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Preparation and Structures of $K_3[V^{III}(ox)_2(\mu\text{-}SO_4)]$ and $K_5[V^{III}(ox)_2(SO_4)_2]$

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Two sulfatovanadium(III) complexes, *trans*-$K_3[V^{III}(ox)_2(\mu\text{-}SO_4)]$ (**1**) and *trans*-$K_5[V^{III}(ox)_2(SO_4)_2]$ (**2**), were prepared. The X-ray crystallography of complex **1** showed that the complex consists of a one-dimensional polymer chain with a bridging sulfate ion. In aqueous solution, however, the sulfate bridge is cleaved and the sulfate ion coordinates to vanadium(III) unidentately. Complex **2** has been characterized by elemental analysis, and Raman and infrared spectra.

Vanadium(III) complexes have attracted significant interest on account of the status of vanadium in ascidians.[1] It has been found that the blood cells of *Ascidia gemmata* contains as high as $0.35\ \mathrm{mol\,dm^{-3}}$ of vanadium.[2] A considerable amount of sulfate coexists with vanadium(III) in the blood cells of ascidians.[3—6] Frank et al. have suggested that the most likely status for vanadium(III) in the blood cells is as the $V(SO_4)(H_2O)_{4-5}^{+}$ complex ion.[4—6] Very recently Bayer et al. have also proposed that a similar sulfato-vanadium(III) complex exists in the blood cells.[7] In this regard it is of importance to study the coordination chemistry of sulfate to vanadium(III). However, there are few sulfatovanadium(III) complexes of which the structure has been well characterized.

We studied the structure of the complexes derived from the reaction of diaquabis(oxalato)vanadate(III), $[V(ox)_2(H_2O)_2]^-$, with SO_4^{2-}. To avoid spontaneous incorporation of a sulfate ion as a counter ion in vanadium(III) complex, the anionic complex, $[V(ox)_2(H_2O)_2]^-$, was used.

This paper describes the preparation and structures of the two sulfatovanadium(III) complexes, *trans*-$K_3[V^{III}(ox)_2(\mu\text{-}SO_4)]\cdot 2H_2O$ and *trans*-$K_5[V^{III}(ox)_2(SO_4)_2]\cdot 3H_2O$. A Raman spectral study on the structure of the sulfato complex in aqueous solution is reported as well.

Experimental

Preparation of Complexes. All procedures were done under an argon atmosphere using a standard Schlenk technique or in a N_2-filled glove box.

***trans*-$K[V(ox)_2(H_2O)_2]\cdot 3H_2O$:** This complex was prepared by a different method from that in the literature.[8]

$V_2(SO_4)_3$ (3.9 g; 10 mmol) was dissolved in 20 cm^3 of water by stirring at 50 °C for a day. A small amount of an insoluble impurity was filtered off. A mixture of $H_2C_2O_4\cdot 2H_2O$ (5.1 g; 40 mmol), KOH (1.2 g; 20 mmol), and $BaCO_3$ (5.9 g; 30 mmol) in 20 cm^3 of water was warmed at 40 °C until the evolution of carbon dioxide stopped. To this mixture the vanadium solution was added and it was stirred at 50 °C for 10 h. Precipitated barium sulfate was removed by filtration. The filtrate was evaporated to about 70% of the initial volume and cooled in an ice bath. Green needle crystals that were deposited were filtered out (yield 0.9 g); this complex was identified as tris(oxalato)vanadate(III), $K_3[V(ox)_3]$.[9] The filtrate was evaporated to 10 cm^3 again and cooled in an ice bath. Purple crystals that appeared were collected by filtration. Yield 3.4 g (49%). Found: C, 13.42; H, 2.73%. Calcd for $K[V(ox)_2(H_2O)_2]\cdot 3H_2O = KVC_4H_{10}O_{13}$: C, 13.49; H, 2.83%.

$K_3[V(ox)_2(\mu\text{-}SO_4)]\cdot 2H_2O$ (1): To a solution containing 0.9 g (2.5 mmol) of *trans*-$K[V(ox)_2(H_2O)_2]\cdot 3H_2O$ and 0.2 g (1 mmol) of K_2SO_4 in a small amount of water, ethanol was added until a small amount of oil appeared. The oily product changed to small green crystals upon heating at 50—55 °C for several hours. The crystals were collected by filtration and washed with aqueous ethanol. The crystalline sample was very resistant to air-oxidation and could be stored in aerial atmosphere. Yield 0.25 g (21%). Found: C, 10.28; H, 0.65%. Calcd for $K_3[V(ox)_2(SO_4)]\cdot 2H_2O = K_3VC_4H_4O_{14}S$: C, 10.09; H, 0.85%.

