



Review

Peroxido complexes of vanadium

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ABSTRACT

Peroxido complexes represent an important group of vanadium compounds having practical applications in distinct areas of chemistry. They possess insulin mimetic properties, antitumor activity and stimulate or inhibit certain enzymes. The bioinorganic chemistry of peroxidovanadates studies also the role of vanadium in the active centers of vanadium dependent enzymes (haloperoxidases and nitrogenases). Peroxidovanadium compounds are intensively studied for their oxidative properties. They can act as catalysts or stoichiometric oxidants in oxidation reactions of organic compounds, e.g. in epoxidation, sulfoxidation, hydroxylation or bromination. This versatility of vanadium peroxido complexes necessitates a critical review of their molecular structure and properties both in solution and in solid state. In this inclusive review we present the complete set of peroxido complexes of vanadium heretofore characterized by X-ray diffraction analysis. Along with the molecular structures we present and discuss the solid state vibrational spectra and thermal decomposition data. Vibrational, UV–vis and ⁵¹V NMR spectra

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of complexes dissolved in various solvents are also discussed. We have extracted the data from several speciation studies in order to clarify the formation conditions for different types of peroxidovanadates and summarize their ^{51}V NMR chemical shifts. We also refer to certain applications of peroxido complexes of vanadium and we place the emphasis on potential applications which have not yet been thoroughly examined but deserve more attention.

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1. Introduction

Soon after discovery of vanadium (Sefström 1831) [1–3] the reaction between V_2O_5 and hydrogen peroxide was studied [4,5]. On dissolution of V_2O_5 in diluted H_2O_2 a red solution is formed, which can serve as a sensitive qualitative proof of vanadium.

First papers describing the synthesis of homoligand¹ peroxidovanadium² [6] complexes appeared by the end of the 19th century when Melikov and Pissarevski reported the preparation of several peroxidovanadates [7]. Later on, Beltrán-Martínez (1943–1956) and Jahr et al. (1934–1960) have prepared a series of homoligand peroxido complexes, e.g. $\text{M}_3[\text{V}(\text{O}_2)_4]$ and $\text{M}_4[\text{V}_2\text{O}_3(\text{O}_2)_4]$ [7]. The first heteroligand¹ peroxido complex of vanadium, $\text{NH}_4[\text{VO}(\text{O}_2)(\text{dipic})(\text{H}_2\text{O})]$, was described by Hartkamp (1959) [8]. Twelve years later, the first crystal structure of peroxidovanadium complex, $(\text{NH}_4)_4[\text{V}_2\text{O}_3(\text{O}_2)_4]$, was published by Svensson and Stomberg [9].

The increasing attention in the last decades to the vanadium chemistry was evoked by important discoveries on the role of vanadium compounds in biological systems. The presence of vanadium in the active center of vanadium dependent enzymes (haloperoxidases and nitrogenases), the insuline mimetic properties and antitumor activity, and even the stimulation and inhibition of many enzymes by vanadium compounds became the main topics in bioinorganic vanadium chemistry. All these aspects of vanadium compounds have been in detail reported in a series of reviews [10] and books [11]. The peroxidovanadium compounds are closely related to at least three biological effects mentioned above. The crystal structure of vanadium chloroperoxidase from *Curvularia inaequalis* has shown that the active site of the peroxido form of the enzyme contains the $\text{V}(\eta^2\text{-O}_2^{2-})$ fragment [12] as a typical part of peroxidovanadium complexes. Structural and functional modelings of the active site of haloperoxidases are subject of many studies [13,14]. Several vanadium peroxido complexes exhibit cytostatic effects [15], e.g. $\text{NH}_4[\text{VO}(\text{O}_2)_2(\text{bpy})]\cdot 4\text{H}_2\text{O}$, $\text{NH}_4[\text{VO}(\text{O}_2)_2(\text{phen})]\cdot 2\text{H}_2\text{O}$ [16,17] and $\text{K}_2[\text{VO}(\text{O}_2)_2(\text{pic})]$ [18,19]. Insuline-enhancing properties were observed for many peroxidovanadium compounds, e.g. $[\text{VO}(\text{O}_2)_2(\text{pic})]^{2-}$ and $[\text{VO}(\text{O}_2)_2(\text{phen})]^-$. The latter complex is a potent protein phosphotyrosine phosphatase inhibitor lowering the blood glucose level even when transdermally delivered to experimental animals (mouse) [12,18]. The well-known inhibition of phosphatases by vanadate (VO_4^{3-}) has stimulated the research on vanadium complexes as phosphatase inhibitors [20], which is very relevant property of vanadate.

