Journal of Engineering and Applied Sciences 13 (23): 9825-9830, 2018
ISSN: 1816-949X

Electronic Structure of Vanadium Tetrachloride Di-Hydroxyl Metal Complex

[1]Faeq A. Mohammed and [2]Hamid I. Abbood
[1]College of Science, Kufa University, Najaf, Iraq
[2]College of Science, Babylon University, Babil, Iraq

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.

Corresponding Author: Faeq A. Mohammed, College of Science, Babylon University, Babil, Iraq

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).

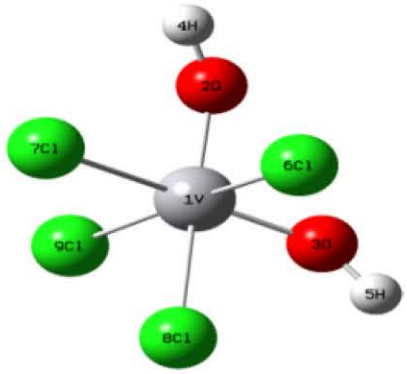

Fig. 1: The relax structure of vanadium tetrachloride di-hydroxyl metal complex

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

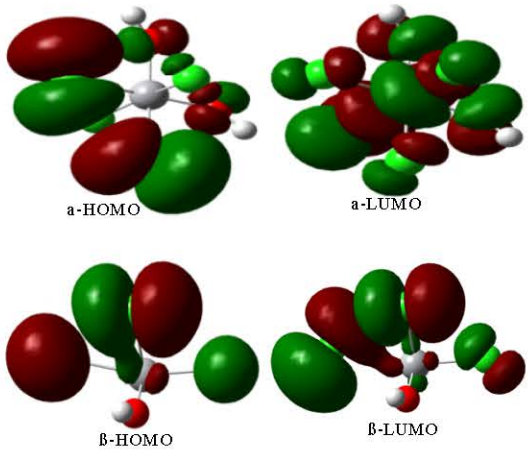

Fig. 2: Frontier orbital surfaces for tetrachloride di-hydroxyl metal complex

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

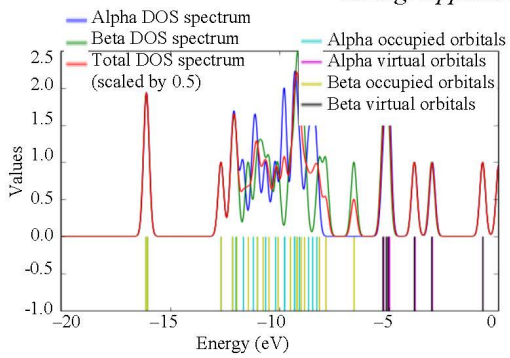

Fig. 3: The DOS for the tetrachloride di-hydroxyl metal complex

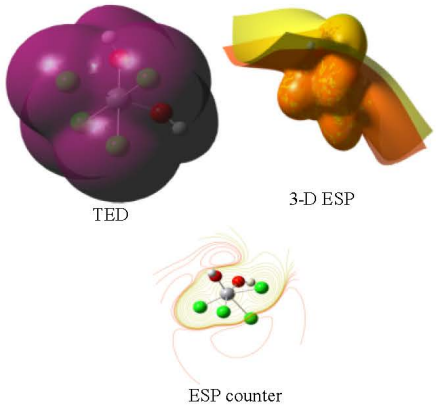

Fig. 4: TED and ESP surfaces of the complex

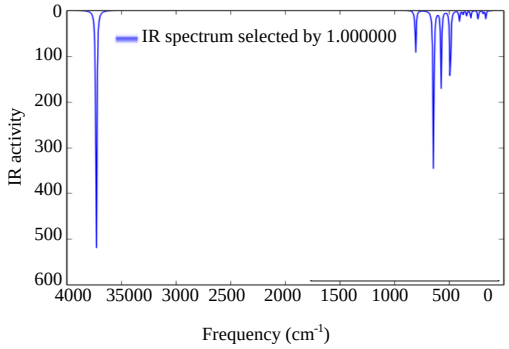

Fig. 5: IR-Spectrum for tetrachloride di-hydroxyl metal complex

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

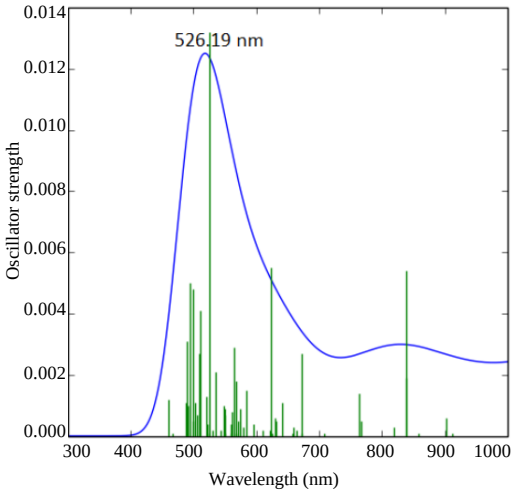

Fig. 6: UV-Vis spectrum of vanadium tetrachloride di-hydroxyl metal complex

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.

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.

REFERENCES

Baes, C.F. and R.E. Mesmer, 1976. The Hydrolysis of Cations. Wiley, Hoboken, New Jersey, USA., Pages: 489.

Becke, A.D., 1993. Density-functional thermochemistry: III, The role of exact exchange. J. Chem. Phys., 98: 5648-5652.

Biernacki, K., A.L. Magalhaes, C. Freire and M. Rangel, 2011. A DFT quantum mechanical study of 3-hydroxy-4-pyrone and 3-hydroxy-4-pyridinone based oxidovanadium (IV) complexes. Struct. Chem., 22: 697-706.

Boas, L.V.V. and J.C. Pessoa, 1987. The Synthesis, Reactions, Properties and Applications of Coordination Compounds. In: Comprehensive Coordination Chemistry, Wilkinson, G., R.D. Gillard and J.A. McCleverty (Eds.). Pergamon Press, New York, USA., ISBN: 9780080359458, pp: 453-583.

