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Formation of V^V Lacunary Polyoxovanadates and Interconversion Reactions of Dodecavanadate Species

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Oxidation reactions of the reduced decavanadate $[V^{IV}{}_2V^V{}_8O_{26}]^{4-}$ (**1**) with halide guest anions were investigated for the synthesis of V^V host molecules. The reaction with Cl^- afforded a new dodecavanadate, $[HV^V{}_{12}O_{32}(Cl)]^{4-}$ (**3**), which incorporated the guest chloride anion. The polyoxovanadate framework of **3** is different from the bowl-shaped dodecavanadate $[V^V{}_{12}O_{32}(CH_3CN)]^{4-}$ (**2**). The structure of **3** is regarded as a trilacunary counterpart of the pentadecavanadate $[V^V{}_9V^{IV}{}_6O_{36}Cl]^{4-}$. Employment of an F^- template yielded the layered polyoxovanadate $[HV^V{}_{11}O_{29}F_2]^{4-}$ (**4**). The framework of **4** is a monolacunary structure of the fluoride-incorporated dodecavanadate $[H_6V^V{}_2V^{IV}{}_{10}O_{30}F_2]^{6-}$, in which one of the VO groups at the belt position is removed. The three vanadium atoms in the capping units are connected by μ^3-F bridges. Reaction with Br^- provided $[HV^V{}_{12}O_{32}(Br)]^{4-}$ (**5**) with minor formation of $[H_3V^V{}_{10}O_{28}]^{3-}$. Interconversion reactions between **2**, **3**, and **4** proceeded as follows: the reaction of **2** with Cl^- prompted an isomerization reaction of the bowl-type framework, affording **3**; the reaction of **3** with F^- gave **4**; the reaction of **4** with CH_3CN reproduced acetonitrile-incorporated **2**. Complexes **3** and **4** were characterized by X-ray analysis. Polyoxovanadates **3** and **4**, with the highest oxidation cores, exhibited distinct signals in the ^{51}V NMR spectra, corresponding to lacunary polyoxovanadate geometries.
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Introduction

Spherical polyoxometalates have attracted attention due to their unique host–guest interactions and their fullerene-like metal–oxido cages, which are sufficiently large to include various types of guest molecules.[1] For spherical polyoxovanadates, guest molecules are anions positioned inside the anionic polyoxovanadate cage. The topology and electrostatic potential distribution explain the encapsulation of the anionic guest.[2] Polyoxovanadate cores are constructed by linkages of square pyramidal VO_5 units. The bifunctionality of the square-pyramidal VO_5 unit may allow the core to interact either as a cationic or an anionic center. For interaction with a cation, the VO_5 unit is able to work as a donor through the negative oxido groups, and for interaction with an anion, the unit may act as an acceptor through the sixth coordination site of the VO_5 square pyramidal unit, which has a positive electrostatic charge on the metal to allow interaction with the anionic guest molecule.[3] For application in host–guest chemistry, such as the recognition of anions, catalytic reactivity, and molecular transportation,[4] a guest anion that is tightly trapped inside the spherical cage is undesirable, because there is no possibility of guest removal without destruction of the cage. The synthesis of open-cage molecules is required for the creation of further applications. The Klemperer-type half-spherical dodecavanadate $[V_{12}O_{32}(CH_3CN)]^{4-}$ (**2**) has an open end at the half sphere from which an acetonitrile guest molecule is free to dissociate.[5] Several dodecavanadates with nitriles or NO^- guest anions have been reported,[6] and the host–guest interactions have been theoretically investigated.[7] The synthesis of dodecavanadate **2** has long been known, and later isolation of the tridecavanadate $[V_{13}O_{34}]^{3-}$ was reported, although the synthetic conditions of the compounds were almost identical, and the only difference was the reflux time.[8a] New and improved synthetic routes are required for further developments in the host–guest chemistry of **2**. We are currently interested in the cyclic polyoxovanadate species $(VO_3)_n{}^{n-}$, which are capable of coordination with cationic templates.[9] Metavanadate species have a 1D or cyclic structure,[10] which can act as a larger macrocyclic oxidoligand to metal centers. An example includes the reduced decavanadate (Figure 1), which can be regarded as a dinuclear vanadyl complex with a macrocyclic octadecavanadate ligand.[11] We recently developed the growth reaction of **1** by using reduction reactions to increase the size of the core.[12] The redox reaction of polyoxometalates is one of the typical methods used to transform polyoxometalate frameworks.[13] In this paper, we report the oxidation reac-

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tions of **1**, with or without guest anions, and utilize the cyclic octavanadate framework as a scaffold towards the synthesis of a spherical compound.

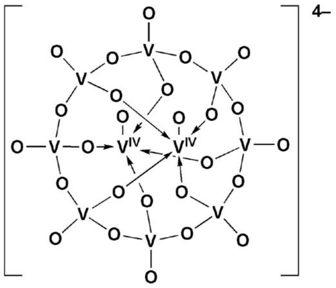


Figure 1. Schematic representation of anion **1**.

