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AQUEOUS SYNTHETIC CHEMISTRY OF VANADIUM(V) WITH CITRATE

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Abstract

*Vanadium's involvement in biological processes entails deep knowledge of its bioavailability and consequently its soluble forms present in aqueous distributions with physiological ligands of variable size and mode of coordination. In a specific manner, V_2O_5, citric acid guanidinium and H_2O_2 reacted, at pH 5.5, with sodium hydroxide and afforded a red crystalline product upon addition of ethanol at 4^oC. Elemental analysis pointed to the molecular formation $[V_2O_2(O_2)_2(C_6H_5O_7)_2][guanidiniumH]_4 \cdot 6H_2O$ **(1).** Complex **1** was further characterized by FT-IR, UV/Visible spectroscopy and X-Ray crystallography.*

Keywords: *vanadium, insulin mimesis, structural speciation*

Introduction

Vanadium is an essential element, which exists in all organisms at low concentration. Vanadium's participation in a plethora of biological systems and abiotic applications has spawn considerable research over its role in nature, its potential use in pharmaceutical therapeutics and generally its role and biological action (Sigel, 1995). The latter action is supported by the fact that vanadium plays a catalytic role in metalloenzyme systems such as nitrogenase and haloperoxidases (Klarlund, 1985).

As an inorganic cofactor, vanadium possesses and promotes bioactivities, ranging from antitumorigenicity to mitogenicity, inhibition of metabolic enzymes such as phosphoglucomutases (Smith, 1983; Lau, 1989; Walton, 1993) and others (Sigel, 1995). Outstanding in this regard is its influence in the heterogeneous syndrome of Diabetes mellitus through its insulin mimetic action (Flynn, 1992; Sakurai, 2002).

The spectrum of activities involving vanadium logically encompasses a variety of interactions that the metal in its predominant oxidation states V(IV and V) develops in the presence of various physiological ligands.

Among the various ligands studied in the presence of vanadium were carboxylate-containing organic ligands, the most biologically relevant of which was citric acid. Citric acid exists in human plasma (Krebs, 1937), promoting chemical interactions with metal ions and variably influencing key metabolic functions. Furthermore, another important physiological ligand, which participates in a large number of biological processes, is hydrogen peroxide.

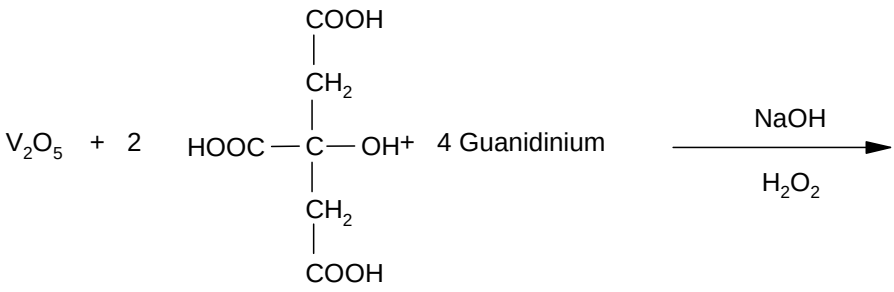
Based on the aforementioned attributes of vanadium interactions with biomolecules, it becomes essential that a) bioavailable species be fully defined in the aqueous media where pertinent vanadium interactions take place, b) soluble species be identified, and ultimately c) the nature, chemical and structural properties of those species be explored, as they constitute the basis on which potential biochemical activity is promoted at the biological level.

In view of the significance of the above mentioned (bio)chemistry, we have embarked on synthetic efforts targeting aqueous vanadium-peroxo-citrate complexes (Kaliva, 2003 and 2006).

