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Synthesis and Characterisation of Macro Cyclic Vanadium Complexes

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Abstract: The design of macro cyclic ligands for the selective complexation of metal ion has been important goal of coordination and bioinorganic chemistry. The cyclam ring continues to be of special interest, and because of its ability to form stable complexes with vanadium. The presence study involves synthesis and characterization of macro cyclic vanadium complexes using synthesized 5, 7, 7, 12, 12, 14 – hexamethyl - 1, 4, 8, 11 – tetraazacyclotetradecane – 4, 11 – diene per chlorate (L1), 5, 5, 7, 12, 12, 14 – hexamethyl 1, 4, 8, 11 – tetraazacyclotetradecane dihydrade (L2) and 5, 5, 7, 12, 12, 14 – hexamethyl 1, 4, 8, 11 – tetraazatrycyclohexadecane (L3) ligands. These complexes were characterized using Fourier transform - Infrared and UV – Visible spectroscopy analysis. Added with this electrochemical studies of the complexes were carried out by cyclic voltammetry technique.

Keywords: Characterization, Macro cyclic vanadium complexes.

I. Introduction

Metal ion plays an important role in living system both in growth and in metabolism. Active sites in the metallobiomolecules are co ordination complexes comprising of one or more metal ions [1]. The potential relation between the properties of active cites biologically active co ordination complexes has contributed significantly to the field of bio inorganic chemistry. The bio inorganic chemistry forms the molecular basis of all the possible interactions between biological molecules and metal ions which is in applied of medicine, biology, environmental science, catalyst, etc, [2]. The potential roles of metal ions in biological systems can be understood based on the structure and activity [3].

Under physiological condition it exists predominantly in the anionic form $H_2VO_4^-$ oxidation state (+5) or (+4) oxidation state as the vanadyl (+4) cationic (VO^{2+}). The anionic form resembles phosphate to some extend while the vanadyl cation resembles Mg^{2+}. Co-ordination complexes of vanadium which may have pharmacological relevance, however, include not only vanadium (V^{5+}) and vanadyl (V^{4+}OLZ) complexes, but also the peroxovanadate $\{V^{+5}O(O_2)(H_2O)(L\text{-}L')^{n-}$, n=0,1$\}$, and $\{V^{+5}O(O_2)_0(H_2O)(L\text{-}L')^{n-}$, n=0,1,2,3$\}$ [4].

Vanadyl (V^{4+}) compound possess less toxicity than vanadate (V^{5+}) compounds and complexes containing thiol functional ligands are more toxic than other functional ligands [5]. From the coordination chemistry point of you vanadium is remarkably flexible (+5) has particularly non rigid streochemical requirements and can form co ordination complexes in geometries ranging from tetra hedral and octahedral to trigonal and pentagonal bi pyramidal V (+4) is much less flexible, with square pyramidal geometry. Complexes may show widely varying thermodynamic stability and kinetic inertness [6].

Vanadium is the one of the most redox active elements, and forms both cationic and anionic complexes in the pH range (2-8) [7]. In vivo, the key redox interplay of vanadium is between V (+5) and V (+4), with the two oxidation states co existing in equilibrium both intra and extra cellularly [8]. Redox balance of vanadium is mediated in vivo by oxygen acidity and the presence of endogenous reducing agent such as ascorbate, glutathione and catechoamine [9]. Although vanadium has been proposed as an in vivo regulated of cell metabolism, and its biochemical functions in mammals is yet to be studied. In certain marine organisms, vanadium is required as a cofactor for a number of haloperoxidases [10]. In rats an extremely low vanadium diet, coupled with high dietary iodine, result in clear aberrations in thyroid hormone metabolism. In vitro effects of vanadium on various compounds of the intracellular signaling cascade are manifested [11]. At higher concentrations (1-5 mM), vanadium insulin like stimulatory or inhibitory effects on specific glucose and lipid related enzyme systems have also been demonstrated [12].

The designs of macrocyclic ligands for the selective complexations of metal ion has been an important goal of coordination and bio inorganic chemistry. The cylam ring contious to be of special interest and because of its ability to form stable complexes with vanadium [13].

