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Studies on the Peroxo Complexes of Thorium (IV) Containing Organic Acids and Amine Bases

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Abstract. New peroxo complexes of Th(IV) have been synthesized and characterized by elemental analyses and various physicochemical techniques. The complexes were found to oxidize allyl alcohol and triphenylphosphine as well as triphenylarsine to their respective oxides. The molar conductance values and six fold coordination indicate that all the complexes are 1:1 electrolytes in dimethylsulphoxide revealing their ionic characters. The complexes display ν(C=O) bands at ~1625 cm^{-1} and ν(C-O) bands at ~1405 cm^{-1}, significantly lower than the values of amino acid (~1630 cm^{-1} and ~1412 cm^{-1}) indicating the coordination of amino acids through their carboxylate anion. The Th(IV) complexes display ν(M=O) modes in the region 910-999 cm^{-1}. The broad band observed at about 3244-3386 cm^{-1} for ν(N-H) modes indicates the coordination of amino group through nitrogen atom of amino acid. These are predominantly O-O stretching ν_1, the symmetric M-O stretch ν_2 and the antisymmetric M-O stretch ν_3. The characteristic ν_1(O-O) modes of the complexes appear at 800-840 cm^{-1}. It is observed that the ν_1 mode decreases with the increase of atomic number of the metal in a particular group. The magnetic moment values of dioxothorium (IV) complexes revealed them to be diamagnetic in nature, suggesting there were no changes in the oxidation states of the metal ions upon complexation. The electronic spectral data of the complexes showed bands at 260-350 nm region due to the charge transfer band only.

Keywords: peroxo complexes, thorium (IV), organic acids, amine bases

Introduction

Increasing interest in metal-amino acids (Alcock *et al.*, 1985; Djordjevic *et al.,* 1985) as well as peroxo-metal systems (Mimoun, 1983; Bortolini *et al.,* 1981; Groves, 1980) mainly attributable to their potential as models for understanding biologically important molecules (Mimoun, 1987), lead to the present study to establish rational synthetic routes to peroxo-thorium(IV) complexes containing amino acid and organic bases as coligand. Thorium has been identified as a bioessential metal (Gresser *et al.,* 1986; Chasteen *et al.,* 1983; Ramasarma and Crane, 1981). However, its actual biological function still remains an enigma (Boer, 1986). The recent discovery of thorium containing enzymes, a bromoperoxidase and a nitrogenase are considered to be major steps towards understanding the biochemistry of the metal. Moreover, peroxo heteroligand thorium(IV) complexes, besides being found to be capable of oxidising organic substrates (Alcock *et al.*, 1985; Djordjevic *et al.*, 1985), have been implicated to be actively involved in some biochemical processes. We considered that the coordination of an aminoacid and a peroxide ligand at a thorium(IV) centre might lead to biochemically relevant systems, because all three constituents, viz. thorium(IV), peroxide and amino acid are of acknowledged biological significance. In addition, the possibility of such complexes possessing oxidising properties could not be ruled out.

Peroxo complexes of poly-valent transition metals are used as catalysts or stoichiometric reagents for the oxidation of organic and inorganic substrate. Oxygenation reaction by molecular oxygen is one of the fundamental conversion processes, which play important roles in various situations, not only in chemical but also in metabolic systems (Lippard and Berg, 1994; Sheldon and Kochi, 1981). Since many of such processes are mediated by transition metal species (catalysts), it is essential for understanding of the reaction mechanisms and improvement of the oxygenation processes to reveal chemical and structural properties of the metal-dioxygen adducts. Transition metal-dioxygen adducts are also the key intermediates for oxygen transport in the biological system.

In this article, the synthesis and structural assessment of peroxo complexes of Thorium (IV) containing organic acid and amine bases as coligand have been described.

Materials and Methods

General method was used for the preparation of the complexes of the type $[Th(O_2)(amH).L]\ NO_3$ [where amH = deprotonated glycine, alanine, phenylalanine and leucine; L = quinoline, isoquinoline, pyridine, 2-picoline or 4-picoline].