Butler, A. and C.J. Carrano, 1991. Coordination chemistry of vanadium in biological systems. Coord. Chem. Rev., 109: 61-105.

Butler, A. and J.V. Walker, 1993. Marine haloperoxidases. Chem. Rev., 93: 1937-1944.

Butler, A., 1998. Vanadium haloperoxidases. Curr. Opin. Chem. Biol., 2: 279-285.

Butler, A., 1999. Vanadium Haloperoxidases. In: Bioinorganic Catalysis, Reedijk, J. and E. Blouwman (Eds.). Marcel Dekker, New York, USA., pp: 55-80.

Chakravarty, J., S. Dutta, A. Dey and A. Chakravorty, 1994. Synthesis, structure and metal redox of new VO^{3+} and VO^{2+} complexes incorporating mixed tridentate-bidentate binding. J. Chem. Soc. Dalton Trans., 4: 557-561.

Chasteen, N.D., 1981. Vanadyl (IV) EPR Spin Probes Inorganic and Biochemical Aspects. In: Biological Magnetic Resonance, Berliner, L. and J. Reuben (Eds.). Plenum Press, New York, ISBN:978-0-306-40612-6, pp: 53-119.

Chasteen, N.D., 1983. The Biochemistry of Vanadium. In: Copper, Molybdenum and Vanadium in Biological Systems, Chasteen, N.D. (Ed.). Springer, Berlin, Germnay, ISBN:978-3-540-12042-1, pp: 105-138.

Chasteen, N.D., 1990. Vanadium in Biological Systems: Physiology and Biochemistry. Springer, Netherlands, ISBN:9780792307334, Pages: 336.

Chasteen, N.D., 1995. Vanadium-Protein Interactions. In: Metal Ions in Biological Systems: Volume 31; Vanadium and its Role for Life, Sigel, A. and H. Sigel (Eds.). Marcel Dekker, New York, USA., pp: 231-231.

Crans, D.C., 1994. Aqueous chemistry of labile oxovanadates: Relevance to biological studies. Comments Inorg. Chem., 16: 1-33.

Crans, D.C., A.D. Keramidas and C. Drouza, 1996. Organic vanadium compounds-a comparison of the transition modification with organophosphorus compounds. Phosphorus Sulfur Silicon Relat. Elem., 109: 245-248.

Diamantis, A.A., J.M. Frederiksen, M.A. Salam, M.R. Snow and E.R.T. Tiekink, 1986. Structures of 2 Vanadium (V) complexes with tridentate ligands. Aust. J. Chem., 39: 1081-1088.