There are only few studies with macro cyclic vanadium complexes are reported. The present study involves synthesis and characterization of macrocylic complexes. There are three ligands, such as L1, L2 and L3 are synthesized. These three macro cyclic ligands are treated with vanadium (+4). These complexes were characterized using FT-IR, UV-Visible spectra. The electrochemical studies of the complexes were also carried out by cyclic voltammetry techniques.

II. Materials and Methods

A. Materials

B. Preparation Methods

a) Synthesis of 5, 7, 7, 12, 12, 14 – hexamethyl - 1, 4, 8, 11 – tetraazacyclotetradeca – 4,11 – dieneperchlorate (L1)

20 g of ethylene diamine is added to 500 mL of acetone. The solution is stirred with drop wise addition of 55.7 g of perchloric acid for 30 min. White crystalline product was obtained with yield of 78%. The meso and racemic mixture of L1 was prepared by adding 500 mL methanol and stirred with 19 g sodium hydro borate and 16.5 g of NaOH for 1 hr. White product was deposited with the yield of 88%.

b) Synthesis of 5, 5, 7, 12, 12, 14 – hexamethyl 1, 4, 8, 11 – tetraazacyclotetradecane dihydrade (L2)

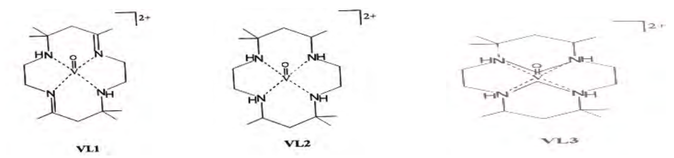
52 g of meso and racemic mixture of L1 is dissolved in 600 mL of methanol and refluxed at 85^0C and filtered. White finely powdered product of meso isomer was precipitated with yield of 37%.

c) Synthesis of 5, 5, 7, 12, 12, 14 – hexamethyl 1, 4, 8, 11 – tetraazatrycyclohexadecane (L3)

A solution containing 25 mL of formaldehyde and 25 mL of formic acid in 50 mL of methanol was added to 50 mL of meso isomer in methanol. The solution was refluxed for 5 hr. The brown residue was extracted with yield of 63%.

d) Synthesis of Vanadium Complexes

The complex of vanadium ligand 1 (VL1) was synthesized by the addition of 1.42 g of L1 and 0.81 g of $VOSO_4H_2O$ in methanol. A green color precipitate was obtained. Similarly the complex of vanadium ligand 2 (VL2) was prepared by using 1.6 g of L2 and the complex of vanadium ligand 3 (VL3) was prepared by using 0.77 g of L3.



C. Experiments

a) FT-IR Spectrum Analysis

Fourier Transform Infrared spectra of the macro cyclic ligand complexes were recorded in the range 4000-400 cm^{-1} using KBr pellets on Perkin Elmer 360 model FT- IR Spectrometer.

b) UV-Visible Spectrum Analysis

UV-Visible spectra of the macro cyclic ligand complexes were recorded using a HITEACI 320 double beam spectrometer.

c) Electrochemical Studies

The Cyclic voltammograms of the sample were recorded by using CH16000A analyzer. A glassy carbon electrode (GCE) as working electrode, Saturated Ag/AgCl electrode as reference and Pt wire was used as auxiliary electrode. Tetra (n-butyl) ammonium perchlorate (TBAP) was used as supporting electrolyte.

III. Results and Discussion

A. Fourier –Transform Infrared Spectroscopy Analysis (FT-IR):

The FT-IR spectra of vanadium complexes VL1, VL2 and VL3 showed a sharp peak around 950-970 cm^{-1} indicating the complexation of vanadium with macro cyclic ligand. The complexes VL1 and VL2 shows a characteristic peak due to N-H bond vibration around 3250 cm^{-1} which is absent in the FT-IR spectrum of VL3. The peak in the range of 2020-2090 cm^{-1} are indicating the co ordination of vanadium metal with nitrogen of corresponding macro cyclic ligand. The FT-IR frequencies were shown in Table 1.