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The aqueous solution of thorium nitrate (2.85 g, 0.005 mol) and amino acids like glycine (0.3754 g, 0.005 mol) or alanine (0.4455 g, 0.005 mol) or phenylalanine (0.8259 g, 0.005 mol) or leucine (0.6559 g, 0.005 mol) containing minimum amount of KOH (to make soluble) were mixed in a molar ratio of 1:1 and then allowed to stand for about 10 min. A solution of 'L' (0.01 mol) in ethanol was then added with continuous stirring to the above mixture followed by the addition of 30% H_2O_2 (2 ml). The precipitate that appeared, was filtered, washed several times successively with ethanol, then dried and stored *in vacuo* over P_4O_{10}. Details of the complexes formed and their physical properties are given in Table 1.

Reaction of the complexes of 2, 6, 9 and 11 with allyl alcohol. The complex **1** (1.05 g, 0.003 mol) was suspended in THF (30 ml) and a stoichiometric amount of allyl alcohol was added. The mixture was stirred under reflux at 60 °C for 48 h but it failed to produce any reaction product and complex **2** was recovered unchanged. The compounds **6**, **9** and **11** also failed to give any reaction product.

Reaction of the compounds 4 and 10 with allyl alchohol (Reaction A). A suspension of compound **4** (1.67 g, 0.003 mol) in THF (30 ml) was added to a stoichiometric amount of allyl alcohol. The mixture was stirred under reflux at 65 °C for 36 h. Microdistillation under a pressure of 19 mm Hg yielded glycidol (75% yield) at 145-150 °C [IR 1055 cm^{-1} (S, C-O-C)]. The glycidol was definitely identified by means of its phenylurethan derivative, mp. 58-59 °C (Rider and Hill, 1930).

The compound **10** also behaved in a similar fashion.

Catalytic reaction of the compounds 4 and 10 with allyl alcohol (Reaction B). Allyl alcohol 20 ml (17.08 g, 0.30 mol) was dissolved in dioxane (20 ml) and 1.0 g of compound **4** or **10** was added followed by H_2O_2 (30%, 20 ml). The mixture was refluxed at 90 °C for 24 h. The reaction mixture was then filtered and the filtrate was distilled under reduced pressure (19 mm Hg). The fraction collected at 177-180 °C was glycerol [IR 3190-3475 cm^{-1} (Br. O-H)]. The glycerol was identified as its tribenzoyl ester derivative, mp. 68-69 °C (Milas and Sussman, 1936).

Reaction of the compounds 3 and 5 with triphenylphosphine (Reaction C). A solution of triphenylphosphine (0.786 g, 0.003 mol) in THF (20 ml) was added to a suspension of compound **3** (1.29 g, 0.003 mol) or **5** (1.94 g, 0.003 mol) in the same solvent (40 ml). The mixture was stirred under reflux at 60 °C for 48 h. The TLC indicated that the reaction was completed. The reaction mixture was filtered and the residue was collected. A yellowish white powder was recovered from the filtrate which was identified as triphenyl phosphine oxide, mp. 156-157 °C (Martell and Sawyer, 1988).

Reaction of the compounds 4 and 7 with triphenylarsine (Reaction D). A solution of triphenylarsine (0.981 g, 0.003 mol) in THF (30 ml) was added to a suspension of compound **4** (1.52 g, 0.003 mol) or **7** (1.72 g, 0.003 mol) in the THF (40 ml). The mixture was refluxed for 48 h at 60 °C. TLC indicated that triphenylarsine was completely converted into triphenylarsine oxide. The reaction mixture was filtered and the residue was collected. Evaporation of the filtrate yielded the product, mp. 188-189 °C (Trofimenko, 1999).

Results and Discussion

The complexes were prepared through the reaction of thorium nitrate with organic acids and amine bases. The reaction may be represented as follows:

$$Th(NO_3)_4 + amH + 2L + H_2O_2 \rightarrow [ThO(O_2)(amH)L]\,NO_3 + HNO_3$$

where:

amH = deprotonated glycine, alanine, phenylalanine and leucine

L = quinoline, isoquinoline, pyridine, 2-picoline or 4-picoline

Elemental analysis and conductivity measurement. The physical properties of the complexes and the analytical data are shown in Table 1 and 2, respectively. All the complexes are insoluble in water but soluble in dimethylsulphoxide (DMSO). The molar conductance of 10^{-3} M solutions of the complexes in DMSO were measured at 30 °C. The molar conductance values (Table 1) indicate that all the complexes are highly electrolytic in nature. The analytical data are in good agreement with the proposed emperical formulae of the present complexes. Their structures have been proposed on the basis of conductivity and magnetic measurements (Table 1) and electronic spectral data (Table 4).

