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Chloride capturing system via proton-induced structure transformation between opened- and closed-forms of dodecavanadates

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Chloride-incorporated dodecavanadates, show two distinct structures of the monoprotonated-form $[HV_{12}O_{32}(Cl)]^{4-}$ (**closed-V12**) with a shperical closed-structure and the opened-form $[V_{12}O_{32}(Cl)]^{5-}$ (**opened-V12**). The reaction of **closed-V12** with stoichiometric amount of ethylenediamine, drives the structure transformation reaction to **opened-V12**, quantitatively. From time dependent observations of ^{51}V NMR, a tube-type intermediate $[V_{12}O_{32}(Cl)]^{5-}$ (**tube-V12**) was observed in the transformation process. Isolation of the intermediate was achieved by the deprotonation reaction of **closed-V12** with diethylamine, and the structure transformation was confirmed by using the isolated intermediate. The reverse transformation from **opened-V12** to **closed-V12** was also proceeded by addition of trifluoroacetic acid. The geometrical difference between **closed-V12** and **opened-V12** is reflected in the reactivity difference to the external reagents, and it was demonstrated by examining the chloride removal reaction by silver cation. Incorporated chloride was preserved in the **closed-V12** cage even in the presence of silver cation. Contrary, chloride in **opened-V12** was removed as AgCl by silver cation. In addition, by the reaction of the chloride-free **opened-V12** with a quantitative amount of $\{Et_4N\}Cl$ retrieved **opened-V12**, showing the capability of **opened-V12** to recapture a guest chloride in the cavity. The transformation between two isomeric dodecavanadate structures is regarded as a move of a molecular mitt to catch a ball and secure it.

Introduction

The design of anion receptors is continuously of great interest because of the important roles of anions in industrial, environmental and biological systems.[1] In addition, anions themselves also act as templates for assembling supermoleculars.[2] The anion binding can be achieved by utilizing several binding forces such as electrostatic, hydrogen bonding between anions and NH or CH groups, anion-π, and/or Lewis acid-anion interactions.[1] In particular, the receptors for halide anions, the simplest anions, have been developed to design molecular-based sensors and transporters.[3] Since halide anions are charged spheres adopting various coordination geometries without specific binding direction, designing a halide host is challenging. The important design factor for halide receptors is the control of the binding sites as well as a spatial arrangement and a size of the cavity formed at the binding sites.[3]

Polyoxometalates are a large class of metal-oxygen anion clusters of highly oxidized early transition metal cations of vanadium, molybdenum, or tungsten.[4] They possess subnanosized and well-defined structures. Their chemical and physical properties can precisely be tuned by selecting constituent elements, structures and counter cations.[4] Polyoxotungstates and polyoxomolybdates can encapsulate the heteroatom in an XO_4 tetrahedron at the centre to form typical Keggin $[XM_{12}O_{40}]^{n-}$ and Dawson type polyoxometalates $[X_2M_{18}O_{62}]^{n-}$ ($M = W^{6+}$ and Mo^{6+}). The XO_4 unit is directly bonded to the tungsten or molybdenum atoms on the anion framework. On the other hands, spherical polyoxovanadates, which are formed by the condensation of VO_5 square pyramidal units, give a structural versatility suited for various types of anion incorporation[5-9]. The strong trans influence of V=O groups in VO_5 square-pyramids allows a weak interaction with an anion at the bottom of the pyramid.[10] By condensation of the units in a spherical form in the manner that all the bottoms of the pyramids are directed to the centre, it enable to accommodate an anion via multiple electrostatic interactions from the

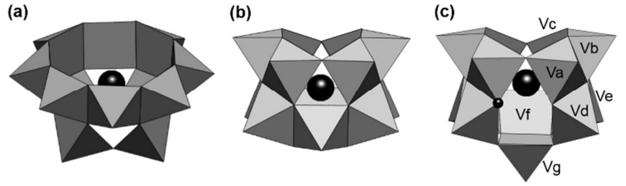

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Fig. 1 Anion structures of chloride-incorporated dodecavanadates, (a) **opened-V12**, (b) **tube-V12**, and (c) **closed-V12**. Large and small spheres, and square-pyramids represent chlorine and protonated-oxygen atoms, and VO_5 units, respectively.

