in HCl should greatly reduce the stability of the HCl antihydrogen-bonded complexes with respect to their HF analogues. This change in relative intensities of the ν_s and $a\nu_s$ absorptions can play a key role in the band assignments of these weak complexes since the absorptions are in the same spectral region.

Conclusions

UF_6 and HCl interact in solid argon to form a well-defined 1:1 hydrogen-bonded complex, UF_6–HCl. The band positions of the UF_6–HCl and the FCl–HCl complexes were very comparable. As the HCl aggregation increased, a 1:2 complex, UF_6–$(HCl)_2$, was observed and characterized by considering the perturbation of the second HCl submolecule on the 1:1 complex. In contrast, the codeposition of WF_6 and MoF_6 with HCl produced hydrogen-bonded 1:1 complexes and antihydrogen-bonded complexes. WF_6 and MoF_6 displayed little preference between the different structural arrangements. In addition, the HCl in the hydrogen-bonded and the antihydrogen-bonded complexes activated several WF_6 and MoF_6 modes that are normally infrared-inactive.

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Raman Spectral Study on the Structure of a Hydrolytic Dimer of the Aquavanadium(III) Ion

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The bridging mode of the hydrolytic dimer of aquavanadium(III) has been determined on the basis of its Raman spectra in resonance with the charge-transfer absorption band in the region 550–380 nm. The Raman spectral characteristics of the hydrolytic dimer are very similar to those of $[V_2O(ttha)]^{2-}$, which has been thought to be a μ-oxo dimer. The hydrolytic dimer formed in a 1:1 mixture of $H_2{}^{18}O/H_2{}^{16}O$ shows no bands which correspond to isotopically mixed species. These observations clearly indicate that the hydrolytic dimer of aquavanadium(III) has a μ-oxo bridge rather than a bis(μ-hydroxo) bridge. The Raman band due to the first overtone of the antisymmetric V–O–V stretching is strongly resonance-enhanced as in the case of binuclear μ-oxo molybdenum complexes (Lincoln, S. E.; Loehr, T. M. *Inorg. Chem.* **1990**, 29, 1907).

Introduction

The chemistry of vanadium in its low oxidation states has been attracting much attention, especially in relation to the status of vanadium in ascidians.[1] Several authors have suggested that the vanadium ion in vanadium-containing blood cells (vanadocytes) is coordinated by organic ligands with low molecular weights (tunichromes).[2] Frank et al., on the other hand, have suggested that the vanadium ion in *Ascidia ceratodes* is present mainly as an unchelated vanadium(III) ion, most likely as the $V(SO_4)(H_2O)_{4-5}{}^+$ complex; they have also pointed out that the pH within the vanadocytes is markedly low (pH 1.1–1.9).[3] Their determination of intracellular pH is consistent with previous[4-8] and recent[9] results, although this subject is still in dispute.[10-13]

It is well-known that the aquavanadium(III) ion is easily hydrolyzed. Pajdowski has studied the hydrolysis of aquavanadium(III) in acidic solution on the basis of spectrophotometric and magnetochemical measurements. He has assigned the intense absorption band observed in the visible region for solutions of pH 2–4 as a charge-transfer transition of the hydrolytic dimer with a bis(μ-hydroxo) bridge.[14] Newton and Baker, on the other hand, have proposed a μ-oxo bridge for the hydrolytic dimer.[15] For the vanadocyte hemolysate from *Ascidia obliqua*, Boeri and Ehrenberg observed an intense absorption band which closely resembles that of the hydrolytic dimer of aquavanadium(III).[16]

Recently, several binuclear complexes of vanadium(III) with several kinds of organic ligands have been prepared and characterized. The μ-oxo bridge has been established in $[V_2OCl_4(THF)_6]$,[17] $[V_2O(bpy)_4Cl_2]Cl_2 \cdot 6H_2O$,[18] and $[V_2O(SCH_2CH_2NMe_2)_4]$[19] by single-crystal X-ray analysis. The μ-oxo bridge has also been proposed for $Na_2[V_2O(ttha)] \cdot dmf \cdot 3H_2O$ (ttha = triethylenetetraminehexaacetate).[20] The (2-hydroxyethyl)ethylenediaminetriacetate (hedta) ligand, on the other hand, has been found to form a bis(μ-alkoxo)-bridged dimer of vanadium(III).[21] It is, therefore, of interest to determine whether the hydrolytic dimer of aquavanadium(III) ion contains a bis(μ-hydroxo) or a μ-oxo bridge.