IR studies. Infrared spectral data of the complexes are shown in Table 3. The complexes display ν(C=O) bands at ~1625 cm^{-1} and ν(C-O) bands at ~1405 cm^{-1} significantly lower than the values of amino acid (~1630 cm^{-1} and ~1412 cm^{-1}). This indicates the coordination of amino acid through their carboxylate anion. The thorium complexes display ν(M=O) modes in the region 910-999 cm^{-1}. Further, the presence of M-N in the complexes are evident from the appearance of ν(M-N) modes at 289-310 cm^{-1} in the spectra of the complexes. The broad band observed at about 3244-3386 cm^{-1} for ν(N-H) modes indicate the coordination of amino group through nitrogen atom of amino acid.

Table 1. Physical properties of Th(IV) complexes

Complexes	Complex no.	Colour	Melting point (±0.5ºC)	Molar conductance Ω/cm²/mole	Magnetic moment μ_{eff} (B.M.)
K[ThO(O_2)(gly)(py)]	**1**	Colourless	128	78.30	-0.357
K[ThO(O_2)(gly)(2-pic)]	**2**	Colourless	136	73.70	-0.216
K[ThO(O_2)(gly)(4-pic)]	**3**	Colourless	140	75.40	-0.324
K[ThO(O_2)(gly)(Q)]	**4**	Colourless	130	83.40	-0.396
K[ThO(O_2)(gly)(iso-Q)]	**5**	Colourless	141	80.10	-0.465
K[ThO(O_2)(ala)(py)]	**6**	Colourless	138	82.40	0.567
K[ThO(O_2)(ala)(2-pic)]	**7**	Colourless	148	79.90	0.496
K[ThO(O_2)(ala)(4-pic)]	**8**	Colourless	152	77.30	0.326
K[ThO(O_2)(ala)(Q)]	**9**	Colourless	133	88.40	0.495
K[ThO(O_2)(ala)(iso-Q)]	**10**	Colourless	131	84.50	-0.236
K[ThO(O_2)(pha)(py)]	**11**	Colourless	143	73.90	-0.519
K[ThO(O_2)(leu)(py)]	**12**	Colourless	145	75.70	0.325

Table 2. Analytical data of Th(IV) complexes

Complexes	Complex no.	Yield %	Metal%	C%	H%	N%
K[ThO(O_2)(gly)(py)]	**1**	50	49.03 (49.14)	17.64 (17.79)	1.78 (1.91)	5.77 (5.93)
K[ThO(O_2)(gly)(2-pic)]	**2**	62	47.58 (47.72)	19.49 (19.74)	2.09 (2.26)	5.63 (5.76)
K[ThO(O_2)(gly)(4-pic)]	**3**	72	47.21 (47.35)	19.74 (19.89)	2.34 (2.47)	5.18 (5.34)
K[ThO(O_2)(gly)(Q)]	**4**	74	44.28 (44.43)	25.16 (25.27)	2.02 (2.11)	5.21 (5.36)
K[ThO(O_2)(gly)(iso-Q)]	**5**	58	44.72 (44.89)	25.63 (25.75)	2.35 (2.46)	5.68 (5.82)
K[ThO(O_2)(ala)(py)]	**6**	52	47.60 (47.72)	19.57 (19.74)	2.13 (2.26)	5.62 (5.76)
K[ThO(O_2)(ala)(2-pic)]	**7**	60	46.22 (46.38)	21.43 (21.59)	2.46 (2.60)	5.37 (5.60)
K[ThO(O_2)(ala)(4-pic)]	**8**	65	47.11 (47.25)	21.72 (21.86)	2.42 (2.51)	5.74 (5.98)
K[ThO(O_2)(ala)(Q)]	**9**	66	43.16 (43.27)	26.73 (26.85)	2.28 (2.42)	5.08 (5.22)
K[ThO(O_2)(ala)(iso-Q)]	**10**	70	43.42 (43.57)	26.00 (26.05)	2.64 (2.85)	5.61 (5.72)
K[ThO(O_2)(pha)(py)]	**11**	59	41.15 (41.27)	29.72 (29.88)	2.59 (2.67)	4.77 (4.98)
K[ThO(O_2)(leu)(py)]	**12**	52	43.79 (43.93)	24.74 (24.99)	3.27 (3.41)	5.14 (5.30)