spherically arranged vanadium atoms. These types of unique frameworks show the diversity of incorporated guest anions at the centre. To date, diverse vanadium-oxygen anion cages with various anions, such as F^-, Cl^-, Br^-, I^-, CN^-, CO_3^{2-}, NO^-, NO_2^-, NO_3^-,N_3^-, PO_4^{3-}, $HCOO^-$, CH_3COO^-, SH^-, SCN^-, SO_3^{2-}, SO_4^{2-}, and ClO_4^- are reported.[5-9] The smaller chloride guest may fit in various cages such as $[V_4O_8(Cl)(CH_3CO_2)_4]^-$, $[V_5O_9(Cl)(O_2CPh)_4]^{2-}$, $[V_{12}O_{32}(Cl)]^{5-}$, $[V_{14}O_{36}(Cl)]^{5-}$, $[V_{14}O_{38}(Cl)]^{7-}$, $[V_{15}O_{36}(Cl)]^{n-}$ (n = 4–6), $[V_{16}O_{38}(Cl)]^{n-}$ (n = 5 or 8), and $[V_{18}O_{42}(Cl)]^{n-}$ (n = 11 or 13).[6-9]

In chloride-incorporated dodecavanadates, three types of structures, a half-spherical structure with a large opened mouth (**opened-V12**), a tube structure (**tube-V12**) and a structure like a ball-grasped form (**closed-V12**) were reported, and more importantly, they all consist of twelve vanadium atoms, thirty two oxygen atoms, and one chlorine atoms (Fig. 1, S1).[7-9] Compounds, **opened-V12**, **closed-V12** and **tube-V12**, are synthesized by different procedures from different vanadium sources of $[Cu_2V_8O_{24}]^{4-}$, $[V_{10}O_{26}]^{4-}$ and $[V_4O_{12}]^{4-}$, respectively.[7-9] There is no report on the relationship among these three compounds. The half-spherical dodecavanadate framework is one of the most thermodynamically stable structures in an organic solvent.[11] While **opened-V12** possesses no proton, **closed-V12** is monoprotonated on the oxygen atom. The distance between the monoprotonated oxygen atom and the nearest-neighbor oxygen atom is 2.63 Å, showing the existence of hydrogen bonding interaction. Thus, proton is essential to stabilize the anion structure of **closed-V12**.[8] These formula resemblance and structure difference provide us the idea that the reversible structure transformations can take place by addition or removal of proton, and that the accessibility by external substrates to the incorporated chloride can be controlled between these two distinct structures. Such system using dynamic molecular motion among two or more distinct geometries induced and controlled by appropriate external stimuli are called molecular machines.[12] Although various molecular machines such as shuttles, rotors, muscles, scissors, loop locks, tweezers have been reported, the design and synthesis of new types of molecular machines are still important.[13] Here, the new molecular capturing system which can be regarded as a molecular mitt, with two switchable structures is demonstrated in terms of the following three points: i) **opened-V12** has ability to capture and release a chloride, ii) **opened-V12** and **closed-V12** are reversibly converted each other, and iii) **closed-V12** tightly holds the incorporated chloride, preventing the dissociation.

Results and discussion

Quantitative structure transformation of closed-V12 to opened-V12. Structure transformation of **closed-V12** to **opened-V12** was monitored by ^{51}V NMR spectra of the reaction solution. ^{51}V NMR spectrum of **closed-V12** showed five signals at −540, −565, −574, −576 and −626 ppm with the intensity ratio of 1:4:4:1:2, and that of **opened-V12** showed three signals at −580, −591 and −601 ppm with the intensity ratio of 1:1:1.[7,8]

By the reaction of **closed-V12** with 0.5 equivalents of ethylenediamine in acetonitrile in the presence of 1 equivalent of $\{Et_4N\}Cl$, the all signals due to **closed-V12** disappeared and the only signals due to **opened-V12** was observed without a signal from any by-products (Fig. 2). Ethylenediamine possesses two proton binding sites, and for the quantitative removal of proton from **closed-V12**, addition of 0.5 equivalents of ethylenediamine is required. Without $\{Et_4N\}Cl$, structure transformation was stopped in the middle of the reaction (see below).