The reaction of *trans*-$K[V(ox)_2(H_2O)_2]$ with an equimolar amount of K_2SO_4, which is required from the composition of **1**, resulted in the precipitation of $K_5[V(ox)_2(SO_4)_2]$ (**2**).

***trans*-$K_5[V(ox)_2(SO_4)_2]\cdot 3H_2O$ (2):** To an aqueous solution of *trans*-$K[V(ox)_2(H_2O)_2]\cdot 3H_2O$ (0.9 g; 2.5 mmol) and K_2SO_4 (0.9 g; 5 mmol), ethanol was added until the solution became cloudy. After the solution was cooled in a refrigerator, green crystals that were deposited were collected by filtration. The crystalline sample of this complex is also very resistant to air-oxidation. Yield. 1.3 g (72%). Found: C, 7.09; H, 0.86%. Calcd for $K_5[V(ox)_2(SO_4)_2]\cdot 3H_2O = K_5VC_4H_6O_{19}S_2$: C, 7.18; H, 0.90%.

Measurements. Raman spectra were recorded on a JASCO R-800 laser Raman spectrophotometer with an excitation by an Ar^+-ion laser line, 514.5 nm. Infrared spectra were recorded on a JASCO FT/IR-8000S. The samples used for Raman and infrared measurements were in the form of KBr disks. For Raman measurements the disks were spun to avoid thermal decomposition induced by laser illumination.

Crystallography. X-Ray Data Collection: A crystal was mounted on a glass fiber and coated with epoxy as a precaution against solvent loss. Unit cell parameters and intensity data for the single crystal (about $0.13\times 0.38\times 0.38\ \mathrm{mm^3}$) of $K_3[V(ox)_2(SO_4)]\cdot 2H_2O$ were measured on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Unit-cell parameters were calculated by least-squares refinement from 25 reflections with $16 < 2\theta < 20°$. Systematic absences led to the space groups $P2_1/n$ (No. 14). Crystal data: $C_4H_4O_{14}SK_3V$,

$M=476.38$, monoclinic, space group $P2_1/n$ (No. 14), $a=10.169(3)$, $b=18.122(4)$, $c=7.578(2)$ Å, $\beta=104.73(1)°$, $V=1350.7(6)$ Å^3, $Z=4$, $D_c=2.34$ g cm^{-3}, $F(000)=944$, $\mu=18.6$ cm^{-1}, and room temperature.

The intensity data were collected by the ω–2θ scan mode up to $2\theta=60°$ (h, k, $l\leq14$, 25, ±10) with scan width $(0.7+0.350\tan\theta)°$ and the scan rate was varied from 1 to 5° min^{-1} (on ω). As a check on crystal and electronic stability, three representative reflections were measured every 120 min of X-ray exposure time and a linear decay correction was applied (correction factor on I, 1.000 to 1.005). The orientation (for the same three reflections) was monitored after every 200th scan. The intensities were corrected for Lorentz and polarization. An empirical absorption correction based on a series of psi-scans were applied (min and max transmission factors, 0.84 to 1.00). A total of 3516 reflections with $F_o>3\sigma(F_o)$ of the unique 4047 reflections on the measured 4342 reflections were considered as "observed" and used for structure analysis.

Analysis of Crystal Structure: The vanadium and donor atom positions were identified by the direct methods. The remaining non-hydrogen atom positions were found by successive difference Fourier techniques to give a trial structure. The structure was refined by the full-matrix least-squares on F using anisotropic thermal parameters for non-hydrogen atoms and their corrections for anomalous dispersion. The hydrogen atoms were not included in the calculation. The final refinement gave $R=0.031$ and $R_w=0.034$ $[w=4F_o^2/\sigma^2(F_o)^2]$, and $\Delta_{\max}=0.02\sigma$. The final difference Fourier synthesis $\Delta\rho_{\max}$ indicated no significant peaks larger than 0.67 e Å^{-3}. All the calculations were done on a VAX computer using the crystallographic package of MOLEN.[10] Atomic positional parameters are given in Table 1.[11]