Syntheses of new polyoxovanadates were attempted with vanadium atoms of the highest oxidation state. In the course of this study, new types of lacunary polyoxovanadates were discovered with incorporation of fluoride, chloride, and bromide guests. The chloride-incorporated dodecavanadate $[HV_{12}O_{32}(Cl)]^{4-}$ (**3**) has a different framework from that of compound **2** and has a new highest oxidation core. Reaction without a guest molecule resulted in the high-yield synthesis of **2** by acetonitrile incorporation. Interconversion reactions of these polyoxovanadates by reaction with halide anions were also investigated.

Results and Discussion

Synthesis

Polyoxometalate frameworks arise through a balance of electrostatic charge distribution between metal cations and anions. The template-directed mechanism is believed to operate in the formation processes of growth reactions from metal-oxido acids. Interaction with an acid causes a condensation reaction of the metal-oxido acids to the oligomers. During the process, even a solvent molecule may be a template, as observed for Klemperer's dodecavanadate, $[V_{12}O_{32}(CH_3CN)]^{4-}$ (**2**).[5] Anion-templated spherical polyoxovanadates have been reported by the group of Müller, and the vanadium atoms of those compounds were in a mixed valence state of V^{VI} and V^{V}, exhibiting a deep blue color.[14] The anion-incorporated spherical polyoxovanadate with all the vanadium atoms in the V^{V} oxidation state is still not known. In principle, the affinity between an anionic guest and a polyoxovanadate host can be increased by decreasing the negative charges on the polyoxovanadate host because of less repulsive forces between the anionic guest and the negatively charged polyoxovanadate. For that reason, an all-V^{V} cage with lower negative charges, compared to the mixed-valence V^{V}/V^{IV} cage of the same framework, may be produced through oxidation of the reduced polyoxovanadates. To develop new polyoxovanadates with the all-V^{V} cage, we explored oxidation reactions of the reduced polyoxovanadate $[V_{10}O_{26}]^{4-}$ (**1**),[11] which is a spherical polyoxovanadate without a guest molecule inside the cage. As a control, reaction in the absence of anionic templates was first attempted to determine the products of oxidation by hydrogen peroxide. In this reaction, despite no guest molecule being added to the mixture, acetonitrile solvent was included in the core of the Klemperer-type dodecavanadate **2**.[6] The synthesis of **2** by this method is selective, thus providing an improved route with high yields. From these control experiments, it was revealed that acetonitrile is a good template for the V^{V} polyoxovanadates, and only **2** was formed when using acetonitrile. The use of polar solvents such as nitromethane also produced the bowl-type dodecavanadate, as confirmed from IR spectroscopy. The nitromethane-incorporated dodecavanadate was not crystallized and characterization was not possible. For the inclusion of halide anions in this system, nonpolar solvents and nonaqueous oxidants were required. The best solvent for anion inclusion was found to be dichloromethane, which was unlikely to be incorporated into the polyoxovanadate core. To survey the best oxidant, hydrogen peroxide, *tert*-butyl hydroperoxide, and *m*-chloroperbenzoic acid were examined, and *tert*-butyl hydroperoxide was found to be the best nonaqueous oxidant, although the reaction rate was slower. The products of oxidation and the guest incorporation reaction were reactive with water, and the use of aqueous hydrogen peroxide solution inhibited the formation of crystals and yielded only oily products. The reaction of **3** with a small amount of water gave an unidentified brown oil. Oxidation of **1** by *tert*-butyl hydroperoxide in dichloromethane produced new types of lacunary polyoxovanadates with various halide anion templates. The reaction in the presence of the Cl^- template afforded a new type of spherical dodecavanadate, $[HV_{12}O_{32}(Cl)]^{4-}$ (**3**), with a different framework from that of **2**, in 35% yield. Employment of the F^- template gave the fluoride-incorporated $[HV_{11}O_{29}F_2]^{4-}$ (**4**) in 54% yield. For the crystallization of **4**, addition of chloroform to the concentrated dichloromethane solution was necessary (see Experimental Section). Reaction with Br^- gave $[HV_{12}O_{32}(Br)]^{4-}$ (**5**) in 15% yield and with minor formation of the decavanadate $[H_3V_{10}O_{28}]^{3-}$.[15] Interestingly, crystallization of the complexes required addition of hydrochlorocarbon solvents such as dichloromethane or chloroform and hydrophobic interactions may control the crystallization of these compounds. The reaction with I^- gave no host–guest species, but only $[V_5O_{14}]^{3-}$[16] was obtained in 70% yield based on vanadium. The order of the yields of the products corresponded with the order of the halides, F^-, Cl^-, and Br^-, which implies the size of the template acts as a key factor for their formation, and the iodide ion may be too large to incorporate into the polyoxovanadates formed in these reactions. In the template incorporation reactions, the total charges of –4 on each polyoxovanadate were maintained. Elemental analyses of these polyoxovanadates were performed by using thoroughly dried samples to avoid partial loss of packing molecules in the lattice, such as volatile $CHCl_3$ or CH_2Cl_2.

