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Preparation and Structure of Oxo-bridged Dinuclear Vanadium(III) Complex $[V^{III}_2(\text{L-his})_4(\mu\text{-O})]\cdot 2H_2O$

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The synthesis, structure, and properties of a L-histidinato vanadium(III) complex, $[V^{III}_2(\text{L-his})_4O]\cdot 2H_2O$, are reported. Crystal structure analysis has revealed that the complex is an oxo-bridged dimer with the V-O-V angle of 153.9(2)° and at each vanadium(III) center one L-his ligand coordinated tridentately and the other didentately. The visible absorption and resonance Raman spectra show the characteristic feature of the oxo-bridged vanadium(III) complexes.

Vanadium(III) chemistry is a topic of current interest with regard to its biological role in the blood cells of tunicates.[1,2] Boeri and Ehrenberg[3] and, more recently, Anderson and Swinehart[4] observed the intense absorption band around 420 nm which is characteristic of oxo-bridged dinuclear vanadium(III) complexes in their spectroscopic studies of the blood cells of *Ascidia obliqua* and *A. ceratodes*. Therefore, it is of importance to study the properties of the oxo-bridged dinuclear vanadium(III) complexes in order to solve the puzzling role of vanadium(III) in tunicates. Although several vanadium(III) complexes with a V-O-V bridge have been characterized by X-ray crystallography, there are no reports about oxo-bridged dinuclear vanadium(III) complexes which contain biologically relevant amino acids. Here we wish to report the first example of an amino acidato vanadium(III) complex with an oxo bridge.

$[V^{III}_2(\text{L-his})_4(\mu\text{-O})]\cdot 2H_2O$ (**1**) was prepared by the reaction of VBr_3 and L-histidine in an aqueous solution under an argon atmosphere using standard Schlenk techniques. $BaBr_2\cdot 2H_2O$ (2.5 g, 7.5 mmol) was added to a suspension of $V_2(SO_4)_3$ (0.98 g, 2.5 mmol) in aqueous solution (20 cm^3). The mixture was heated at 70 °C for 12 h. Precipitated $BaSO_4$ was filtered out. To the filtrate was added an aqueous solution of L-histidine (1.55 g, 10 mmol) neutralized by $LiOH\cdot H_2O$ (0.42 g, 10 mmol). The brown solution was evaporated to dryness under reduced pressure. To the residue, ethanol was added to extract lithium bromide and the crude powder of **1** was collected by filtration. Crystallization was done by dissolving the crude powder in a small amount of water, adding more than twice the volume of ethanol, and then keeping the solution at 50 °C. The crystalline sample was resistant to air-oxidation while a diluted aqueous solution of **1** was very unstable in air. Yield; 0.5 g. Found: C, 37.88; H, 4.67; N, 21.72%. Calcd for $C_{24}H_{36}N_{12}O_{11}V_2$: C, 37.40; H, 4.68; N, 21.82%.

The structure of complex **1** was determined by X-ray crystallography.[5] As the ORTEP drawing in Fig. 1 shows, the histidinato vanadium(III) complex obtained here is an oxo-bridged dinuclear complex. Table 1 summarizes the selected bond distances and angles of **1**. Five dinuclear vanadium(III) complexes with a single oxo bridge have been structurally characterized so far: $[V_2OCl_4(THF)_6]$ (**2**),[6] $[V_2O(SCH_2CH_2NMe_2)_4]$ (**3**),[7] $[V_2O(acac)_2L_2]I_2$ (L=1,4,7-trimethyl-1,4,7-triazacyclononane) (**4**),[8] $[V_2OCl_2(bpy)_4]Cl_2$ (**5**),[9] $[V_2OCl_2(phen)_4]Cl_2$ (**6**).[10] Complex **1** has the smallest V-O-V angle among them; 153.9(2)° for **1**, 180.0° for **2**, 177.84(25)° for **3**, 180.0° for **4**, 173.5° for **5**, 167.9(6)° for **6**. The average V-O(oxo) distance of **1** is 1.792 Å, being in the range of 1.769-1.813 Å which was obtained for **2** to **6**. Each vanadium(III) atom is in a distorted octahedral environment comprising a tridentately coordinated L-his ligand, a didentately coordinated L-his ligand, and a bridging oxo ligand. The didentate L-his ligand coordinates to the vanadium(III) ion via the amino and imidazolyl nitrogen atoms, leaving the carboxylate group as a pendant group. In each octahedron, the two imidazolyl nitrogens and also the two amino nitrogens are in the cis position, respectively. The V-N distance in the trans position with respect to the bridging oxo group is elongated due to a strong structural trans influence of the oxo ligand.