Results and Discussion

Crystal structure of *trans*-[V(ox)$_2$(μ-SO$_4$)] (1). A perspective view of the complex **1** is shown in Fig. 1. The selected bond distances and angles are summarized in Table 2. The vanadium(III) atom was in a distorted octahedral environment made up by the four O atoms of the two oxalato ligands and the two O atoms of the two sulfate ligands in the trans positions. The complex anion constituted a one-dimensional polymer chain linked by a bridging ligand sulfato as shown in Fig. 2 and thus formulated as *trans*-[V(ox)$_2$(μ-SO$_4$)]$^{3-}$. The bond distances and angles in the equatorial plane agreed fairly well with those found in *trans*-K[V$^{\text{III}}$(ox)$_2$(H$_2$O)$_2$].[8] That is, the average distances in *trans*-K$_3$[V$^{\text{III}}$(ox)$_2$(μ-SO$_4$)] and *trans*-K[V$^{\text{III}}$(ox)$_2$(H$_2$O)$_2$] were: r(V–O(ox))=2.008 and 2.011 Å, r(C=O)=1.224 and 1.216 Å, r(C–O)=1.288 and 1.281 Å, and r(C–C)=1.546 and 1.545 Å. The bite angles, 81.21(7) and 81.39(7)°, of the oxalato ligand of this complex were somewhat larger than those (average 80.4°) found in *trans*-K[V(ox)$_2$(H$_2$O)$_2$].

The V–O (SO$_4$) distance of this complex were 1.990(2) and 1.995(2) Å, which were comparable to 1.994 Å (average) found in VOSO$_4$·5H$_2$O[12] in which the sulfate ion coordinates to VO^{2+} unidentately. The two S–O distances were long (1.519(2) and 1.494(2) Å) and the other two short (1.446(2) and 1.456(2) Å) in this complex, corresponding to the bridging coordination of the sulfate.

Figure 3 shows the infrared and Raman spectra of **1**. The observed vibrational characteristics were consistent with the structure obtained from the X-ray analysis. Thus the mutual exclusion rule between the Raman and infrared spectra, which was recognized in the ν_a (CO$_2^-$) (1650—1750 cm^{-1}) and ν_s (CO$_2^-$)+ν (C–C) (around 1400 cm^{-1}) regions, was in accordance with the trans configuration of **1**. In the SO$_4^{2-}$ stretching vi-

Table 1. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) ($B_{\text{eq}}=(8\pi/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$)

Atom	x	y	z	B_{eq}
V	0.39380(4)	0.21584(2)	0.11666(5)	0.998(6)
C1	0.4622(2)	0.3504(1)	0.2971(3)	1.31(4)
C2	0.5278(2)	0.3522(1)	0.1346(3)	1.27(4)
C3	0.3365(2)	0.0721(1)	−0.0120(3)	1.39(4)
C4	0.2685(2)	0.0812(1)	0.1477(3)	1.40(4)
O1	0.3904(2)	0.29207(9)	0.3029(2)	1.45(3)
O2	0.4781(2)	0.4013(1)	0.4056(3)	2.23(4)
O3	0.5173(2)	0.29126(9)	0.0441(2)	1.40(3)
O4	0.5852(2)	0.4076(1)	0.1001(3)	2.08(3)
O5	0.3931(2)	0.13051(9)	−0.0552(2)	1.51(3)
O6	0.3312(2)	0.0117(1)	−0.0877(3)	2.33(4)
O7	0.2712(2)	0.14754(9)	0.2084(2)	1.47(3)
O8	0.2179(2)	0.0280(1)	0.2045(3)	2.65(4)
O9 W1	0.5593(2)	0.2410(1)	0.7180(3)	2.20(3)
O10 W2	0.4270(3)	0.0435(1)	−0.3933(3)	3.57(5)
S	0.20110(6)	0.33060(3)	−0.15659(8)	1.330(9)
O11	0.2336(2)	0.25546(9)	−0.0674(3)	1.78(3)
O12	0.5495(2)	0.1651(1)	0.2869(3)	1.83(3)
O13	0.2518(2)	0.3886(1)	−0.0259(3)	2.19(4)
O14	0.2569(2)	0.3332(1)	−0.3154(3)	2.43(4)
K1	0.66416(6)	0.10599(3)	0.83114(9)	2.23(1)
K2	0.31061(6)	0.18701(4)	0.56666(8)	2.42(1)
K3	0.94538(6)	0.04055(3)	0.23295(8)	2.08(1)

W: Crystallization water.