IR Spectroscopy

The IR spectrum of **3** shows strong bands around 989 cm^{-1}, which correspond to the $\nu(V{=}O_{terminal})$ stretching frequencies (Figure 2b). Stretching of the V–O$_{bridge}$ bond appears in the range 500–900 cm^{-1}. Notable differences between lacunary complex **3** and the spherical pentadecavanadate[17] $[V^V{}_9V^{IV}{}_6O_{36}Cl]^{4-}$ are observed in the IR pattern of the V–O$_{bridge}$ stretching region. The pentadecavanadate has distinct peaks in the range 500–750 cm^{-1}, but the peaks in the range 750–900 cm^{-1} are insignificant. The structure of the pentadecavanadate consists of μ^3-O bridges and no μ^2-O bridges were observed in the reduced core. The lack of μ^2-O bridges is consistent with the weak spectrum in the 750–900 cm^{-1} range. Complex **3** has μ^2-O bridges at the lacunary positions in addition to μ^3-O bridges.

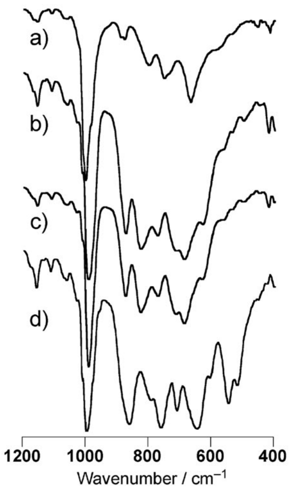


Figure 2. Infrared spectra of (a) $[V^V{}_9V^{IV}{}_6O_{36}Cl]^{4-}$, (b) complex **3**, (c) complex **5**, and (d) $[V_{12}O_{32}(CH_3CN)]^{4-}$ (**2**).

Complex **2** also has μ^2-O bridges and exhibits distinct peaks in the 750–900 cm^{-1} region. The peaks in the 750–900 cm^{-1} range are due to $\nu(V{-}\mu^2{-}O)$ stretching frequencies. The infrared spectra of **3** and **5** are quite similar, which supports that both complexes have the same lacunary spherical frameworks with halide ion incorporation.

Structures

The ORTEP view of **3** is depicted in Figure 3. The polyoxovanadate framework of **3** is a geometrical isomer of the precedented Klemperer dodecavanadate, and **3** has chloride inclusion with protonation at the core. It is the first example of an anion-incorporated spherical polyoxovanadate with all the vanadium atoms in the V^V oxidation state.[18] The 12 VO$_5$ units are joined by vertex or edge-sharing to form the spherical structure. Bond valence sum (BVS) calculations suggest O9 and O20 have low BVS values of 1.35 and 1.73, respectively.[19] All the other oxygen atoms have BVS values in the range 1.88–2.14. From these observations, the best estimate of the protonated site has to be on O9, which is able to interact with O20 through a hydrogen bond. Unfortunately, six molecules of dichloromethane were present in the lattice with relatively larger thermal motion, and we were unable to locate the positions of the protons from the Fourier map. The structure may be regarded as a lacunary counterpart of the reduced pentadecavanadate $[V^V{}_9V^{IV}{}_6O_{36}Cl]^{4-}$.[17] The addition of two missing vanadium groups of VO and V$_2$O$_3$ units to **3** reconstructs the framework of the pentadecavanadate, as shown in Figure 4. The first lacunary group is the V=O unit at the site surrounded by four oxygen atoms (O9, O20, O8, and O19) and the coordination of these four oxygen atoms to the V=O group rebuilds the VO$_5$ unit at the lacunary position. The second lacunary group is the V$_2$O$_3$ unit at the site surrounded by six oxygen atoms (O5, O10, O11, O23, O16, and O15) and also the coordination of these oxygen atoms retrieve the complete spherical framework of the pentadecavanadate instead of the lacunary structure. The range of V=O terminal distances of **3** is 1.579(4)–1.612(4) Å, and the distances of V–O$_{bridge}$ are in the range 1.708(4)–2.060(4) Å. The V=O terminal distances of the precedented pentadecavanadate are in the range 1.578(8)–1.607(10) Å, and the distances of V–O$_{bridge}$ are in the range 1.823(5)–2.060(8) Å.

