J. Iran. Chem. Soc., Vol. 5, No. 2, June 2008, pp. 328-335.

JOURNAL OF THE
Iranian
Chemical Society

Template Synthesis and Characterization of Oxovanadium(IV) Complexes with Tetraaza Macrocyclic Ligands and Their Activity on Potato Virus X

S.N. Thakur[a], K.S. Yadav[a], N.P. Singh[b] and H.S. Yadav[a,*]

[a]*Department of Chemistry, North Eastern Regional Institute of Science and Technology (NERIST), Nirjuli, Arunachal Pradesh, India*

[b]*Department of Chemistry, U.P. Autonomous College, Varanasi, India*

(Received 3 May 2007, Accepted 30 September 2007)

The oxovanadium(IV) complexes (I) of the type $[VO(L)]SO_4$ have been prepared using an in-situ method of synthesis with ligands derived from di-2-thienylethanedione with 1,2-diaminobenzene or 2,3-diaminopyridine. These parent complexes have been further reacted with β-diketones to yield macrocyclic complexes (II) of types $[VO(mac)]SO_4$ (where mac = macrocyclic ligands derived by condensation of amino group of parent complex with β-diketones), wherein the VO^{2+} cation acts as a template. Tentative structures of these complexes have been proposed on the basis of elemental analysis, electrical conductance, magnetic moments and spectral (infrared, electronic and electron spin resonance) data. The oxovanadium(IV) complexes are five coordinated wherein the tetraaza macrocyclic ligands act as tetradentate chelating agents. All the complexes are found to inhibit the infectivity of potato virus X, when checked using the test plant *Chenopodium amaranticolor.*

Keywords: Oxovanadium(IV), Macrocyclic complexes, Template, Potato virus X

INTRODUCTION

Interest in vanadium chemistry is due to its importance in industry, the environment and physiological functions in plants as well as in animals [1-4]. Vanadium is accumulated in high concentrations in sea squirts [5] and mushrooms of the genus *Amanita* [6]. The function of vanadium in living systems is yet to be ascertained with conformity, despite some hypotheses that have been put forward [7]. Moreover, two classes of vanadium-dependent enzymes, namely vanadium-nitrogenases [8] and vanadate haloperoxidases [9], have been discovered in nature. Vanadium has the ability to produce significant physiological effects such as the inhibition of phosphate-metabolizing enzymes [10], the stimulation of phosphomutases [11] and phosphoisomerases [12], anticancer activity [13] and insulinomimetic activity [14].

Much research has been devoted to the exploration of the potential of thiosemicarbazones and their complexes to exhibit biological activity, such as antibacterial, antimalarial, antiviral and antitumor effects [15-17]. Planar Schiff base ligands capable of imposing rigid coordination environments about metal ions have stimulated widespread interest [18]. Therefore, in this communication we report the syntheses and characterization of oxovanadium(IV) complexes with macrocyclic ligands derived from di-2-thienylethanedione and 1,2-diaminobenzene or 2,3-diaminopyridine and their cyclization reactions with β-diketones, including acetylacetone, benzoylacetone, thenoyltrifluoroactone and dibenzoylmethane. The activity of these oxovanadium(IV) complexes on potato virus X has been determined using the

*Corresponding author. E-mail: hardeoy@yahoo.co.in

test plant *Chenopodium amaranticolor*.

EXPERIMENTAL

1,2-Diaminobenzene and 2,3-diamiopyridine were distilled before use. Acetylacetone, benzoylacetone, thenoyltrifluoro-acetone and dibenzoylmethane (Sisco Research Laboratories, Mumbai, India) were used as supplied. Vanadium sulfate and di-2-thienylethanedione were obtained from E. Merck. All the solvents used were reagent grade products.

Synthesis of the Complexes

Preparation of oxovanadium(IV) complexes with ligands derived by condensation of di-2-thienylethanedione with 1,2-diaminobenzene or 2,3-diaminopyridine. Vanadium sulfate (2.0 mmol, 0.43 g) dissolved in methanol (25 ml) was added to a refluxing solution of di-2-thienylethanedione (2.0 mmol, 0.44 g) and 1,2-diaminobenzene (4.0 mmol, 0.43 g) or 2,3-diamino pyridine (4.0 mmol, 0.44 g) in aqueous ethanol (25 ml). The mixture was refluxed for 6 h, when the color of the solution turned green. The complexes were filtered and the solvent was removed under vacuum at room temperature and the dark green product was isolated. The complex was thoroughly washed with a methanol/aqueous ethanol mixture, with a yield of 70%.

