions are presented in section 3, and the conclusions are given in section 4.

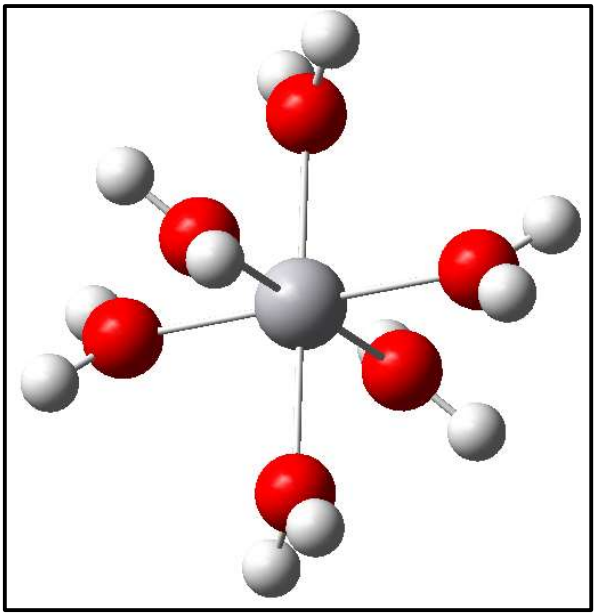
II. Computational Details

In order to account the most stable electronic structures of all the four hydrated complex ions of vanadium: $V(H_2O)_6]^{2+}$, $[V(H_2O)_6]^{3+}$, $[VO(H_2O)_5]^{2+}$, and $[VO_2(H_2O)_3]^{+}.H_2O$, the starting (trial) structures for geometry optimization of each of them were carefully built by using *GaussView*: the Gaussian graphical interface [19], and the respective Cartesian coordinates of the atoms were extracted. All the four trial structures are displayed in **chart 1** where ash-brown, white, and red colored spheroids represent Vanadium (V), Hydrogen (H), and Oxygen (O) atoms respectively. For each optimization process, all the Gaussian keywords and methodologies were selected as instructed in *Gaussian 09* manual [20]. The hybrid functional based DFT method known as B3LYP was used with the basis set of this type: 6−31G (*d*, *p*) i.e. the methodology used was DFT: B3LYP/6−31G (*d*, *p*). The better and more reliable computational results were assured by using the greater basis set of the type 6−31G (*d*, *p*), where "6−31G" is the standard, split-valence double-zeta basis set: the functions that were used in *Gaussian* script computationally while describing the core and valence orbitals of the atoms; and the functions in parentheses "(*d*, *p*)" are polarization functions on heavy atoms and

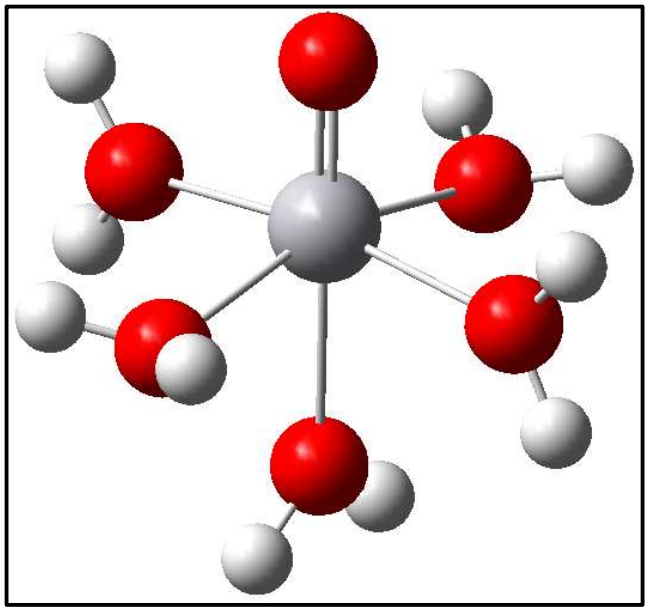
Chart 1: Trial structures



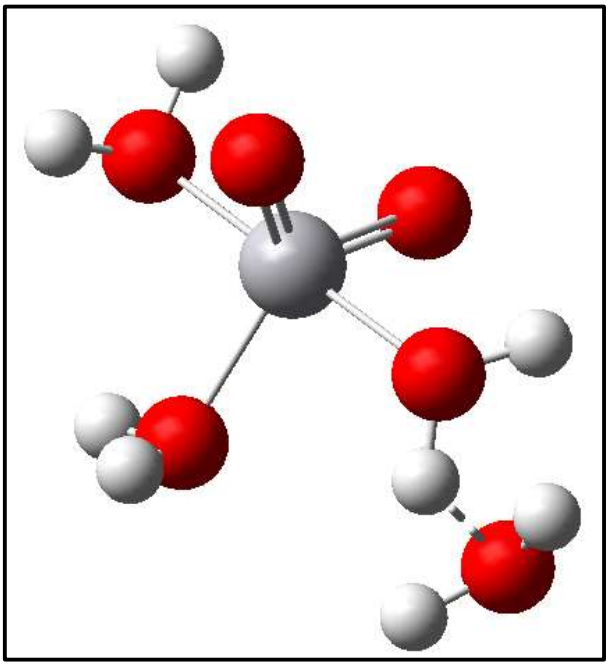
$[V(H_2O)_6]^{2+}$



$[V(H_2O)_6]^{3+}$



$[VO(H_2O)_5]^{2+}$



$[VO_2(H_2O)_3]^{+}.H_2O$

hydrogen that was used to properly describe chemical bonds. Again, to direct *Gaussian* for running desirable computations, the ionic charge and spin multiplicity were specified as two integers accordingly. Here, all the four complex ions are cationic with almost dissimilar positive charge units, *i.e.* $V(H_2O)_6]^{2+}$, $[V(H_2O)_6]^{3+}$, $[VO(H_2O)_5]^{2+}$, and $[VO_2(H_2O)_3]^{+}.H_2O$ have charge = +2, +3, +2, and +1 respectively. Thus, the respective set of integers (charge, spin multiplicity) used in the *Gaussian* input file to describe each cationic complex was (2, 2), (3, 1), (2, 2), and (1, 1) respectively. Moreover, while solving the electronic Schrodinger equation

iteratively, the self-consistent field (hereafter, SCF) with both default SCF procedure (SCF=Tight) and Berny algorithm for optimizations to a local minimum were selected in *Gaussian* 09 [20], [21]. To verify all the four theoretically converged geometries as the energetically minimum structures, the frequency calculation job (*Gaussian* keyword: *Freq*) for each structure was run computationally by using the atomic Cartesian coordinates of the concerned optimized geometry without changing computational methodology and basis set [20], [21], [22]. For this verification, the terminology "imaginary frequencies (negative signs)" was carefully searched in each *Gaussian* output file. Furthermore, while reading the concerned *Gaussian* output files such as *.log*, *.fchk*, and *.chk* for extracting three dimensionally displayed chemical data and visualizing each optimized geometry in the three dimensional space, the *GaussView* was used.

III. Results and Discussions

Usually, theoretical computations based on the first principles DFT method provide comparatively more reliable basis for quantum mechanical determination of the most stable ground state electronic structures of the multi-electron and/or many-body giant molecular systems [14], [17], [18], [23], [24], [25], [26], [27], [28], [29], [30]. More particularly, this spatially dependent electron density based computational method gives impressive explanation while interpreting experimentally observed molecular properties of the coordination and transition metal compounds [14],[17],[18], [31]. In this study, the trial structures for all the four hydrated complexes of V^{n+} (n = +II, +III, +IV, and +V): $[V(H_2O)_6]^{2+}$, $[V(H_2O)_6]^{3+}$, $[VO(H_2O)_5]^{2+}$, and $[VO_2(H_2O)_3]^{+}.H_2O$ (**chart 1**) existing in their aqueous type solutions are optimized separately by applying the DFT: B3LYP/6−31G (*d, p*) methodology, and identified their energetically most stable equilibrium structures theoretically/computationally. The detailed DFT derived coordination chemistry of each hydrated complex ion is explained separately in the following subsections.