Structural transformation proceeded by the amount of ethylenediamine added. By the reaction of **closed-V12** with 0.13, 0.25 and 0.38 equivalents of ethylenediamine, the ratio of **opened-V12** observed in ^{51}V NMR after a sufficient time were ca. 25, 50 and 75 %, respectively. (Fig. 2). For the proton elimination, the selection of base is important. For example, $\{Et_4N\}OH$ and $\{n\text{-}Bu_4N\}OH$ were not suitable for the structure transformation, since water presented or formed by the reaction induced the isomerization of dodecavanadates to $[H_3V_{10}O_{28}]^{3-}$ or $[V_{14}O_{38}(Cl)]^{7-}$. Triethylamine was also unsuited because it worked as a reductant, giving partly reduced polyoxovanadates.

Although ^{51}V NMR measurement is useful to identify the solution state of fully oxidized vanadium species, the presence of paramagnetic species formed by partial reduction of vanadium with inter-valence charge transfer prevent the detection of polyoxovanadate species. Therefore, other spectroscopic analysis was necessary to estimate the presence of paramagnetic by-products. UV spectrum of the reaction solution after the structure transformation of **closed-V12** to **opened-V12** shows no peaks in the range over 500 nm, suggesting that any by-products with inter-valence charge transfer are not formed. After addition of excess amount of diethyl ether, the precipitates containing all vanadium species in the reaction solution were collected**.** IR spectra of the samples obtained with various equivalents of base were in good agreement with those simulated from the two authentic samples (Fig. 2). These results show that transformation of **closed-V12** to **opened-V12** completely proceeds stoichiometrically.

Estimated reaction path of structure transformation of closed-V12 to opened-V12. Time dependent observations of ^{51}V NMR allow us to detect kinetically tentative intermediate on the course of the transformation reaction (Fig. 3, S2). In the first stage of the reaction, signals at −561 and −580 ppm were appeared and disappeared over the time. Without the presence of additional {Et_4N}Cl in the reaction solution, the signals due to the intermediate and **opened-V12** were observed with the proportion of ca. 1:9, while the signals due to **closed-V12** disappeared. These results indicate that the intermediate is **tube-V12,** which is stabilized by the protonated amine.[9]

We survey the best cation to stabilize the intermediate, and found that diethylammonium cation gave the single crystals of the intermediate. From NMR, elemental analysis and the single crystal X-ray crystallographic analysis, the formula of this compound is {n-Bu_4N}{Et_2NH_2}$_4$[$V_{12}O_{32}$(Cl)] and the anion structure is **tube-V12** (Table S1 and Fig. S3). The anion structure was stabilized by the hydrogen bonding interaction between the oxygen atoms of the **tube-V12** framework and secondary ammonium cations, as mentioned by Streb's group.[9]