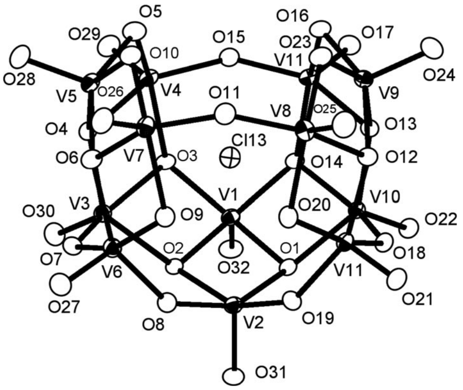


Figure 3. ORTEP view of compound **3**.

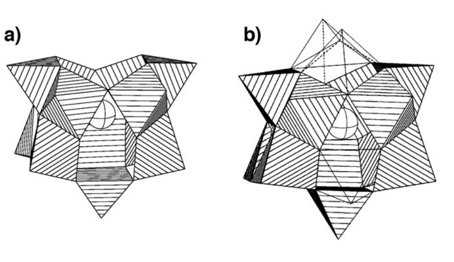


Figure 4. Polyhedral views showing the lacunary positions of **3**. The VO$_5$ units are represented by striped polyhedrons: polyhedral representation of (a) **3** and (b) $[V^V{}_9V^{IV}{}_6O_{36}Cl]^{4-}$. The structure of **3** is considered to be a trilacunary-type pentadecavanadate. The VO unit at the front and the V$_2$O$_3$ unit on the top are missing in **3**. The lacunary units corresponding to the structure of **3** are represented by the frame polyhedrons in (b).

Although some of the V–O bridging distances of **3** are shorter than the precedented pentadecavanadate, the overall cluster size of lacunary **3** is very close to that of the precedented pentadecavanadate. The structural differences between lacunary complex **3** and the pentadecavanadate are observed in the differences in the V···Cl distances. The V···Cl distances of **3** are in the narrow range 3.22–3.49 Å, whereas the distances of the pentadecavanadate are distributed in the range 3.07–3.71 Å. Observation of a smaller variation in the distances of **3** is due to the spherical framework with all the vanadium atoms in the same V^V oxidation state. The shorter V···Cl distances in **3** indicate that the negative–negative charge repulsions are compensated in the highest oxidation core of **3**. The large variation in the V···Cl distances in the reduced pentadecavanadate are due to the existence of shorter V^V···Cl distances and longer V^{IV}···Cl distances despite the charge delocalization in the spherical core. It is noted that the six dichloromethane molecules are in close contact with the cluster framework. The dichloromethane protons point in the direction of the cluster oxido surface. Unfortunately, the crystals of bromide-incorporated complex **5** were not suitable for X-ray analysis, although the spectroscopic and analytical data are in good agreement with the formation of the same core of **3**, especially the IR spectroscopic data.

Fluoride-incorporated complex **4** has a monolacunary framework, and the ORTEP view is shown in Figure 5. The asymmetric unit of **4** is related by a center of symmetry, and it can be considered as a layered polyoxovanadate.

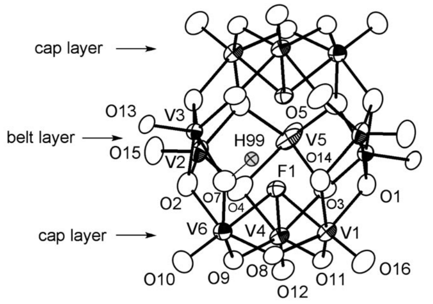


Figure 5. ORTEP view of compound **4**. The anion is shown to represent the nondisordered framework by removal of the (V5*)=O group from the belt layer. The lacunary positions are disordered over four positions at V3, V3*, V5, and V5* with total occupancy of three.

The cluster consists of five VO_5 units on the belt layer and two capping groups of three VO_5F units sandwiched the belt layer. Each unit is edge-shared to form the layered structure. The μ^3-F bridge connects V1, V4, and V6 octahedrons. The structure of **4** resembles that of $[H_6V^V{}_2V^{IV}{}_{10}O_{30}F_2]^{6-}$ reported by the group of Müller.[20] The removal of one VO unit from $[H_6V^V{}_2V^{IV}{}_{10}O_{30}F_2]^{6-}$ gives the structure of **4**. The lacunary position of the VO unit of **4** is disordered over four positions at V3, V5, V3*, and V5*. The total occupancy of the VO units from V3 and V5 is 3, and this corresponds to having three V=O groups out of the four positions when the symmetrically related positions are taken into account. The V=O group from V2 has full occupancy and it gives two symmetrically related V=O groups at the belt layer. Thus, the belt layer has five V=O groups out from the six positions of V2, V3, and V5 with the symmetrically related groups. The V=O, V–O_{bridge}, and V–F distances of **4** are in the range 1.588(4)–1.602(4), 1.802(3)–2.098(5), and 2.203(3)–2.221(3) Å, respectively. The protonation sites were estimated from BVS calculations. The BVS values of O3, O4, O7, and O14 are 1.57, 1.54, 1.25, and 1.28, respectively. The BVS values of the remaining oxygen atoms are in the range 1.85–2.11. Thus, the protonation site is estimated at O7 or O14 and hydrogen bonded to O3* or O4*, respectively. One of the protons, H99, was found on the Fourier map.

