Crystal Structure of an L-Cysteine Methyl Ester–Vanadyl(IV) Complex

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Since vanadate ion (+5 oxidation state) was found to be a potent inhibitor of Na^+, K^+-ATPase [1], interest in the physiology, biochemistry and bioinorganic chemistry of vanadium has been focused on the structure of this element in living systems [2, 3]. When vanadate ion was given to animals, vanadyl ion (+4 oxidation state or oxovanadium) was exclusively detected in organs and organelles, indicating that vanadate ion was reduced to vanadyl and subsequently bound to proteins or other higher molecular weight compounds [4, 5].

The importance of sulfur–metal binding in various types of metalloproteins is well known. Vanadium nitrogenase, for example, may include a vanadium–sulfur coordination [6–8].

Based on these findings, the importance of vanadyl –sulfur bonding in biological systems has recently been recognized. Thus several vanadyl–thiolate complexes have been investigated [9–11], and the crystal structure of the vanadyl–ethane-1,2-dithiolate complex was established [12–14]. However, few vanadyl complexes containing a biologically significant thiol-amino acid, which might be detected in biological systems, have been studied.

During investigation of the chemical nature of the vanadyl ion [4, 5, 15–20], we found that cysteine and its derivatives form stable purple complexes with vanadyl ion [21], and that the vanadate ion is reduced by cysteine [22], glutathione and other related compounds [23], followed by complex formation as vanadyl–thiolate complexes in aqueous solution under physiological conditions. This paper reports the first crystal structure of a purple colored vanadyl–cysteine methyl ester complex.

Thin leaf crystals of vanadyl–cysteine methyl ester complex **A** were prepared from a mixture of L-cysteine methyl ester hydrochloride and vanadyl sulfate in 0.2 M borate buffer, pH 10.5, as described previously [21]. The crystals of the complex are monoclinic with the following crystallographic data: space group C_2 with $a = 6.770(2)$, $b = 8.212(2)$, $c = 12.747(4)$ Å, $\beta = 104.09(2)^\circ$; $U = 687.3(3)$ Å; $Z = 4$ and $D_x = 1.62$ g/cm^3. The diffraction intensities with 2θ up to 50° were collected on a computer-controlled Rigaku four-circle diffractometer with a graphite-monochromated Mo Kα radiation, in ω scan mode, and were corrected for Lorentz, polarization and background effects. The structure was determined by the heavy atom method and refined by the block-diagonal least-squares calculations with anisotropic temperature factors for non-hydrogen atoms. The hydrogen atoms were located from difference maps and were included only in the calculations of the structure factors. The final R value was 0.0406 for 663 reflections ($F > 6\sigma F$).

The structure with the absolute configuration of the complex A is depicted in Fig. 1. Bond distances and angles are shown in Table I. The coordination geometry around the central vanadium atom is square-pyramidal with two-fold symmetry, and nitrogen and sulfur atoms are in *trans* positions. The bond angles O_1–V–N and O_1–V–S are 98.06° and 114.13°, respectively, which indicates an out-of-plane distance for the vanadium atom. The intramolecular and intermolecular bond distances of N···O_1 are 3.14 Å and 2.8 Å, respectively, indicating that both intra- and intermolecular hydrogen bonding may be present in the crystals. The bond distances of V–S (2.322 Å) and V=O (1.616 Å) in complex A are comparable to those (V–S, mean value 2.378 Å and V=O, 1.625 Å) in the vanadyl–ethane-1,2-dithiolate complex [13].

The present complex **A** is a good chemical model for a protein containing vanadyl–cysteine coordination. This complex may also be useful in characterization of vanadyl–sulfur bonding, which might be detected in biological systems.

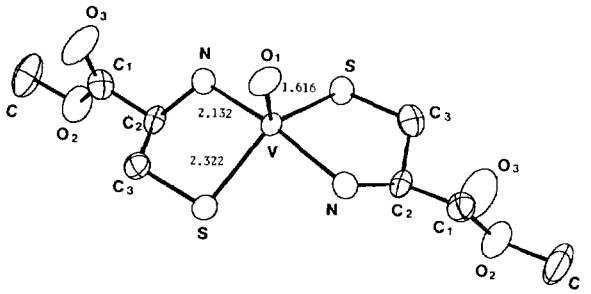

Fig. 1. Structure of vanadyl(IV)–cysteine methyl ester complex.

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TABLE I. Selected Interatomic Distances (Å) and Angles (deg) for Complex A

Bonds			
$V-O_1$	1.616(7)	C_2-C_1	1.514(11)
V–N	2.132(6)	C_3-S	1.823(8)
V–S	2.322(3)	C_1-O_2	1.314(11)
$N-C_2$	1.489(10)	C_1-O_3	1.180(11)
C_2-C_3	1.497(13)	O_2-C_4	1.436(12)
Angles			
O_1-V-N	98.06(18)	$N-C_2-C_1$	111.87(69)
O_1-V-S	114.13(6)	$C_3-C_2-C_1$	108.89(69)
N–V–S	84.37(20)	$C_2-C_1-O_2$	112.65(74)
$V-N-C_2$	115.99(49)	$O_2-C_1-O_3$	123.33(78)
$V-S-C_3$	97.83(31)	$C_1-O_2-C_4$	116.36(77)
$N-C_2-C_3$	110.15(64)	$C_2-C_1-O_3$	123.87(80)
$S-C_3-C_2$	111.09(54)		

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