3.1 Coordination chemistry of hydrated vanadium (II) complex ion

A vanadium (II) ion in its aqueous solution is a divalent cation, dissolved in water, of the molecular formula $[V(H_2O)_6]^{2+}$ as mentioned earlier in section 1. The DFT derived equilibrium structure (starting from the trial molecular model) of the $[V(H_2O)_6]^{2+}$ ion is shown in Figure 1, where ash-brown, white, and red colored spheroids represent Vanadium (V), Hydrogen (H), and Oxygen (O) atoms respectively. Generally, in theoretical/computational chemistry, the optimized geometry is specified in reference to the following structural parameters: a) bond length: an intermediate distance between the two bonding atomic nuclei in any given molecule; and b) bond angle: an angle formed by three atomic nuclei across the two bonds, those that are involved to determine the specific coordination geometry of the $[V(H_2O)_6]^{2+}$ complex ion more precisely in the three dimensional space are carefully chosen here. The explicitly measured dimensions of these parameters are listed in Table 1, where DFT derived and originally (trial structure) present bond lengths and bond angles are expressed in Angstrom (Å) and degree (°) respectively for comparison purpose. They are found to be reasonably close for the trial and DFT produced structures. This quantitative result can be used to claim that the trial molecular model built for the $[V(H_2O)_6]^{2+}$ complex ion (**chart 1**) is in accordance with the computational/theoretical modeling rules. Likewise, if we analyze all the DFT derived V−OH_2 bond lengths (first row third column) carefully, we may reveal that the oppositely aligned H_2O molecules have equal bond lengths, suggesting such trans type H_2O molecules are equally bound to the central vanadium atom. This is quite logical as the chemical bonding principle tells: a shorter bond length always means a stronger bond and vice versa, *i.e.* those atoms that are closer to each other most often form strong chemical bonds, and those that are far apart to each other form weak bonds. Most importantly, all the DFT derived V−OH_2 dimensions (~2.0 Å) listed in Table 1 are very much consistent with the experimentally derived values (V−OH_2 bond length: 2.1Å) reported by Shannon elsewhere [31]. It is quite common in theoretical chemistry that an electron density map (mapped with the total density) for the concerned optimized geometry can be used to examine the bonding patterns and a closed three dimensional molecular geometry. It is also applicable to visualize the areas where electrons are present and where they are not, which in turn lead to image the molecular shape in the three dimensional space. This type of mapping for the $[V(H_2O)_6]^{2+}$ complex ion is displayed in Figure 2, where charge distributions around the ion is illustrated three dimensionally. This map demonstrates well about the position of all the six centrally bound H_2O molecules whose electron densities are seen to be concentrated clearly around the central vanadium atom, signifying the presence of all the six bonding sites of the central vanadium around its immediate vicinity. The six distinguished protrusions (electron dense region) observed around the central V atom further speculates that all the associated but inbound H_2O molecules are distributed symmetrically and bonded firmly to it. Likewise, to account the molecular geometry three dimensionally, each corner of the protrusions must be interconnected ideally to each other. While doing so, an imaginary object with a specific shape can be brought out through which one may unveil easily that all the six H_2O molecules are almost symmetrically arranged around the central V atom by defining six vertices, twelve edges, and eight faces of an octahedron, signifying an octahedral geometry of the $[V(H_2O)_6]^{2+}$

ion in the three dimensional space. This generic term used here to refer a closed 3−dimensional shape of the $[V(H_2O)_6]^{2+}$ ion can also be reconfirmed by inspecting the concerned bond angles listed in Table 1. As we see, none of these angles are exactly 90°: a required value for all the concerned bond angles to attain an octahedral shape as proposed by valence shell electron pair repulsion (VSEPR) theory, but an exactly equal each and every opposite bond angle that are measured in the average range of 90° produces a definite shape of slightly distorted octahedral geometry for $[V(H_2O)_6]^{2+}$ ion as predicted by many experimental as well as simulation studies [2], [32], [33]. This distortion in the coordination geometry is agreeable because the central V atom is surrounded by six bond pairs of electrons, and while developing coordinate covalent bonds between the central V and the coordinated H_2O molecules, the overlapping directions of the completely fulfilled 2*p* orbitals of the H_2O molecules (more specifically a 2*p* orbital of an "O" containing a lone pair electrons) and the completely vacant *d* orbitals (V^{2+} has d^3 configuration with vacant and occupied *d*-orbitals) of the central V may play vital role to fix that particular molecular shape, as proposed by the valence bond theory (VBT) applicable to coordination and transition metal compounds. It is very important to note here that every geometry of the coordination compound always has a specific number of molecules that a central metal atom/ion holds at its immediate vicinity, more commonly called coordination number (hereafter, CN) of that central metal/ion. In the $[V(H_2O)_6]^{2+}$ complex ion, the central V atom is attached directly to six H_2O molecules (CN = 6) each having a donor atom "O", *i.e.* in terms of coordination chemistry, the six monodentate H_2O ligands are directly involved to make coordinate covalent bonds to the central V atom through their donor atoms "O", resulting a formation of primary coordination sphere or a first solvation sphere. As all the six H_2O molecules are neutral type ligands, the charge carried by the central V atom can be calculated as +2 (same as the charge unit of the complex ion). Therefore, the V^{2+} with a fixed CN must have a definite value of the ionic radius unlike to those metal ions which preferentially make clusters with the number of ligands around them. Shanon has reported the experimentally determined ionic radius of the V^{2+} elsewhere [31] as 0.80Å which signifies that the V^{2+} ion is comparatively a bigger sized vanadium ion (than other higher oxidation states of V) that obviously shows a less tendency to attract the bonding ligands (here, H_2O ligands) towards its center but, more intensely attract in comparison to other more bigger sized 3*d* metal ions, resulting its CN limited to six. The same poor binding ability of the central V^{2+} ion (in comparison to higher oxidation states of V) towards its six coordinated H_2O molecules would be a root cause to set the V−OH_2 bond lengths in $[V(H_2O)_6]^{2+}$ as one of the highest values (the V−OH_2 bond lengths in $[V(H_2O)_6]^{2+}$ (Table 1) can be compared to the concerned values in $[V(H_2O)_6]^{3+}$ (Table 2) and $[VO(H_2O)_5]^{2+}$ (Table 3)). Lastly, in theoretical research, an electronic structure produced from the geometry optimization technique is usually reassured by examining whether it represents energetically low structure or not. This can be enquired usually by determining the frequencies on the final nuclear Cartesian coordinates of the optimized geometry without changing *Gaussian* methodology and basis set. In this study, a DFT derived electronic structure of the $[V(H_2O)_6]^{2+}$ complex ion is reconfirmed by computing the concerned frequencies on its final nuclear Cartesian coordinates by employing *B3LYP/6−31G (d, p)* methodology, and successively found no any imaginary frequency (zero negative frequency) as mentioned in Table 1. This theoretical result not only guaranties that the DFT-produced low energy electronic structure (Figure 1) of the $[V(H_2O)_6]^{2+}$ ion represents a true minimum of the potential energy surface but also underscores the validation of the DFT computing criteria endorsed during geometry convergence process.

Table 1. The DFT derived structural parameters for $[V(H_2O)_6]^{2+}$ ion. All the bond lengths and angles are measured in Angstrom (Å) and degree (°) respectively. The O−H bond length and H−O−H bond angle are expressed in average values.

