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The (biological) speciation of vanadate(V) as revealed by ^{51}V NMR: A tribute on Lage Pettersson and his work

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ABSTRACT

Four decades of research carried out by Lage Pettersson, his group and his coworkers are reviewed, research that has been directed predominantly towards the speciation of vanadate and systems containing, along with vanadate and co-reactants such as phosphate and peroxide, biologically relevant organics. In particular, those organics have been addressed that either are (potential) ligands for vanadate-derived coordination compounds generated at physiological conditions and/or function as constituents in medicinally interesting oxidovanadium compounds. Examples for molecules introduced in the context of the physiological vanadate–ligand interaction include the dipeptides Pro-Ala, Ala-Gly, Ala-His and Ala-Ser, the serum constituents lactate and citrate, and the nucleobases adenosine and uridine. The speciation in the vanadate–picolinate and vanadate–maltol systems is geared towards insulin-enhancing vanadium drugs. The speciation as a function of pH, ionic strength and the concentration of vanadate and the ligand(s) is based on potentiometric and ^{51}V NMR investigations, a methodical combination that allows reliable access to composition, formation constants and, to some extent, also structural details for the manifold of species present in aqueous media at physiological pH and beyond. The time frame 1971 to 2014 is reviewed, emphasizing the interval 1985 to 2006, and thus focusing on *biologically* interesting vanadium systems. Figurative representations from the original literature have been included.

1. Introduction

Lage Pettersson received his Ph.D. in Inorganic Chemistry in 1974 under the supervision of Nils Ingri at the University of Umeå in the North of Sweden. He continued to work in the Chemistry Department in Umeå, with his research focusing on the solution speciation and reactivity of inorganic and coordination compounds of molybdenum and vanadium. With respect to vanadium, his research activities increasingly addressed issues of biochemical and medicinal relevance. In order to access the speciation within the aqueous vanadate(V) system as such, and vanadium(V)-based coordination compounds generated in the presence of (biogenic) ligands, Lage developed basic strategies in the application of ^{51}V NMR spectroscopy, allowing for pivotal insight into, and perception of, vanadate–ligand interactions of biological relevance. He became appointed Professor of Chemistry at the Umeå University in 1999. Lage Pettersson, a tireless ally in the vanadium community, passed away in 2013 at the age of 73. My first encounter with Lage goes back to the 22nd International Conference on Coordination Chemistry (ICCC) in Budapest in 1982, where he presented a poster displaying the pH- and concentration-dependent speciation of vanadate in aqueous solutions, Fig. 1 [1,2]. Four years thereafter, I received a letter, stating that "… we have worked further with the H^+-HVO_4^{2-} system … [and] also studied the vanadooxalate system. … The last three years we have focused on the molybdophosphate and molybdophenylphosphate systems. Having solved these, we plan to resume the study of the extremely complicated molybdovanadate system." Lage's very first publications in fact describe details of the molybdophosphate systems [3,4], a topic which decades later he resumed in close cooperation with, inter alia, Masato Hashimoto from the Wakayama University [5], who also dedicated one of his recent papers (on chloridooxidoperoxidomolybdate) to Lage [6]. The last paper co-authored by Lage Pettersson, and published posthumously in 2014, once more addresses structural information on a molybdate system in aqueous solution [7]. For the molybdovanadates and molybdovanadophosphate systems mentioned in Lage's letter, and

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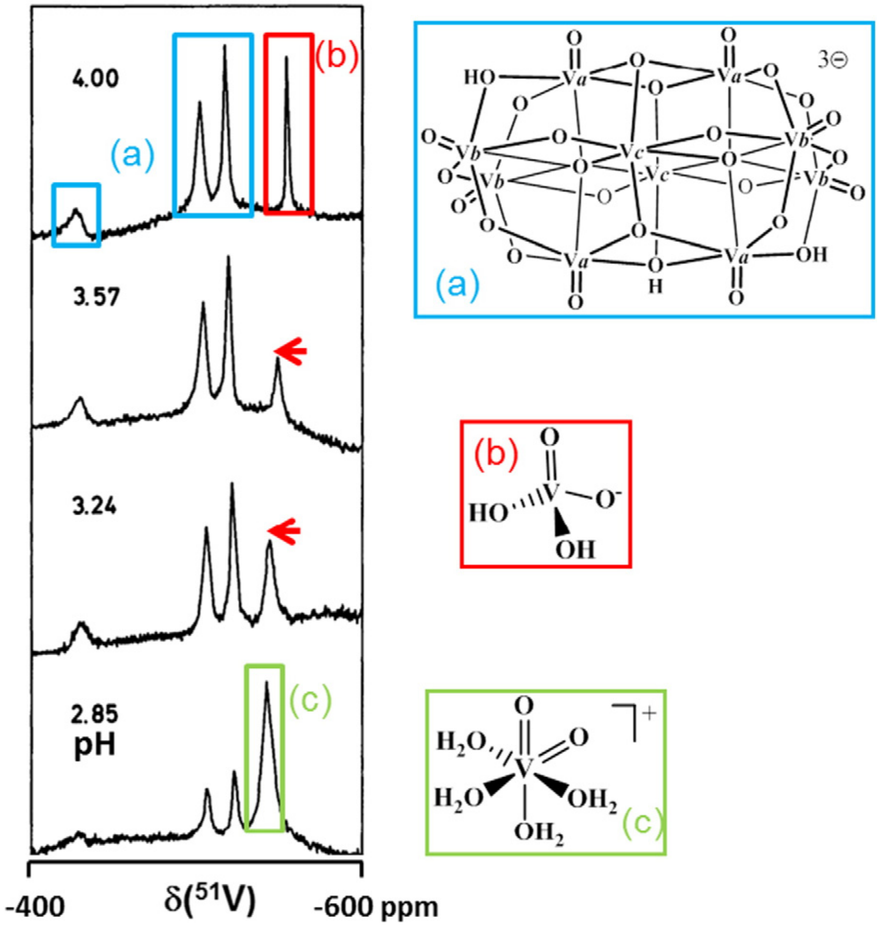