We present here Raman spectral studies on the structure of the binuclear aquavanadium(III) complex formed by hydrolysis

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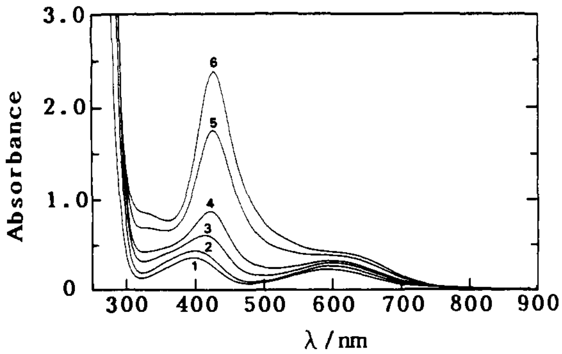

Figure 1. pH dependence of the absorption spectrum of $V_2(SO_4)_3$ (40 mM/V(III) atom). pH: (1) 0.8; (2) 1.1; (3) 1.5; (4) 1.7; (5) 2.0; (6) 2.2.

in acidic solution. It has been shown that the vanadium ion is present in high concentration (40–150 mM) in the blood cells of ascidians.[22-25] Hence, the presence of the hydrolytic dimer of the aquavanadium(III) ion in vanadocytes could not be negligible even if the intracellular pH is rather low.

Experimental Section

Materials. VCl_3 was obtained from Wako Pure Chemical Industries (99.5%) and used as received. $V_2(SO_4)_3$ was prepared according to the literature.[26] A stock solution of $V_2(SO_4)_3$ was prepared by dissolving solid $V_2(SO_4)_3$ in deaerated and argon-saturated water containing 15 mM H_2SO_4. $Na_2[V_2O(ttha)]\cdot dmf\cdot 3H_2O$[20] and $[V_2O(bpy)_4Cl_2]Cl_2\cdot 6H_2O$[18] were prepared according to the methods in the literature. Preparations of air-sensitive materials were carried out under an argon atmosphere by using a standard syringe and vacuum-line techniques. Argon gas was purified by passage through a gas-purification column (Gasclean, Nikka Seiko Co.) before use.

Measurements. Raman tubes and cuvettes equipped with airtight stopcocks were used for Raman and UV–vis measurements, respectively. Transfer of vanadium(III)-containing solutions to the Raman tubes or cuvettes was carried out under a positive argon pressure. Solid $Na_2[V_2O(ttha)]\cdot dmf\cdot 3H_2O$ and $[V_2O(bpy)_4Cl_2]Cl_2\cdot 6H_2O$ were formed into disks for the Raman measurements. The disks were spun so as to avoid any thermal decomposition induced by local laser illumination. The Raman spectra of the solid samples were measured under open air, since no spectral changes due to oxidation of vanadium(III) were observed during the measurements. Raman spectra were obtained on JASCO R-800 laser Raman spectrophotometers equipped with a Spectra-Physics Model 2016 Ar^+ ion laser or NEC Model GLG-5800 He-Ne laser. Raman intensity measurements were made relative to the ν_1 band of sulfate. Corrections of the observed intensity were applied to the fourth power of the wavenumber of scattered radiation and the instrumental response. Infrared spectra were recorded on a JASCO FT/IR-8000 spectrometer. UV–vis spectra were recorded on a JASCO Ubest 50 spectrophotometer.

Results and Discussion

Raman Bands Due to the Hydrolytic Dimer of Aquavanadium(III). Figure 1 shows the visible absorption spectra of aqueous $V_2(SO_4)_3$ solution as a function of pH. It is reasonably concluded that below pH 0.8 monomeric aquavanadium(III) species are predominantly present, since the visible spectrum is virtually identical with that of $[V(H_2O)_6]^{3+}$.[27-29] At pH 1.5, the visible absorption band due to the hydrolysis product of aquavanadium(III) appears at 415 nm. Upon an increase in the pH of the solution, the intensity of this band increases, while its band maximum moves slightly to lower energy. This shift in the absorption maximum may be due to the equilibrium between the monomeric and dimeric species. The band maximum at pH 2.2 was at 425 nm, which is in agreement with the observation by Newton and Baker,[15] while Pajdowski[14c] reported the band maximum at 436 nm. Pajdowski has assigned the intense absorption band as a charge-transfer transition of the binuclear vanadium(III) complex with a bis(μ-hydroxo) bridge; he has also shown that the monomeric hydroxo complex shows no intense bands in the visible region.[14]