Structural parameters	Structures		Imaginary frequency
	Trial	Optimized DFT *calc*	
Bond Lengths			
V1−O2	2.12	2.06	
V1−O10	2.14	2.12	
V1−O6	2.15	2.08	
V1−O8	2.12	2.06	
V1−O4	2.14	2.12	
V1−O12	2.16	2.08	
O−H	0.97	0.98	0
Bond Angles			
O12−V1−O10	93.9	72.4	
O10−V1−O2	100.9	103.7	

O2−V1−O6	96.1	75.3	
O6−V1−O4	93.9	72.4	
O4−V1−O8	100.9	103.7	
O8−V1−O12	96.1	75.3	
H−O−H	107.0	110.0	

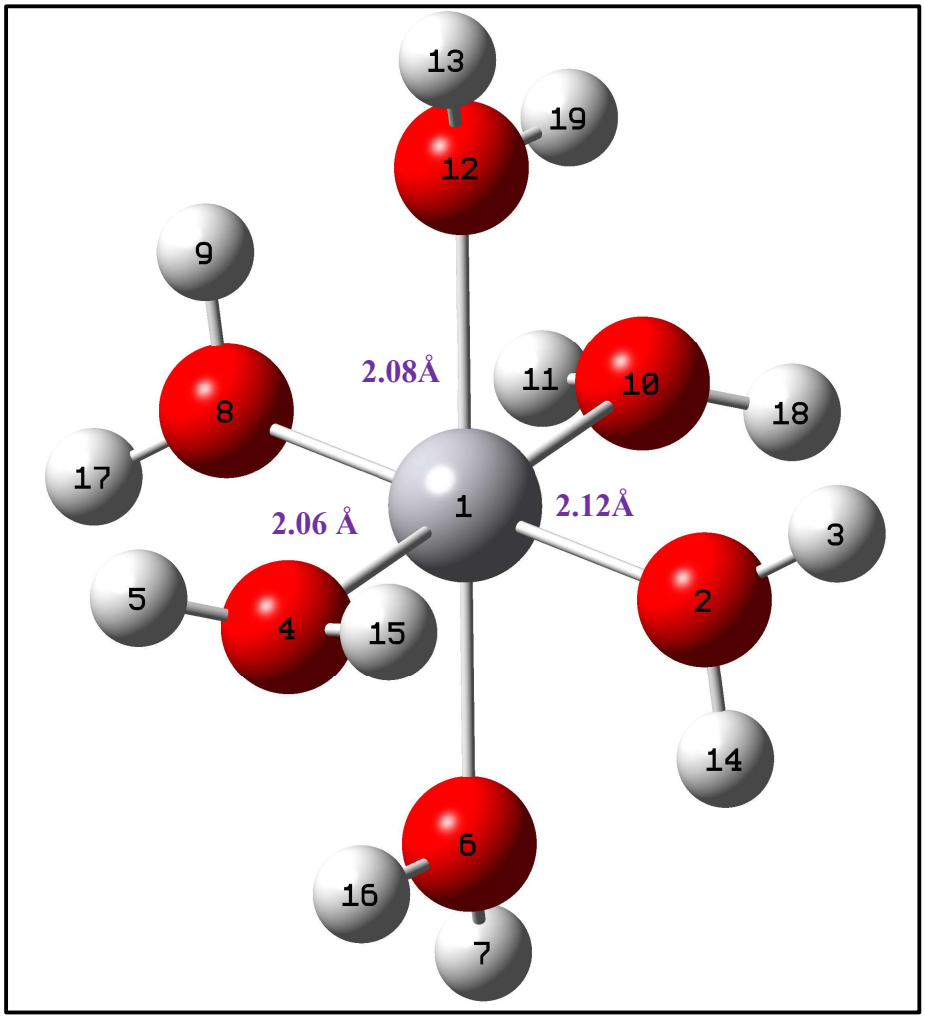


Figure 1. A DFT optimized geometry of $[V(H_2O)_6]^{2+}$ complex ion. The ash-brown, white, and red colored spheroids represent Vanadium (V), Hydrogen (H), and Oxygen (O) atoms respectively. For simplicity, a formal charge of the complex ion is omitted, and all the atoms are labeled numerically.

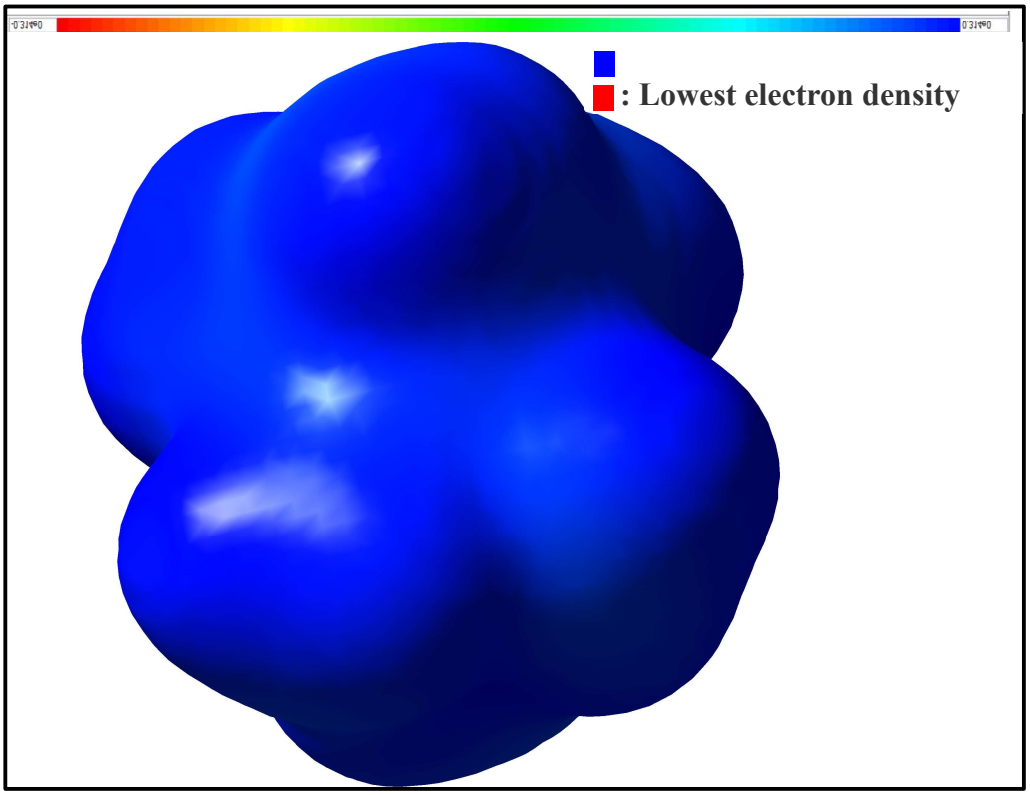


Figure 2. A DFT produced electron density map (mapped with total density) of the [V(H2O)6]2+ complex ion. The six protrusions approximate the position of six H2O ligands around the central vanadium atom.

3.2 Coordination chemistry of hydrated vanadium (III) complex ion

A vanadium (III) ion attains a molecular formula $[V(H_2O)_6]^{3+}$ in its aqueous solution as mentioned earlier in section 1. The DFT derived equilibrium structure (from the trial structure) of this trivalent complex ion is shown in Figure 3, where ash-brown, white, and red colored spheroids represent Vanadium (V), Hydrogen (H), and Oxygen (O) atoms as before. Alike in subsection 3.1, the structural parameters that are considered as quite significant tools to predict the molecular geometry quantitatively are explicitly measured and presented in Table 2, where DFT derived and original (trial structure) bond lengths and bond angles are measured in Angstrom (Å) and degree (°) respectively. In this case as well, the dimensions of these parameters for both of the structures are not noticeably different, specifying that the molecular model used as a trial structure is approvable. Likewise, the careful analyses of all the DFT derived V−OH_2 bond lengths (first row third column of Table 2) reveal that all the H_2O molecules are equally bound to the central vanadium atom. This is not surprising because an equally-dimensioned bond lengths always have an identical binding force to the central metal atom/ion. The most influential point is that the DFT determined dimensions for all the V−OH_2 bonds (1.98 Å in average) are very much compatible to the experimentally derived values reported by Shannon (V−OH_2 = 1.994 Å) [31] and Joanna *et al.* (V−OH_2 = 1.99 Å) [2]. As in $[V(H_2O)_6]^{2+}$ complex ion, the electron density map (mapped with the total density) of the $[V(H_2O)_6]^{3+}$ ion displayed in Figure 4 is used here to portray its charge distributions three dimensionally, and to envision the areas where electrons are present and where they are not, which in turn assist to depict the molecular geometry in the three dimensional space. This map demonstrates quite well about the position of all the six centrally bound H_2O molecules whose electron densities are concentrated clearly around the central V atom, showing the existence of six bonding sites in the immediate proximity of V center. Again, the six very centralized, symmetric and recognizable protrusions (electron dense region) present around the central V atom tells us that all the associated but inbound H_2O molecules are bonded firmly to it. Moreover, the exact molecular shape can be set out if we interconnect each corner of the protrusions through the imaginary lines. If we do so, all the six H_2O molecules appears to be symmetrically arranged around the central V atom by defining six vertices, twelve edges, and eight faces