Fig. 1. ^{51}V NMR spectra of a ca. 0.31 M vanadate solution at different pH values. Chemical shifts relative to $VOCl_3$ are indicated on the abscissa. Blue: the three signals of the three different vanadium centers V_a, V_b and V_c in decavanadate $H_nV_{10}O_{28}^{(6-n)-}$ (the dominant species at low pH; shown is the triprotonated form); red: monovanadate $H_nVO_4^{(3-n)-}$ (with decreasing pH this signal shifts to the left, indicated by a red arrow); green: $[VO_2(H_2O)_4]^+$. Spectra modified from ref. [1]. For the pH-dependence of the ^{51}V shielding see also Fig. 2.

investigated by multinuclear (^{31}P, ^{51}V, ^{95}Mo) NMR plus potentiometry, see for example ref. [8,9]; for tungstovanadates ref. [10].

The greater part of Lage Pettersson's work focuses on a detailed analysis of the speciation in the vanadate system as a function of pH, the ionic strength and the presence of biogenic ligands. This work had in part been carried out in the frame of the European COST actions on “Metals in Proteins.” A main issue in these studies is ^{51}V nuclear magnetic resonance, an analytical method that, combined with H^+ potentiometric data, provides detailed insight into the speciation of the vanadate-based systems; Lage Pettersson has crucially contributed to the development and appreciation of this methodological approach. Correspondingly, and since this special issue is dedicated to the Vanadium Symposium, the present overview emphasizes Lage's input and share to the present level of awareness with respect to the speciation of vanadate and vanadium coordination compounds with biogenic ligands in media mimicking physiological conditions.

EPR investigations, also sporadically carried out in Lage's group in view of the redox-lability of several of the systems (such as the vanadate–maltol system), as well as ^{17}O, ^{95}Mo and ^{183}W NMR will not be addressed. Here, the interested reader is referred to, for example, refs. [8–11].

2. Technical notes

2.1. Nomenclature

In order to adapt to IUPAC recommendations, the terms oxo, hydroxo and peroxo for the *ligands* O^{2-}, OH^- and O_2^{2-} employed in the original literature have throughout been replaced by oxido, hydroxido and peroxido.

2.2. Species denotation

In the original literature, the vanadate species characterized in solution are commonly denoted $H_pV_qX_rL_s$, where X represents O_2^{2-}, and L is any ligand. Reference point is dihydrogenvanadate $H_2VO_4^-$: $(p,q,r,s) = (0,1,0,0)$. Examples for other species are as follows:

$HVO_4^{2-} \equiv (-1,1,0,0)$
$HVO_2(O_2)_2^{2-} \equiv HVX_2^{2-} \equiv (-1,1,2,0)$
$V_{10}O_{28}^{6-} \equiv (4,10,0,0)$; according to the reaction for the formation of decavanadate(6−):

$$\mathbf{4}H^+ + \mathbf{10}H_2VO_4^- \rightarrow V_{10}O_{28}^{6-} + 12H_2O$$

$[VO(O_2)_2Pi]^{2-} \equiv (0,1,2,1)$; according to the following reaction equation:

$$H_2VO_4^- + 2H_2O_2 + Pi^- \rightarrow [VO(O_2)_2Pi]^{2-} + 3H_2O;\ Pi^- \text{ is the picolinato}(1-) \text{ ligand}$$

In most instances discussed in the present overview, I have “translated” the $H_pV_qX_rL_s$ descriptors employed in Pettersson's publications into formulae familiar to the majority of coordination chemists.