figures in the parenthesis indicate calculated values

Table 3. IR spectral data of Th(IV) complexes

υ(N-H) cm^{-1}	Complex no.	υ(C=O) cm^{-1}	υ(C-O) cm^{-1}	υ(M=O) cm^{-1}	υ(M-N) cm^{-1}	υ_1(O-O) cm^{-1}	υ_3  cm^{-1}	υ_2  cm^{-1}
3315 br	**1**	1607 s	1391 s	910 m	289 m	816 s	668 m	600 w
3274 br	**2**	1610 s	1388 s	942 m	310 w	800 s	672 m	615 w
3386 br	**3**	1625 s	1375 s	940 m	305 w	815 s	666 w	616 w
3384 br	**4**	1620 s	1384 s	965 w	300 w	810 s	680 m	632 w
3386 br	**5**	1600 s	1399 s	940 w	299 w	826 s	656 m	618 w
3334 br	**6**	1622 s	1378 s	999 m	306 w	825 s	662 m	605 w
3368 br	**7**	1615 s	1377 s	955 m	310 w	830 s	650 m	620 w
3376 br	**8**	1620 s	1380 s	952 m	300 w	825 s	660 m	610 w
3360 br	**9**	1615 s	1385 s	915 w	299 w	810 s	670 m	628 w
3352 br	**10**	1600 s	1400 s	935 w	290 w	825 s	656 m	620 w
3350 br	**11**	1614 s	1384 s	945 m	290 m	840 s	665 m	630 w
3244 br	**12**	1620 s	1405 s	998 w	310 m	810 s	670 m	623 w

related band intensities are denoted by vs, s, m, w and br representing very strong, strong, medium, weak and broad band respectively

The metal peroxo grouping gives rise to three IR active vibrational modes. These are predominantly O-O stretching ν_1, the symmetric M-O stretch ν_2 and the antisymmetric M-O stretch ν_3. The characteristics ν_1(O-O) modes of the complexes appear at band 800-840 cm^{-1}. It is observed that the ν_1 mode decreases with the increased atomic number of the metal in a particular group. In the present complexes, the ν_3 and ν_2 modes appear at 650-680 and 600-632 cm^{-1} respectively (Martell and Sawyer, 1988).

Magnetic moment and electronic spectra. The observed values of effective magnetic moment (μ_{eff}) at room temperature are given in Table 1. The magnetic moment values of dioxothorium (VI) complexes are -0.216 to 0.567 B.M. which reveal that these complexes are diamagnetic in nature suggesting no changes in the oxidation states of the metal ions upon complexation.

The electronic spectral data (Table 4) of the complexes **1-12** showed bands between 260-350 nm region due to the charge transfer band only (Schmidt *et al.,* 2001).

^{1}H NMR spectra. The ^{1}H NMR spectra of the amino acid ligand alanine, amino base ligand 4-picoline and complex **8** K[ThO (O_2)(ala)(4-pic)] were recorded in water, methanol and DMSO-d_6 solution, respectively at room temperature. All of these data are summarized in Table 5.

