

^{51}V solid-state NMR investigations and DFT studies of model compounds for vanadium haloperoxidases

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Dedicated to Prof. Hans-Heinrich Limbach on the occasion of his 65th birthday

Abstract

Three *cis*-dioxovanadium(V) complexes with similar *N*-salicylidenehydrazide ligands modeling hydrogen bonding interactions of vanadate relevant for vanadium haloperoxidases are studied by ^{51}V solid-state NMR spectroscopy. Their parameters describing the quadrupolar and chemical shift anisotropy interactions (quadrupolar coupling constant C_Q , asymmetry of the quadrupolar tensor η_Q , isotropic chemical shift δ_{iso} , chemical shift anisotropy δ_σ , asymmetry of the chemical shift tensor η_σ and the Euler angles α , β and γ) are determined both experimentally and theoretically using DFT methods. A comparative study of different methods to determine the NMR parameters by numerical simulation of the spectra is presented. Detailed theoretical investigations on the DFT level using various basis sets and structural models show that by useful choice of the methodology, the calculated parameters agree to the experimental ones in a very good manner.

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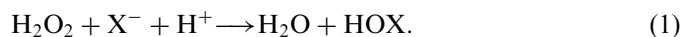
Keywords: Haloperoxidase; Model system; ^{51}V NMR; *Cis*-dioxovanadium(V) complex; Quadrupolar interaction; Ab initio calculation; Numerical optimization

1. Introduction

The scientific interest in vanadium-dependent enzymes was sparked in 1984 by the isolation of the bromoperoxidase from the marine algae *Ascophyllum nodosum* [1]. Since that time, several vanadium haloperoxidases (V-HPOs) have been found in marine algae as well as in some fungi and lichens. They are involved in the biosynthesis of halogenated natural products [2–4]. Due to numerous potential biological, medicinal and industrial applications of vanadium compounds and vanadium enzymes, the study of these enzymes became a field of intensive research [5–9].

V-HPO enzymes are capable of catalyzing the two electron oxidation (Eq. (1)) of a halide ion (X^-) to

hypohalous acid (HOX) in the presence of hydrogen peroxide:



The hypohalous acid can further halogenate an appropriate organic substrate or react with another equivalent of hydrogen peroxide, forming singlet-oxygen [10]. In the last decade, the structures of several V-HPOs have been determined by X-ray crystallography, indicating the presence of an extended hydrogen bonding network [11–13] in the active site of the enzymes. This finding led to the proposal that the catalytic activity of V-HPO enzymes is driven by those hydrogen bonding interactions [9,14], similar to many other enzymes, where hydrogen bonds play a crucial role [15–19]. In order to study the influence of the hydrogen bonding network a number of systems was synthesized that model the hydrogen bonding of vanadate species [20–28].

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Despite the great interest and the large number of investigations concerning V-HPOs, many aspects of their chemistry and their molecular reaction mechanism are still not fully understood. This is mainly due to the fact that the enzymes are colorless and diamagnetic in their active form. Thus most of the common spectroscopic methods are not available for their study. An exception is the solid-state NMR spectroscopy [29–32], in particular in the combination with quantum chemical calculations [33–38].

In the case of the V-HPOs, ^{51}V solid-state NMR spectroscopy is an especially suitable tool to investigate the active site of the enzymes [39], as their spectra are very sensitive on the chemical environment of the vanadium atom, owing to the simultaneous presence of chemical shift anisotropy (CSA) and quadrupolar interactions.

For the structural and functional interpretation of such spectra, it is essential to have reference spectra and parameters available from various model systems [40–46] with well established structures.

While such reference data are easily available in databases for common nuclei like ^{13}C or ^{15}N , this is not the case for less frequently studied nuclei like ^{51}V . As an alternative, quantum chemical or empirical calculations of these parameters might be employed for the interpretation. However, until now only a few examples with calculations of ^{51}V NMR shifts of model complexes have been reported [47–49]. The situation is even more difficult for solid-state NMR parameters, like chemical shift (CS) or quadrupolar tensors, where only few DFT calculations on vanadates and vanadium model complexes [39,50–53] have been reported. In particular, to the best of our knowledge, there are no ^{51}V solid-state NMR investigations of model complexes with hydrogen bonding ability up to now. To address this problem we started to study these model complexes employing ^{51}V solid-state MAS NMR spectroscopy and quantum chemical calculations. Since the ^{51}V quadrupolar interaction is much larger than the available spectral window of the ^{51}V MAS NMR experiment, we had

to establish both a reliable method for the simulation of the spectra and for the quantum chemical calculation of the NMR parameters. In this paper we present and discuss the results of the ^{51}V MAS NMR measurements of three model complexes for V-HPOs, which are able to build up complex hydrogen bonding networks. Next, two different methods for the evaluation of the spectral data will be presented and compared. These results are complemented by DFT calculations of the CS and electric field gradient (EFG) tensors which allow to extract the relevant solid-state NMR parameters. The obtained experimental and theoretical data will be compared in order to validate the capability of the employed methodologies for the determination of ^{51}V solid-state NMR parameters. These methods can be later employed to study a larger number of model complexes, which can serve as an empirical database for further studies of the enzymes.

2. Investigated vanadium complexes

The *cis*-dioxovanadium(V) complexes under investigation in this study are depicted in Fig. 1 [20,26]. They are based on *N*-salicylidenehydrazide ligands and part of a series of compounds intended to model the hydrogen bonding of vanadate species by varying the side chain of the carbonic acid fragment of the ligand system [54]. The three compounds **I**, **II** and **III** exhibit relatively similar molecular structures, solely differing in the length of the hydroxyl side chain and their water content. For the vanadium atom a square pyramidal coordination geometry is observed. The crystal structures reveal a complex hydrogen bonding system around the vanadate moiety, which includes interactions with the ammonium cation leading to a hydrogen bonding relay between the hydroxyl side chain and one of the oxo groups. In the case of complex **I** this hydrogen bonding relay is extended by an additional water molecule.

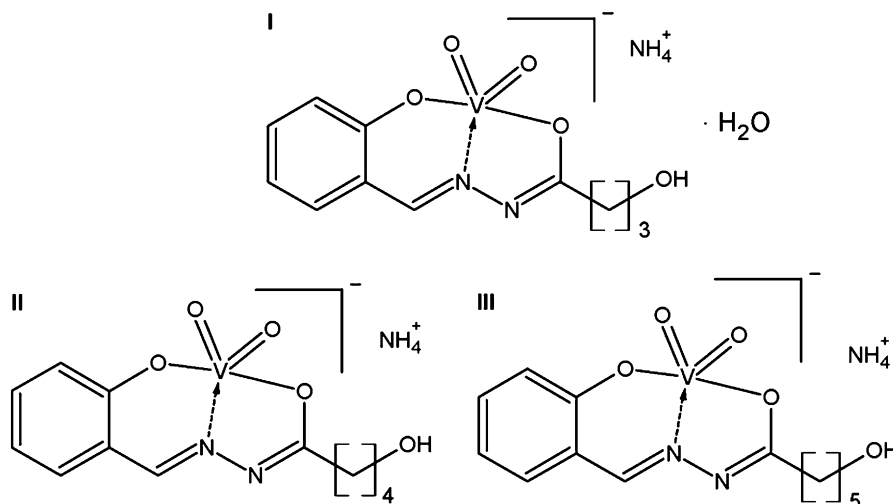


Fig. 1. Chemical structure of the model complexes **I**, **II** and **III**.

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