to be Sc^+–ethylbenzene rather than Sc^+–*o*-xylene. This suggests initial cleavage of the central C–C bond, in contrast to bare Sc^+, where preference for the terminal C–C bond is observed.

All of the alkenes studied also react with $ScC_6H_4^+$ to give a variety of product ions. Its reaction with ethylene appears to give Sc^+–phenylacetylene, exclusively. One of the frequently observed ions in this study is $ScC_9H_7^+$. Its unusual formulation and low CID efficiency all indicate a high stability for this ion, with its structure most likely being that of indenylscandium ion.

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Registry No. Sc^+, 14336-93-7; C_6H_6, 71-43-2; $ScC_6H_6^+$, 107494-94-0; ScC_6H_4, 135865-29-1; ScO^+, 134627-16-0; CH_4, 74-82-8; C_2H_6, 74-84-0; C_3H_8, 74-98-6; *n*-C_4H_{10}, 106-97-8; *i*-C_4H_{10}, 75-28-5; *n*-C_5H_{12}, 109-66-0; *neo*-C_5H_{12}, 463-82-1.

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Matrix Infrared Spectra of HCl Complexes with UF_6, WF_6, and MoF_6

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HCl complexes with UF_6, WF_6, and MoF_6 were prepared in solid argon at 12 K. The FTIR spectrum of UF_6/HCl contained a doublet at 2850.6 and 2849.7 cm^{-1} due to the hydrogen-bonded UF_6–HCl complex. In contrast, the HCl interaction with WF_6, as well as MoF_6 produced two distinctly different 1:1 complexes. The 2862.1-cm^{-1} absorption due to the antihydrogen-bonded complex, WF_6–ClH, was slightly more intense than the 2866.2-cm^{-1} absorption of the hydrogen-bonded complex, WF_6–HCl. The frequencies and relative intensities of the absorptions for the MoF_6 complexes with HCl were very similar to those of their WF_6 counterparts.

Introduction

Hydrogen bonds and Lewis acid–base interactions play important roles in determining the intermolecular structures and the properties of weak complexes. The possibility of direct competition between these two means of intermolecular binding has been the focus of several recent investigations.[1–6] The Cl_2 and ClF complexes with HF serve as prime examples of this competition. Even though the molecular beam electric resonance studies[1,2] have only detected the Cl_2–FH and FCl–FH complexes, the most recent ab initio calculations[3] have shown that the hydrogen-bonded complexes, Cl_2–HF and ClF–HF, are only slightly less stable than their antihydrogen-bonded counterparts. These theoretical results have been confirmed by a matrix infrared investigation[4] of HF complexes with Cl_2 and ClF. In this matrix IR study, complexes with both structural arrangements were characterized because the matrix cage quickly quenches internal energy and prevents rearrangement. In contrast to the HF complexes, a matrix IR investigation[5] on HCl complexes with Cl_2 and ClF detected only the hydrogen-bonded complexes, Cl_2–HCl and ClF–HCl.

The most recent case of direct competition between hydrogen bonding and Lewis acid–base interactions involved a matrix IR investigation[6] on HF complexes with UF_6, WF_6, and MoF_6. While the UF_6–HF complex was more stable than the UF_6–FH complex, HF complexes with WF_6 and MoF_6 preferred the antihydrogen-bonded arrangements. The characterization of the HF complexes with metal hexafluorides can be corroborated by substituting HCl for HF since the larger covalent radius of chlorine in HCl should significantly reduce the preference for antihydrogen-bonded complexes. The present study reports the infrared observation and characterization of HCl complexes with UF_6, WF_6, and MoF_6.

Experimental Section

The apparatus and spectroscopic techniques for the hydrogen halide experiments with the metal hexafluorides in solid argon at 12 K have been described in detail earlier.[4] Samples of UF_6, WF_6, MoF_6 (Oak Ridge National Laboratory), HCl (Matheson), and DCl (MSD Isotopes) were condensed at 77 K and evacuated to remove any volatile impurities. HCl and DCl were codeposited from passivated stainless-steel manifolds. Samples were diluted between 100/1 and 200/1 mol ratios with argon (Air Products) and deposited on a CsI window at total rates of 14–17 mmol/h for 3.3–3.8 h. In order to promote further aggregation of the HCl, each matrix was annealed to 25 K for 10 min and then recooled to 12 K. Finally, each matrix was warmed to 30 K for an additional 10 min and then cooled back to 12 K. IR spectra were obtained before, during, and after the sample codeposition as well as after the matrix annealings. All spectra were recorded on a Nicolet 7199 FTIR spectrometer at resolutions ranging from 0.24 to 1.0 cm^{-1}.