Eady, R.R., 2003. Current status of structure function relationships of vanadium nitrogenase. Coord. Chem. Rev., 237: 23-30.

Faeq, A.M. and H.I. Abbood, 2017. Structural and electronic properties of cis-platin metal complex: B3LYP-SDD/DFT calculations. Intl. J. Adv. Eng. Res. Sci., 4: 082-086.

Frisch, M.J.E.A., G.W. Trucks, H.B. Schlegel, G.E. Scuseria and M.A. Robb *et al*., 2009a. Gaussian 09, revision A.02. Gaussian Inc., Wallingford, Connecticut.

Frisch, M.J.E.A., G.W. Trucks, H.B. Schlegel, G.E. Scuseria and M.A. Robb *et al*., 2009b. Gaussview version 5.0.8. Gaussian Inc., Wallingford, Connecticut.

Gresser, M.J., A.S., Tracey and P.J. Stankiewicz, 1987. The interaction of vanadate with tyrosine kinases and phosphatases. Adv. Prot Phosphatases, 4: 35-57.

Hasan, A.S. and H.I. Abbood, 2016. Density function theory calculations of graphene sheet. J. Kufa Phys., 8: 59-65.

Hay, P.J. and W.R. Wadt, 1985. Ab initio effective core potentials for molecular calculations: Potentials for K to Au including the outermost core orbitals. J. Chem. Phys., 82: 299-310.

Kustin, K., G.C. McLeod, T.R. Gilbert and B.R.L. Briggs, 1983. Vanadium and Other Metal Ions in the Physiological Ecology of Marine Organisms. In: Copper, Molybdenum and Vanadium in Biological Systems, Structure and Bonding, Clarke, J.B., J.B. Goodenough, P. Hemmerich, J.A. Ibers and C.K. Jorgenson (Eds.). Springer, Berlin, Germany, ISBN:978-3-540-12042-1, pp: 139-160.

Kustin, K., W.E. Robinson and M.J. Smith, 1990. Tunichromes, vanadium and vacuolated blood cells in tunicates. Invertebrate Reprod. Dev., 17: 129-139.

Lee, C., W. Yang and R.G. Parr, 1988. Development of the colle-salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B, 37: 785-789.

Liu, H.X., W. Wang, X. Wang and M.Y. Tan, 1994. Synthesis, characterization and the crystal structure of a cis-dioxovanadium (V) complex of a tridentate schiff base ligand. J. Coord. Chem., 33: 347-352.

Liu, S.X. and S. Gao, 1998. Synthesis and characterization of two novel monooxovanadium (V) complexes with bidentate benzohydroxamate ligand. Inorg. Chimica Acta, 282: 149-154.

Liu, S.X. and S. Gao, 1998. Synthesis, crystal structure and spectral properties of VO (acetylacetone benzoylhydrazone)(8-quinolinol). Polyhedron, 17: 81-84.

Liu, T., H.X. Zhang and B.H. Xia, 2007. Theoretical studies on structures and spectroscopic properties of a series of novel cationic [trans-$(C^N)_2Ir(PH_3)_2$]+(C^N= ppy, bzq, ppz, dfppy). J. Phys. Chem. A, 111: 8724-8730.

Mazhir, S.N., H.I. Abbood and H.A. Abdulridha, 2016. Electron transport in graphene-B/P compound heterojunction using LDA/SZ. Intl. J. Adv. Eng. Res. Sci., 3: 154-156.

Michibata, H., N. Yamaguchi, T. Uyama and T. Ueki, 2003. Molecular biological approaches to the accumulation and reduction of vanadium by ascidians. Coord. Chem. Rev., 237: 41-51.

Michibata, H., T. Uyama, T. Ueki and K. Kanamori, 2002. Vanadocytes, cells hold the key to resolving the highly selective accumulation and reduction of vanadium in ascidians. Microsc. Res. Tech., 56: 421-434.

Mokry, L.M. and C.J. Carrano, 1993. Steric control of vanadium (V) coordination geometry: A mononuclear structural model for transition-state-analog RNase inhibitors. Inorg. Chem., 32: 6119-6121.

Nielsen, F.H. and E.O. Uthus, 1990. In Vanadium in Biological Systems. Kluwer Academic Publisher, Boston, Massachusetts,.

Pee, K.H.V., S. Keller, T. Wage, I. Wynands and H. Schnerr *et al*., 2000. Enzymatic halogenation catalyzed via a catalytic triad and by oxidoreductases. Biol. Chem., 381: 1-5.