Preparation of macrocyclic complexes of oxo-vanadium(IV). Vanadium sulfate (2.0 mmol, 0.43 g), dissolved in methanol (25 ml), was added to a refluxing solution of di-2-thienylethanedione (2.0 mmol, 0.44 g) and 1,2-diaminobenzene (4.0 mmol, 0.43 g) or 2,3-diamino-pyridine (4.0 mmol, 0.44 g) in aqueous ethanol (25 ml). The mixture was refluxed for 5 h, when the color of the solution intensified and turned green. To this reaction mixture, an ethanolic solution (10 ml) of acetylacetone (2.0 mmol, 0.10 g) and glacial acetic acid (5 ml) were added. The reaction mixture was further refluxed for about 5 h, after which a green precipitate was obtained. The complex was filtered and purified by washing with 10 ml of a mixture of methanol/aqueous ethanol (1:1), with a yield of 60%.

The same procedure was adopted for the synthesis of other oxovanadium(IV) macrocyclic complexes using benzoyl-acetone (2.0 mmol, 0.16 g), thenoyltrifluoroacetone (2.0 mmol, 0.22 g) and dibenzoylmethane (2.0 mmol, 0.22 g).

Analytical Procedure and Physical Measurements

Microanalyses for carbon, hydrogen, nitrogen and sulfur were performed at the Central Research Facility, NERIST, Nirjuli, Itanagar. The amount of vanadium was estimated gravimetrically as its vanadate [15] after decomposing the complex with concentrated nitric acid.

Conductance measurements were performed in dimethyl-formamide using a Toshniwal conductivity bridge (model no. CL0102A) at room temperature. The magnetic susceptibility measurements were made by the Gouy's balance using mercuric tetrathiocyanatocobaltate(II) as the calibrant. Electronic and infrared spectra were recorded in dimethyformamide at the RSIC, NEHU, Shillong. The room temperature (298 K) and liquid nitrogen temperature (77 K) electron spin resonance spectra (ESR, X-band) were recorded at the RSIC, IIT, Chennai, and analyzed by previously published methods [30,31,32].

Activity of Oxovanadium(IV) Complexes on the Infectivity of Potato Virus X

A pure culture of potato virus X was maintained on tobacco plant (*Nicotiana tabacum*, var. White Burley). For the assay of the virus, a local viral host, *C. amaranticolor,* was used as a test plant. Plants having the same age, height and vigor were used in all treatments, leaving the youngest leaves close to the apex. The local lesion method was used for virus assay [19]. The whole leaves were used for various treatments and a control plant was maintained separately. An inoculum of the virus was prepared by macerating young infected leaves showing severe symptoms with double-distilled water (1 ml per 1 g of leaf material) in a sterilized mortar. The extract was filtered through two folds of muslin cloth and centrifuged at 5000 rpm for 10 min. The supernatant fluid was separated and suitably diluted with double distilled water and was used as an inoculum. The stock solution of vanadium complexes (1 mg ml^{-1}) was prepared in double-distilled water and was further diluted as and when required. The inoculum was mixed with different dilutions of vanadium complexes in equal proportions, left for 10 min and then used as virus inoculum. For each set of inoculations, the leaves of healthy and vigorously growing *C. amaranticolor* plants at the four-

leaf stage were uniformly dusted with carborandum powder (600 mesh) on the upper surface of the leaf in one direction along both sides of the midrib from their base to the top. Then, the leaves were washed with distilled water. The control plant leaves received a mixture of 1 ml of the infective sap in 1 ml of distilled water. The experiments were performed in an insect-free glass house under natural light. The incubation period after inoculation was seven days.