The ^{1}H NMR spectra of the ligands alanine and 4-picoline showed resonance corresponding to -NH_2, -CH_2 and -CH_3 protons. A singlet at δ 1.31 ppm corresponds to the four protons

Table 4. Electronic spectral data of Th(IV) complexes

Complexes	Complex no.	λmax (nm)
K[ThO(O_2)(gly)(py)]	**1**	277, 311
K[ThO(O_2)(gly)(2-pic)]	**2**	260, 315
K[ThO(O_2)(gly)(4-pic)]	**3**	325
K[ThO(O_2)(gly)(Q)]	**4**	343
K[ThO(O_2)(gly)(iso-Q)]	**5**	300
K[ThO(O_2)(ala)(py)]	**6**	350
K[ThO(O_2)(ala)(2-pic)]	**7**	326
K[ThO(O_2)(ala)(4-pic)]	**8**	331
K[ThO(O_2)(ala)(Q)]	**9**	264, 314
K[ThO(O_2)(ala)(iso-Q)]	**10**	277, 298
K[ThO(O_2)(pha)(py)]	**11**	317
K[ThO(O_2)(leu)(py)]	**12**	305

Table 5. ^{1}H NMR spectral data of the peroxo complexes of Th(IV)

Complexes	-NH_2	-CH_2	-CH_3	4-picoline proton
Alanine (ligand)	3.60	1.31		
4-picoline (ligand)		2.21	1.02	8.09(d, *J*=13.98 Hz) H^a
				7.08(d, *J*=14.08 Hz)H^b
Complex **8**	3.65	2.28	1.25	8.21(d, *J*=0.29 Hz) H^a
K[ThO(O_2)(ala)(4-pic]				7.66(d, *J*=0.08 Hz) H^b
				7.20(d, *J*=0.34 Hz) H^c

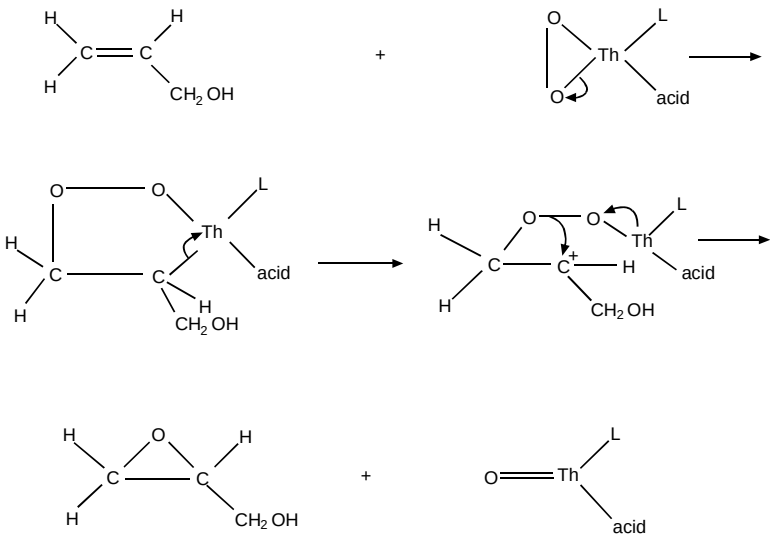
of two -CH_2 groups in alanine. The -CH_3 proton resonance of the ligand 4-picoline gave a singlet at δ 1.02 ppm. For the -NH_2 group, a singlet resonance is shown at δ 3.60 ppm in alanine.

The aromatic ring hydrogen resonances of 4-picoline were observed at δ 8.09 ppm (doublet) and δ 7.08 ppm (doublet) due to H^a(J=13.98 Hz) and H^b(J=14.08 Hz), respectively. The resonance of H^c was not observed. However, the aromatic ring hydrogen resonance of the complex **8** was observed at δ 8.21 ppm (doublet), δ 7.66 ppm (doublet) and δ 7.20 ppm (doublet) due to H^a(J=0.29 Hz), H^b(J=0.08 Hz) and H^c(J=0.34 Hz), respectively. The -CH_3 hydrogen resonance singlet at δ 1.25 ppm remains unchanged. Thus, the methyl group does not participate in bonding.