Results

Matrix infrared observations of UF_6, WF_6, and MoF_6 complexes with HCl and DCl will be described in turn.

Uranium Hexafluoride. A series of uranium hexafluoride experiments were conducted with hydrogen chloride at different concentrations in argon at 12 K. After the most concentrated samples were deposited, the spectrum in Figure 1a shows absorptions due to the HCl monomer (labeled HCl, Q and P bands), dimer (labeled D), and trimer (labeled T); these band positions are in agreement with earlier matrix IR studies.[7,8] Absorptions for the N_2–HCl and $N_2(HCl)_2$ complexes[8] (labeled N and M, respectively) were also observed. Due to the small HF and DF impurities in the hexafluoride sample, absorptions due to the HF–HCl and HCl–DF complexes[9] were also detected at 2834.5, 2832.5, and 2807.2 cm^{-1}. A new product absorption at 2850.5 cm^{-1} (labeled ν_s) appeared as a shoulder of the P branch of HCl. The spectra at a resolution of 0.24 cm^{-1} clearly revealed that this new shoulder was actually a doublet at 2850.6 and 2849.7 cm^{-1}. In addition, weak product absorptions were observed at 2827.2 and 2805.0 cm^{-1} (labeled ν_{sa} and ν_{sb}, respectively). No perturbed UF_6 modes were observed. The spectrum in Figure 1b exhibits the effect of annealing the matrix to 30 K for 10 min. While the

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Table I. Infrared Absorptions (cm^{-1}) in HCl Complexes with Metal Hexafluorides in Solid Argon

UF_6 + HCl	UF_6 + DCl	WF_6 + HCl	WF_6 + DCl	MoF_6 + HCl	MoF_6 + DCl	assignt
2850.6	2064.9	2866.2	2075.4	2866.0	...	ν_s
2849.7						ν_s
		2862.1	2072.2	2859.0	...	$a\nu_s$
2827.2	2049.5					ν_{sa}
2805.0	2031.3					ν_{sb}
		772.9	772.9			$\nu_1{}^c$
		678.9	679.0	651.4	651.4	$\nu_2{}^c$
		670.2	668.3	647.9	646.6	$a\nu_2{}^c$
				644.6	643.7	$a\nu_2{}^c$

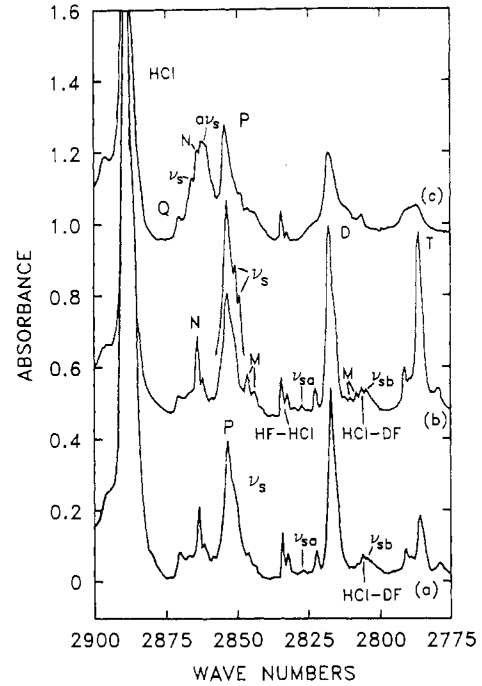

Figure 1. FTIR spectra at 1.0-cm^{-1} resolution in the 2900–2775-cm^{-1} region for HCl, UF_6, and WF_6 in solid argon: (a) after codeposition of 31 mmol of Ar/UF_6 = 150/1 and 33 mmol of Ar/HCl = 150/1 at 12 K in 3.8 h; (b) after warming of the matrix displayed in (a) to both 25 and 30 K for 10 min and then recooling of the matrix to 12 K [(inset) 2857–2846-cm^{-1} region at 0.24-cm^{-1} resolution]; (c) after the codeposition of 31 mmol of Ar/WF_6 = 200/1 and 30 mmol of Ar/HCl = 200/1 at 12 K in 3.7 h.