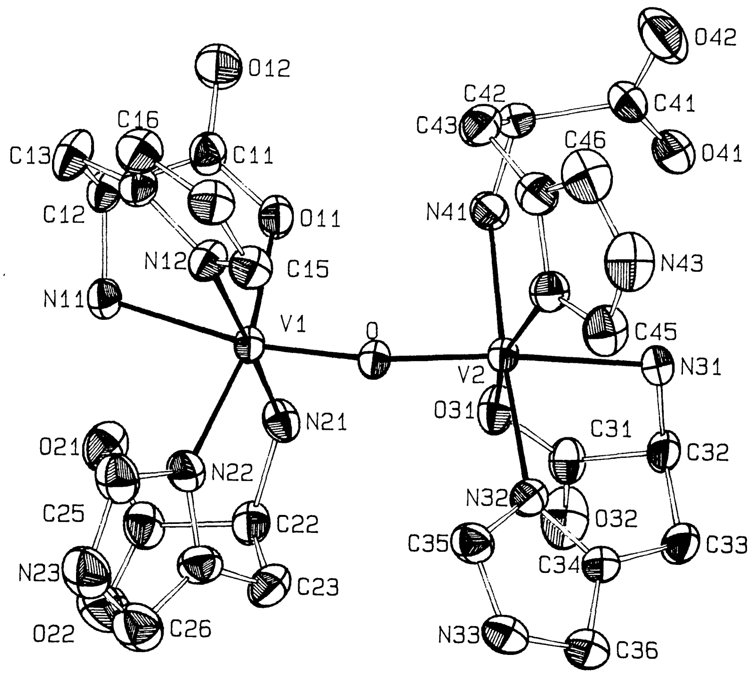

Fig. 1. ORTEP drawing of **1**.

Table 1. Selected bond distances (Å) and angles (degree) of **1**

V1-O	1.792(2)	O-V1-O11	94.0(1)	O-V2-O31	94.1(1)
V1-O11	2.060(4)	O-V1-N12	95.2(1)	O-V2-N32	95.1(1)
V1-N11	2.214(3)	O-V1-N21	90.1(1)	O-V2-N41	90.0(1)
V1-N12	2.112(4)	O-V1-N22	101.3(1)	O-V2-N42	101.1(1)
V1-N21	2.176(4)	O11-V1-N11	75.1(1)	O31-V2-N31	75.0(1)
V1-N22	2.091(4)	O11-V1-N12	89.1(2)	O31-V2-N32	89.2(2)
V2-O	1.791(2)	O11-V1-N21	86.6(2)	O31-V2-N41	86.6(2)
V2-O31	2.058(4)	N11-V1-N12	83.2(1)	N31-V2-N32	83.3(1)
V2-N31	2.212(3)	N11-V1-N21	90.9(1)	N31-V2-N41	90.9(1)
V2-N32	2.113(4)	N11-V1-N22	89.7(1)	N31-V2-N42	89.9(1)
V2-N41	2.176(4)	N12-V1-N22	92.5(2)	N32-V2-N42	92.5(2)
V2-N42	2.093(4)	N21-V1-N22	90.3(2)	N41-V2-N42	90.3(2)
V1•••V2	3.4905(5)	V1-O-V2	153.9(2)		

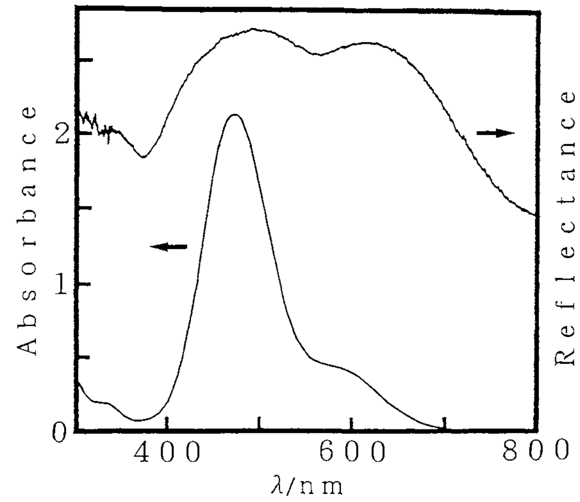

Fig. 2. Diffuse reflectance and absorption spectra of **1**. Conditions: reflectance spectrum; powdered sample of **1** was diluted with MgO in 1:1 ratio; absorption spectrum, [**1**] = 6.75×10^{-4} moldm^{-3}, [L-histidine] = 1.68×10^{-2} moldm^{-3}, pH=7.67. Without free ligands, the diluted aqueous solution of **1** was very unstable.