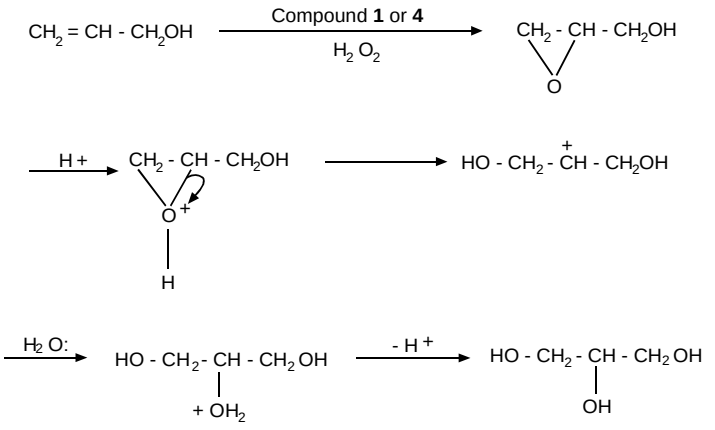
In the complex **8**, the observed -NH_2 singlet resonance at δ 3.65 ppm which was a shifted downfield compared to the free -NH_2 group of alanine. This downfield shift indicates that the -NH_2 group is coordinated to the thorium metal centre. This result is also consistent with the IR data.

Reactivity. The resulting products were found to liberate iodine within 3 min on treatment with aqueous potassium iodide. Based on these observations the possible reactivity of the complexes towards olefinic compounds could be explored. Compounds **2**, **6**, **9** and **11** were inert towards oxidation of allyl alcohol. However, compound **4** and **10** react stoichiometrically with allyl alcohol (reaction A) producing glycidol as indicated by IR band at 1055 cm^{-1} due to the C-O-C stretching mode (Kurosawa *et al.*, 1991). A possible reaction path is shown in Scheme 1 and 2.

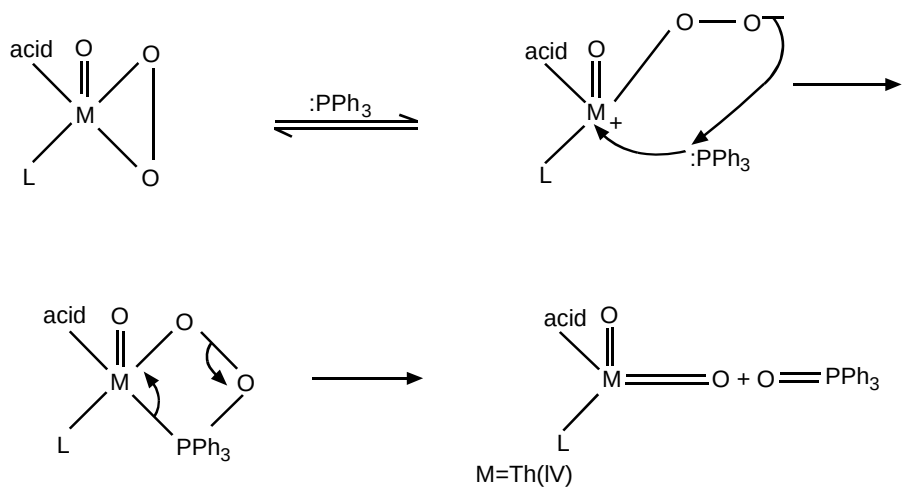
In reaction B, compound **4** or **10** was used to catalyze the oxidation of allyl alcohol by H_2O_2 and in this case, the product



Scheme 1



Scheme 2



Scheme 3

isolated was glycerol. The IR spectrum of this product was identical with that of an authentic sample. A possible reaction path is shown in Scheme 2. The reactions C and D produced triphenylphosphine oxide and triphenylarsine oxide, respectively. The products display IR bands at 1195 cm^{-1} and 888 cm^{-1} due to ν(P=O) and ν(As=O) modes, respectively. The IR spectra of the residue of reactions C and D displayed the disappearance of ν_1(O-O) bands which indicates the transfer of peroxo oxygen to the substrate. A possible reaction path is shown in Scheme-3.

On the basis of spectroscopic interpretation and physical measurements the molecular structure of complex **8** could be illustrated as shown in Fig. 1.