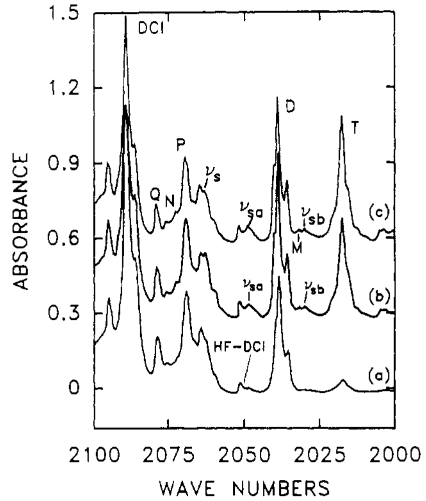

Figure 2. FTIR spectra at 1.0-cm^{-1} resolution in the 2100–2000-cm^{-1} region for DCl/HCl and UF_6 in solid argon: (a) after codeposition of 27 mmol of Ar/UF_6 = 200/1 and 31 mmol of Ar/(DCl/HCl) = 150/1 at 12 K in 3.3 h; (b) after warming of the matrix to 25 K for 10 min and then recooling to 12 K; and (c) after annealing of the matrix to 30 K for 10 min and then cooling back to 12 K.

ν_s shoulder displayed very little change, the intensity of the ν_{sa} absorption increased, and the ν_{sb} absorption became more prominent with respect to the HCl–DF absorption. The $N_2(HCl)_2$ and $(HCl)_3$ complexes also exhibited dramatic increases. The other HCl and UF_6 experiments produced similar results.

In the analogous UF_6 study with DCl/HCl mixtures (>75% DCl), the principal absorptions in the HCl experiments and their DCl counterparts were observed as shown in Figure 2, and the new product absorptions are listed in Table I. Even at a resolution of 1.0 cm^{-1}, the sharp ν_s DCl doublet at 2064.9 and 2063.3 cm^{-1} was clearly resolved from the P branch of DCl. While sample annealings up to 30 K did not effect the overall intensity of the ν_s doublet, a new product absorption at 2031.3 cm^{-1} (labeled ν_{sb}) appeared. On the basis of a comparison of the HF-$D^{35}Cl$ absorption at 2052.2 cm^{-1}, the increases in the 2049.5-cm^{-1} absorption (labeled ν_{sa}) were too large to be due the HF–$D^{37}Cl$ complex only. Again, no perturbed UF_6 modes were detected.

Tungsten Hexafluoride. A similar study was performed with tungsten hexafluoride and hydrogen chloride in solid argon. The spectrum in Figure 1c is typical of the spectra observed after codeposition of WF_6 and HCl. The ν_s and $a\nu_s$ absorptions at 2866.2 and 2862.1 cm^{-1}, respectively, were the only new spectral feature in the HCl stretching region. In contrast to the UF_6 study, three perturbed WF_6 absorptions were observed at 772.9, 678.9, and 670.2 cm^{-1} (labeled $\nu_1{}^c$, $\nu_2{}^c$, and $a\nu_2{}^c$, respectively in Table I), and no secondary product absorptions were observed before or after the sample annealings. In the corresponding WF_6 experiments with DCl/HCl mixtures, the DCl counterparts of the ν_s and $a\nu_s$ absorptions appeared at 2075.4 and 2072.2 cm^{-1}, respectively. While no significant shift in the frequencies of the $\nu_1{}^c$ and $\nu_2{}^c$ modes was observed, the $a\nu_2{}^c$ mode exhibited a 1.9-cm^{-1} red shift.

Molybdenum Hexafluoride. A parallel investigation was conducted with molybdenum hexafluoride and hydrogen chloride in argon matrices. The new product absorptions, which are listed in Table I, were comparable to those results for WF_6 and HCl. After sample codeposition, the ν_s and $a\nu_s$ absorptions at 2866.0 and 2859.0 cm^{-1}, respectively, were observed. Also, three perturbed MoF_6 modes were seen at 651.4, 647.9, and 644.6 cm^{-1} (labeled $\nu_2{}^c$, $a\nu_2{}^c$, and $a\nu_2{}^c$, respectively). Sample annealings failed to produce any secondary product absorptions. In the DCl/HCl studies with MoF_6, no new product absorptions were detected in the DCl stretching region. However, the $a\nu_2{}^c$ absorptions at 646.6 and 643.7 cm^{-1} were slightly red-shifted from their HCl counterparts. No shift in the $\nu_2{}^c$ absorption was observed.

Discussion

The product absorptions of the HCl–hexafluoride complexes will be identified and assigned. In addition, the physical properties of the metal hexafluorides and their complexes will be discussed.