of an octahedron, meaning is the $[V(H_2O)_6]^{3+}$ complex ion secures an octahedral geometry in the three dimensional space. The inclusive term used just above to deduce the three dimensional shape of the $[V(H_2O)_6]^{3+}$ complex ion can be reconfirmed by measuring its specific bond angles listed in Table 2. Here, none of these angles are exactly 90°: a required value for attaining an exactly octahedral geometry according to the VSEPR theory, but an perfectly equal each and every opposite bond angle that are observed in the average range of 90° indicates a particular shape of slightly distorted octahedral geometry of $[V(H_2O)_6]^{3+}$ (but less distorted than the shape of $[V(H_2O)_6]^{2+}$) as claimed by the experimental as well as simulation studies [2], [32], [33]. This distortion in the octahedral coordination geometry is acceptable theoretically because the central V atom is surrounded by six bond pairs of electrons, and while developing coordinate covalent bond between the central V and the surrounded H_2O molecules, the overlapping directions of the completely fulfilled *p*-orbitals of the "O" atom of each H_2O ligand and the completely vacant *d*-orbitals (V^{3+} has d^2 configuration) of the central V may play cardinal role to maintain that particular shape as highlighted by the VBT applicable to coordination and transition metal compounds. Similarly, in the $[V(H_2O)_6]^{3+}$ complex ion, the central V atom is attached directly to six H_2O molecules (CN = 6) each having a donor atom "O" *i.e.* in terms of coordination chemistry, the six monodentate ligands are directly bonded to the central V atom through their donor atoms "O". And, all the six H_2O ligands are neutral, the charge carried by the central V atom is +3 (same as the charge unit of the complex ion). Therefore, the V^{3+} ion having a constant CN must have a definite ionic radius value equal to 0.654 Å, as reported by Shanon elsewhere [31]. It is obvious that the V^{3+} ion is smaller in size than the V^{2+} ion and bigger than V^{4+} and V^{5+}, the V^{3+} ion shows a more tendency to attract H_2O ligands towards its center than the V^{2+}, implies that a former trivalent ion restricts its CN to six more preferentially than the latter divalent ion. The same stronger binding ability of the central V^{3+} ion to its six coordinated H_2O ligands would be a root cause to set the V−OH_2 bond lengths in $[V(H_2O)_6]^{3+}$ shorter than that in $[V(H_2O)_6]^{2+}$ (refer Table 1 and Table 2 for comparison). Lastly, to reconfirm whether the DFT acquired electronic structure of the $[V(H_2O)_6]^{3+}$ complex ion truly represents energetically low ground state structure or not, the concerned frequencies on its final nuclear Cartesian coordinates were computed as in $[V(H_2O)_6]^{2+}$ ion (sub section 3.1), and successively found no any imaginary frequencies (zero negative frequencies) (Table 2). It ascertains that the DFT produced low energy electronic structure of the $[V(H_2O)_6]^{3+}$ ion shown in Figure 3 depicts a true minimum of the potential energy surface.

Table 2. The DFT derived structural parameters for the $[V(H_2O)_6]^{3+}$ complex ion. All the bond lengths and angles are measured in Angstrom (Å) and degree (°) respectively. The O−H bond length and H−O−H bond angle are expressed in average values.

Structural parameters	Structures		Imaginary frequency
	Trial	Optimized DFT *calc*	
Bond Lengths			
V1−O2	2.02	1.98	
V1−O10	2.02	1.98	
V1−O6	2.02	1.98	
V1−O8	2.02	1.98	
V1−O4	2.02	1.98	
V1−O12	2.02	1.98	
O−H	0.97	0.98	0
Bond Angles			
O2−V1−O6	86.6	94.1	
O6−V1−O10	87.6	85.8	
O10−V1−O8	86.6	94.1	
O8−V1−O12	86.6	94.1	
O12−V1−O4	86.6	85.8	
O4−V1−O2	86.6	94.1	
H−O−H	109	108.8	

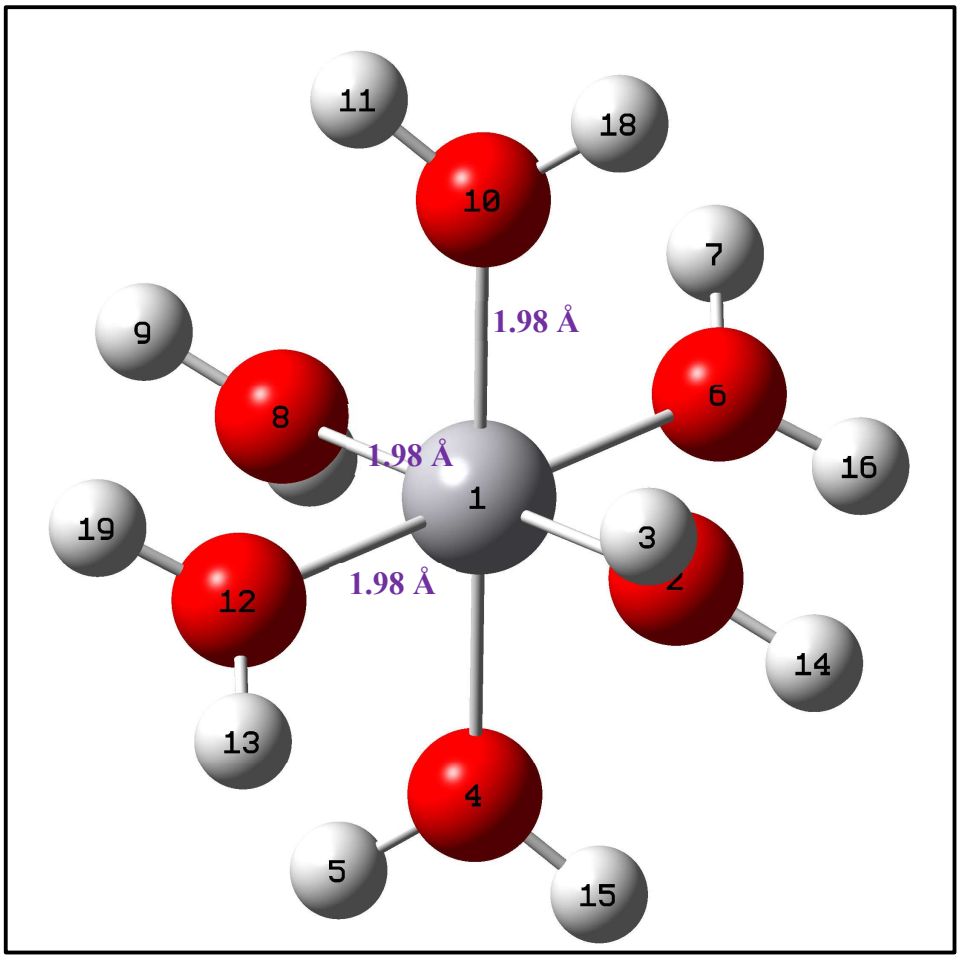


Figure 3. A DFT optimized geometry of [V(H2O)6]3+. The ash-brown, white, and red colored spheroids represent Vanadium (V), Hydrogen (H), and Oxygen (O) atoms respectively. For simplicity, a formal charge of the complex ion is omitted, and all the atoms are labeled numerically.