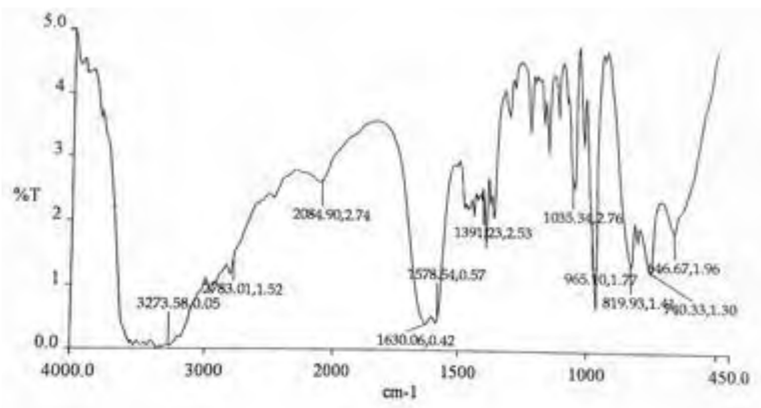


Fig. 1: FT-IR spectrum of complex VL1

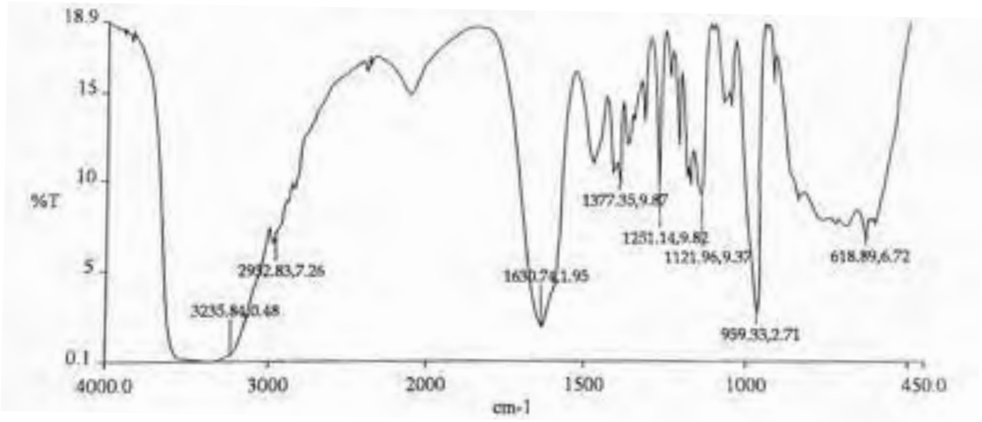


Fig. 2: FT-IR spectrum of complex VL2

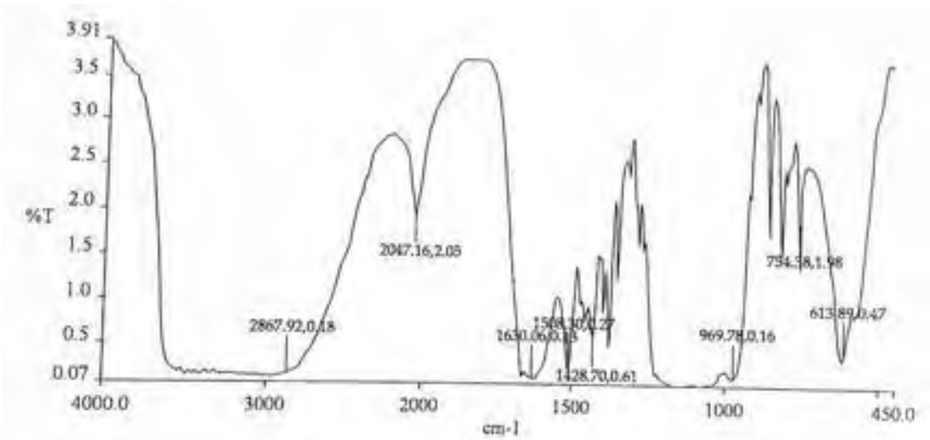


Fig. 3: FT-IR spectrum of complex VL3

TABLE I: FT-IR FREQUENCIES OF VANADIUM COMPLEXES

Complexes	cm^{-1}		
	Vanadium (IV)-oxo	Vanadium (IV)- Nitrogen	N-H
VL1	965	2084	3273
VL2	959	2022	3235
VL3	969	2047	Nil