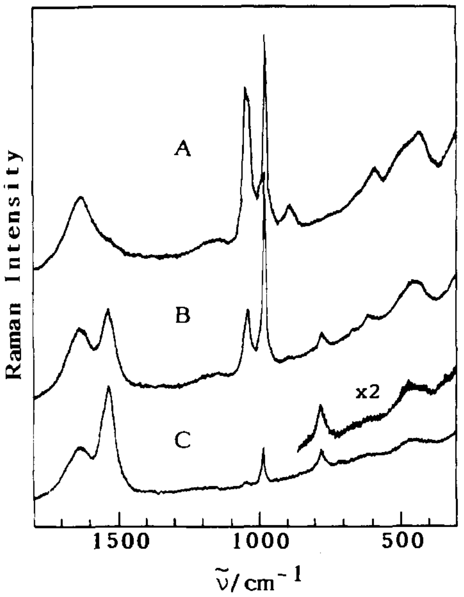

Figure 2. Raman spectra (514.5-nm excitation) of aqueous $V_2(SO_4)_3$ as a function of pH: (A) 40 mM/V(III) atom, pH 0.4; (B) 40 mM/V(III) atom, pH 1.3; (C) 10 mM/V(III) atom, pH 2.4.

We studied the pH dependence of the Raman spectra of $V_2(SO_4)_3$ (40 mM) in aqueous solution in order to identify the Raman bands due to the binuclear complex formed by hydrolysis. Figure 2 shows the Raman spectra excited with a 514.5-nm line as a function of pH. The Raman bands observed at pH 0.4, where the binuclear aquavanadium(III) ion is negligibly present, are assigned to SO_4^{2-}, HSO_4^-, and $V(H_2O)_6^{3+}$ ions. The most intense band at 978 cm^{-1} is assigned as the totally symmetric stretching of the SO_4^{2-} ion. The bands at 1047 and 890 cm^{-1} are due to the symmetric S–O stretchings of the HSO_4^- ion, since the bands increase in intensity with increasing acidity and formation of HSO_4^-. The degenerate S–O stretchings of SO_4^{2-} and HSO_4^- are assigned as the broad band at ca. 1140 cm^{-1}. The bands in the 550–650-cm^{-1} region are assignable to the degenerate bendings of SO_4^{2-} and HSO_4^-. The detailed assignment in this region will be discussed later in relation to the possible coordination of sulfate to vanadium(III). The E bending modes of SO_4^{2-} and HSO_4^- are expected around 450 cm^{-1}. Since the V^{3+}–OH_2 stretchings of solid cesium vanadium alum, $Cs_2SO_4\cdot[V(H_2O)_6]_2(SO_4)_3\cdot 12H_2O$, have been assigned to the bands in the 400–500-cm^{-1} region,[30] the V^{3+}–OH_2 stretchings of the present aqueous V^{3+} solution are also expected to appear around 450 cm^{-1}. It was found that the Raman profile of the aqueous $V_2(SO_4)_3$ solution in the 400–500-cm^{-1} region changed slightly when D_2O was used as the solvent. This deuterium isotope effect suggests that the bands due to V^{3+}–OH_2 stretchings overlap with those due to the E bending modes of SO_4^{2-} and HSO_4^-. This assignment was confirmed by the observation of a broad Raman band centered at 430 cm^{-1} for VCl_3 solution.