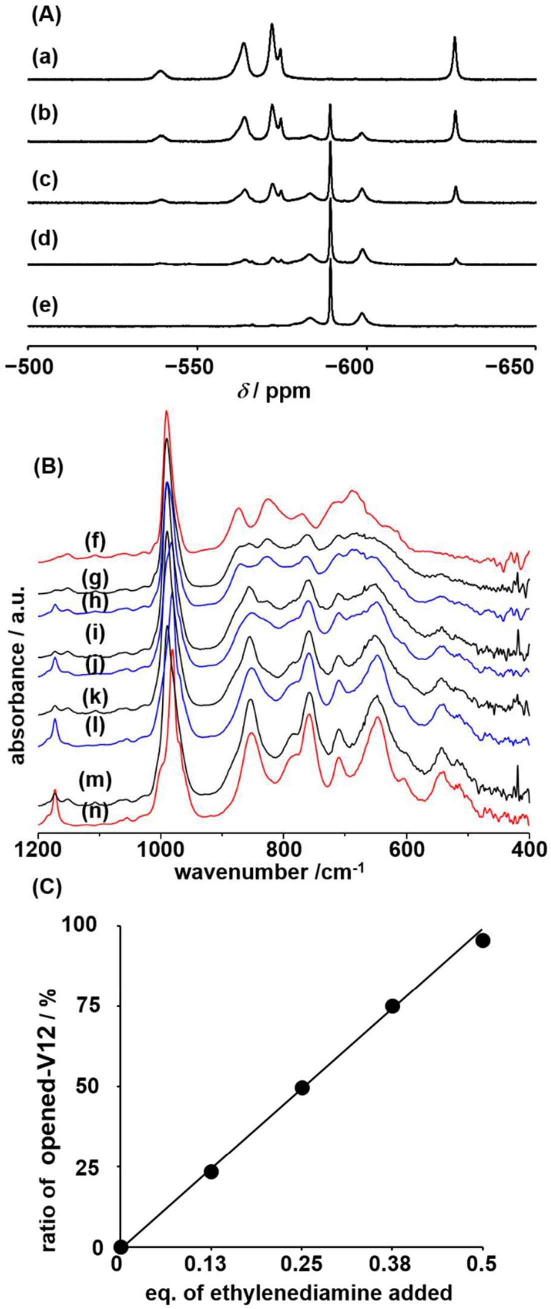


Fig. 2 (A) ^{51}V NMR spectra of the acetonitrile solution of **closed-V12** in the presence of (a) 0, (b) 0.13, (c) 0.25, (d) 0.38 and (e) 0.5 equivalents of ethylenediamine. To the solution of **closed-V12**, two equivalents of {Et_4N}Cl with respect to ethylenediamine were added. In all these spectra, only signal sets due to **closed-V12** and **opened-V12** were observed. (B) IR spectra of the samples obtained after the reaction of **closed-V12** with (g) 0.13, (i) 0.25, (k) 0.38 and (m) 0.5 equivalents of ethylenediamine (black lines), IR spectra of authentic samples of (f) **closed-V12** and (n) **opened-V12** (red line), and the simulated spectra from authentic **closed-V12** and **opened-V12** with the ratio of (h) 3:1, (j) 1:1, and (l) 1:3 (blue line). (C) Plots of the equivalents of ethylenediamine added to **closed-V12** versus estimated molar ratio of **opened-V12** from ^{51}V NMR.

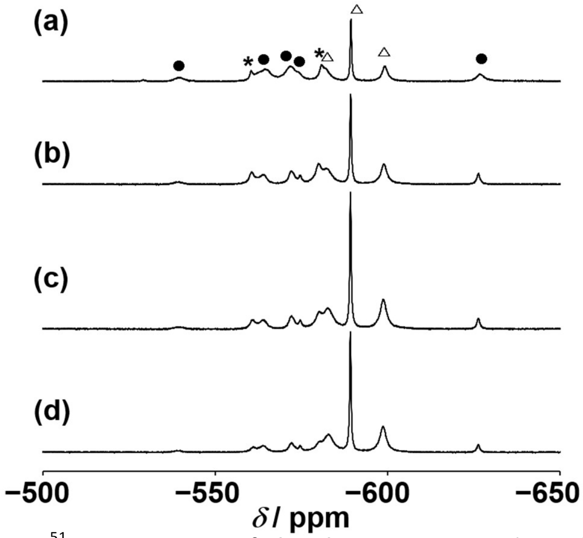


Fig. 3 ^{51}V NMR spectra of **closed-V12** in acetonitrile in the presence of 0.5 equivalents of ethylenediamine after (a) 10 min, (b) 120 min, (c) 960 min and (d) 1920 min in an NMR sample tube. Asterisks, circles and triangles represent the peaks assigned to **tube-V12**, **closed-V12** and **opened-V12**, respectively.

The expected transformation of **tube-V12** to **opened-V12** was separately confirmed by choosing the counter cation. In the presence of 200 equivalents of {Et_4N}Cl, **tube-V12** was converted to **opened-V12**, showing that **tube-V12** is indeed the intermediate for the transformation of **closed-V12** to **opened-V12**. While transformation of **tube-V12** to **opened-V12** completely proceeded, the yield of reverse reaction in the presence of 200 equivalents of dimethylamine hydrochloride for the same reaction time, reached only ca. 85% partly due to the thermodynamic stability of **opened-V12** (Fig. S4).

Based on the point of structural similarity, the reaction path was estimated. The difference of the frameworks between **closed-V12** and **tube-V12** is the position of one VO_5 unit. Both **tube-V12** and **opened-V12** possess two layers of vanadium rings; two stacked six-vanadium rings for **tube-V12** and eight- and four-vanadium rings for **opened-V12**. Therefore, we propose the following reaction scheme. Removal of proton by base triggered the rearrangement of the VO_5 unit, Vg in Fig. 1, to fill the ex-protonated site, resulting the formation of **tube-V12** intermediate. Then, further rearrangement may complete the structure transformation to **opened-V12** in the presence of tetraethylammonium cation (Fig. 4).