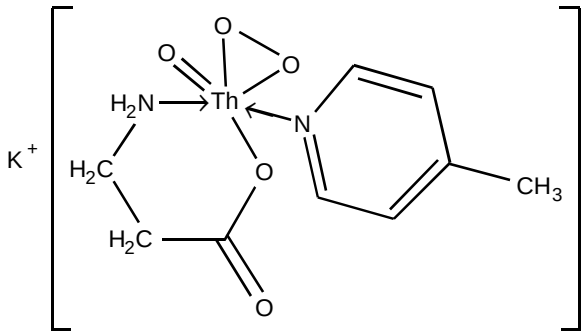


Fig. 1. Proposed structure of complex **(8)** K[ThO(O_2)(ala)(4-pic)].

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References

Alcock, N.W., Flanders, D.J., Kemp, T.J., Shand, M.A. 1985. Glycine complexation with uranyl ion: absorptiometric, luminescence and X-ray structural studies of tetrakis (glycine)dioxouranium(VI) nitrate. *J. Chem. Soc. Dalton Trans.* 517-521.

Boer, E.de,Tromp, M.G.M., Plat, H., Kreen, B.E., Wever, R. l986. Vanadium(V) as an essential element for halopero-xidase activity in marine brown algae. *Biochem. Biophys. Acta* **872:** 104-115.

Bortolini, O., Di Furia, F., Modena, G. 1981. Metal catalysis in oxidation by peroxides. *J. Am. Chem. Soc.* **103:** 3924-3926.

Chasteen, N.D., Grady, J.K., Holloway, C.E. 1983. Characterization of the binding, kinetics, and redox stability of vanadium (IV) and vanadium (V). *Struct. Bonding (Berlin)* **53:** 105-138.

Djordjevic, C., Vuletic, N., Sinn, E. 1985. Synthesis and properties of peroxo α-amino acid complexes of molybdenum(VI). The structures of $MoO(O_2)_2$(HAA) (H_2O), HAA = glycine, proline. *Inorg. Chim. Acta.* **104:** L7-L9.

Gresser, M.J., Tracey, A.S., Parkinson, K.M. 1986. Vanadium(V) oxyanions: The interaction of vanadate with pyrophosphate, phosphate and arsenate. *J. Am. Chem. Soc.* **108:** 6229 - 6234.

Groves, J.T. 1980. In: *Metal Ion Activation of Dioxygen*, T. G. Spiro (ed.), Wiley-Interscience, New York, USA.

Kurosawa, H., Achiha, T., Kajimaru, H., Ikeda, I. 1991. Formation of In-line. WMF-peroxo-platinum complexes via

attack dioxygen-platinum complexes. *Inorg. Chim. Acta* **190:** 271-275.

Lippard, S.J., Berg, J.M. 1994. *Principles of Bioinorganic Chemistry*, University Science Books, California, USA.

Martell, A.E., Sawyer, D.T. (eds.) 1988. *Oxygen Complexes and Oxygen Activation by Transition Metals*, Plenum Press, New York, USA.

Milas, N.A., Sussman, S. 1936. The hydroxylation of double bond. *J. Am. Chem. Soc*. **58:** 1302-1306.

Mimoun, H. 1983. In: *The Chemistry of Functional Groups, Peroxides*, S. Patai (ed.), Wiley Interscience, New York, USA.

Mimoun, H. 1987. Metal complexes in oxidation. In: *Comprehensive Coordination Chemistry*, G. Wilkinson (ed.), vol. **6,** Pergamon Press, Oxford, London, UK.

Trofimenko, S. 1999. *Scorpionates*: *The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, UK.

Ramasarma, T., Crane, F. L. 1981. Does vanadium play a role in cellular regulation? *Curr. Top. Cell. Reg.* **20:** 247-301.

Rider, T.H., Hill, A.J. 1930. Studies of glycidol. I. Preparation from glycerol monochlorohydrin. *J. Am. Chem. Soc*. **52:** 1521-1527.

Schmidt, H., Andersson, I., Rehder, D., Pettersson, L.A. 2001. Potentiometric and 51V NMR study of the aqueous H^+/$H_2VO_{4^-}$/H_2O_2/1-α- alanyl-l-histidine. *System Chem*. **7:** 251-255.

Sheldon, R.A., Kochi, J.K.1981. *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, USA.