At pH 1.3, the Raman spectrum exhibits new bands at 1533 and 774 cm^{-1} (see Figure 2B). These bands show no deuterium

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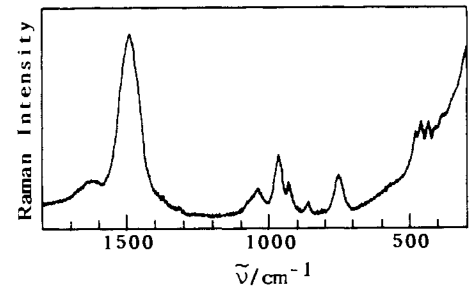

Figure 3. Raman spectrum (514.5-nm excitation) of solid $Na_2[V_2O(ttha)]\cdot dmf\cdot 3H_2O$.

isotope shifts; this clearly rules out the possibility that these bands are due to an OH_2 or OH group. The Raman spectrum at pH 2.4 (Figure 2C) was obtained for the solution diluted to ca. 10 mM, since the 40 mM solution completely absorbed the laser beam. The intensities of the 1533- and 774 cm^{-1}-bands increase considerably at this pH; the band at 1533 cm^{-1} becomes dominant in the spectrum, and the band at 774 cm^{-1} has an intensity comparable to that of the band due to the totally symmetric stretching of SO_4^{2-}. These observations appears to indicate that the bands at 1533 and 774 cm^{-1} are in resonance with the charge-transfer transition. Therefore, these bands are assigned as the vibrations of the binuclear aquavanadium(III) complex formed by hydrolysis.

The bands at 1533 and 774 cm^{-1} were also observed for aqueous solutions of VCl_3, indicating that the appearance of the 1533- and 774-cm^{-1} bands does not depend on the counterion, Cl^- or SO_4^{2-}.

The Raman profile in the 350–500-cm^{-1} region depends on the pH of the solution; the band maximum moved to the higher wavenumbers with an increase in the content of the hydrolytic dimer in the solution (see Figure 2). This suggests that another band, which is assignable to the hydrolytic dimer of aquavanadium(III), overlaps with the bands due to the SO_4^{2-} degenerate bending and V^{3+}–OH_2 stretchings in this region.

Although the monomeric hydroxovanadium(III) complex should be present in the solutions studied, the Raman band due to the monomeric species could not be identified, since the monomeric species have no absorption bands in the visible region[14] by which the Raman bands are resonance-enhanced.

The binuclear complexes of vanadium(III) with organic ligands, $[V_2OCl_4(THF)_6]$,[17] $[V_2O(bpy)_4Cl_2]Cl_2$,[18] $[V_2O(SCH_2CH_2NMe_2)_4]$,[19] and $Na_2[V_2O(ttha)]$,[20] have been prepared and characterized. Of these binuclear complexes, the ttha complex has been found to show an intense charge-transfer band which is similar to that of the hydrolytic dimer of the aquavanadium(III) ion; λ_{max} = 450 nm, $\epsilon = 2.63 \times 10^3$ M^{-1} cm^{-1}/mol of V(III).[20] The binuclear complex with ttha has been thought to be a μ-oxo dimer on the basis of its spectral characteristics.[20] Figure 3 shows the Raman spectrum of solid $Na_2[V_2O(ttha)]$ in resonance with the charge-transfer band in the region of 600–400 nm. The aqueous solution of the ttha complex gives a spectrum similar to that of the solid-state one. It is recognized at first sight that the Raman spectrum of $Na_2[V_2O(ttha)]$ closely resembles that of the hydrolytic dimer of aquavanadium(III). Namely, the Raman spectrum exhibits a dominant band at 1494 cm^{-1} and a medium-intensity band at 753 cm^{-1}. In the 400–500-cm^{-1} region three distinct bands were observed in this case. The similarity in the visible and Raman spectra between the hydrolytic dimer of aquavanadium(III) and $[V_2O(ttha)]^{2-}$ allows one to affirm that $V_2O(ttha)^{2-}$ is a μ-oxo complex and not a bis(μ-hydroxo) dimer.

Figure 4 shows the infrared spectrum of $Na_2[V_2O(ttha)]^{2-}$. No infrared bands were observed around 1500 cm^{-1}. This fact confirms that the Raman band at 1494 cm^{-1} is a resonance-enhanced mode. The infrared band at 750 cm^{-1} may be the counterpart of the Raman band at 753 cm^{-1}.