Quantitative structure transformation of opened-V12 to closed-V12. Structure transformation of **opened-V12** to **closed-V12** was investigated by addition of acid. Quantitative addition of weak acid such as acetic acid gave a partial structure transformation to **closed-V12**. ^{51}V NMR spectrum of the reaction solution of **opened-V12** with *p*-toluenesulfonic acid monohydrate showed signals at −579 and −590 ppm. These signals were assignable to $[V_{14}O_{38}(Cl)]^{7-}$, which was formed by hydrolysis reaction of **closed-V12**. To avoid contamination of water, trifluoroacetic acid was selected. By the reaction of **opened-V12** with 0.25, 0.5, 0.75 and 1 equivalents of trifluoroacetic acid, the ratio of **closed-V12** observed in ^{51}V NMR after a sufficient time were ca. 0, 25, 50 and 100 %, respectively without a formation of any by-products (Fig. 5). UV spectrum of the reaction solution showed no existence of reduced vanadium species. IR spectra of samples obtained after the reaction with different equivalents of acid without any purification were in good agreement with the simulated spectra from the two authentic samples. These spectra shows additional features of the overlapped peaks due to the trifluoroacetate since tetra-*n*-butylammonium trifluoroacetate formed was precipitated with vanadium species by addition of excess amount of diethyl ether. The ratio of **closed-V12** to **opened-V12** quantitatively increased in accord with the amount of acid added with the overlapped peaks. This is the first report on the proton-induced reversible structure transformation of polyoxometalates between two distinct structures maintaining the number of metal and oxygen atoms.‡ Structure transformation of polyoxometalates sometimes proceeds by addition or removal of proton in association with the formula change.[4,11] Isomerization of polyoxometalates with maintaining the formula is restricted to quite similar structures, for example, structure transformation between α- and β-Keggin isomers is observed by adjustment of pH.[4] It is also reported that in organic media, polyoxometalate structures are just protonated or deprotonated without changing the number of metal and oxygen atoms by addition of acid or base.[14]

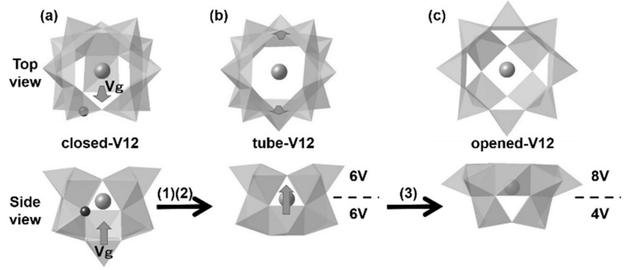


Fig. 4 Estimated reaction path of the transformation of (a) **closed-V12** to (c) **opened-V12** via (b) **tube-V12** as an intermediate. The reaction triggered by (1) removal of proton of **closed-V12** by base. (2) The Vg unit was moved to the ex-protonated site, resulting in the formation of **tube-V12**. Compound **opened-V12** may be converted from **tube-V12** by (3) moving two VO_5 units from the bottom to the top layer. The proposed scheme only suggests the mechanism based on the point of structural similarity.

For the dynamic structure transformation, VO_5-based polyoxovanadates with weak electrostatic interaction between the guest anion with vanadium atoms, have an advantage in terms of structural freedom over molybdenum- and tungsten-