Identification and Assignment. The products bands that are listed in Table I were not observed when the hexafluorides and HCl were deposited separately. However, these absorptions were detected when both reagents were permitted to interact during the condensation and annealing processes. Three groups of HCl product absorptions can be identified on the basis of concentration, annealing behavior, and band position. In the UF_6 and WF_6 studies, the HCl nature of the product absorptions was confirmed by similar DCl counterparts with HCl/DCl frequency ratios of 1.378–1.381, which are characteristic of the fundamental vibration of the HCl ligand. Unfortunately, the DCl product absorptions in the MoF_6 experiments were probably masked by the Q and P absorption of DCl. Even though all of the absorptions in the first group (labeled ν_s) were clearly present after the sample codeposition, the ν_s absorption for UF_6 and HCl merits special consideration due to its close proximity to the P branch of HCl. In the 1-cm^{-1} resolution spectra, the UF_6 ν_s absorption at 2850.5 cm^{-1} appeared as a shoulder of the $P(H^{35}Cl)$ absorption at 2853.6 cm^{-1}. However, higher resolution spectra of UF_6 and HCl unquestionably revealed that the ν_s doublet at 2850.6 and 2849.7 cm^{-1} is distinctly different from the 2851.7 cm^{-1} $P(H^{37}Cl)$ absorption that was observed without UF_6. Furthermore, Figure 2, which is representative of the UF_6 and DCl spectra, shows that the ν_s absorption is completely resolved from the P(DCl) absorption. The frequency of the UF_6 ν_s absorption was slightly blue-shifted from the HCl stretching mode in the FCl–HCl complex[5] at 2849.9 cm^{-1}, and the band positions of the MoF_6 and WF_6 ν_s, which were less intense than ν_s for UF_6, were slightly blue-shifted from the 2863.4 cm^{-1} absorption due to the N_2–HCl complex.[5] With WF_6 and MoF_6, the second group of HCl absorptions (labeled aν_s) also appeared after codeposition. The frequencies of the aν_s absorptions were slightly red-shifted from the N_2–HCl absorption. No evidence of an aν_s absorption in the UF_6 study was found. The third group of product absorptions (labeled ν_{sa} and ν_{sb}) were observed only in the UF_6 experiments. These absorptions, which were produced primarily by matrix annealings, were red-shifted from the absorptions due to the N_2–$(HCl)_2$ complex.[8]

The HCl product absorptions of the ν_s and aν_s groups that were produced primarily on sample deposition indicate the presence of two unique 1:1 complexes in the WF_6 and MoF_6 studies. The ν_s absorptions are assigned to a hydrogen-bonded complex, MF_6–HCl, while the aν_s bands are assigned to a different 1:1 complex with an antihydrogen-bonded form, MF_6–ClH. These assignments are based on comparison of the frequencies of the ν_s and aν_s absorptions in the HF and metal hexafluoride investigation[6] and the anticipated effects of replacing an HF with an HCl in these 1:1 complexes. The HCl substitution for HF should not dramatically change the band positions of the ν_s absorptions relative to other absorptions of weak hydrogen-bonded 1:1 complexes since the substitution should affect these weak complexes to a similar degree. Depending on the dominant matrix site, the ν_s absorption for UF_6 should be comparable to the ν_s bands of the Cl_2–HCl or FCl–HCl complexes.[5] In addition, the frequencies of the ν_s absorptions for WF_6 and MoF_6 should remain virtually identical and should be blue-shifted from the 2863.4-cm^{-1} absorption of the N_2–HCl complex.

While the HCl substitution for HF should have little impact on the relative population of the hydrogen-bonded 1:1 complexes, the substitution should have dramatic effects on the antihydrogen-bonded 1:1 complexes. The HCl substitution dramatically reduces the stability of the antihydrogen-bonded complexes as seen in the earlier matrix IR studies on HF and HCl complexes with diatomic halogens.[4,5] Therefore, the relative intensities of the HCl aν_s absorptions with respect to their corresponding HCl ν_s absorptions should be much smaller than their HF counterparts. For the 1:1 HF complexes with WF_6 (and MoF_6), the intensity ratio of the aν_s absorption to the ν_s absorption was 5:1 while the same ratio for its HCl counterpart was approximately 2:1. Even though the relative band positions of the aν_s absorptions with respect to hydrogen-bonded complexes may change, the aν_s absorption for the WF_6–ClH complex should be slightly blue-shifted from its MoF_6 counterpart since MoF_6 is a stronger Lewis acid than WF_6.[6]. With the proposed ν_s and aν_s assignments, every anticipated effect of the HCl substitution was indeed observed and provided further support for the ν_s and aν_s assignments in the HF study with metal hexafluorides.[6]