RESULTS AND DISCUSSION

The reaction appears to proceed according to the following equation:

$$L^1 \text{ (or } L^2) + VOSO_4.3H_2O \xrightarrow{\text{Ethanol}} [VO(L^1)]SO_4 \text{ (or } [VO(L^2)]SO_4) + 5\ H_2O \quad (1)$$

where L^1 = Di-2-thienylethanedione + 1,2-Diaminobenzene and L^2 = Di-2-thienylethanedione + 2,3-Diaminopyridine.

The parent complex $[VO(L^1)]SO_4$ (or $[VO(L^2)]SO_4$) then reacts with β-diketones to yield $[VO(mac)]SO_4$ as given below:

$$[VO(L^1)]SO_4 \text{ (or } [VO(L^2)]SO_4) + \beta\text{-Diketones} \longrightarrow [VO(mac)]SO_4 + 2H_2O \quad (2)$$

where mac = tetraaza macrocyclic ligands derived from condensation of L^1 or L^2 with β-diketones in the presence of oxovanadium(IV) cations.

The elemental analyses of the complexes show a 1:1 metal to ligand stoichiometry (Table 1). The molar conductivity of the oxovanadium(IV) complexes in dimethylformamide showed values of Λ_M between 120-138 $ohm^{-1}\ cm^2\ mol^{-1}$, which indicate their electrolytic nature.

Infrared Spectra

The macrocyclic complexes of oxovanadium(IV) exhibit ν (>C=N) absorption around 1625-1610 cm^{-1}, which normally appears at 1660 cm^{-1} in free ligands. The lowering of this band in type I complexes indicates the coordination of the azomethine group nitrogen atoms to the vanadium [20-22]. The presence of a band at approximately 300 cm^{-1} may be assigned to ν(V-N) vibration [23]. The appearance of a >C=N band and the absence of the >C=O band around 1700 cm^{-1} is conclusive evidence for condensation of diamines with the 2-keto group of di-2-thienylethanedione [22]. The bands appearing at 3350 and 3180 cm^{-1} may be assigned to asymmetrical and symmetrical N-H stretching modes of the coordinated terminal amino group [24]. The oxovanadium(IV) complexes show a band at around 980 cm^{-1}, which is assigned to the ν(V=O) vibration [25]. The presence of ionic sulfate groups in the complexes are confirmed by the appearance of three bands at ca. 1130-1135 cm^{-1} (ν_3), 955-960 cm^{-1} (ν_1) and 600-610 cm^{-1} (ν_4). The absence of a ν_2 band and non-splitting in the ν_3 band indicate that the Td symmetry is retained [26]. The infrared spectra of type-II macrocyclic complexes show the same pattern of bands, but the asymmetrical and symmetrical N-H stretching modes of terminal amino groups disappear due to the condensation of these amino groups with the carbonyl group of β-diketones in the cyclization reactions.

Magnetic Moments and Electronic Spectra

Oxovanadium(IV) complexes show magnetic moment values in the range of 1.71-1.76 B.M. at room temperature, which has been reported for oxovanadium(IV) complexes with one unpaired electron [27]. The electronic spectra show bands in the regions of 835-906 nm, 628-665 nm and 447-474 nm, similar to other five-coordinate oxovanadium(IV) complexes involving nitrogen donor atoms. According to the energy level scheme reported by Stocklosa *et al.* [28] for distorted five-coordinate square pyramidal oxovanadium(IV) complexes, the observed bands can be assigned to $^2B_2 \rightarrow {}^2E$, $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2A_1$ transitions, respectively. One more band is observed in the region 280-284 nm, which may be due to transitions of the azomethine linkages [29].

ESR Spectra

The X-band ESR spectra of oxovanadium(IV) complexes show eight lines at room temperature (Fig. 1), which are due to hyperfine splitting arising from the interaction of the unpaired electron and a ^{51}V nucleus with a nuclear spin number of I = 7/2. This confirms the presence of a single oxovanadium(IV) cation as the metallic center in the complex. The anisotropy is clearly visible in the spectra at liquid nitrogen temperature and eight bands, each due to $g_{\parallel}$ and $g_{\perp}$, are observed separately. The $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$ and $A_{\perp}$ values (Table 2),