B. Ultra-Violet Visible Spectroscopy Analysis (UV-Visible):

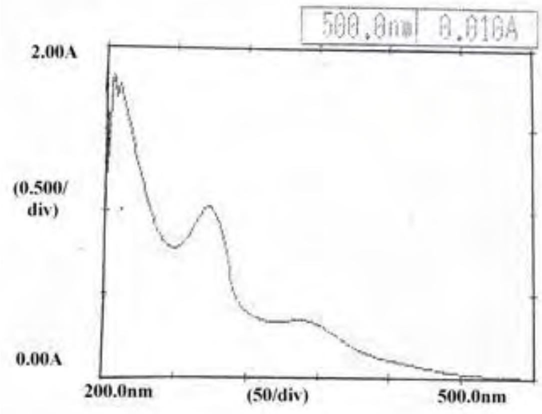


Fig. 4: UV- spectrum of complex VL1

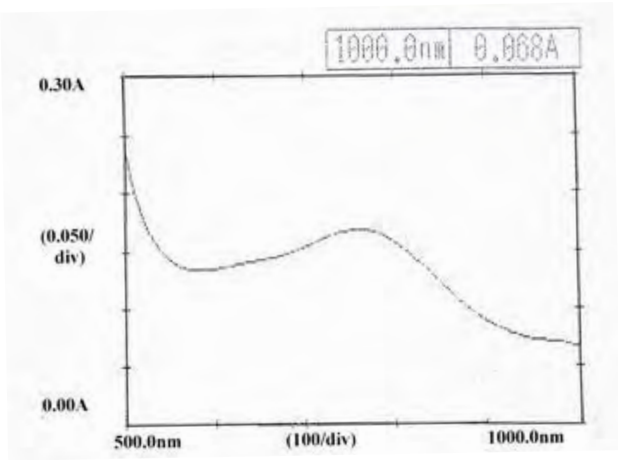


Fig. 5: Visible- spectrum of complex VL1

The UV- Visible spectra shows broad absorption peaks in the visible range at 930-700 nm due to d-d transition are the indicative of characteristic vanadium (IV) oxo complexes. Moderatively intense peaks around 310-250 nm were found in the UV spectra of the complexes due to ligand to ligand charge transfer transition. Λ_{max} values are compiled in the Table 2.