The unsymmetrical contour of the absorption spectrum in the 600–400-nm region of the hydrolytic dimer of V(III) suggests that the spectrum consists of at least two bands besides the weak band around 600 nm. The result of the band contour analysis from 13 500 to 26 000 cm^{-1} using Gaussian curves is shown in the upper part of Figure 5. The bands at 21 500 and 23 500 cm^{-1} are both assignable to charge-transfer transitions on the basis of their intensities, while the weak band at 15 800 cm^{-1} is assignable to a d–d transition. The upper part of Figure 6 shows the result of a similar analysis for the charge-transfer band of $[V_2O(ttha)]^{2-}$. For this complex three components were found at 15 400, 20 000, and 22 500 cm^{-1}. The resonance Raman excitation profiles of the hydrolytic dimer of V(III) and of $[V_2O(ttha)]^{2-}$ are shown in the lower parts of Figures 5 and 6, respectively. The Raman band around 760 cm^{-1} and the band around 1500 cm^{-1} appear to resonate with the lower energy component of the charge-transfer transitions. On the other hand, the bands in the 400–500-cm^{-1} region of $[V_2O(ttha)]^{2-}$ seem to follow the envelope of the higher energy component.

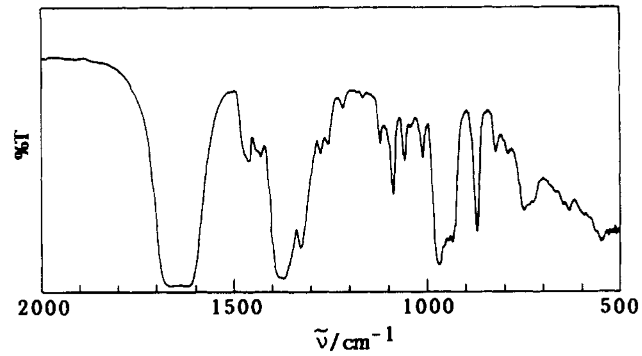

Figure 4. Infrared spectrum of $Na_2[V_2O(ttha)]\cdot dmf\cdot 3H_2O$ (KBr pellet).

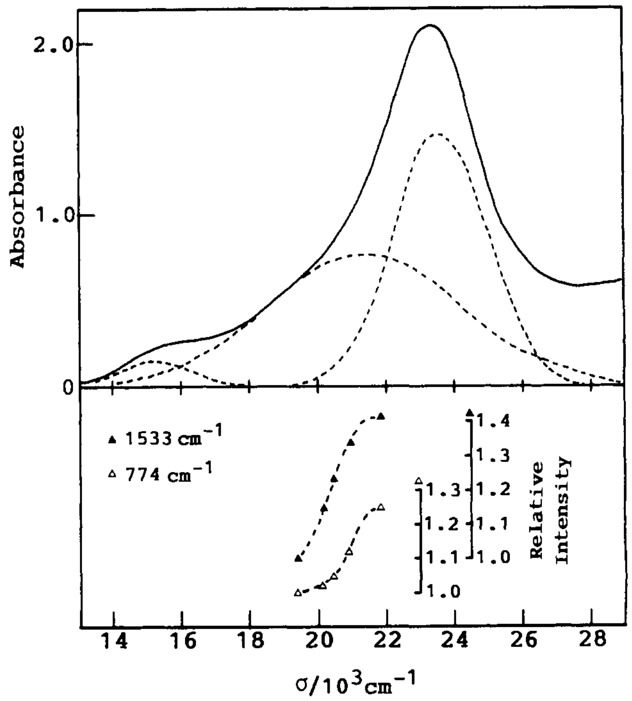

Figure 5. Band contour analysis for the visible absorption spectrum of the hydrolytic dimer of V(III) (1.97×10^{-2} mol dm^{-3}/V(III), pH 2.5) and resonance Raman excitation profiles. Raman intensity was measured relative to the height of $\nu_1(SO_4^{2-})$, and the weakest intensity was normalized to unity.