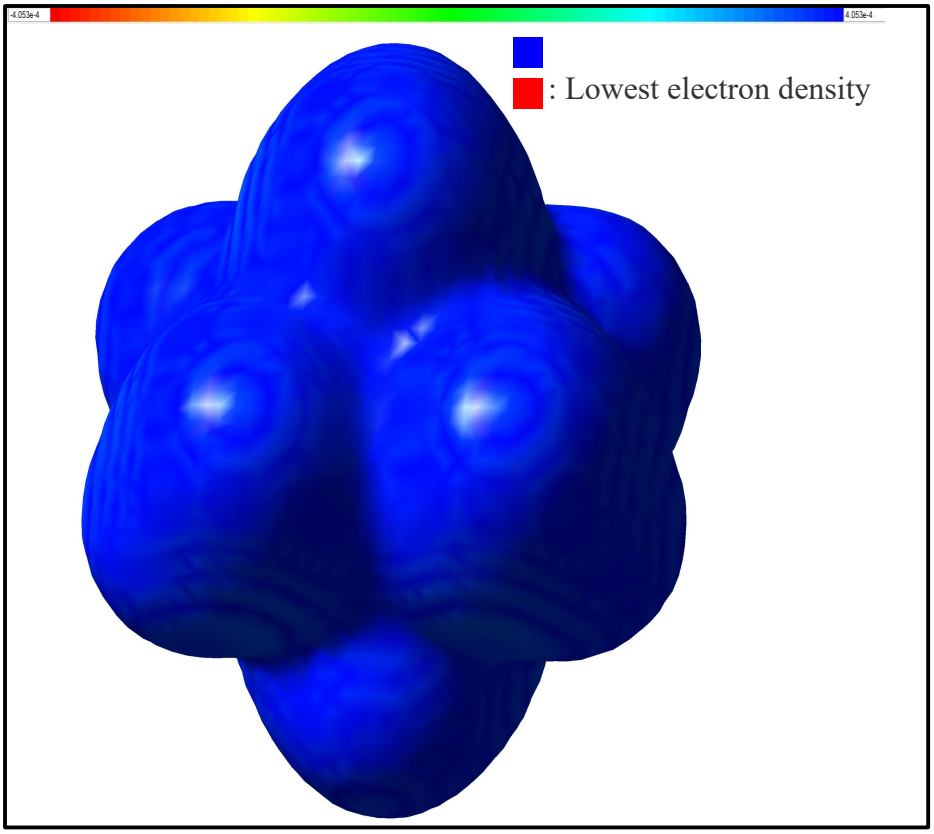


Figure 4. A DFT produced electron density map (mapped with total density) of the complex ion [V(H2O)6]3+.The six protrusions approximate the position of six H2O ligands around the central vanadium atom.

3.3 Coordination chemistry of hydrated vanadium (IV) complex ion

The tetravalent vanadium (V (IV)) ion has comparatively a small ionic radius due to which the density of positive charge around it is comparatively higher just like in other small and highly charged transition metal ions such as Ti (IV) and U (VI) [3]. This is why, the V (IV) ions behave as Lewis acids (electron pair acceptor) and can attract H_2O molecules (electron pair donor) more strongly than the intermolecular force of interactions in bulk water/solution system. This explanation reflects that the V(IV) ions have very high propensity to undergo hydrolysis reactions in the aqueous type solutions, leading to the formation of vanadyl ions VO^{2+} with highly reduced charge density [2], [3]. The main characteristic features of such most stable diatomic ion (vanadyl functional group) known so far are their unique structural unity (proposed bonding pattern with polarity is $V^{4+} \equiv O^{2-}$ [34]) while taking part in many redox reactions, and their high tendency of forming characteristically blue paramagnetic type complex compounds by coordinating either with neutral, negative, or positive type ligands. Accordingly, the VO^{2+} ions in the aqueous solution must have high preference to stabilize themselves by coordinating with the specific number of neutral and monodentate H_2O ligand with an "O" as a donor atom that has a completely fulfilled 2*p* orbital (lone pair electrons). The hydrated form of this VO^{2+} ion is reported as $[VO(H_2O)_5]^{2+}$ by many experimental as well as simulation studies [2], [3], [32], [33]; where central vanadium has +4 oxidation state. In this contribution, the trial molecular model of the $[VO(H_2O)_5]^{2+}$ complex ion (**chart 1**) is optimized through the DFT model and derived its equilibrium structure as displayed in Figure 5, where ash-brown, white, and red colored spheroids represent Vanadium (V), Hydrogen (H), and Oxygen (O) atoms respectively. Alike in $[V(H_2O)_6]^{2+}$ and $[V(H_2O)_6]^{3+}$ complex ions (subsection 3.1 and 3.2), the theoretically computed dimensions of the structural parameters are used here as well to interpret the coordination chemistry quantitatively. All the DFT derived and the original (trial structure) bond lengths and bond

angles are presented (Table 3) in Angstrom (Å) and degree (°) respectively. If we examine these comparable values for the both structures, it can be ascertained that the molecular model used here as a trial structure is quite appropriate. In a similar way, if we analyze all the DFT generated V−OH_2 bond lengths (first row third column) carefully, we can reveal that four out of five H_2O molecules are almost equally bound (bond length = 2.03 Å) to the central vanadium atom whereas a remaining H_2O trans to oxo (double bonded O atom) group is comparatively weakly bound at 2.17Å, and that oxo group is most strongly bound at 1.57 Å. This is as anticipated because an equally-dimensioned bond lengths always have an identical binding force to the central metal atom/ion and contrastingly, double bonded atoms have a shorter bond length meaning is possessing a strong binding force. Most relevantly, all these DFT generated dimensions for all six chemical bonds (five V−OH_2 and an V=O) are very much consistent to the experimentally derived values: Shannon reported that four similar type V−OH_2, a trans V−OH2, and an V=O bonds have length equal to 2.03 Å, 2.20 Å, and 1.59 Å respectively [31], and Joanna *et al.* reported for the same bonds as 2.0 Å, 2.2 Å and 1.6 Å [2]. Again, as in lower oxidation states vanadium hydrated complexes: $[V(H_2O)_6]^{2+}$ and $[V(H_2O)_6]^{3+}$, the electron density map of the $[VO(H_2O)_5]^{2+}$ complex ion (Figure 6) can be used to illuminate the charge distributions around it three dimensionally, and to visualize the areas where electrons are present and where they are not, leading to sketch out more clear molecular geometry. This map demonstrates the position of all the five H_2O molecules and an oxo group whose electron densities are found to be concentrated around the central V atom, predicting the presence of all the six bonding sites in the immediate environs of that central V atom. Similarly, the six distinguishable protrusions (electron dense region) of the map observed around the central V atom further speculates that all the associated but inbound bonding atoms/molecules are coordinated firmly to it. If we examine the map more closely, an uppermost protrusion (shown by red colored arrow in Figure 6) is found to be centralized more intensely towards the central V atom, reassuring the occurrence of exceptionally asymmetric distribution of the electron density which can be assigned to the shortly bonded yet strongly bound oxo group to the V center. Moreover, we can also speculate the molecular shape of the $[VO(H_2O)_5]^{2+}$ ion from its electron density map. For it, each tip of the protrusions must be interconnected through the imaginary lines and visualize thus achieved ideal shape three dimensionally. While doing so, it is appeared as: all the four H_2O molecules are symmetrically arranged around the central V atom but form a plane slightly below that center, an H_2O trans to oxo group and the oxo group itself forms a base and an apex of the pyramidal shape, giving a pyramidal coordination geometry for the $[VO(H_2O)_5]^{2+}$ complex ion in the three dimensional space. Such a universal term used to refer a closed 3-dimensional shape of the $[VO(H_2O)_5]^{2+}$ ion can also be judged by analyzing the concerned DFT generated bond angles listed in Table 3. As the angle O2=V1−OH_2(*trans*) is measured as 180°, and the four equatorial H_2O molecules align differently with almost dissimilar bond angles in the plane slightly below the V center, we expect a specific shape of slightly distorted pyramidal geometry as determined earlier by several experimental as well as simulation studies [2], [32], [33]. This distortion in the coordination geometry is agreeable because the central V atom is surrounded by six bonding groups, out of which the strongly bound oxo group affects the four equatorial H_2O molecules strongly, which then induces a trans H_2O molecule for shifting slightly away from the V center (make the trans H_2O molecule less strongly bound), and same would be their orbital overlapping tendencies while making coordinate covalent bonds between themselves. These mutual effects may involve directly for giving a definite coordination geometry to the $[VO(H_2O)_5]^{2+}$ complex ion as featured by the VSEPR and VBT bonding concepts of the coordination compounds.