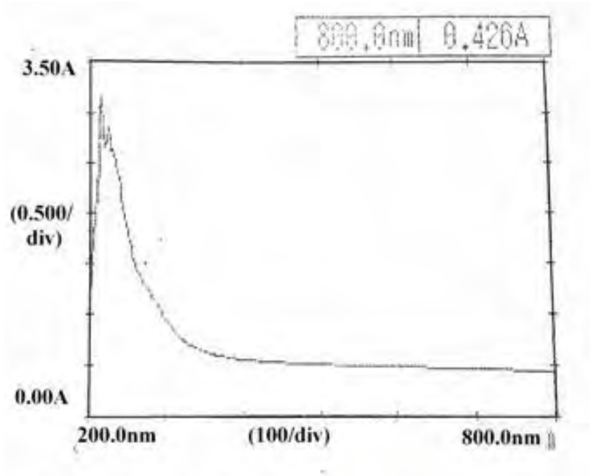


Fig. 6: UV- spectrum of complex VL2

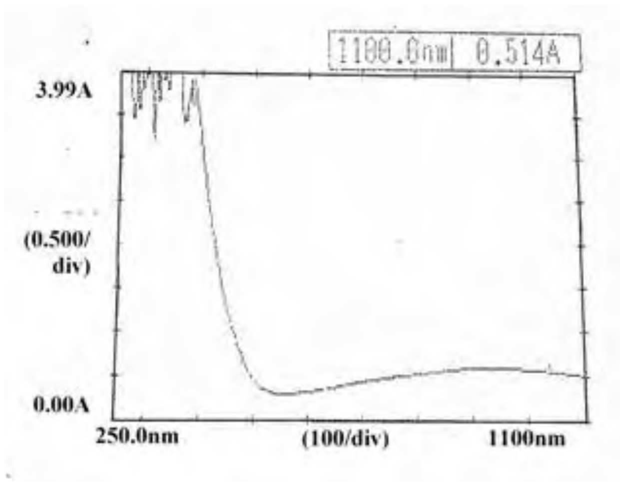


Fig. 7: UV- spectrum of complex VL3

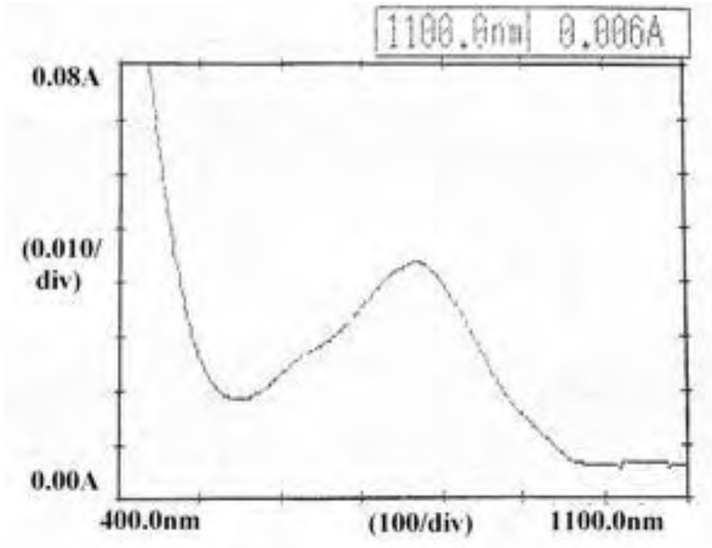


Fig. 8: Visible- spectrum of complex VL2

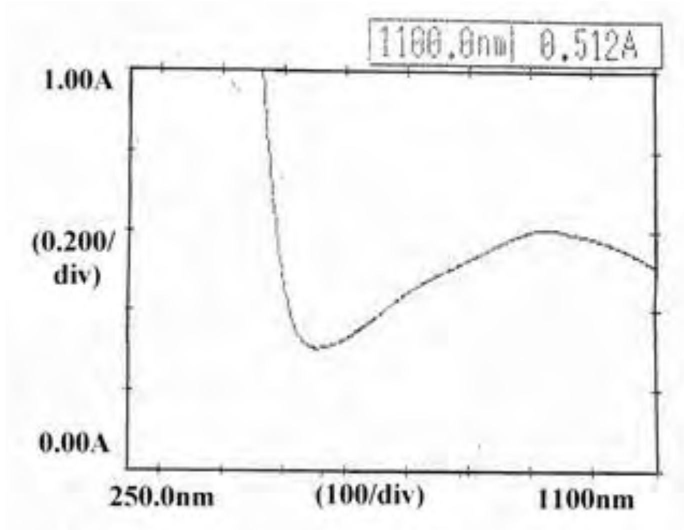


Fig. 9: Visible- spectrum of complex VL3

TABLE II: UV-VISIBLE ABSORPTION SPECTRAL DATA OF VANADIUM COMPLEXES

Complexes	Electronic spectra			
	Ligand to Ligand transition		d-d transition of vanadium complexes	
	Λ_{max}, nm	E, $M^{-1}cm^{-1}$	Λ_{max}, nm	E, $M^{-1}cm^{-1}$
VL1	273	10260	760	168
VL2	272	14000	770	430
VL3	269	18900	926	306

C. Potential Ranges of Vanadium Complexes:

The cyclic voltammograms of the complexes were recorded in the potential range -0.2V to 0.8V. All the vanadium (IV) complexes showed an irreversible single electron redox peak in the range -0.8 to -1.6V as it is evidenced from the criteria that the cathodic peak potential (E_{pc}) does not show a reverse peak. The E_{pc} of the complexes are shown in Table 3.