The ν_{sa} and ν_{sb} absorptions in the UF_6 study displayed a higher order dependence on HCl concentration, which is characteristic of a 1:2 complex. Since no evidence of antihydrogen-bonded 1:1 complexes was discovered, the ν_{sa} and ν_{sb} absorptions should be attributed to a 1:2 complex with an UF_6–H_aCl–H_bCl structure. The $N_2(HCl)_2$ complex, which has absorptions at 2846, 2843.5, 2812.5, 2810.8, and 2809.0 cm^{-1} (labeled M), served as an useful model in the identification of these new product absorptions. Since the ν_s absorption for UF_6 is red-shifted from the ν_s absorption for N_2, the ν_{sa} and ν_{sb} absorptions for UF_6 should be red-shifted from its nitrogen counterparts, and the UF_6 ν_{sa} absorption should exhibit a larger red shift than the UF_6 ν_{sb} band due to the more direct interaction of H_aCl with UF_6. The absorptions for the $UF_6(HCl)_2$ complex display the appropriate red shifts.

In conjunction with these HCl product absorptions, new product bands (labeled ν^c and aν^c) were assigned to several HCl-perturbed WF_6 and MoF_6 modes that were normally infrared-inactive. These absorptions were identified by close proximity to their gas-phase fundamentals[10] and exhibited the same HCl concentration dependence as the ν_s and aν_s absorptions. Similar HCl activation of normally infrared-inactive fundamentals has been observed for H_2, O_2, and N_2 complexed to HCl.[11,12] In these complexes, the infrared activation of these hexafluoride modes is due to the electrical asymmetry induced by the HCl ligand. The presence of two different perturbed ν_2 modes for WF_6 and MoF_6 is unique. The aν_2^c absorptions exhibited larger perturbations from the gas-phase fundamentals than their ν_2^c counterparts. Since the antihydrogen-bonded complexes displayed a stronger binding interaction than the hydrogen-bonded complexes, these frequencies shifts appeared quite sensible. The relative intensities of the aν_2^c and aν_s absorptions with respect to the ν_2^c and ν_s absorptions were also significantly reduced from the earlier HF study with WF_6 and MoF_6.[6] The destabilizing effect of the HCl also reduced the perturbation of the aν_2^c with respect to its HF counterpart.

Finally, the aν_s modes play a crucial role in determining the structure of the antihydrogen-bonded complexes. The small perturbations on the aν_s absorptions clearly indicate the chlorine of the HCl bonds directly to a fluorine of the hexafluoride and not to the metal center. A direct interaction between the chlorine and the metal center would have a tremendous effect on the hexafluoride submolecule modes since the symmetry of the hexafluorides would be lowered. In addition, the larger perturbation by DCl than by HCl of the aν_s mode is probably due to the smaller librational amplitude of DCl. With the antihydrogen-bonded complexes, the time average position of electron density, which is directly related to the average position of the hydrogen or the deuterium, determines the average binding interactions of these complexes. Therefore, the MF_6–ClD complexes should be slightly more stable than their HCl counterparts.

Physical Properties. Several interesting comparisons between the physical properties of the metal hexafluorides and their hydrogen halide complexes can be made. Since the aν_a absorptions for WF_6 (2962.1 cm^{-1}) and MoF_6 (2859.0 cm^{-1}) are due to the Lewis acid–base interaction between the fluorine of MF_6 and the HCl, these bonds can supply useful information about the relative Lewis acidity of WF_6 and MoF_6. Clearly, MoF_6 is a slightly stronger Lewis acid than WF_6. Similarly, the ν_s absorptions provide details about the relative proton affinities of the hexafluorides. Since the ν_s modes are 2866.2 cm^{-1} for WF_6, 2866.0 cm^{-1} for MoF_6, and 2850.6 cm^{-1} for UF_6, the order of Bronsted base strength is $WF_6 \cong MoF_6 < UF_6$ with HCl serving as a proton donor. Both of these bonding trends were also observed in the HF study with hexafluorides.[6]

The most noticeable difference between the HF and HCl complexes with metal hexafluorides is the relative populations of the antihydrogen-bonded and hydrogen-bonded complexes. While each metal hexafluoride in the HF study[4] formed hydrogen-bonded and antihydrogen-bonded complexes, the UF_6–HF, WF_6–FH, and MoF_6–FH complexes were clearly dominant. In the present HCl investigation, WF_6 and MoF_6 showed a significantly reduced preference for the antihydrogen-bonded complexes, which were still dominant. UF_6 formed only the hydrogen-bonded complex, UF_6–HCl. This increased preference for the hydrogen-bonded arrangements can be readily explained. While the HCl hydrogen-bonded complexes are slightly less stable than their HF counterparts, the effect of the large covalent radius of chlorine

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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 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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