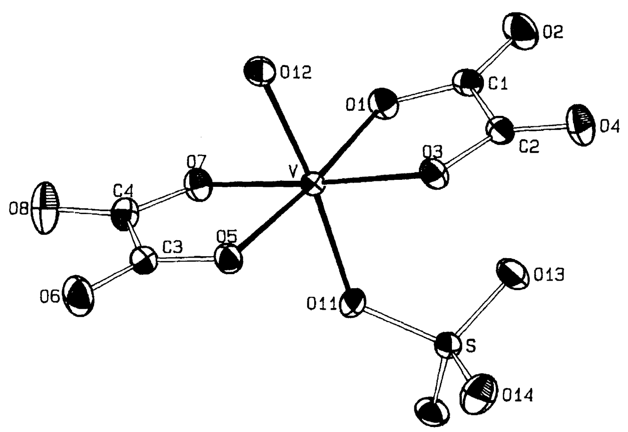

Fig. 1. Ortep drawing of *trans*-[V$^{\text{III}}$(ox)$_2$(μ-SO$_4$)]$^{3-}$.

Table 2. Selected Bond Distances (Å) and Angles (degree)

V–O1	1.982(2)	O1–V–O3	81.21(7)
V–O3	2.025(2)	O1–V–O5	174.16(7)
V–O5	2.021(2)	O3–V–O7	174.55(7)
V–O7	2.003(2)	O5–V–O7	81.39(7)
V–O11	1.990(2)	O11–V–O12	173.48(7)
V–O12	1.995(2)	O3–V–O5	104.02(7)
S–O11	1.519(2)	O11–S–O13	110.3(1)
S–O12	1.494(2)	O11–S–O14	108.1(1)
S–O13	1.446(2)	O12–S–O13	108.7(1)
S–O14	1.456(2)	O12–S–O14	110.6(1)
		O13–S–O14	113.4(1)
		V–O1–C1	115.7(2)
		V–O3–C2	114.0(2)
		V–O5–C3	113.2(2)
		V–O7–C4	114.4(2)
		V–O11–S	133.0(1)
		V–O12–S	138.8(1)

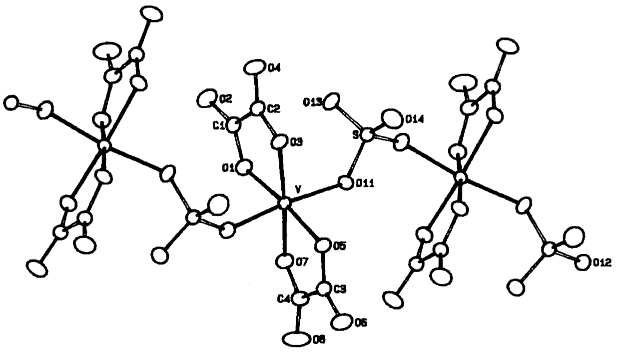

Fig. 2. One-dimensional polymer chain of *trans*-$K_3[V^{III}(ox)_2(\mu\text{-}SO_4)]$.

bration region, the most intense Raman band appeared at 1008 cm^{-1}. This was distinct from the Raman spectral behavior of a free or unidentately coordinated sulfate, which has a very intense Raman band around 980 cm^{-1}.

Solid State Structure of *trans*-$K_5[V(ox)_2(SO_4)_2]$ (2). Crystals good enough for an X-ray analysis were not obtained for complex **2**, so its structure was analyzed on the basis of the Raman and infrared spectra shown in Fig. 4. In the ν_a (CO_2^-), and ν_s (CO_2^-)+ν (C–C), and ν_s (CO_2^-)+δ (CO_2^-) (900—950 cm^{-1}) regions, the mutual exclusion rule applied to the observed Raman and infrared bands except for the 1708 cm^{-1} band. This observation implies that the complex **2** has a symmetry near to centrosymmetry, and thus has a trans conformation.

The SO_4^{2-} stretching vibrations were of great use to identify the coordination mode of sulfate.[13] The S–O stretching vibrations of a free sulfate ion were reduced to the A_1+F_2 modes under a Td symmetry. In general the Raman band due to the A_1 mode appeared at about 980 cm^{-1} as a very intense, sharp band, and that due to the F_2 mode appeared at about 1100 cm^{-1} as a very weak, broad band. In the infrared spectrum, the A_1 mode was inactive while the F_2 mode was observed as an intense band. The unidentate coordination of a sulfate ion lowered its symmetry to approximately C_{3v} and then the F_2 mode split into the A_1+E modes. All of the modes, two A_1 (one correlated to A_1 and the other to F_2 of Td) and E modes, were Raman and infrared active. Generally the A_1 (A_1), the A_1 (F_2), and the E modes were observed in the 970 cm^{-1}, the 1030—1070 cm^{-1}, and the 1120—1150 cm^{-1} regions, respectively.