The Raman spectra of a variety of complexes containing a M–O–M bridge have been studied.[31-33] Generally, in the reso-

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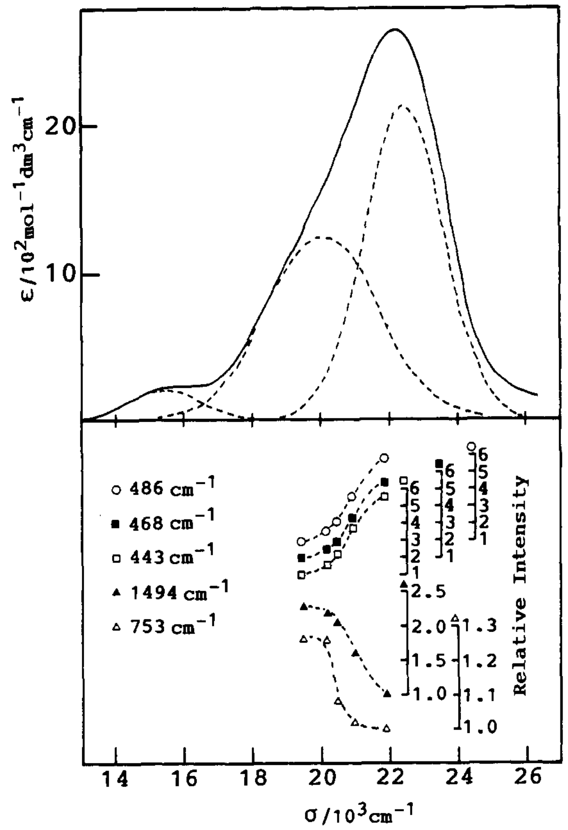

Figure 6. Band contour analysis for the visible absorption spectrum of $[V_2O(ttha)]^{2-}$ and resonance Raman excitation profiles. Relative Raman intensity was measured as in Figure 5.

nance Raman spectra of the complexes with a M–O–M bridge, the symmetric stretching of the M–O–M moiety in the 200–500-cm⁻¹ region is a dominant mode and it is thought to be characteristic of the μ-oxo dimer. The Raman band due to the antisymmetric stretching of a M–O–M moiety is usually weak or not observed. Very recently, however, Lincoln and Loehr have observed the resonance Raman spectra for several binuclear complexes consisting of a Mo–O–Mo bridge, where the first overtone of the antisymmetric Mo–O–Mo stretching has surprisingly high intensity.[34] In fact, in the resonance Raman spectrum of $[Mo_2O_3Cl_8]^{4-}$, the first overtone of the antisymmetric Mo–O–Mo stretching is dominant at 1608 cm⁻¹, while the symmetric Mo–O–Mo stretching at 380 cm⁻¹ has only an intensity comparable to that of the fundamental vibration of the antisymmetric Mo–O–Mo stretching at 805 cm⁻¹. The reason for the appearance of the strongly enhanced overtone has been discussed by Lincoln and Loehr.[34]

The hydrolytic dimers of aquavanadium(III) and $[V_2O(ttha)]^{2-}$ are apparently new examples of μ-oxo complexes where the first overtone of the antisymmetric M–O–M stretching is strongly resonance-enhanced. Referring to the assignment of Lincoln and Loehr,[34] the resonance-enhanced bands at 774 and 1533 cm⁻¹ of the hydrolytic dimer of aquavanadium(III) are reasonably assigned as the antisymmetric V–O–V stretching and its first overtone, respectively. The bands at 753 and 1494 cm⁻¹ of $[V_2O(ttha)]^{2-}$ are similarly assigned. The symmetric V–O–V stretching of the binuclear aquavanadium(III) ion is expected to be in the 400–500-cm⁻¹ region but was not distinguished due to the broad feature that resulted from band overlapping.

The depolarization ratio of the antisymmetric V–O–V stretching of the hydrolytic dimer of aquavanadium(III) was determined to be ca. 0.5 with a 514.5-nm excitation. This value suggests that the overall molecular symmetry of the complex in solution is lost. This symmetry lowering may be responsible for the appearance of the antisymmetric V–O–V stretching in the Raman spectrum.

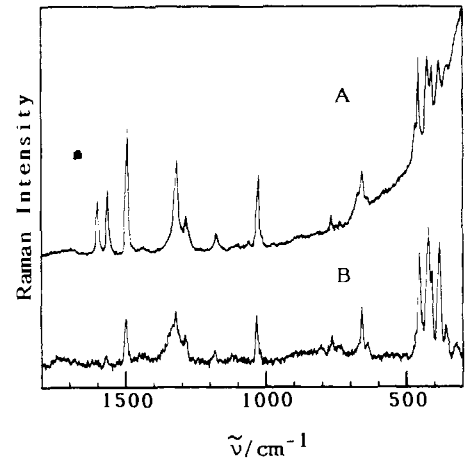

Figure 7. Raman spectra of solid $[V_2O(bpy)_4Cl_2]Cl_2$: (A) 514.5-nm excitation, 200 mW; (B) 632.8-nm excitation, 50 mW.

