

## Crystal and Molecular Structure of a New Hydroxylamido/Amino Acid Oxovanadium(V) Complex, $[\text{VO}(\text{NH}_2\text{O})_2(\text{DL-methioninato})]\cdot\text{H}_2\text{O}$

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The crystal and molecular structure of the  $[\text{VO}(\text{DL-meth})(\text{NH}_2\text{O})_2]\cdot\text{H}_2\text{O}$  complex has been determined by X-ray diffraction methods (monoclinic,  $P2_1/c$  with  $a = 5.8138(2)$ ,  $b = 27.3496(8)$ ,  $c = 7.5663(2)$  Å,  $\beta = 103.059(3)^\circ$ , and  $Z = 4$ ). The vanadium(V) cation is in a pentagonal bipyramidal environment axially coordinated to the oxo group and equatorially to two hydroxylamido groups in a side-on fashion. The fifth equatorial binding site and the other apical position are occupied by an N and an O atom, respectively, from the methioninate anion acting as a bidentate ligand.

**Key words:** Oxovanadium(V) Complex, Amino Acid Complex, Hydroxylamido Complex, Crystal Structure

### Introduction

Vanadium is one of the trace elements of which the essentiality for higher forms of life remains controversial [1–3]. Notwithstanding, it is well known that it plays an important role in certain metalloenzymes and in insulin regulation [1, 3–6].

Peroxovanadium complexes received increasing attention during the last years because they are involved as intermediates in halide oxidation by vanadate-

dependent peroxidases [1, 3, 6–8] and, additionally, some of them have interesting pharmacological properties [9, 10]. In this context, renewed interest has also arisen on vanadium complexes with hydroxylamine,  $\text{NH}_2\text{OH}$ , a molecule which is isoelectronic with hydrogen peroxide,  $\text{H}_2\text{O}_2$ .

In a recent paper, we described the synthesis of a number of oxovanadium(V) complexes of the type  $[\text{VO}(\text{NH}_2\text{O})_2(\text{amino acid})]$  and investigated in detail the vibrational-spectroscopic behavior of the hydroxylamido ligand present in them [11].

As structural information on this type of complexes remains relatively scarce, we have made efforts to obtain single crystals of some of them adequate for X-ray diffraction studies. Usually, the obtained crystals are extremely small or of poor quality but, after several attempts with DL-methionine as the chelating amino acid, we could finally obtain a number of small, well-shaped, single crystals. Therefore, here we report the structure of the  $[\text{VO}(\text{NH}_2\text{O})_2(\text{DL-met})]\cdot\text{H}_2\text{O}$  complex.

### Experimental Section

#### *Synthesis of the complex*

$\text{NH}_4\text{VO}_3$ , NaOH, and  $\text{NH}_2\text{OH}\cdot\text{HCl}$  were purchased from Merck, DL-methionine was obtained from Aldrich. All these reagents were used as supplied. Samples of the investigated complex were obtained by the general procedure previously outlined [11], as follows: 0.117 g (1.0 mmol) of  $\text{NH}_4\text{VO}_3$  and 0.230 g (5.8 mmol) of NaOH were dissolved in 10 mL of distilled water, and the mixture was heated at 50 °C under stirring. After cooling to r.t., 0.463 g (3.1 mmol) of DL-methionine was added in small portions, under continuous stirring. The resulting solution was ice-cooled, and then 0.375 g (5.4 mmol) of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  was added in small portions. After completion of the addition, the solution was kept for 5 min. over ice and finally stored in a refrigerator at 3–5 °C. After a few hours the complex precipitated as a colorless microcrystalline powder, which was separated by filtration, washed with small portions of cold water and absolute ethanol, and finally dried under vacuum. Single crystals adequate for structural X-ray diffraction studies were selected from this mass, aided by a microscope.

The purity of the obtained material was confirmed by elemental analysis, using a Carlo Erba model EA 1108 elemental analyzer, as well as by IR and Raman spectroscopy [11]. –  $\text{C}_5\text{H}_{16}\text{N}_3\text{O}_6\text{SV}$  (297.21): calcd. C 20.19, H 5.38, N 14.13, S 10.78; found C 20.05, H 5.45, N 14.00, S 10.70.



der deposition number CCDC 826986. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## Results and Discussion

An ORTEP [15] drawing of the [VO(DL-meth)-(NH<sub>2</sub>O)<sub>2</sub>].H<sub>2</sub>O complex is shown in Fig. 1. Intramolecular bond lengths and angles around the vanadium center are given in Table 2.

The vanadyl V=O bond [ $d(\text{V}=\text{O})$  1.601(3) Å] defines the axis of a distorted pentagonal bipyramidal environment around the vanadium(V) cation. The metal atom is equatorially coordinated in a side-on fashion to two hydroxylamido anions through both their oxygen [V–O distances of 1.908(3) and 1.918(3) Å] and nitrogen atoms [V–N distances of 2.028(4) and 1.989(4) Å]. The remaining equatorial and axial coordination sites are bridged by the amino acid molecule acting as a bidentate ligand through its nitrogen atom [ $d(\text{V}-\text{N})$  2.120(4) Å] and one carboxylic oxygen atom [ $d(\text{V}-\text{O})$  2.175(3) Å].

The atoms equatorially coordinated to vanadium lie nearly on a common plane [rms deviation of atoms from the least squares plane of 0.015 Å] and at the rim of a Chinese umbrella-like shape that gently slopes down opposite to the VO bond direction [O(carboxyl)-V-L(eq) angles in the range from 76.0(1) to 84.1(1)°].

The conformation and intramolecular bond lengths and angles agree well with those of the few complexes of this type which have been structurally characterized, namely [VO(NH<sub>2</sub>O)<sub>2</sub>(glycine)].H<sub>2</sub>O [16], [VO(NH<sub>2</sub>O)<sub>2</sub>(serine)].H<sub>2</sub>O [16], [VO(NH<sub>2</sub>O)<sub>2</sub>(alanine)].2H<sub>2</sub>O [17] and [VO(NH<sub>2</sub>O)<sub>2</sub>(threonine)] [17]. It is interesting to mention that while in these latter compounds the two hydroxylamido ligands are coordinated with the nitrogen atoms *cis* to the remaining equatorial ligands [16, 17], in the present case these N ligands are in *trans* position to each other (see Fig. 1). It has been suggested that the steric requirements of the other equatorial ligands dictate the orientation of the hydroxylamido groups [16].

The solid is further stabilized by a complex network of intermolecular N–H...O [N...O distances of 2.85(5) and 3.12(5) Å], N–H...S [ $d(\text{N}\cdots\text{S})$  3.68(5) Å], N–H...Ow [ $d(\text{N}\cdots\text{Ow})$  2.77(6) Å], and Ow–H...O [Ow...O distances of 2.85(5) and 3.14(6) Å] hydrogen bonds (see Fig. 1).

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