Table 3. The DFT derived structural parameters for the $[VO(H_2O)_5]^{2+}$ complex ion. All the bond lengths and angles are measured in Angstrom (Å) and degree (°) respectively. The O−H bond lengths and H−O−H bond angles are expressed in average value.

Structural parameters	Structures		Imaginary frequency
	Trial	Optimized DFT *calc*	
Bond Lengths			
V1=O2	1.52	1.57	
V1−O3	1.98	2.03	
V1−O4	1.97	2.03	
V1−O5	2.12	2.17	
V1−O6	1.98	2.02	
V1−O7	1.97	2.02	
O−H	1.01	0.98	0
Bond Angles			

O2=V1−O7	98.02	99.7	
O7−V1−O3	92.34	88.6	
O3−V1−O5	79.21	83.9	
O5−V1−O4	83.08	80.3	
O4−V1−O6	91.73	88.6	
O6−V1=O2	100.63	96.1	
O2=V1−O5	179.50	179.9	
H−O−H	105	104.5	

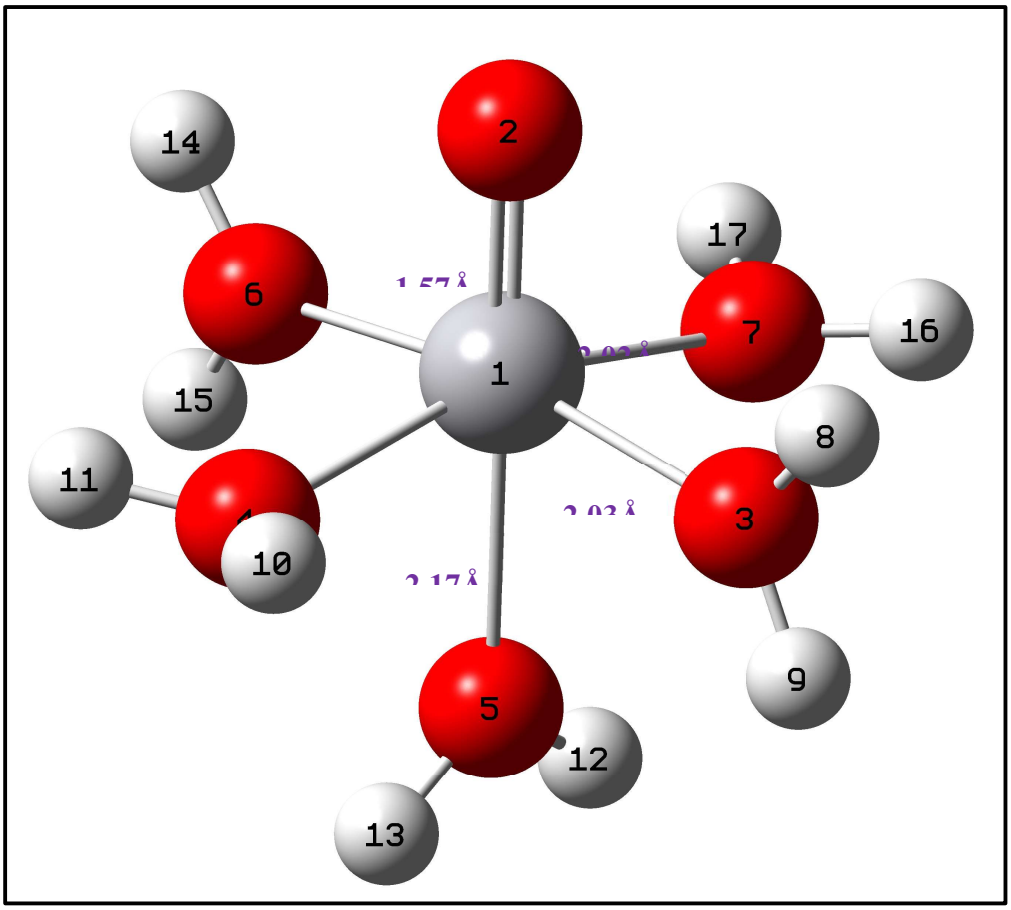


Figure 5. A DFT optimized geometry of [VO(H2O)5]2+ complex ion. The ash-brown, white, and red colored spheroids represent Vanadium (V), Hydrogen (H), and Oxygen (O) atoms respectively. For simplicity, a formal charge of the complex ion is omitted, and all the atoms are labeled numerically.

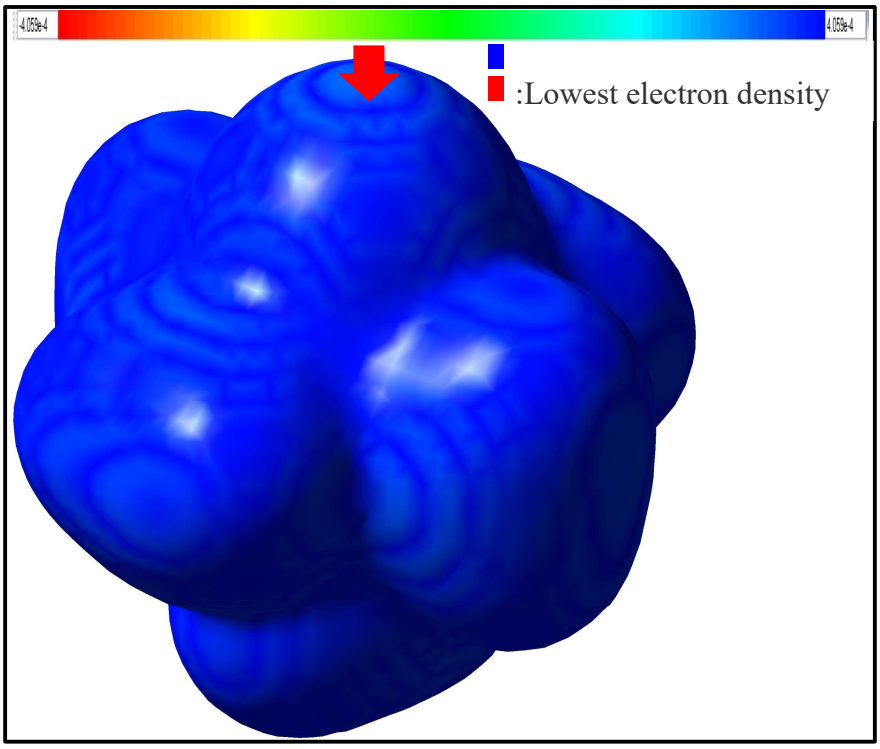


Figure 6. A DFT produced electron density map (mapped with total density) of the complex ion [VO(H2O)5]2+. An uppermost protrusion (pointed by an arrow) approximates the position of an oxo group, and the remaining five approximates that for five H2O ligands around the central vanadium atom.