The Raman spectra of $[V_2O(bpy)_4Cl_2]Cl_2$, whose structure has been established to consist of a linear V–O–V bridge by single-crystal X-ray analysis,[18] were studied for comparison. This binuclear bpy complex is dark purple and has two intense absorption bands at 524 and 627 nm, while the hydrolytic dimer of aquavanadium(III) and $[V_2O(ttha)]^{2-}$ are dark brown and have a single intense absorption band around 430 nm. The Raman spectra of the binuclear bpy complex obtained with 514.5- and 632.8-nm excitation are shown in Figure 7. The spectra do not show a strongly enhanced overtone of the antisymmetric V–O–V stretching. A series of bands in the 1450–1600-cm⁻¹ region are assigned as the vibrations of bpy.[35] We attempted to assign the antisymmetric V–O–V stretching of the bpy complex using the sample prepared in $^{18}OH_2$. However, the band for the expected isotope shift was not observed. This would imply that the band due to the V–O–V moiety may be weak and overlap with the intense and broad band due to the bpy ligand.

The difference in the resonance Raman behavior between the two types of binuclear vanadium(III) complexes already mentioned may be a result of the difference in the geometry of the V–O–V unit (for example, linear versus bent) and/or more likely in the nature of the resonant charge-transfer transition, since the visible absorption spectrum of the bpy complex is significantly different from those of the hydrolytic dimer of V(III) and the ttha complex. Crystallization of $[V_2O(ttha)]^{2-}$ was attempted unsuccessfully by using alkali-metal ions, Ba^{2+}, $(C_4H_9)_4P^+$, $(Ph)_4P^+$, $(C_4H_9)_4N^+$, $(PhCH_2)(CH_3)_3N^+$, $(enH_2)^{2+}$, and $(tnH_2)^{2+}$ as counterions. Attempts to isolate the binuclear aquavanadium(III) complex were also unfruitful. Therefore, the previous question still needs to be answered.

Raman Spectra of the Hydrolytic Dimer of Aquavanadium(III) in $H_2{}^{16}O/H_2{}^{18}O$. We examined the ^{18}O-isotope substitution effect on the Raman spectra of the hydrolytic dimer of the aquavanadium(III) complex with the view of further confirming the bridging mode. In this experiment, VCl_3 was used instead of $V_2(SO_4)_3$, since VCl_3 is quite soluble in water and, therefore, convenient to treat with a small quantity of $H_2{}^{18}O$. Figure 8 shows the Raman spectra of the hydrolytic dimer of aquavanadium(III) formed in $H_2{}^{16}O$, $H_2{}^{18}O$, and a 1:1 mixture of $H_2{}^{16}O/H_2{}^{18}O$. The 1533- and 774-cm⁻¹ bands observed in normal water moved to 1460 and 737 cm⁻¹, respectively, upon ^{18}O substitution. The observed isotope shifts are −73 and −37 cm⁻¹, respectively, being consistent with those observed for the complexes with the Mo–O–Mo bridge.[34] The isotope shift could not be determined for the band at ca. 460 cm⁻¹, because of the broad feature due to the band overlapping.

The bridging mode of the hydrolytic dimer of aquavanadium(III) was definitely determined from the Raman spectra of the hydrolytic dimer formed in a 1:1 $H_2{}^{16}O/H_2{}^{18}O$ mixture. If the binuclear aquavanadium(III) complex takes a bis(μ-hydroxo)

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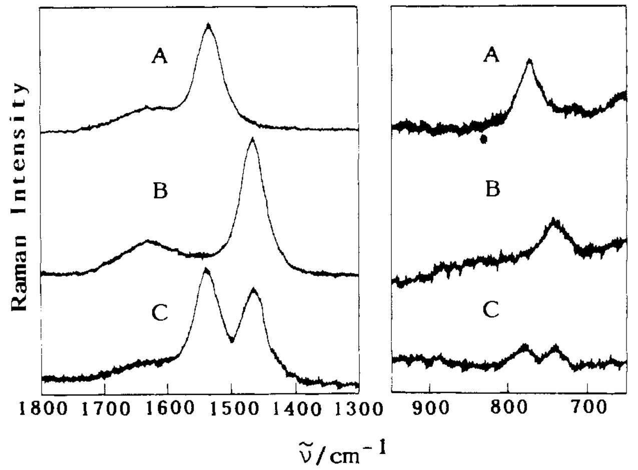