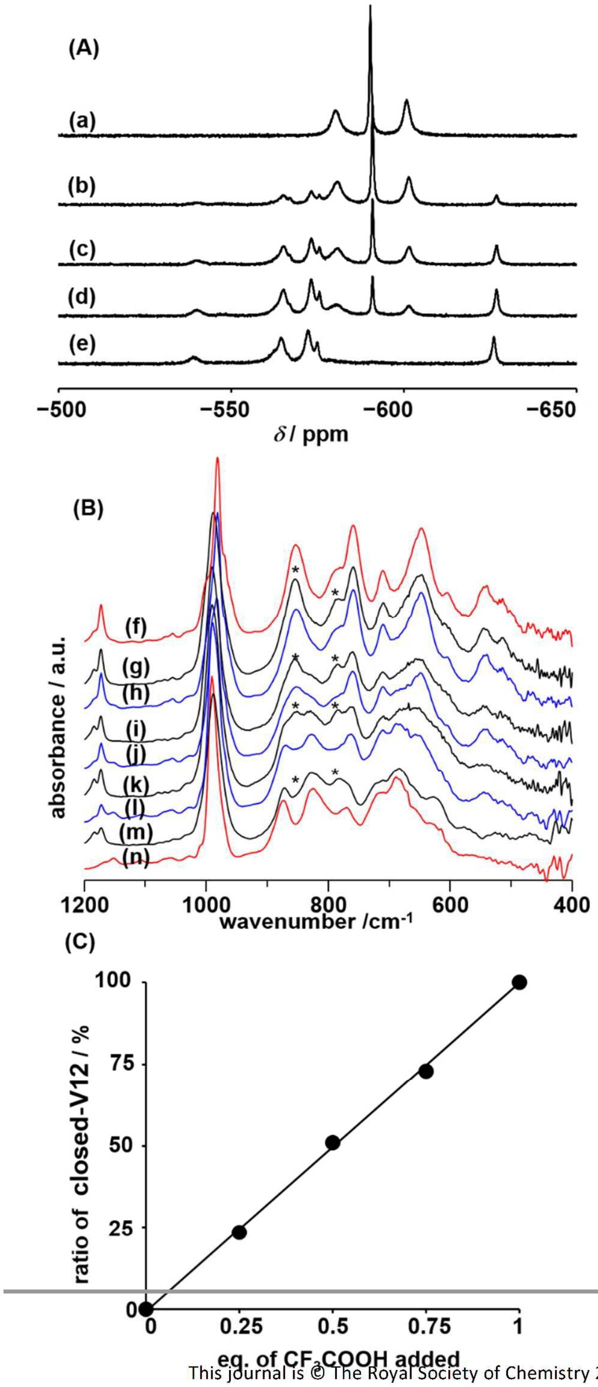


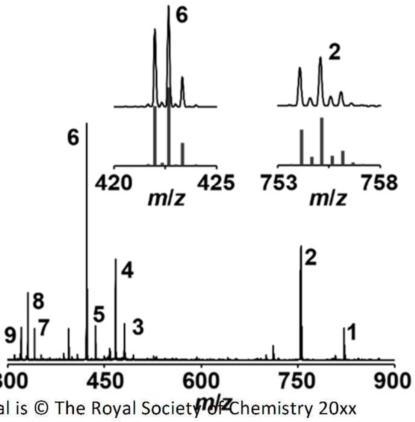
Fig. 5 (A) ^{51}V NMR spectra of the acetonitrile solution of **opened-V12** in the presence of (a) 0, (b) 0.25, (c) 0.5, (d) 0.75 and (e) 1 equivalents of CF_3COOH. In all these spectra, signal sets due to **closed-V12** and **opened-V12** were observed exclusively. (B) IR spectra of the samples obtained after the reaction of **opened-V12** with (g) 0.25, (i) 0.5, (k) 0.75 and (m) 1 equivalents of CF_3COOH (black lines), IR spectra of authentic samples of (f) **opened-V12** and (n) **closed-V12** (red line), and the simulated spectra from authentic **opened-V12** and **closed-V12** with the ratio of (h) 3:1, (j) 1:1, and (l) 1:3 (blue line). (C) Plots of the equivalents of CF_3COOH added to **opened-V12** versus estimated molar ratio of **closed-V12** from ^{51}V NMR.

based Keggin or Dawson polyoxometalates with direct bond between molybdenum or tungsten atoms and hetero units via oxygen atoms.

In the early stage of the transformation of **opened-V12** to **closed-V12**, a signal at −550 ppm was observed in ^{51}V NMR spectra (Fig. S5). This signal position was different from that of **tube-V12**, showing that the transformation of **opened-V12** to **closed-V12** proceeds via different paths from reverse one.

Reactivity of the chloride incorporated in dodecavanadates with silver cation. Compound **closed-V12** possesses V_6O_6 ring and the hole size with considering Van der Waals radius is ca. 2.0 Å. This value is smaller than the size of chloride (3.4 Å) inferring the confinement of the guest anion. In contrast, **opened-V12** possesses V_8O_8 ring and the hole size is 4.2 Å (Fig.S1). It seems that chloride is able to pass the largely opened ring freely. However, once chloride is stabilized in the **opened-V12** cage, the removal of chloride is difficult even at high temperature.[7]

The geometrical difference between **closed-V12** and **opened-V12** induces the reactivity difference against silver cation. The reaction of **closed-V12** with 1 equivalent of $AgBF_4$ yielded no precipitates of AgCl and it gave **closed-V12’**. From IR spectra, the anion structure of **closed-V12’** was identical to **closed-V12** (Fig. S6). ESI-MS spectrum showed signal sets at *m*/*z* = 755.2, 436.4 and 422.7 assigned to $\{(n\text{-}Bu_4N)[AgHV_{12}O_{32}(Cl)]\}^{2-}$, $\{[AgHV_{12}O_{32}(Cl)]CH_3CN\}^{3-}$, and $\{[AgHV_{12}O_{32}(Cl)]\}^{3-}$, respectively (Fig. 6). These results and elemental analysis show that the formula of **closed-V12’** is $\{n\text{-}Bu_4N\}_3Ag[HV_{12}O_{32}(Cl)]$, with maintaining the structures of the **closed-V12** framework before and after the reaction.