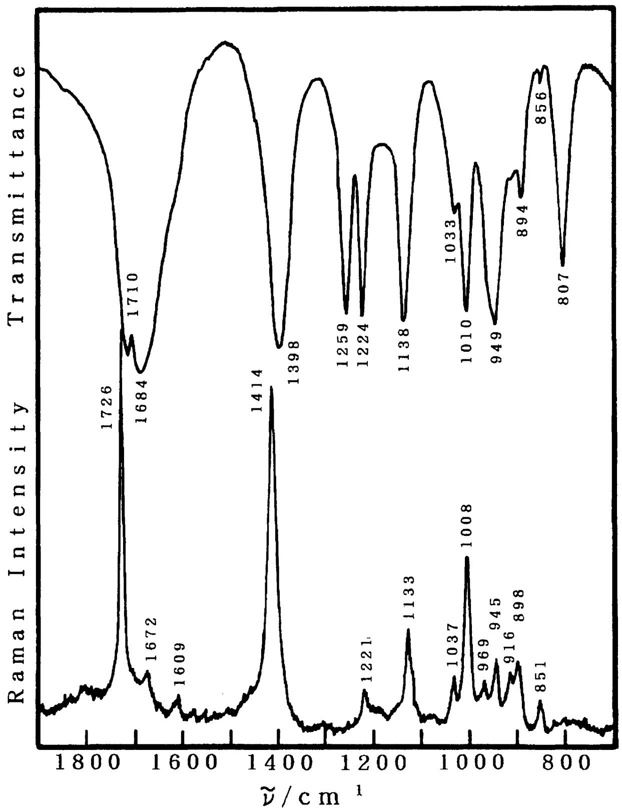

Fig. 3. Infrared (upper) and Raman (lower) spectra of *trans*-$K_3[V^{III}(ox)_2(\mu\text{-}SO_4)]\cdot 2H_2O$.

The vibrational bands due to the sulfate ions in the complex **2** can be satisfactorily interpreted as of a C_{3v} symmetry. Thus, the 978 cm^{-1} Raman band and the 979 cm^{-1} infrared band can be assigned to the A_1 (A_1) mode. The two Raman bands at 1030 and 1058 cm^{-1} and the two infrared bands at 1030 and 1060 cm^{-1} are assignable to the A_1 (F_2) mode. The observation of the two A_1 (F_2) bands in the infrared and Raman spectra would be due to the vibrational coupling between the two sulfato groups and the deviation from a rigorous centrosymmetric structure. The very weak Raman band at about 1150 cm^{-1} and the intense infrared band at 1143 cm^{-1} are assignable to the E mode. These vibrational characteristics exclude the possibility that the sulfate ion may exist as a free ion in the double salt (i.e., $K[V(ox)_2(H_2O)_2]\cdot 2K_2SO_4$), and indicate that the

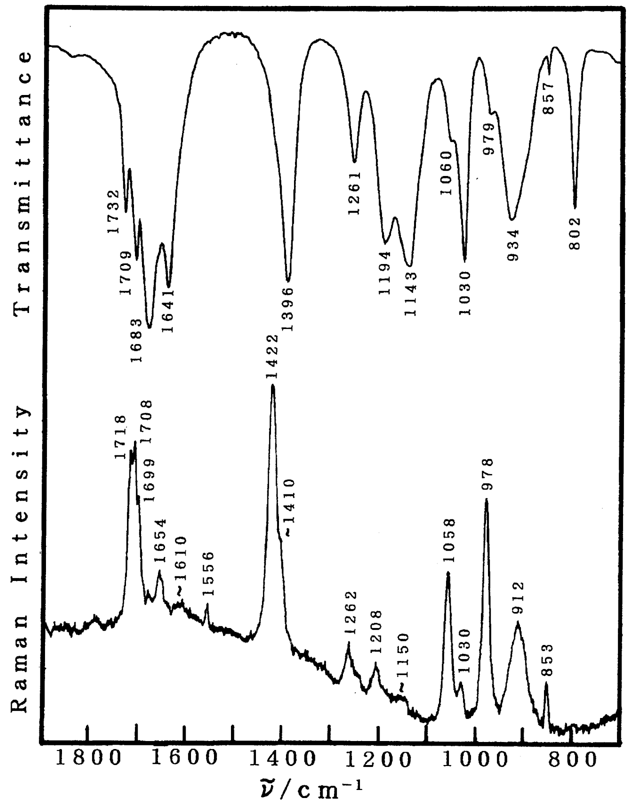

Fig. 4. Infrared (upper) and Raman (lower) spectra of *trans*-$K_5[V^{III}(ox)_2(SO_4)_2]\cdot 3H_2O$.