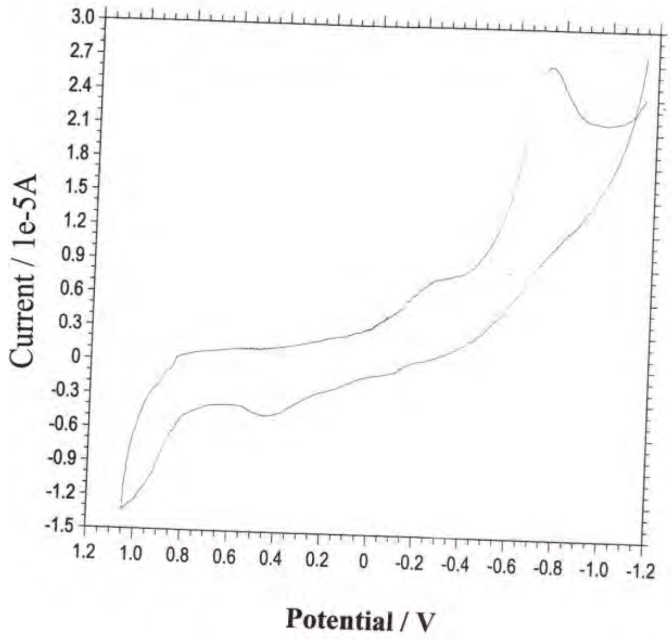


Fig. 10: Electro chemical studies of complex VL1

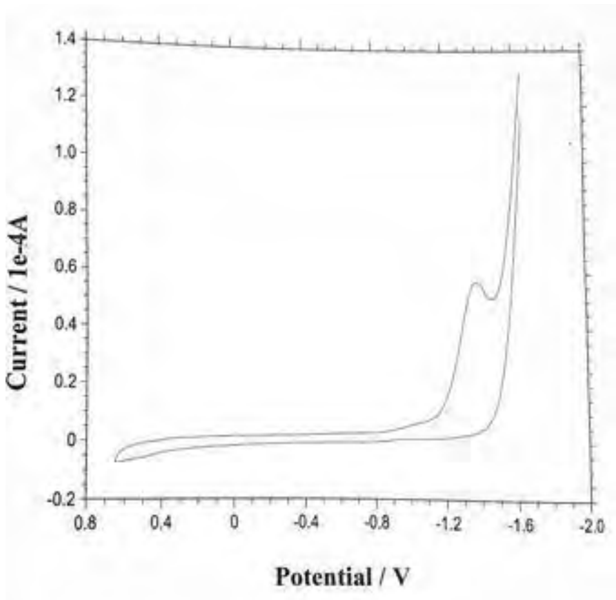


Fig. 11: Electro chemical studies of complex VL2

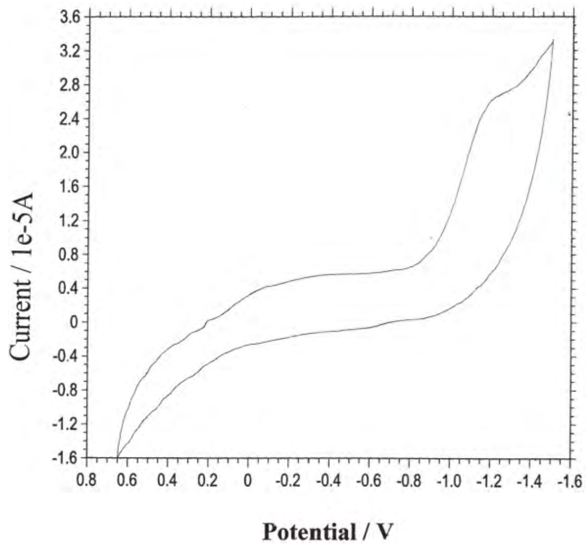


Fig. 12: Electro chemical studies of complex VL3

TABLE III: POTENTIAL RANGES OF VANADIUM COMPLEXES

S.NO	COMPLEXES	E_{PC}(v)
1	VL1	-0.70
2	VL2	-1.39
3	VL3	-1.22

IV. CONCLUSION

The interest in the synthesis of new vanadium (IV) complexes is mainly due to their applications in bioinorganic chemistry, magneto chemistry and pharmacology. Our present work deals with the synthesis of L1, L2, L3 and their vanadium complexes and their characterization.