Table 1. Physical and Analytical Data of the Oxovanadium(IV) Complexes

Complex	Empirical formula	Decomp. temp. (°C)	%Calc. (Found)					μ_{eff} B.M. (300 °K)
			C	H	N	V	S	
$[VO(L^1)]SO_4$	$C_{22}H_{18}N_4VS_3O_5$	212	46.7 (46.6)	3.2 (3.1)	9.9 (9.8)	9.0 (9.0)	17.0 (16.9)	1.73
$[VO(L^2)]SO_4$	$C_{20}H_{16}N_6VS_3O_5$	210	42.3 (42.1)	2.8 (2.7)	14.8 (14.7)	9.0 (9.0)	16.9 (16.8)	1.75
$[VO(mac^{1)})]SO_4$	$C_{27}H_{22}N_4VS_3O_5$	217	51.5 (51.4)	3.5 (3.4)	8.9 (8.8)	8.1 (8.0)	15.3 (15.2)	1.72
$[VO(mac^2)]SO_4$	$C_{32}H_{24}N_4VS_3O_5$	220	55.6 (55.6)	3.5 (3.4)	8.1 (8.0)	7.4 (7.3)	13.9 (13.8)	1.74
$[VO(mac^3)]SO_4$	$C_{30}H_{19}N_4VS_4O_5F_3$	215	47.9 (47.8)	2.5 (2.4)	7.5 (7.4)	6.8 (6.8)	17.0 (16.9)	1.71
$[VO(mac^4)]SO_4$	$C_{37}H_{26}N_4VS_3O_5$	218	59.0 (58.9)	3.5 (3.4)	7.4 (7.3)	6.8 (6.8)	12.8 (12.7)	1.76
$[VO(mac^5)]SO_4$	$C_{25}H_{20}N_6VS_3O_5$	215	47.5 (47.4)	3.2 (3.1)	13.3 (13.2)	8.1 (8.0)	15.2 (15.1)	1.75
$[VO(mac^6)]SO_4$	$C_{30}H_{22}N_6VS_3O_5$	220	52.0 (51.9)	3.2 (3.1)	12.1 (12.0)	7.4 (7.3)	13.9 (13.8)	1.73
$[VO(mac^7)]SO_4$	$C_{28}H_{17}N_6VS_4O_5F_3$	217	44.6 (44.6)	2.3 (2.2)	11.2 (11.1)	6.8 (6.8)	17.0 (16.9)	1.72
$[VO(mac^8)]SO_4$	$C_{35}H_{24}N_6VS_3O_5$	218	55.6 (55.5)	3.2 (3.1)	11.1 (11.0)	6.7 (6.6)	12.7 (12.6)	1.75

L^1 = Ligand derived by condensation of di-2-thienylethanedione with 1,2-diaminobenzene (1:2)
L^2 = Ligand derived by condensation of di-2-thienylethanedione with 2,3-diaminopyridine (1:2)
Mac^1 = macrocyclic ligand derived by condensation of L^1 with acetylacetone
Mac^2 = macrocyclic ligand derived by condensation of L^1 with benzoylacetone
Mac^3 = macrocyclic ligand derived by condensation of L^1 with thenoyltrifluoroacetone
Mac^4 = macrocyclic ligand derived by condensation of L^1 with dibenzoylmethane
Mac^5 = macrocyclic ligand derived by condensation of L^2 with acetylacetone
Mac^6 = macrocyclic ligand derived by condensation of L^2 with benzoylacetone
Mac^7 = macrocyclic ligand derived by condensation of L^2 with thenoyltrifluoroacetone
Mac^8 = macrocyclic ligand derived by condensation of L^2 with dibenzoylmethane

measured from the spectra, indicate a square-pyramidal structure [33-34]. The g_{iso} value from the mobile solution at room temperature and g_{av} values from the frozen solution at liquid nitrogen temperature are not in close agreement, since the g and A tensors are corrected for second-order. Furthermore, g values are all very close to the spin-only value (free electron value) of 2.0023, suggesting little spin-orbit coupling. On the basis of the above studies, the tentative

