

## **VANADIUM (V)-PEROXO-CITRATE COMPLEX FROM AQUEOUS SOLUTIONS**

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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 fashion, V<sub>2</sub>O<sub>5</sub>, citric acid and H<sub>2</sub>O<sub>2</sub> reacted at pH 5.5-6.0 and afforded a red crystalline product. Elemental analysis pointed to the molecular formation K<sub>10</sub>[V<sub>2</sub>O<sub>2</sub>(O<sub>2</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>2</sub>][V<sub>2</sub>O<sub>2</sub>(O<sub>2</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>O<sub>7</sub>)<sub>2</sub>]·20H<sub>2</sub>O(I). Complex I, was further characterized by FT-IR and X-Ray crystallography.*

**Key words:** *vanadium, peroxo-citrate complex*

### **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 and its potential use in pharmaceutical therapeutics (Sigel, 1995). In that sense, vanadium has been found to play a catalytic role in metalloenzyme systems such as nitrogenases and haloperoxidases (Klarlund, 1985; Smith, 1983).

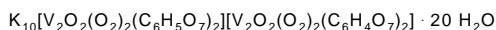
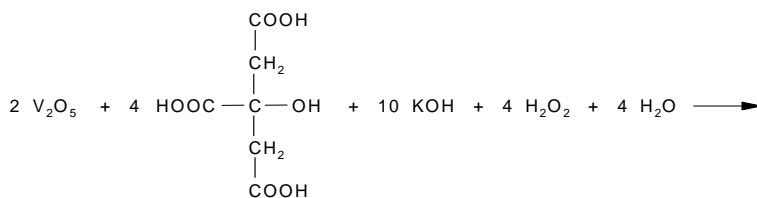
As an inorganic cofactor, vanadium possesses and promotes bioactivities, ranging from antitumorigenicity to mitogenicity, inhibition of metabolic enzymes such as phosphoglucomutases (Klarlund, 1985; Lau, 1989; Smith, 1983; Walton, 1993) and others (Sigel, 1995). The most important of all properties, however, is its influence on the heterogeneous syndrome of Diabetes mellitus through its insulin mimetic action (Flynn, 1992; Sakurai, 2002).

In that context, the spectrum of activities involving vanadium logically encompasses a variety of interactions that the metal develops in its predominant oxidation states V(IV and V) with 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, H<sub>2</sub>O<sub>2</sub>. 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).

### Experimental

We investigated the aqueous chemistry of the ternary system vanadium-citric-hydrogen peroxide, from which the complex  $K_{10}[V_2O_2(O_2)_2(C_6H_5O_7)_2][V_2O_2(O_2)_2(C_6H_4O_7)_2] \cdot 20H_2O$  (**1**) was isolated.

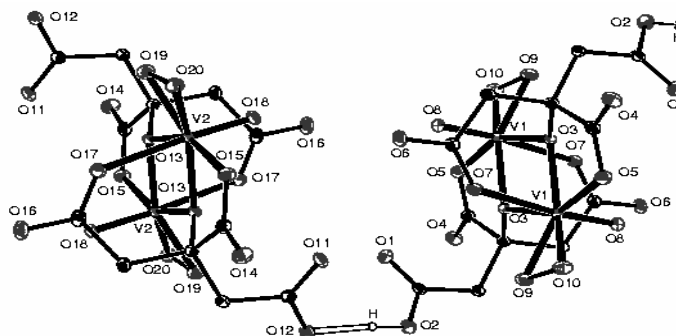
In a typical reaction, V<sub>2</sub>O<sub>5</sub> reacted with citric acid in the presence of KOH at pH 5.5-6.0. Aqueous KOH was important for two reasons. It helped adjust the pH of the reaction medium, at which the specific synthesis was carried out, while at the same time provided the cations necessary for balancing the large negative charge on the derived anionic complex **1**. Addition of dilute hydrogen peroxide solution promoted the peroxidation of the compound efficiently. The overall stoichiometric reaction leading to complex **1** is shown below:



## Results and Discussions

The product of the aforementioned reaction was well characterized by elemental analysis, X-Ray crystallography, and FT-IR spectroscopy.

The structure of the peroxy complex  $K_{10}[V_2O_2(O_2)_2(C_6H_5O_7)_2][V_2O_2(O_2)_2(C_6H_4O_7)_2] \cdot 20H_2O$  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 in both sunubits of the complex is pentagonal biryramidal.



**Fig. 1.** Structure of **1** with the atom-labeling scheme. Thermal ellipsoids are drawn by ORTEP and represent 50% probability surfaces.

The FT-Infrared spectrum of **1** was recorded in KBr and reflected the presence of vibrationally active carboxylate groups. The antisymmetric stretching vibrations  $\nu_{as}(COO^-)$  for the carboxylate carbonyls emerged in the range  $1630-1562\text{ cm}^{-1}$ . Symmetric vibrations  $\nu_s(COO^-)$  for the same groups appeared around  $1400\text{ cm}^{-1}$ .

## Conclusions

The anionic complex **1** is essentially composed of two dinuclear and discrete subunits A and B. 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 in both subunits of the complex is pentagonal bipyramidal.

The citrates participating in the coordination sphere around each vanadium ion differ in their protonation state in the two-dinuclear subunits A and B of complex **1**. The bound citrate ligands donating their alkoxide terminals as bridges between the vanadium ions, their central carboxylates and the variably deprotonated terminal carboxylate groups as anchors to the metal ion(s), fulfill the coordination requirements of the metal ions V(V). Peroxide groups are bound to each vanadium of the core.

The peroxo vanadium complex may represent bioavailable soluble species participating in biologically relevant chemistry. The implications of such chemistry may be a significant part of the (bio)chemical interactions of vanadium V(V) with chemical targets in biologically relevant fluids.

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