Figure 2 shows the diffuse reflectance spectrum (upper) of a powder sample of **1** and the absorption spectrum (lower) of an aqueous solution of **1**. The absorption spectrum exhibits an intense band at 478.5 nm (ε=3220 mol^{-1}dm^{3}cm^{-1}) which is due to a ligand-to-metal charge transfer (LMCT) band of the $[\mathrm{V\text{-}O\text{-}V}]^{4+}$ unit[11]) and a medium intense band at 590 nm. These two bands correspond well in their positions to those observed for the solid sample though the relative intensities of the two bands are rather different in both states. These observations indicate that the $[\mathrm{V\text{-}O\text{-}V}]^{4+}$ unit was preserved in aqueous solutions.

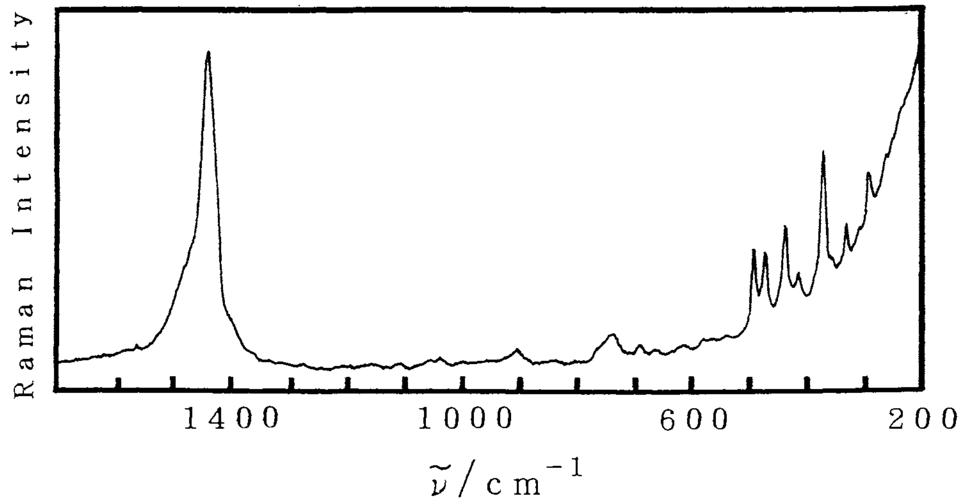

Fig. 3. Resonance Raman spectrum of **1**. Conditions: sample, KBr disk; laser, Ar^{+} ion, 488.0 nm (200 mW).

Figure 3 shows the Raman spectrum measured on resonance with the LMCT band. In accordance with the earlier observation[11]) the first harmonics of the antisymmetric V-O-V stretching, which was observed at 1437 cm^{-1}, was strongly resonance enhanced . The bands at 730 and 436 cm^{-1} can be assigned to the fundamental vibrations of antisymmetric and symmetric V-O-V stretchings, respectively.

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5) Crystal data for $[V_2(\text{L-his})_4(\mu\text{-O})]\cdot 2H_2O$: M=770.51, 0.25x0.25x0.30 mm^3, triclinic, P1, a=10.100(1), b=10.100(1), c=10.646(1) Å, α=62.54(1), β=62.52(1), γ=87.68(1)°, V=834.1 Å^3, Z=1, D_{calc}=1.53 gcm^{-3}, λ(Mo Kα)=0.71073 Å, F(000)=398, μ(Mo Kα)=6.1 cm^{-1}, room temperature, R(R_w)=0.039 (0.049) for 4906 independent reflections with $|Fo|>3\sigma|Fo|$ ($2\theta \leq 60°$). The data collection and the structure determination were performed by the same procedure described in a previous paper (K. Okamoto, J. Hidaka, M. Fukagawa, and K. Kanamori, *Acta Cryst.*, **C48**, 10925 (1992)).
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