Figure 8. Raman spectra of VCl_3 in $H_2{}^{16}O/H_2{}^{18}O$ at pH 2.0: (A) $H_2{}^{16}O$; (B) $H_2{}^{18}O$; (C) 1:1 mixture of $H_2{}^{16}O/H_2{}^{18}O$.

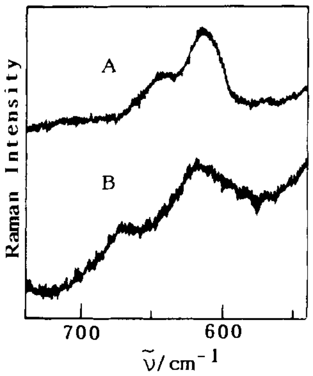

Figure 9. Raman spectra in the F_2 bending region of $SO_4{}^{2-}$: (A) solid $VOSO_4{\cdot}5H_2O$; (B) aqueous $V_2(SO_4)_3$, 250 mM/V(III) atom, pH 1.2.

bridge as suggested by Pajdowski,[14] three isotopic species, $V(^{16}OH)_2V$, $V(^{16}OH)(^{18}OH)V$, and $V(^{18}OH)_2V$, should be present in a 1:2:1 ratio. On the other hand, $V{-}^{16}O{-}V$ and $V{-}^{18}O{-}V$ species should be present in a 1:1 ratio due to the μ-oxo bridge. The Raman spectra in Figure 8C show only two bands in both the 700–800- and the 1400–1600-cm^{-1} regions. These two bands correspond to the isotopically pure species; there is no indication of the presence of the mixed-isotope species. This observation unequivocally proves that the hydrolytic dimer of the aquavanadium(III) complex is a μ-oxo one.

Coordination of Sulfate. Coordination of the sulfate ion has been suggested for vanadium(III) in vanadium-containing blood cells of ascidians.[3] The Raman spectra of $V_2(SO_4)_3$ in aqueous solution may provide useful information as to the possibility of the coordination of sulfate to vanadium(III) in the blood cells. When the sulfate ion coordinates to vanadium in a monodentate fashion, the symmetry of the sulfate ion is reduced to C_{3v} from T_d; this results in splitting of the F_2 mode into the A_1 and E modes. The examination of the Raman spectrum of $VO(SO_4){\cdot}5H_2O$, containing a monodentately coordinate sulfate ligand,[36] demonstrates that the F_2 bending (ν_4) mode is diagnostic of whether a sulfate ion coordinates to vanadium or not; the Raman band due to the F_2 stretching (ν_3) mode is very weak and broad and, therefore, not appropriate for this purpose.

Figure 9A shows the Raman spectrum in the ν_4 region of solid $VO(SO_4){\cdot}5H_2O$. The observed band splitting is consistent with the symmetry reduction of the sulfate ion caused by coordination to VO^{2+}. Similar splitting was also observed for the aqueous solution of 250 mM $V_2(SO_4)_3$ (see Figure 9B). The measurement of the depolarization ratio indicates that the higher wavenumber component is due to the A_1 mode and the lower one to the E mode. The reduction of the symmetry of the $SO_4{}^{2-}$ ion could also be caused by protonation of $SO_4{}^{2-}$. However, Raman spectra of the free sulfate ion exhibit one broad band and do not show such splitting even at pH 0.2. Therefore, the coordination of the sulfate ion to vanadium(III) should be responsible for the splitting observed in the aqueous solution of $V_2(SO_4)_3$. Such band splitting was discernible even for a solution of 40 mM $V_2(SO_4)_3$ (see Figure 2). The observed splitting is larger for the $V^{3+}{-}SO_4{}^{2-}$ pair than for the $VO^{2+}{-}SO_4{}^{2-}$ pair; this is suggestive of a larger affinity of $SO_4{}^{2-}$ for V^{3+} than for VO^{2+}.

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