Peak number	Ionic species	m/z
1	$\{\{(n\text{-}C_4H_9)_4N\}_2[HV_{12}O_{32}Cl]\}^{2-}$	822.3
2	$\{\{(n\text{-}C_4H_9)_4N\}[AgHV_{12}O_{32}Cl]\}^{2-}$	755.2
3	$\{\{(n\text{-}C_4H_9)_4N\}[HV_{12}O_{32}Cl]CH_3CN\}^{3-}$	480.8
4	$\{\{(n\text{-}C_4H_9)_4N\}[HV_{12}O_{32}Cl]\}^{3-}$	467.1
5	$\{[AgHV_{12}O_{32}Cl]CH_3CN\}^{3-}$	436.4
6	$\{[AgHV_{12}O_{32}Cl]\}^{3-}$	422.7

Fig. 6 ESI-MS spectrum of **closed-V12’**. The lines in the insets are the calculated patterns for $\{Ag[HV_{12}O_{32}(Cl)]\}^{3-}$ (*m*/*z* = 422.7) and $\{(n\text{-}C_4H_9)_4N\}Ag[HV_{12}O_{32}(Cl)]\}^{2-}$ (*m*/*z* = 755.2). A table shows assignments of peaks.

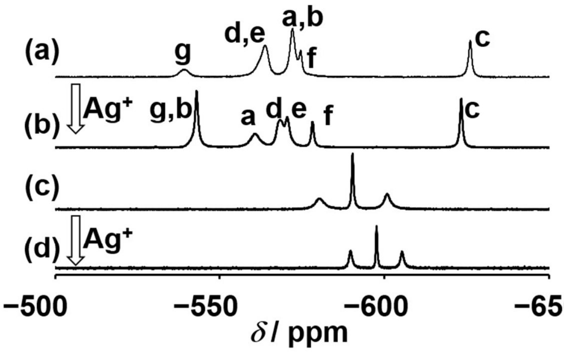


Fig. 7 ^{51}V NMR spectra of (a) **closed-V12**, (b) **closed-V12’**, (c) **opened-V12** and (b) **opend-V12’**. Signal assignment of **closed-V12’** based on ^{51}V-^{51}V COSY NMR spectra were shown according the labelling in Fig. 1.

^{51}V NMR spectrum of **closed-V12’** was different from that of **closed-V12**. From the intensity ratio of signals and ^{51}V-^{51}V COSY NMR spectrum, signals at −531, −541, −558, −568, −578 and −622 ppm are assigned to Vb and Vg, Va, Vd, Ve, Vf and Vc, respectively (Fig. 7, S7). The signals due to the V_6O_6 ring, Va, Vb and Vc were downfield shifted, while the other peaks were upfield shifted, indicating that the silver cation was interacted on top of the V_6O_6 ring.[§]

On the other hand, the reaction of **opened-V12** with 1 equivalent of $AgBF_4$ resulted in the formation of white precipitates of AgCl because of the accessible hole. ^{51}V NMR spectrum of the reaction solution showed upper field shift for all three signals at −589, −597 and −605 ppm, and these signal position was the same as that of the previously reported acetonitrile-incorporated $[V_{12}O_{32}(CH_3CN)]^{4-}$ (**opened-V12’**) (Fig. 7).[§§,15] As a control experiment, no dissociation of chloride from **opened-V12** was observed in acetonitrile at room temperature over 34 h without the presence of silver cation. IR spectrum was investigated for the compound after removing the chloride by silver cation from **opened-V12**. The isolated compound shows almost the same peak feature to **opened-V12** in V−O stretching region, suggesting that the anion structure is maintained during the reaction (Fig. S8). The only difference was observed on the bands attributed to *v*(V=O) due to the different charges on the complexes with or without chloride anion. The chloride incorporation weaken the V=O bonds to give V=O stretching at 981 cm^{-1}, and **opened-V12** gave the bands at 992 cm^{-1}. The overall V−O framework is rigid and the structures of **opened-V12** and **opened-V12’** is almost identical except V=O bond lengths. These observation is consistent with the X-ray crystallographic analysis, and the average V=O bond length of **opened-V12** was 1.60 Å and **opened-V12’** was 1.59 Å.[7,15]

The complete removal of chloride was confirmed by elemental analysis of the obtained compounds. All these results suggest that the **opened-V12** has an open cavity that is accessible by external reagents such as silver cation, resulting the formation of the chloride free complex without the decomposition of **opened-V12** framework.