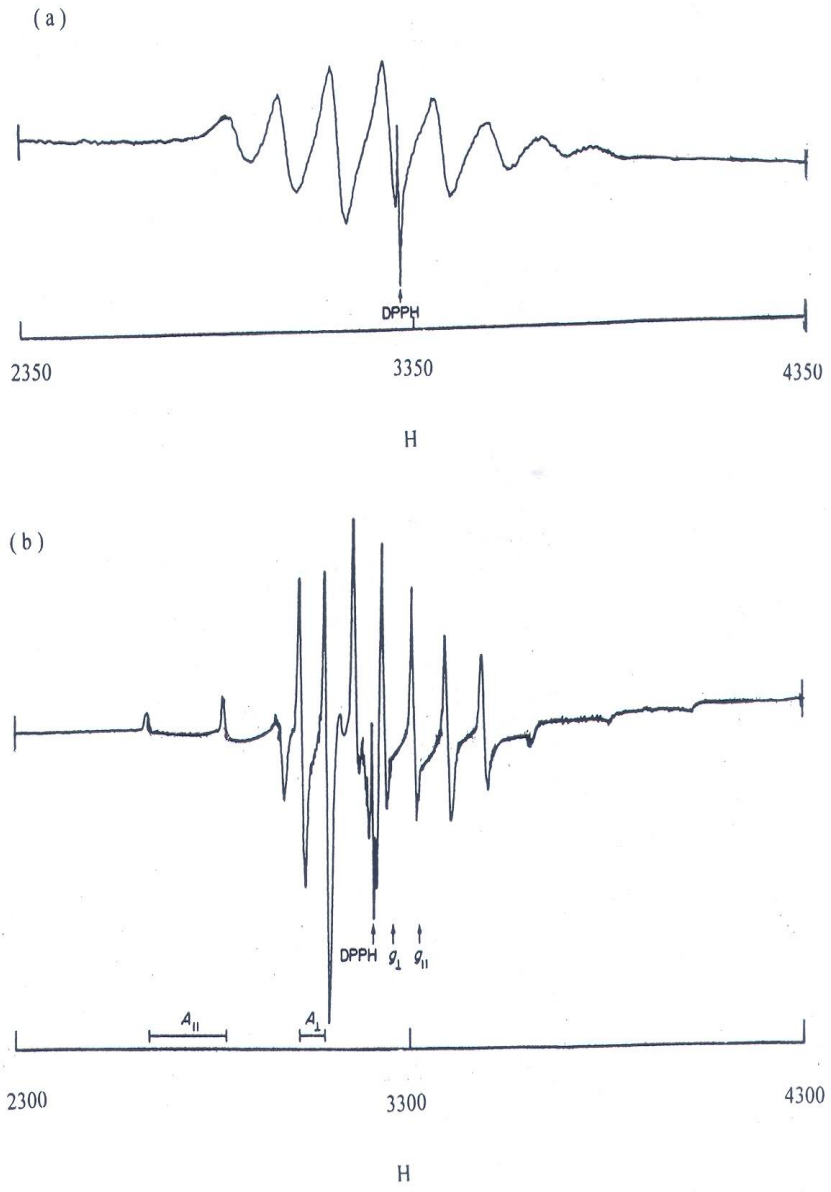


Fig. 1. Electron paramagnetic resonance (EPR) spectra of $[VO(L^1)]SO_4$ in DMSO at 298 K (a) and77 K (b).

structures in Scheme 1 may be proposed for these oxovanadium(IV) complexes.

Activity of Oxovanadium(IV) Complexes on Potato Virus

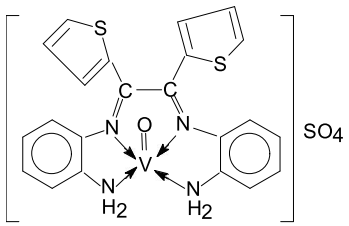
The effect of the complexes on the infectivity of potato virus X was analyzed statistically by comparing viral activity in the control to that in the individual treatment, as summarized in Table 3.

ACKNOWKLEDGEMENTS

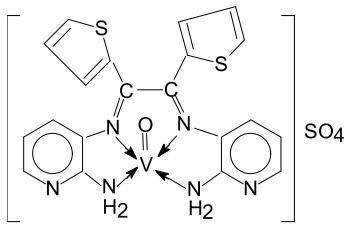
The authors thank the Director of NERIST for providing laboratory facilities, and the CSIR, New Delhi for financial help.