NMR Spectroscopic Studies

Despite the high sensitivities of ^{51}V NMR spectroscopy, there are only a small number of isolated isopolyoxovanadates, and lacunary-type polyoxovanadates provide good examples for the chemical shifts. The ^{51}V NMR spectra of **3** were recorded at –25, 25, and 75 °C, and are given in Figure 6. The NMR spectrum at 75 °C reveals seven well-resolved lines at –536, –558, –560, –567, –569, –571, and –627 ppm with a relative intensity ratio of 2:2:2:2:1:1:2. At –25 °C, these signals are merged into four signals at –544, –569, –578, and –632 ppm with an intensity ratio of 1:4:5:2 with the higher-field shift. The signals are broader at low temperature and sharper at high temperature. The temperature dependency of the line widths was reversible. The intensity ratio and the number of signals are consistent with the geometry observed in the crystal structure. Although the complexity of structures with similar chemical environments prevents unambiguous assignments, the distinct signals matched to the chemical environments provides confident evidence regarding the host–guest structure in solution, as is also supported by the 2D COSY NMR spectra with temporal assignments (see Supporting Information). For the full assignments of these signals, synthesis of the derivatives or substituted complexes is required by taking advantage of the lacunary structure. No apparent sign of dynamic behavior was observed from the variable-temperature observations. However, small signals that arose around 600 ppm at 75 °C did not disappear when the temperature was reduced to room temperature, and these signals are most likely due to decomposed materials that are yet unidentified (Supporting Information, Figure S1). As the temperature increases, the line widths decreased due to the quadrapole effects of the ^{51}V nuclei.[21] From the structural points, complex **3** is a geometrical isomer of **2**, and similar chemical shifts between **2** and **3** are expected when chloride incorporation is not taken into account. However, the signal of **3** in the range of the chemical shifts of complex **2** was observed only at –627 ppm. The remaining six signals were significantly downfield shifted. These downfield shifts are indicative of chloride inclusion in the cluster and are consistent with the shift of $[VOX_4]^-$, which was also downfield shifted when X^- was substituted for Cl^-.[22] Bromide complex **5** in acetonitrile was susceptible to decomposition, even at room temperature. However, as the signals from decomposition products increased, the chemical shifts of the main signals could be identified and were almost identical to complex **3**. This is consistent with the formation of the bromide inclusion with the same structure as **3**. The ^{35}Cl NMR signal of **3** was recorded in CD_3CN at room temperature. A singlet at 162 ppm ($\Delta\nu_{1/2}$ = 1400 Hz) was observed and the line width was significantly sharper when compared with typical compounds such as that from CH_2Cl_2 (7500 Hz). The relatively sharp signal reflects the spherical environments of the chloride anion in the polyoxovanadate host. The ^{35}Cl NMR signal of compound **3** was observed even 3 d after sampling, with a new accompanying signal at 91 ppm, which indicated minor decomposition.

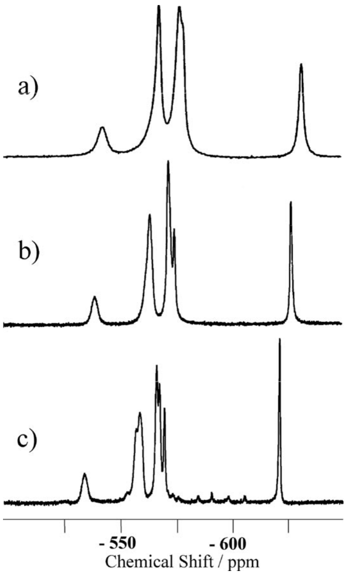


Figure 6. ^{51}V NMR spectra of **3** in CD_3CN at (a) –25, (b) 25, and (c) 75 °C.

The ^{51}V NMR spectrum of **4** is shown in Figure 7. At 25 °C, complex **4** showed six signals at –462, –467, –485, –499, –525, and –533 ppm with an intensity ratio of 1:2:3:1:2:2. The number of signals and the intensity ratio was consistent with the geometry of the monolacunary structure. The compound was not stable at 75 °C and showed a substantial decrease in the intensity of the six signals and an increase in intensity of new signals at –474, –518, and –556 ppm due to the formation of unidentified decomposition products. Prolonged heating at 75 °C increased the distinct triplet-like signals at –586, –592, and –600 ppm; the chemical shifts and the pattern of the signals became comparable to complex **2**. The downfield shifts of these signals from that of **2** may suggest the formation of new fluoride-included dodecavanadate $[V_{12}O_{32}F]^{3-}$ with the same framework as **2**; however, isolation of the products was not successful.