The reaction of **opened-V12’** with 1 equivalent of {Et$_4$N}Cl in nitromethane, chloride was incorporated again into the framework and the host-guest structure of **opened-V12** was retrieved. Such molecules with the catch-and-release property are called molecular baskets.[16] More importantly, the guest release and capturing processes for the **opened-V12** framework were quantitative under this condition. In acetonitrile, the incorporated chloride in **opened-V12** was not dissociated. The twelve electrostatic interactions between vanadium and chlorine atoms is strong enough to hold the chloride at the cavity due to its cavity shape preferable to the chloride anion and the negative charge to gain a stabilization by the interactions with pentavalent vanadium centres.

The electrochemical potentials of **opened-V12** were controllable by incorporation or removal of chloride. The cyclicvoltammograms showed two reversible waves at −0.71 and −1.37 mV vs Fc/Fc^{+} (Fc = ferrocene) for **opened-V12** and −0.38 and −1.11 V vs Fc/Fc^{+} for **opened-V12’**, respectively (Fig. S9). The different anion charges of –5 on **opend-V12** and –4 on **opened-V12’** are responsible for the switch of the redox potentials.[17] On the other hands, the redox potentials of **opened-V12’** and **closed-V12** were observed in the similar range, because both of the complexes have the same –4 charges on the vanadium frameworks. The presence of the chloride guest in the cluster strongly perturbed the redox potentials resulting the apparent negative shifts of the redox waves.

Conclusions

Between the two distinct structures of chloride-incorporated dodecavanadates, **closed-V12** and **opened-V12**, structure transformation reversibly took place by quantitative addition or removal of proton. The geometrical accessibility of silver cation to the incorporated chloride of **closed-V12** and **opened-V12** was different each other. While the guest chloride in **closed-V12** was protected from silver cation, the guest chloride in **opened-V12** was removed as AgCl. Also, the reaction of chloride-free **opened-V12** with {Et$_4$N}Cl retrieved **opened-V12** by recapturing the guest chloride. The reversible transformation with controlling accessibility to chloride in two distinct dodecavanadate structures is regarded as a move of a molecular mitt: A free chloride is captured in the half-spherical opened framework, and the incorporated chloride is grasped by the proton-induced structure transformation to be protected from the external stimuli. The dodecavanadate framework is opened again by deprotonation, and then the captured chloride can react with a substrate. Although the reversible opened and closed conformation change was demonstrated with the steroid cyclophanes induced by the macroscopic pressure stimuli, the reversible one induced by chemical stimuli have not been reported, as far as we know.[18]

Acknowledgements

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Notes and references

‡. The reactivity difference was also demonstrated through the condensation of benzaldehyde with malononitrile (Knoevenagel condensation). This reaction is generally considered to proceed by subtraction of proton from the activated methylene moiety.[19] The higher reactivity of **opened-V12** (84% yield) and **tube-V12** (86%) than that with **closed-V12** (20%) is consistent with the higher acceptability of proton. It is reported that the deprotonated polyoxometalates showed the higher reactivity for the Knoevenagel condensation than original ones (Fig. S10)[20]

§. Chloride in **tube-V12** with the same six-vanadium rings as that of **closed-V12** was maintained in the framework even in the presence of silver cation. The stable isolation of **tube-V12** by the interaction with a different type of cation on the V$_6$O$_6$ ring is reported.[21]

§§. The reaction of **opened-V12’** with quantitative trifluoroacetic acid gave the complicated ^{51}V NMR spectrum, showing the decomposition to the several unknown products. The electrostatic interaction of the incorporated chloride with each VO$_5$ square pyramidal unit could allow the required transformation.

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Chloride capturing system via proton-induced structure transformation between opened- and closed-forms of dodecavanadates

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Reactivity of incorporated chloride was controlled by the reversible structure transformation between two distinct structures of dodecavanadates.