Inorganica Chimica Acta, 46 (1980) L119–L120
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Cysteine Methyl Ester–Oxovanadium(IV) Complex, Preparation and Characterization

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Received August 12, 1980

A recent topic of interest in bioinorganic chemistry is the physiology of vanadium ion, that is, the properties and function of vanadocytes found in the blood of ascidians [1, 2] and the inhibitory effect of vanadium on Na, K-ATPase [3]. Although complexes of various ligands with vanadium (III and IV) or oxovanadium (IV) have been prepared and studied, few oxovanadium complexes with sulfur and nitrogen donor atoms have been isolated from solution and characterized. During investigations on vanadium complexes formed with various types of ligands, we isolated the bis(cysteine methyl ester)-oxovanadium(IV) complex *1* for the first time. We wish to report herein the preparation and characterization of *1*.

When a mixture of cysteine methyl ester hydrochloride and vanadyl sulfate in a molar ratio of 5:1 in 0.2 *M* borate buffer (pH 10.5) was stirred in air for 5–6 hours, a purple solid was precipitated. The precipitate was collected, washed with water several times and dried *in vacuo* over P_2O_5 at room temperature. *Anal.* Calcd. for $C_8H_{16}O_5N_2S_2V$: C, 28.65; H, 4.82; N, 8.36. Found: C, 28.47; H, 4.78; N, 8.33. From the result of elemental analysis we deduced that in this complex two cysteine methyl ester ligands form a penta-coordinate array around the vanadium (IV) center. Conformation of this penta-coordinate geometry containing oxovanadium(IV) was obtained by IR, Raman, ESR and visible absorption spectroscopies. The IR (KBr disk) and Raman spectra of *1* showed two strong split absorption bands at 956 and 945 cm^{-1} attributable to the vanadyl group (V=O) [4] (Fig. 1), suggesting the presence of *cis* and *trans* isomers in the complex. No absorption band due to the thiol group of the ligand in the purple complex *1* was detectable by Raman spectrometry and the amino group coordinated to the metal ion was detectable by IR spectrometry. The oxovanadium(IV) complex showed a typical isotropic eight line ESR

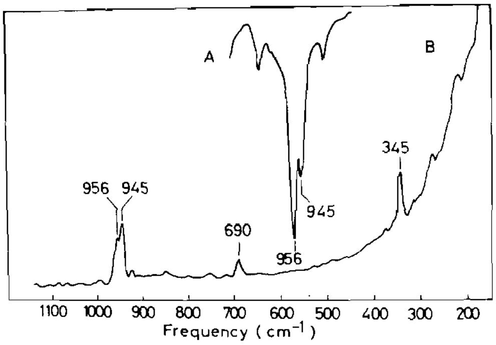

Fig. 1. IR (KBr-disk) (A) and Raman (B) spectra of the cysteinemethylester-oxovanadium(IV) complex. Instrument conditions for B: laser, 514.5 nm line; power, 200 mW at laser output; slit width, 5 cm^{-1}; time constant, 0.2 sec; temperature 20 °C.

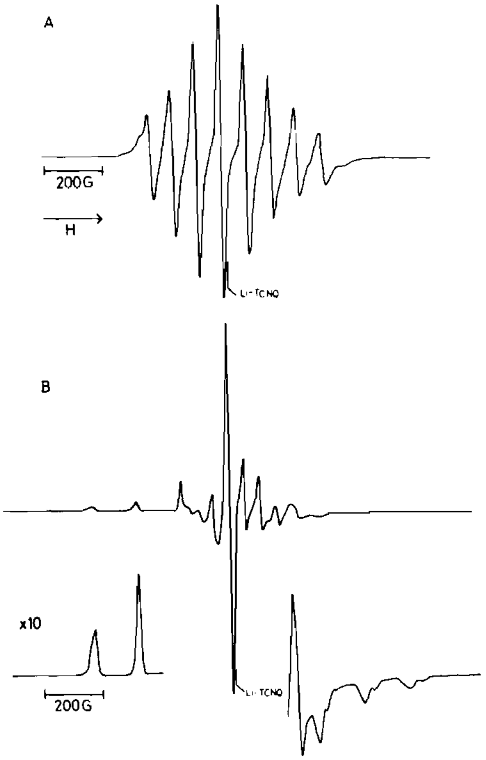

Fig. 2. ESR spectra of the cysteinemethylester-oxovanadium(IV) complex. Instrument conditions: modulation frequency, 100 KHz; modulation amplitude, 2.5 gauss; microwave frequency, 9.4112 GHz for A and 9.2476 GHz for B; microwave power, 50 mw; time constant, 0.3 sec for A and 0.03 sec for B; gain, 710 for A and 10 for B; temperature, 293 K for A and 77 K for B. The complex was prepared from 2 m*M* vanadyl sulfate and 10 m*M* cysteinemethylester hydrochloride in 0.2 *M* borate buffer (pH 10.5).

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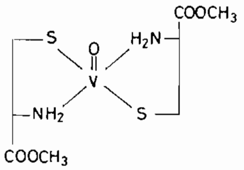
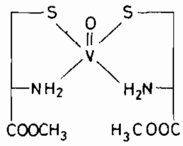
spectrum at room and liquid nitrogen temperature [5, 6] (g_o; 1.990, $g_\parallel$; 1.964, $g_\perp$; 2.003; A_o; 79.2 X 10^{-4} cm^{-1}, $A_\parallel$; 143.6 X 10^{-4} cm^{-1}, $A_\perp$; 47.0 X 10^{-4} cm^{-1}) (Fig. 2). A minor oxovanadium(IV) component was also detectable in the ESR spectrum, as in the IR and Raman spectra. The visible absorption band of *1* is also typical of oxovanadium(IV) complexes [7, 8]. A ligand to metal ion stoichiometry of 2:1 in the product was confirmed by spectrophotometric titration monitoring 530 and 678 nm of its absorption maxima at pH 10.5.

The most interesting characteristic of *1* deduced from the above results is the apparent, square pyramidal geometry of the thiolate-amino coordination of the cysteine methyl ester ligand containing the oxovanadium(IV) center. The relative stability of this complex *1* can be considered with the results obtained by comparison of empirical ligand field parameters calculated from ESR parameters and maximum values in visible region absorption spectrum [6]. The K-value, the Fermi contact term, which is related to the amount of unpaired electron density at the vanadium nucleus, and the $(\beta_1^*)^2$-value of the in-plane σ-bonding coefficient for *1* are 0.61 and 0.61, respectively. In contrast, those of oxovanadium(IV) complexes containing oxygen–oxygen, oxygen–nitrogen and nitrogen–nitrogen donor sets ranged from 0.69 to 0.75 and from 0.70 and 0.79, respectively, and the K-value for the sulfur–sulfur set is reported as 0.50 [6]. Therefore, those of *1* having sulfur–nitrogen set fall within those of oxygen–nitrogen and sulfur–sulfur sets. This clearly shows that sulfur-containing ligands can be covalently bonded to the oxovanadium(IV) center. The structure of *1* can be depicted as follows.





The stable purple solid complex *1* can also be prepared using sodium vanadate(V) in place of vanadium sulfate.

The finding that cysteine and oxovanadium(IV) form a stable complex should be useful in understanding the physiology of the vanadium ion in biological systems.

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