Table 2. Values of g and A for Oxovanadium(IV) Complexes

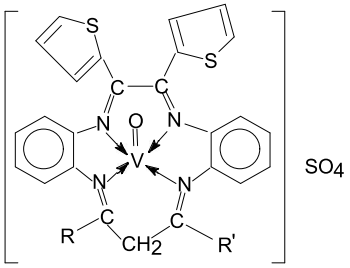
Complex	298 K			77 K			
	|g|	$g_{\parallel}$	$g_{\perp}$	|g|	$10^{-4}A_{\parallel}$ (cm^{-1})	$10^{-4}A_{\perp}$ (cm^{-1})	10^{-4} |A| (cm^{-1})
$[VO(L^1)]SO_4$	1.972	1.930	1.970	1.956	190.70	66.40	107.83
$[VO(L^2)]SO_4$	1.983	1.935	1.979	1.964	191.64	65.80	107.74
$[VO(mac^1)]SO_4$	1.986	1.933	1.977	1.962	188.53	64.81	106.05
$[VO(mac^2)]SO_4$	1.979	1.934	1.976	1.962	185.46	65.50	105.55
$[VO(mac^3)]SO_4$	1.980	1.936	1.984	1.968	186.45	66.74	106.64
$[VO(mac^4)]SO_4$	1.978	1.932	1.975	1.960	184.37	64.50	104.52
$[VO(mac^5)]SO_4$	1.978	1.935	1.984	1.967	188.26	66.79	107.28
$[VO(mac^6)]SO_4$	1.977	1.934	1.977	1.962	187.47	66.59	106.88
$[VO(mac^7)]SO_4$	1.979	1.936	1.978	1.964	187.48	66.60	106.89
$[VO(mac^8)]SO_4$	1.978	1.935	1.977	1.963	187.47	66.61	106.89



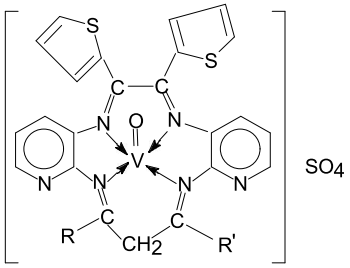
(I)



(I)



(II)



(II)

R	R´	β-Diketone
CH_3	CH_3	Acetylacetone
C_6H_5	CH_3	Benzoylacetone
C_4H_3S	CF_3	Thenoyltrifluoroacetone
C_6H_5	C_6H_5	Dibenzoylmethane

Scheme 1

Table 3. Effect of Oxovanadium(IV) Complexes on the Infectivity of Potato Virus X Using *C. amaranticolor* as a Test Plant

Complex	Dilution (g ml^{-1})	Average no. of local lesions/leaf[a]		Decrease in viral activity (%)
		Treated	Control	
$[VO(L^1)]SO_4$	1000	23	72	68
	100	34	66	48
$[VO(L^2)]SO_4$	1000	22	70	69
	100	32	63	49
$[VO(mac^1)]SO_4$	1000	22	71	69
	100	32	66	52
$[VO(mac^2)]SO_4$	1000	22	72	69
	100	32	63	49
$[VO(mac^3)]SO_4$	1000	22	72	69
	100	32	66	52
$[VO(mac^4)]SO_4$	1000	23	71	68
	100	32	63	49
$[VO(mac^5)]SO_4$	1000	24	70	66
	100	32	63	49
$[VO(mac^6)]SO_4$	1000	23	70	67
	100	32	63	49
$[VO(mac^7)]SO_4$	1000	22	70	69
	100	33	66	50
$[VO(mac^8)]SO_4$	1000	23	70	67
	100	34	66	48

[a]Averaged from 10 leaves.

REFERENCES

[1] K. Gavazov, V. Lekova, G. Patronov, Acta Chim. Slov. 53 (2006) 506.

[2] D.C. Crans, J.J. Smee, E. Gaidamauskas, L. Yang, Chem. Rev. 104 (2004) 849.

[3] D. Rehder, Coord. Chem. Rev.182 (1999) 297.

[4] D. Rehder, J. Inorg. Biochem. 80 (2000) 133.

[5] P. Frank, R.M.K. Carlson, E.J. Carlson, K.O. Hodgson, Coord. Chem. Rev. 31 (2003) 237.