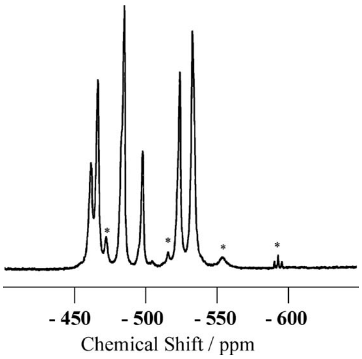
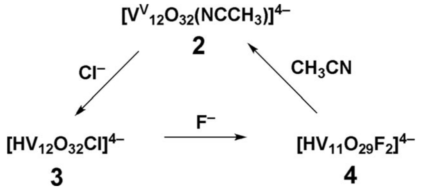


Figure 7. ^{51}V NMR spectrum of **4** at –25 °C in CD_3CN. The signals designated by * are from decomposition products.

Interconversion Reaction of the Cages

Template exchange reactions were studied by the group of Yamase by using the V^{IV} spherical polyoxovanadate $[V_{18}O_{42}(H_2O)]^{12-}$.[23] Air oxidation reactions of the compound with template anions led to the isolation of various types of incorporated complexes with different ratios of reduced sites. In our case, reactions with the halide templates revealed interconversion reactions of the dodecavanadate framework with the highest oxidation state vanadium atoms. A summary of the interconversion reactions is shown in Scheme 1.



Scheme 1. Interconversion reactions of the V^{V} open-cage lacunary polyoxovanadates.

First, dodecavanadate **2** was treated with chloride anion. Addition of *n*Bu_4NCl to an acetonitrile solution of **2** was heated at 60 °C and the brown solution gradually turned deep red. After recrystallization, high-quality crystals of **3** were obtained. The nucleophilic chloride was incorporated into the bowl-type dodecavanadate and the structure was transformed into **3**. The protonation of **3** suggested the reaction was not simply a guest exchange, but an acid-promoted reaction. The reverse reaction, that of **3** with acetonitrile, was not observed from ^{51}V NMR spectroscopy. The pattern of the ^{51}V NMR spectrum of **3** in acetonitrile solution was not affected by an increase in temperature except the line width, and the formation of **2** was not observed from NMR studies. The results suggest that the rigid framework of chloride compound **3** is stable in acetonitrile without dissociation of the chloride, as expected from the lacunary geometry of **3**, which is an isomer of bowl-shaped **2**. The second attempted reaction was that of chloride compound **3** with fluoride anions. When compound **3** was heated with an excess amount of *n*$Bu_4NF\cdot 3H_2O$ in dichloromethane, the color of the solution changed from deep red to orange, and crystals of compound **4** were produced. The electronegative and nucleophilic fluoride anion promoted the conversion of the trilacunary dodecavanadate into the layered undecavanadate with the inclusion of two fluoride ions. On the contrary, no reaction was observed for **4** with an excess amount of chloride anions according to the ^{51}V NMR spectra. The ^{51}V NMR spectrum of **4** showed six signals consistent with the geometry revealed by structural analysis; however, the complex gradually decomposed in acetonitrile. In addition to these signals, new signals were observed at –474, –518, and –556 ppm along with triplet-like signals at –600 ppm. At 75 °C, the intensities of the signals of **4** were significantly decreased and the triplet-like signals increased at –593, –600, and –608 ppm. The isolation of **2** from an acetonitrile solution of **4** was possible after recrystallization. Fluoride-incorporated complex **4** was unstable, as observed from the ^{51}V NMR spectrum at 75 °C, and polar solvents promoted the decomposition reactions. The reaction of **2** with $n\mathrm{Bu_4NF{\cdot}3H_2O}$ was unable to yield **4**, and the product formed was confirmed as $[\mathrm{V_5O_{14}}]^{3-}$ from ^{51}V NMR spectroscopy.

Conclusions

Guest incorporation reactions of lacunary polyoxovanadates were demonstrated by oxidation reactions of reduced decavanadate **1**. Two types of polyoxovanadates with vanadium atoms in the $\mathrm{V^V}$ oxidation state were isolated and characterized. The polyoxovanadate framework of fluoride complex **4** was a layered monolacunary undecavandate, and chloride complex **3** was a trilacunary dodecavanadate. Oxidation reaction without the halide anion in acetonitrile resulted in the improved synthesis of bowl-type dodecavanadate **2**. Reactivity studies of these open-cage polyoxovanadates revealed interconversion reactions between the species. Further investigation of these species, such as the addition of heterometals, by taking advantage of the lacunary structure, will lead to the development of new lacunary polyoxovanadate chemistries. We assert these new $\mathrm{V^V}$ polyoxovanadate derivatives will provide further understanding of the host–guest chemistry of polyoxovanadates through ^{51}V NMR spectroscopic studies, of which only a limited number of compounds, typically metavanadates and decavanadates, are presently known.