Rath, S.P., S. Mondal and A. Chakravorty, 1997. Chemistry of hydrazonato oxovanadium (V) alkoxides derived from dihydric/monohydric alcohols. Inorg. Chimica Acta, 263: 247-253.

Rehder, D. and S. Jantzen, 1998. Structure, function and models of biogenic vanadium compounds. Adv. Environ. Sci. Technol. N. Y., 30: 251-284.

Rehder, D., 1991. The bioinorganic Chemistry of vanadium. Angew. Chem. Intl. Ed., 30: 148-167.

Rehder, D., 1995. Inorganic Considerations on the Function of Vanadium in Biological Systems. In: Metal Ions in Biological Systems: Volume 31; Vanadium and its Role for Life, Sigel, A. and H. Sigel (Eds.). Marcel Dekker, New York, USA., pp: 1-43.

Rehder, D., 1999. The coordination chemistry of vanadium as related to its biological functions. Coord. Chem. Rev., 182: 297-322.

Rehder, D., 2000. Vanadium nitrogenase. J. Inorg. Biochem., 80: 133-136.

Rehder, D., 2003. Biological and medicinal aspects of vanadium. Inorg. Chem. Commun., 6: 604-617.

Sigel, H. and A. Sigel, 1995. Vanadium and its Role in Life. Marcel Decker, New York, USA.,.

Slebodnick, C., B.J. Hamstra and V.L. Pecoraro, 1997. Modeling the Biological Chemistry of Vanadium: Structural and Reactivity Studies Elucidating Biological Function. In: Metal Sites in Proteins and Models, Hill, H.A.O., P.J. Sadler and A.J. Thomson (Eds.). Springer, Berlin, Germany, ISBN:978-3-540-62874-3, pp: 51-108.

Smith, M.J., D.E. Ryan and K. Nakanishi, 1995. Vanadium in Ascidians and the Chemistry of Tlinichromes. In: Metal Ions in Biological Systems: Volume 31; Vanadium and its Role for Life, Sigel, A. and H. Sigel (Eds.). Marcel Dekker, New York, USA., pp: 423-490.

Stankiewicz, P.J., A.S. Tracey and D.C. Crans, 1995. Inhibition of phosphate-metabolizing enzymes by oxovanadium (V) complexes. Met. Ions Biol. Syst., 31: 287-324.

Taylor, S.W., B. Kammerer and E. Bayer, 1997. New perspectives in the Chemistry and biochemistry of the tunichromes and related compounds. Chem. Rev., 97: 333-346.

Tracey, A.S. and D.C. Crans, 1998. Vanadium Compounds: Chemistry, Biochemistry and Therapeutic Applications. Vol. 711, ACS Publisher, ýWashington, USA., ISBN:9780841235892, Pages: 381.

Vilter, H., 1995. Vanadium-dependent haloperoxidases. Metal Ions Biol. Syst., 31: 325-362.

Wever, R. and K. Kustin, 1990. Vanadium: A biologically relevant element. Adv. Inorg. Chem., 35: 81-115.

Wever, R., P. Barnett and W. Hemrika, 1997. Structure and Physiological Function of Vanadium Chloroperoxidase. In: Transition Metals in Microbial Metabolism, Winkelmann, G. (Ed.). Harwood Academic Publishers, Amsterdam, Netherlands, pp: 415-433.

Yeh, G.Y., D.M. Eisenberg, T.J. Kaptchuk and R.S. Phillips, 2003. Systematic review of herbs and dietary supplements for glycemic control in diabetes. Diabetes Care, 26: 1277-1294.

Zhou, X., A.M. Ren and J.K. Feng, 2005a. Theoretical studies on the ground states in M (terpyridine) 22+ andM (n-butyl-phenylterpyridine) 22+(M= Fe, Ru, Os) and excited states in Ru (terpyridine) 22+ using density functional theory. J. Organomet. Chem., 690: 338-347.

Zhou, X., H.X. Zhang, Q.J. Pan, B.H. Xia and A.C. Tang, 2005b. Theoretical studies of the spectroscopic properties of [Pt (trpy) C? CR]+(trpy= 2, 2 ‘, 6 ‘, 2 ‘‘-Terpyridine; R = H, CH2OH and C6H5). J. Phys. Chem. A, 109: 8809-8818.