[6] R.E. Berry, E.M. Armstrong, R.L. Beddes, D. Collison, S.N. Ertok, M. Helliwell, C.D. Garner, Angew. Chem., Int. Ed. Engl. 38 (1999) 795.

[7] K. Kanamori, Coord. Chem. Rev. 147 (2003) 237.

[8] R.R. Eady, Coord. Chem. Rev. 23 (2003) 237.

[9] J.N. Carter-Franklin, J.D. Parrish, R.A. Tschirret-Guth, R.D. Little, A.J. Butler, J. Am. Chem. Soc. 125 (2003) 3688.

[10] P.J. Stankiewicz, A.S. Tracey, D.S. Crans, in: H. Sigel, A. Sigel (Eds.), Vanadium and Its Role in life, Metal Ions in Biological Systems, Marcel Dekker, New York, 1995, p. 31.

[11] G.L. Mendz, Arch. Biochem. Biophys. 201 (1991) 291.

[12] A. Evangelou, Oncol. Hematol. 42 (2002) 249.

[13] D.C. Crans, L.Q. Yang, J.A. Alfano, L.A.H. Chi, W.Z. Jin, M. Mahroof- Tahir, K. Robbins, M.M. Toloue, L.

K. Chan, A.J. Plante, R.Z. Grayson, G.R. Willsky, Coord. Chem. Rev. 13 (2003) 237.

[14] M. Kaliva, E. Kyriakakis, A. Salifoglou, Inorg. Chem. 41 (2002) 7015.

[15] N.C. Kasuga, K. Sekino, M. Ishikawa, A. Honda, M. Yokoyama, S. Nakano, N. Shimada, C. Koumo, K.J. Nomiya, Inorg. Biochem. 96 (2003) 298.

[16] K. Nomiya, K. Sekino, M. Ishikawa, A. Honda, M. Yokoyama, N.C. Kasuga, H. Yokoyama, S. Nakano, K. Onodera, J. Inorg. Biochem. 98 (2004) 601.

[17] M.C. Rodriguez-Arguelles, E.C. Lopez-Silva, J. Sanmartin, A. Bacchi, C. Pelizzi, F. Zani, Inorg. Chim. Acta 357 (2004) 2543.

[18] M.S. Shongwe, N.R. Huda, Al-Kharousi, H. Adams, M.J. Morris, E. Bill, Inorg. Chem. 45 (2006) 1103.

[19] J.H. Jensen, Phytopathology 27 (1937) 69.

[20] M. Nonoyama, S. Tomita, K. Yamasaki, Inorg. Chim. Acta 12 (1975) 33.

[21] S.K. Sahni, Trans. Met. Chem. 4 (1979) 73.

[22] J.R. Dyer, Applications of Absorption Spectroscopy of Organic Compounds. Prentice-Hall, Inc., Englewood Cliffs, NJ, 1965.

[23] J.R. Ferraro, Low Frequency Vibrations of Inorganic and Coordination Compounds, Plenum Press, New York, 1971.

[24] D.P. Madden, M.M. daMota, S.M. Nelson, J. Chem. Soc. A (1970) 890.

[25] K. Sakata, M. Kuroda, S. Yanagida, M. Hashimoto, Inorg. Chim. Acta 156 (1989) 107.

[26] H.S. Yadav, Bull. Soc. Chim. France 127 (1990) 641.

[27] A. Symal, Coord. Chem. Rev. 21 (1975) 309.

[28] H.J. Stocklosa, J.R. Wasson, M.J. McCormick, Inorg. Chem. 13 (1964) 592.

[29] P.C.H. Mitchell, J.A. Valero, Inorg. Chim. Acta 71 (1983) 179.

[30] F.K. Kneubuhl, J. Chem. Phys. 3 (1960) 1074.

[31] R.H. Sands, Phys. Rev. 99 (1955) 1222.

[32] H.R. Garman., J.D. Swalen, J. Chem. Phys. 56 (1962) 3221.

[33] A. Syamal, K.S. Kale, Ind. J. Chem. 17A (1979) 518.

[34] L.J. Boucher, E.C. Tynan, T.F. Yen, Inorg. Chem. A (1968) 731.