Experimental Section

Measurements: IR spectra were measured in mineral oil or KBr pellets by using a Horiba FT-720 IR spectrometer. NMR samples were measured in $\mathrm{CD_3CN}$ solution at 25 °C. ^{51}V NMR spectra were recorded with a JEOL JNM-LA400 at 105.04 MHz. Chemical shifts were externally referenced to pure $\mathrm{VOCl_3}$ (δ = 0 ppm). ^{35}Cl NMR spectra were recorded with a JEOL JNM-LA400 at 40.25 MHz. Chemical shifts were externally referenced to saturated KCl aqueous solution (δ = 0 ppm).

Synthesis: All reagents were reagent grade and used without further purification. Solvents were dried and distilled, then stored under an atmosphere of nitrogen. Compound **1** was synthesized by using modified methods of published procedures[11] (see Supporting Information) and purity was confirmed by IR spectroscopy and elemental analysis. Elemental analyses of C, H, and N were performed by the Research Institute for Instrumental Analysis at Kanazawa University. Elemental analyses of F, Cl, and Br were performed by the Center for Organic Elemental Microanalysis Laboratory at Kyoto University.

Improved Synthesis of $(n\mathrm{Bu_4N})_4[\mathrm{V^V}_{12}\mathrm{O_{32}(CH_3CN)}]$ (2): Hydrogen peroxide (30%, 284 mg) was added to a violet solution of **1** (948 mg, 0.50 mmol) in acetonitrile (10 mL). The resulting brown solution was stirred for 1 h at room temperature, and ethyl ether (40 mL) was added to yield a brown powder. Yield: 798 mg (90% based on V). The solid obtained was sufficiently pure for the subsequent synthesis. X-ray quality crystals were obtained by recrystallization from acetonitrile and ethyl acetate. IR (KBr): $\tilde{\nu}$ = 521 (s), 550 (s), 608 (sh.), 646 (vs), 710 (s), 760 (vs), 791 (sh.), 860 (vs), 993 (vs) cm^{-1}. ^{51}V NMR (105.04 MHz, $\mathrm{CD_3CN}$, 25 °C, $\mathrm{VOCl_3}$): δ = –593 (4 V), –600 (4 V), –608 (4 V) ppm. $(n\mathrm{Bu_4N})_4[\mathrm{V_{12}O_{32}}]$ (2093.2): calcd. C 36.72, H 6.93, N 2.68; found C 36.38, H 6.99, N 2.69.

$(n\mathrm{Bu_4N})_4[\mathrm{HV^V}_{12}\mathrm{O_{32}(Cl)}]$ (3): To a solution of **1** (948 mg, 0.50 mmol) and tetra-*n*-butylammonium chloride (556 mg, 2.0 mmol) in dichloromethane (30 mL) was added *tert*-butyl hydroperoxide (120 mg, 1.0 mmol); the purple solution gradually turned intense red. The solution was stirred for 30 min and then cooled in a refrigerator. Red crystals were formed over 2 d. Yield: 313 mg (35% based on V). IR (KBr): $\tilde{\nu}$ = 528 (w), 571 (sh.), 629 (m), 669 (sh.), 687 (s), 714 (s), 779 (m), 824 (s), 874 (m), 989 (vs) cm^{-1}. ^{51}V NMR (105.04 MHz, $\mathrm{CD_3CN}$, 25 °C, $\mathrm{VOCl_3}$): δ = –540 (1 V), –565 (4 V), –573 (5 V), –626 (2 V) ppm. ^{35}Cl NMR (40.25 MHz, $\mathrm{CD_3CN}$, 25 °C, saturated KCl aqueous solution): δ = +162 ($\Delta\nu_{1/2}$ = 1400 Hz) ppm. $(n\mathrm{Bu_4N})_4[\mathrm{HV_{12}O_{32}(Cl)}]$ (2129.6): calcd. C 36.10, H 6.86, N 2.63, Cl 1.66; found C 36.25 H 6.91, N 2.64, Cl 1.63.