The vanadium complexes of corresponding ligands were synthesized by the stichiometric addition of vanadyl sulphate. Monohydrate to their ligands in acetonitrile methanol mixture. All the complexes were characterized by IR and UV visible spectra. The IR spectral studies indicate peak around 950-970cm^{-1} due to the presence of vanadium (IV) oxo coordination to the ligand. The UV- Visible spectra investigation of the complex shows a peak in the visible range above 700nm in the complexes are also an indication of vanadium (IV) complexes. The electrochemical studies carried on these complexes show single electron irreversible reduction process.

Reference

[1] J. A. Jbers, and R. H. Holm, "Modeling coordination sites in metallobiomolecules," *Science*, vol. 209, no. 4453, pp. 223-235, Jul. 1980.

[2] E. Bouwman, and J. Reedijk, *Bioinorganic Catalysis* (2nd ed.), Marcel Dekker Inc. New York, Basel, 1999.

[3] D. E. Fenton, *Biocoordination Chemistry*, Oxford University Press, Oxford, UK, pp. 1-96, 1995.

[4] K. H. Thompson, J. H. McNeill, and C. Orvig, "Vanadium-containing insulin biomimetic drugs," *Biological Inorganic Chemistry,* vol. 2, pp. 139-158, 1999.

[5] D. Rehder et. al. "In vitro study of the insulin-mimetic behaviour of vanadium (IV, V) coordination compounds," *Journal of Biological Inorganic Chemistry,* vol. 7, pp. 384-396, 2002.

[6] C. Djordjevic, B. C. Puryear, N. Vuletic, C. J. Abelt, and S. J. Sheffield, "Preparation, spectroscopic properties and characterization of novel peroxo complexes of vanadium (V) and molybdenum (VI) with nicotinic acid and nicotinic acid N-oxide," *Inorganic Chemistry*, vol. 27, no. 17, pp. 2926-2932, 1988.

[7] G. R. Willsky, "Vanadium in the biosphere," In *Vanadium in Biological Systems: Physiology and Biochemistry,* N. D. Chasteen Ed. Dordrecht: Kluwer Academic Publishers, 1990, ch. 1, pp. 1-24.

[8] E. M. Page, and S. A. Wass, "Vanadium 1995," *Coordination Chemistry Review,* vol. 164, pp. 203-259, 1997

[9] F. H. Nielsen, "Vanadium in mammalian physiology and nutrition. In H. Sigel and A. Sigel (eds)," *Metal Ions in Biological Systems, Vanadium and its Role in Life*, vol. 31, no. 16, pp. 543-574, Marcel Dekker, New York, 1995.

[10] A. Butler, and J. V. Walker, "Marine haloperoxidases," *Chemical Reviews*, vol. 93, pp. 1937-1944, 1993.

[11] G. Elberg, J. Li, and Y. Shechter, "Mechanism of action of vanadium in mediating the biological effect of insulin," In: J. O. Nriagu (ed.), *Vanadium in the Environment. Part II: Health Effects*, no. 14, Wiley, New York, 1998.

[12] P. J. Stankiewicz, and A. S. Tracey, *Metal Ions in Biological Systems* (ed.), H. Sigel, and A. Sigel, Marcel Dekker, New York, vol. 31, no. 8, pp. 249-285, 1995.

[13] N. D. Chasteen, E. M. Lord, H. J. Thompson, and J. K. Grady, "Vanadium complexes of transferrin and ferritin in the rat," *Biochimica et Biophysica Acta (BBA)*, vol. 884, no. 1, pp. 84-92, Oct. 1986.