3.4 Coordination chemistry of hydrated vanadium (V) complex ion

Among the different hydrated complex ions of the V^{n+}(n = II, III, IV, V) in the aqueous type solutions, the electronic stabilities and the ground state electronic structures of the hydrated vanadium (V) complex ions (yellow colored) are very debatable. Krakowiak *et al.* reported VO_2^+ as unhydrated and $[VO_2(H_2O)_4]^+$ as the hydrated V^{5+} complex ions elsewhere [2], Barceloux *et al.* [35] reported VO_3^- or $[VO_3(H_2O)_3]^-$ as the predominating V^{5+} complex ions in the extracellular body fluids, and Vijayakumar *et al.* [36] reported the existence of $[VO_2(H_2O)_3]^+$ as the hydrated V^{5+} complex ions (no any evidences of $[VO_2(H_2O)_4]^+$) in the vanadium redox flow battery catholyte solution. Therefore, either $[VO_2(H_2O)_4]^+$ or $[VO_2(H_2O)_3]^+.H_2O$ form of the hydrated V^{5+} ion may exist predominantly in the low pH scaled aqueous type solution (vanadium solution is usually prepared in the matrix of bench H_2SO_4 solution) unlike in the less acidic type extracellular body fluids. The author of this article has already confirmed $[VO_2(H_2O)_3]^+.H_2O$ as the most stable electronic structure of the V(V) ion with a stabilization energy ΔE = 25.73 *kJ/mol.* lower than that of the $[VO_2(H_2O)_4]^+$ complex ion by employing the DFT model, and reported the detailed structural consequences and electronic stabilities elsewhere [14]. However, in this contribution, the DFT generated molecular structure of the $[VO_2(H_2O)_3]^+.H_2O$ complex ion is reproduced (Figure 7) for the purpose of comparing it with the structures of lower oxidation states hydrated complexes. As can be seen in Figure 7, each V=O bond length is 1.6Å and each V−OH_2 bond length is 2.0Å in average. These values are as equal as the experimentally (X-ray absorption fine structure (EXAFS) and large-angle X-ray scattering (LAXS) techniques) determined values [35], [37]. While analyzing these data sets carefully, one may find that both oxo groups are bound to the central V atom with almost equal strength and alike this, all the single bonded three H_2O molecules are also bound to the same V atom with identical strength. But, as expected, the intensity of the binding force is stronger in the two oxo groups than in the three V−OH_2 groups. Again, there is no any true trans group exists in the structure (unlike in V(IV) complex ion) , but the two oxo groups in cis-configuration affects directly to the orientation of the three H_2O molecules making their plane slightly below to the central vanadium atom. Thus, the molecular geometry of the complex ion enclosed within the square bracket $[VO_2(H_2O)_3]^+$ is visualized as trigonal-bipyramidal. Unlike in the stable hydrated complexes of V(II), V(III), and V(IV), the V(V) hydrated complex has an H_2O molecule just outside

the first co-ordination sphere *i.e.* an H_2O molecule is present in the outer co-ordination sphere, where it remains in direct connection to the nearby H_2O molecule of the inner co-ordination sphere as can be seen clearly in Figure 7. This sort of direct linkage is developed due to the intermolecular interaction exists in between the electronegative atom O (δ^- atom) of the outer H_2O molecule and an H atom (δ^+ atom) bonded to the inner H_2O molecule (interacting atoms are labelled as 7H 8O in Figure 7). This special type of dipole-dipole attraction between the two nearby (inner and outer sphered) H_2O molecules is called hydrogen bond (hereafter, H−bond) whose length is theoretically estimated as 1.6Å. Interestingly, this length is quite shorter than the intermolecular H−bond length (1.8Å) exists in the liquid bulk water system. It reflects that the binding force between the first and the second co-ordination sphere in the $[VO_2(H_2O)_3]^+.H_2O$ complex ion is stronger than the force created by the single H−bond (out of many) of the bulk water system. Such DFT produced most stable hydrated V(V) complex ion is believed to play a crucial role for making the V^{5+} ions

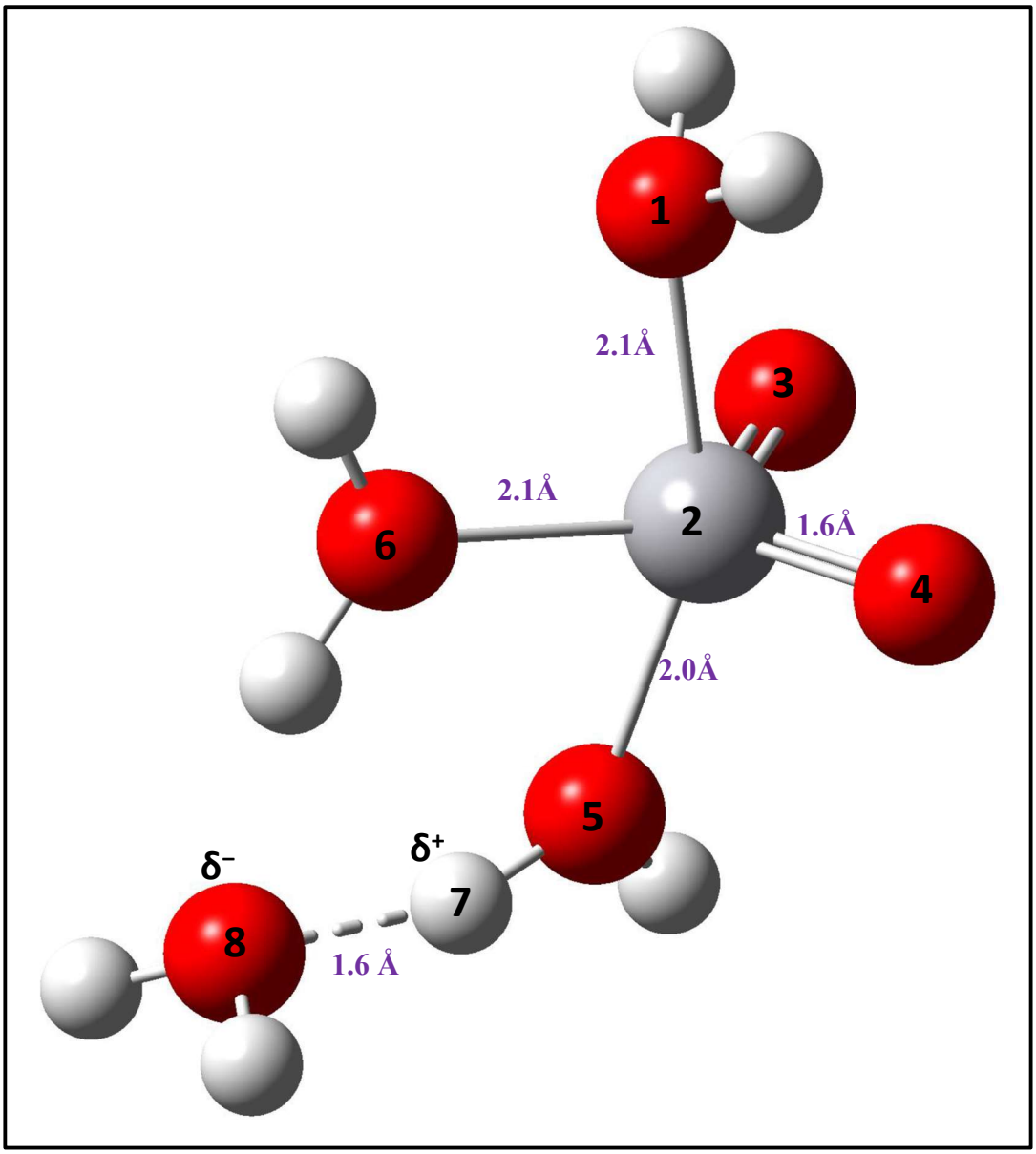


Figure 7. A DFT optimized geometry of [VO2(H2O)3]+.H2O. The ash-brown, white, and red colored spheroids represent Vanadium (V), Hydrogen (H), and Oxygen (O) atoms respectively. For simplicity, a formal charge of the complex ion is omitted, and all the atoms are labeled numerically.

thermally unstable as it leads to the conversion of V^{5+} ions into the precipitate of V_2O_5. For the detailed structural relationships and the pathway of V_2O_5 precipitation process, see a contribution of the same author elsewhere [14].