$(n\mathrm{Bu_4N})_4[\mathrm{HV^V}_{11}\mathrm{O_{29}F_2}]$ (4): To a solution of **1** (379 mg, 0.20 mmol) and tetra-*n*-butylammonium fluoride (315 mg, 1.0 mmol) in dichloromethane (20 mL) was added *tert*-butyl hydroperoxide (60 mg, 0.5 mmol); the purple solution gradually turned intense red. The solution was dried with anhydrous magnesium sulfate and then concentrated to 10 mL by heating; chloroform (20 mL) was then added. Red crystals were obtained after 2 d. Yield: 200 mg (54% based on V). IR (KBr): $\tilde{\nu}$ = 625 (m), 660 (m), 739 (m), 800 (s), 854 (m), 876 (m), 966 (s), 982 (vs), 991 (vs) cm^{-1}. ^{51}V NMR (105.04 MHz, $\mathrm{CD_3CN}$, 25 °C, $\mathrm{VOCl_3}$): δ = –462 (1 V), –467 (1 V), –485 (3 V), –499 (1 V), –525 (2 V), –533 (3 V) ppm. ^{19}F NMR (377.44 MHz, $\mathrm{CD_3CN}$, 25 °C, $n\mathrm{Bu_4NPF_6}$): δ = –72 (d, $^{1}J_{\mathrm{F,V}}$ = 55 Hz), –77 (d, $^{1}J_{\mathrm{F,V}}$ = 58 Hz) ppm. $(n\mathrm{Bu_4N})_4[\mathrm{HV_{11}O_{29}F_2}]$ (2033.2): calcd. C 37.81, H 7.19, N 2.76, F 1.87; found C 37.31 H 7.14, N 2.74, F 1.73.

$(n\mathrm{Bu_4N})_4[\mathrm{HV^V}_{12}\mathrm{O_{32}(Br)}]$ (5): To a solution of **1** (379 mg, 0.20 mmol) and tetra-*n*-butylammonium bromide (322 mg, 1.0 mmol) in dichloromethane (20 mL) was added *tert*-butyl hydroperoxide (60 mg, 0.5 mmol); the purple solution turned intense red. The solution was stirred for 30 min and cooled in a refrigerator. Both red crystals and crystals of decavanadate $[\mathrm{H_3V_{10}O_{28}}]^{3-}$ were formed together after 2 d. The mixture of crystals was placed in dichloromethane solution with the addition of tetra-*n*-butylammonium bromide (64 mg, 0.20 mmol). Under these conditions, only the red crystals of **5** were dissolved in the solution, and the undissolved decavanadate was filtered out. Red crystals of **5** were obtained. Yield: 134 mg (15% based on V). IR (KBr): $\tilde{\nu}$ = 501 (w), 536 (sh.), 629 (m), 688 (s), 712 (s), 771 (m), 825 (s), 872 (m), 991 (vs) cm^{-1}. ^{51}V NMR (105.04 MHz, $\mathrm{CD_3CN}$, 25 °C, $\mathrm{VOCl_3}$): δ = –540 (1 V), –565 (4 V), –573 (5 V), –627 (2 V) ppm. $(n\mathrm{Bu_4N})_4[\mathrm{HV_{12}O_{32}(Br)}]$ (2174.1): calcd. C 35.36, H 6.72, N 2.58, Br 3.68; found C 35.72 H 6.87, N 2.67, Br 3.85.

Table 1. Crystal data for **3** and **4**.

	3	**4**
Formula	$(n\mathrm{Bu}_4\mathrm{N})_4[\mathrm{HV}_{12}\mathrm{O}_{32}\mathrm{Cl}]\cdot 6\mathrm{CH}_2\mathrm{Cl}_2$	$(n\mathrm{Bu}_4\mathrm{N})_4[\mathrm{HV}_{11}\mathrm{O}_{29}\mathrm{F}_2]\cdot 6\mathrm{CHCl}_3$
Crystal system	monoclinic	orthorhombic
Space group	$P2_1$	*Pbca*
a / Å	18.175(2)	19.256(3)
b / Å	16.981(2)	20.312(3)
c / Å	18.631(2)	29.808(4)
α / °	90	90
β / °	99.635(2)	90
γ / °	90	90
V / Å^3	5669(1)	11658(3)
Z	2	4
No. of data collected	63857	13280
No. of data used	27097	9379
No. of variables	1180	650
$R(R_\mathrm{w})$	0.0528(0.1509)	0.0830(0.258)
GOF	1.248	1.06

X-ray Crystallography: Single crystal structure analyses were performed at –150 °C by using a Rigaku/MSC Mercury diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71070 Å) and with 0.5° ω-scans at 0° and 90° in ϕ. The crystal data are summarized in Table 1. Data were collected and processed by using the CrystalClear program (ver 1.3.5, Rigaku).[24] Numerical absorption corrections were applied by using CrystalClear and corrections for Lorenz and polarization effects were performed. The structures were solved by direct methods (SHELXS-86). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not included in the refinement of **3** due to the larger thermal motion of tetra-*n*-butylammonium salts and dichloromethane. Hydrogen atoms of **4** were included but not refined. The SHELX-97 program[25] was used for full-matrix least-squares refinements. CCDC-737788 (for **3**) and -737789 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Modified synthesis of $(n\mathrm{Bu}_4\mathrm{N})_4[\mathrm{V}_{10}\mathrm{O}_{26}]$ (**1**); variable-temperature ^{51}V NMR spectra of **3**; ^{35}Cl NMR spectra of **3**; variable-temperature ^{51}V NMR spectra of **4**; ^{51}V–^{51}V COSY spectrum of **3**.

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