Experimental

We investigated the aqueous chemistry of the ternary system vanadium-citric-hydrogen peroxide system, from which we discovered the complex $[V_2O_2(O_2)_2(C_6H_5O_7)_2][quanidiniumH]_4 \cdot 6H_2O$**(1).**

In a typical reaction, V_2O_5 reacted with citric acid and guanidinium in the presence of NaOH at pH 5.5. NaOH was added in order to generate sodium metavanadate in the first step. Aqueous guanidinium was important for two reasons. It helped adjust the pH of the reaction medium, at which the specific synthesis was carried out, and at the same time provided the cations necessary for balancing the large negative charge on the derived anionic complex **1**. Addition of dilute hydrogen peroxide solution promoted the peroxidation of the assembled compound efficiently. The reaction leading to complex **1** is shown schematically below:



$[V_2O_2(O_2)_2(C_6H_5O_7)_2][GuanidimiumH]_4 \cdot 6H_2O$

Results and Discussions

The synthesized complex was well characterized by elemental analysis, X-Ray crystallography, FT-IR, and UV/Visible spectroscopy.

The structure of the peroxo complex $[V_2O_2(O_2)_2(C_6H_5O_7)_2][quanidiniumH]_4 \cdot 6H_2O$ (**1**) is presented in Figure 1. The anionic complex subunit contains a $V^V{}_2O_2$ core with the two vanadium ions in the oxidation state +5. The coordination geometry around each of the vanadium ions of the complex is distorted pentagonal pyramidal.

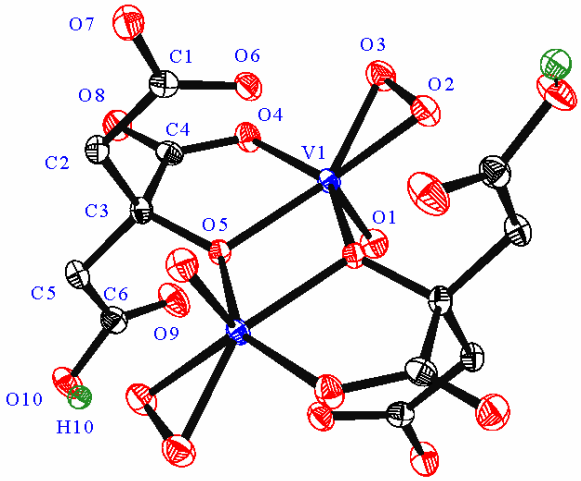


Figure 1. Structure of the anion in **1** with the atom-labeling scheme

***UV/Visible spectroscopy*:** The electronic spectrum of **1** was recorded in H_2O. The spectrum showed a band at 406 nm (ε = 253 $M^{-1}cm^{-1}$) with a rising absorbance into the ultraviolet region. An additional feature was observed at around 221 nm (ε = 4984.126 $M^{-1}cm^{-1}$). The spectrum was featureless beyond 450 nm. The band at 406 nm has been attributed to the presence of a peroxo to vanadium Ligand to Metal Charge Transfer (LMCT).

***FT-IR spectroscopy*:** The FT-Infrared spectra of **1** were recorded in KBr and reflected the presence of vibrationally active carboxylate groups. Antisymmetric and symmetric vibrations for the carboxylate groups of the coordinated citrate ligands were observed. The antisymmetric stretching vibrations $v_{as}(COO^-)$ for the carboxylate carbonyls emerged in the range 1673-1548cm^{-1}. Symmetric vibrations $v_s(COO^-)$ for the same groups appeared around 1409cm^{-1}.

Conclusions

- The anionic complex contains a $V^V_2O_2$ core with the two vanadium ions in the oxidation state +5.
- The coordination geometry around each of the vanadium ions of the complex is distorted pentagonal pyramidal.
- The citrates participating in the coordination sphere around each vanadium ion have the same (de)protonation state in complex **1**.
- Peroxide groups bound to each vanadium of the core.
- Protonation-deprotonation produces discrete structures in aqueous media, and confirms the stability of the basic $V^V_2O_2$ core.
- The peroxo vanadium complex may represent bioavailable soluble species participating in biologically relevant chemistry.
- The implications of such a ternary system chemistry may be a significant part of the (bio)chemical interactions of vanadium V(V) with key targets in biological fluids.

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