IV. Conclusion

As the transition metals of the periodic table are characterized by their incomplete *d*-orbital of electrons, large coordination sphere, variable oxidation states, intense hydration reactions, high tendency of forming colored complexes etc., their complex compounds featuring metal-ligand coordinate bonds and coordination centers (metallic atoms/ions) are of both scholarly and practical interests. More especially, the same type but hydrated complex compounds (metal aquo complexes) with H_2O as ligands [molecular formula $[M(H_2O)_n]^{z+}$] are captivating much attention as their detailed theoretical characterizations are more crucial not only for modeling the metal hydrolysis reactions in the aqueous type solutions but also for understanding their ground state electronic stabilities. Being the coordination chemistry of hydrated vanadium more prominent due to the accessibility of its four adjacent oxidation states (V^{n+}; n = +II, +III, +IV, and +V), present theoretical study was mainly aimed at deducing detailed contrasting structural stabilities and coordination geometries of these four distinctive colored vanadium aquo complexes: $[V(H_2O)_6]^{2+}$, $[V(H_2O)_6]^{3+}$, $[VO(H_2O)_5]^{2+}$, and $[VO_2(H_2O)_3]^{+}.H_2O$ in the aqueous type media (both in medicinal and biological fluid matrices). By employing a computationally robust density functional theory (DFT) method, an energetically low ground state electronic structure of each of these complex ions was predicted separately from the respective trial molecular structure (computationally designed). Interestingly, the DFT derived (*Th.*) dimensions of all the chemical bonds present in the ground state electronic structure of each complex ion are found to be very much consistent with the experimentally derived (*Exp.*) values: (a) $[V(H_2O)_6]^{2+}$: V−OH_2 bond length *Th.* 2.0 Å, *Exp.* 2.1 Å; (b) $[V(H_2O)_6]^{3+}$: V−OH_2 bond length *Th.* 1.98 Å, *Exp.* 1.99 Å; (c) $[VO(H_2O)_5]^{2+}$: equatorial V−OH_2 bond length *Th.* 2.03 Å, *Exp.* 2.03 Å, trans V−OH_2 bond length *Th.* 2.17 Å, *Exp.* 2.20 Å, and V=O bond length *Th.* 1.57 Å, *Exp.* 1.59 Å; (d) $[VO_2(H_2O)_3]^{+}$. H_2O: V=O bond length *Th.* 1.6 Å, *Exp.* 1.6 Å, V−OH_2 bond length *Th.* 2.0 Å, *Exp.* 2.0 Å, and an H−bond length *Th.* 1.6 Å. Similarly, the bonding patterns and a closed three dimensional molecular geometry of each DFT derived structure was determined from the respective electron density map (mapped with the total density); $[V(H_2O)_6]^{2+}$, and $[V(H_2O)_6]^{3+}$ ions: distorted octahedral shape, $[VO(H_2O)_5]^{2+}$ ion: distorted pyramidal, and $[VO_2(H_2O)_3]^{+}$ ion: trigonal-bipyramidal as reported earlier by many experimental and simulation studies. Furthermore, to reconfirm whether the DFT acquired electronic structure of each hydrated complex ion truly represents energetically low ground state electronic structure or not, the ground state frequencies on the nuclear Cartesian coordinates of each optimized geometry were computed, and successively found no any imaginary frequencies (zero negative frequencies), reassuring that each DFT produced structure depicts a real minimum of the potential energy surface.

Even though the above mentioned theoretically derived coordination chemistries of all the four hydrated vanadium complexes are as accurate as those obtained from very sophisticated experimental techniques and hence, are highly useful while simulating vanadium based redox flow battery systems and modeling the vanadium hydrolysis reactions in the aqueous type solutions, this research work was only restricted to computationally cheap yet decent DFT method with B3LYP hybrid functional (DFT: B3LYP/6−31G (*d*, *p*) methodology) due to the unavailability of enough computational resources. One may use systematically convergent basis sets recommended for the transition metals (especially for the 3*d* metals) such as relativistic and nonrelativistic type that range in quality from triple-ζ to quintuple-ζ [37] to strengthen the results reported here.

References

[1] R. D. Madan, Modern Inorganic Chemistry (S. Chand & Company Ltd., India, 1997).

[2] J. Krakowiak, D. Lundberg, I. Persson, *Inorganic Chemistry* 51, 9598 (2012).

[3] I. Persson, *Pure and Applied Chemistry* 82(10), 1901 (2010).

[4] T. Yamamura, A. B. Marahatta, S. Yoshida and N. Tanno, Inventors; 2016, Tohoku University (Japan), WIPO (PCT) Patent WO2016158295A1.

[5] T. Yamamura, A. B. Marahatta, S. Yoshida and N. Tanno, Inventors; 2016, Tohoku University (Japan), Japan Patent JP2016/057602.

[6] B. Mukherjee, B. Patra, S. Mahapatra, P. Banerjee, A. Tiwari, M. Chatterjee, *Toxicology Letters* 150(2), 135(2004).

[7] A. F. Rowley, *Journal of Invertebrate Pathology* 37(1), 91 (1981).

[8] J. C. Pessoa, S. Etcheverry, D. Gambino, *Coordination Chemistry Reviews* 301, 24 (2015).

[9] A. Bishayee, A. Waghray, M. A. Patel, M. Chatterjee, *Cancer Letter* 294 (1), 1 (2010).

[10] MedicineNet, VANADIUM, *https://www.medicinenet.com/vanadium/supplements-vitamins.htm*

[11] R. Wever, R. Renirie, Z. Hasan, Vanadium in Biology: Encyclopedia of Inorganic Chemistry (John Wiley & Sons: New York, 2006).

[12] B. R. Nechay, *Annual Reviews of Pharmacology and Toxicology* 24, 501 (1984).

[13] D. Rehder, *Coordination Chemistry Reviews* 182(1), 297 (1999).

[14] A. B. Marahatta, *International Journal of Progressive Sciences and Technologies,* 20(2), 348 (2020).

[15] M. Bühl, H. Kabrede, *Journal of Chemical Theory and Computations* 2(5), 1282 (2005).

[16] B. I. Kruft, "Density Functional Theory for the Investigation of Transition Metal Complexes: Structure, Binding, and Spectroscopy of Metal-Siderophores and the Catalase-Peroxidase Enzyme", A dissertation submitted as part of the requirements for the degree of Doctor of Philosophy (Ph. D.), The City University of New York, USA, 2015.

[17] C. J. Cramer, D. G. Truhlar, *Physical Chemistry Chemical Physics* 11(46), 10757(2009).

[18] A. C. Tsipis, *Coordination Chemistry Reviews* 272, 1(2014).

[19] Æ. Frisch, H. P. Hratchian, R. D. Dennington II, T. A. Keith, J. Millam, Gauss view 05 Reference (Gaussian, Inc. 2009).

[20] Gaussian 09 manual. *http://gaussian.com/geom/?tabid=1#GeomkeywordReadOptimi zeoption*

[21] Æ Frisch, Gaussian 09W Reference (Gaussian, Inc., 2009).

[22] J. B. Foresman, Æ Frisch, Exploring Chemistry with Electronic Structure Methods (Gaussian, Inc., 2015).

[23] J. B. Adams, Encyclopedia of Materials: Science and Technology (Elsevier, 2001).

[24] A. B. Marahatta, *International Journal of Progressive Sciences and Technologies* 16(1), 51 (2019).

[25] A. B. Marahatta, *International Journal of Progressive Sciences and Technologies* 16(2), 01(2019).

[26] A. B. Marahatta, *International Journal of Progressive Sciences and Technologies* 19(1), 100 (2020).

[27] A. B. Marahatta, H. Kono, *International Journal of Progressive Sciences and Technologies* 20(1), 109 (2020).

[28] A. B. Marahatta, *International Journal of Progressive Sciences and Technologies* 19(2), 48 (2020).

[29] A. B. Marahatta, M. Kanno, K. Hoki, W. Setaka, S. Irle, H. Kono, *The Journal of Physical Chemistry C* 116, 24845 (2012).

[30] Y. H. Zhao, J. X. Liu , H. Y. Su, K. Sun , W. X. Li, *ChemCatChem* 6(6), 1755 (2014).

[31] R. D. Shannon, *Acta Crystallographica* Sect. A (32), 751 (1976).

[32] F. H. Allen, *Acta Crystallographica* Sect. B (58), 380 (2002).

[33] Inorganic Crystal Structure Database 1.4.6, release 2011-2; FIZ Karlsruhe: Eggenstein-Leopoldshafen, Germany, 2011.

[34] H. B. Gray, J. R. Winkler, *Accounts of Chemical Research* 51(8), 1850 (2018).

[35] D. G. Barceloux, D. Barceloux, *Journal of Toxicology: Clinical Toxicology* 37(2), 265(1999).

[36] M. Vijayakumar, L. Li, G. Graff, J. Liu, H. Zhang, Z. Yang, J. Z. Hu, *Journal of Power Sources* 196(7), 3669 (2011).

[37] N. B. Balabanov, K. A. Peterson, *Journal of Chemical Physics* 123, 064107-1(2005).