Since the classical work published by Mimoun et al. [21], many results have been obtained in the field of oxidations of organic compounds under involvement of peroxidovanadium compounds as catalysts or stoichiometric oxidants. In these reactions, peroxidovanadium compounds are usually formed in situ from vanadium containing precursors, mostly ammonium or alkaline metal vanadates, resp. V_2O_5 and hydrogen peroxide or an alkyl hydrogen peroxide. Peroxidovanadium compounds are able to oxidize

aliphatic and aromatic hydrocarbons, sulfides, alcohols, etc. The reactivity of vanadium peroxido complexes in oxidation reactions was, in addition to the already mentioned books [11], the subject of a series of excellent reviews [22]. Recently, studies on catalytically active polymer anchored peroxidovanadium complexes have been reported [23–25].

In this review we deal only with compounds with molecular structure unequivocally determined by X-ray analysis. We discuss the synthesis, molecular and crystal structures and vibrational spectra of solid complexes and their thermal decomposition as well as some solution properties of the complexes: vibrational, UV–vis and ^{51}V NMR spectra, and stability in various solvents. We would like to present here a thorough and, to the best of our knowledge, a complete overview of crystallographically characterized peroxido complexes of vanadium with all $n(\text{O}_2^{2-})/n(\text{V})$ ratios known so far in mono-, di-, tri-, tetranuclear and polymeric solid state structures. This topic was already partially dealt in our previous publication on monoperoxidovanadates [26].

2. Peroxidovanadium species in solution

Most of heteroligand peroxidovanadium complexes can be derived from the homoligand complexes. Therefore, in this part we describe the speciation of homoligand complexes in aqueous and partially also in other solvents. The first consistent data on speciation were obtained by UV–vis spectroscopy and cryoscopy (extensive studies were performed by Chaveau [27,28]), but the most consistent data were later obtained using potentiometry and ^{51}V NMR spectroscopy. The formulation of species differs by various authors. In the summarizing Table 1 we used, when possible, the formulae derived from molecular structures found for solid state homoligand and heteroligand peroxido vanadium complexes. When necessary, the formulae were completed by water molecule(s) to achieve the pentagonal pyramidal surroundings around the vanadium center. As can be seen from Table 1, the positions of the ^{51}V NMR signals found by individual authors slightly differ due to the influence of ionic strength, temperature and vanadium concentration (c_v), but the overall picture is similar. In aqueous solution, there were found 14 homoligand species with $n(\text{O}_2^{2-})/n(\text{V})$ ratios equal to 0.5, 1, 2, 3 and 4. The data in Table 1 were mainly taken from the papers by Howarth et al. [29,30], Tracey et al. [31], and from the most thorough studies published by Pettersson et al. [32–34]. In the cited references the reader can find also formation constants and distribution curves calculated for various experimental conditions. Other speciation studies published by Griffith et al. [35] and Conte et al. [36] have confirmed the general picture on composition of peroxido vanadium complexes in aqueous solutions.

It must be noted that nearly all speciation studies were performed for relatively low c_v . The precise equilibrium studies require an adjustment of the ionic strength which is, however, in fact limiting the highest possible values of c_v . Moreover, most of the investigations were aimed at the modeling of vanadium compounds in biological systems with naturally low c_v . The physiological conditions ($c_{\text{NaCl}} = 0.150$ mol/L) limit the maximum vanadium concentration to several tenths of mmol/L. The highest c_v studied was mostly profoundly lower than c_v during the crystallization of solid complexes. There is some indication that the situation in solutions with $c_v > 1$ mol/L might be different [37].

¹ In this review, the term “homoligand” is used for peroxido complexes containing O^{2-} , O_2^{2-} , H_2O and/or OH^- ; the term “heteroligand” is used for all other peroxido complexes.

² According to IUPAC recommendations on the nomenclature of inorganic chemistry (IUPAC Red Book 2005), $(\text{O}_2)^{2-}$ is the “peroxido” ligand, although in majority of papers still “peroxo” is used. The Scopus database search provided 155 results for “vanadium peroxo” or “peroxovanadates”, but only 20 for “peroxido” (in 2005–2014).

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