two sulfate ions coordinates unidentately in the trans positions. Thus the vanadium(III) complex (**2**) with two sulfate ions obtained here is reasonably formulated as *trans*-$K_5[V(ox)_2(SO_4)_2]$.

Coordination of Sulfate Ion in Aqueous Solution. It is important to investigate the coordination of sulfate ion to vanadium(III) in aqueous solution, in relation to the status of vanadium(III) in the blood cells of ascidians. Kimura et al. have reported the association constant of V^{3+} with SO_4^{2-} being 29 on the basis of the UV spectral study.[14)] However, they did not discriminate the inner-sphere (coordination) and outer-sphere (ion-pair) association. There are few studies that demonstrate the direct bonding between V^{3+} and SO_4^{2-} in aqueous solution.

We examined the interaction of the sulfate ion with vanadium(III) on the basis of the Raman spectroscopy. Figure 5 shows the Raman spectra in the SO_4^{2-} stretching region of the aqueous solution of *trans*-$K_3[V(ox)_2(\mu\text{-}SO_4)]$ (about 0.4 mol dm^{-3}) and that of $VOSO_4\cdot 5H_2O$ (about 1 mol dm^{-3}), of which the formation constant, $[VOSO_4]/([VO^{2+}][SO_4^{2-}])$, was calculated to be 63[15)] for comparison. The Raman spectra are very similar to each other. The Raman bands due to the bridging sulfate observed for complex **1** (945, 1008, 1037, and 1133 cm^{-1}) were not observed in aqueous solution, indicating that the complex had no sulfato bridge in the solution. The sharp band at 1041 cm^{-1} can be assigned to the A_1 (F_2) mode of the sulfate ion of C_{3v} symmetry, suggesting that at least one of the vanadium(III) species equilibrating in aqueous solution had a direct bond between V^{3+} and SO_4^{2-} since the reduction of the symmetry of the SO_4^{2-} ion would not be expected for the ionic outer-sphere interaction.

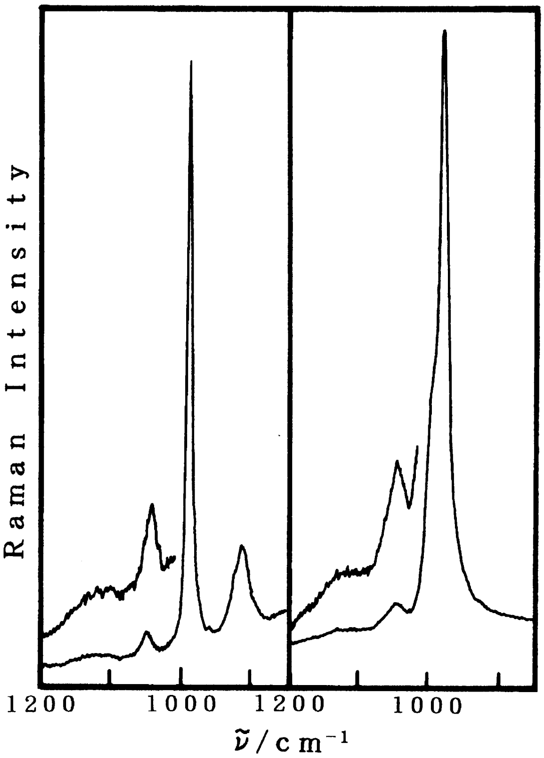

Fig. 5. Raman spectra of the aqueous solution of *trans*-$K_3[V^{III}(ox)_2(\mu\text{-}SO_4)]$ (left) and $VOSO_4\cdot 5H_2O$ (right).

The isolation of the two sulfatovanadium(III) complexes as well as the Raman spectral evidence for the complex formation of V^{3+} with SO_4^{2-} in aqueous solution support the view that the sulfate ion in the blood cells of ascidians coordinates to V^{3+} ion.

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