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Evaluation of Chemo- and Shape-Selective Association of a Bowl-Type Dodecavanadate Cage with an Electron-Rich Group

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The host-guest interaction between a half spherical-type dodecavanadate (**V12**) and a neutral molecule guest was evaluated by monitoring the flip of a VO₅ unit caused by the presence or absence of a guest in the cavity of **V12**. In *N,N*-dimethylformamide (DMF), **V12** adopted the guest-free-form (**V12-free**). By addition of several guest molecules, such as acetonitrile, nitromethane, dichloromethane, the structure conversion to the guest-inserted form (**V12(guest)**) were observed with the affinity constants of 137±10, 0.14±0.1, and 0.15±0.1 M⁻¹, respectively. In the case of 1,2-dichloroethane, 1,2-dibromoethane, and 1,2-diiodoethane, the constants were 35±5, 114±5, and 2.1±0.5 M⁻¹, respectively, suggesting that the bromo group is best fit to the cavity of the bowl. A cyclic carbonate and 5- and 6-membered lactons, cyclobutanone, and hexanal were inserted to the **V12** host, while non-cyclic carbonate, non-cyclic and 7-membered cyclic ester, ketone with a 6-membered ring, and benzaldehyde showed no effect on the guest insertion. The **V12** host preferred to hold a guest with an electron-rich group and the bowl type structure showed the unique shape-selective interaction with a guest.

Introduction

The cavity with a well-defined size and functionalization acts as a molecular flasks, in which only a few molecules can be included.¹ By using such a cavity, several size-selective transformation reactions are accomplished. The design and synthesis of the cavity for the single molecule manipulation have been developed, especially by the synthesis of macrocyclic and cage-type structures.¹ The phenomena of the molecular hosts can be explained in detail by the crystallographic and spectroscopic analysis and DFT calculation.¹ Since the unique host property and reactivity are strongly depend on the structures, the development of novel host materials with a designed cavity are important. While most reported molecular hosts were built by organic frameworks, discrete inorganic molecular hosts were rare. Molybdenum-oxygen cluster anion with a porous spherical structure, [Mo₁₃₂O₃₇₂(L)₃₀(H₂O)₇₂]⁴²⁻ (L = carboxylate, sulfate, or phosphate), showed the unique host-guest systems.² Through 20 pores of the cluster, the size-selective inclusion of organic molecules and cation exchange were achieved.³ In addition, the space and the catalytic performance of the inside sphere can be controlled by the inner ligands.⁴

Discrete metal-oxygen clusters are classified into Polyoxometalates.⁵ They exhibit (sub-)nano sized well-defined molecular structures. Many structure types of

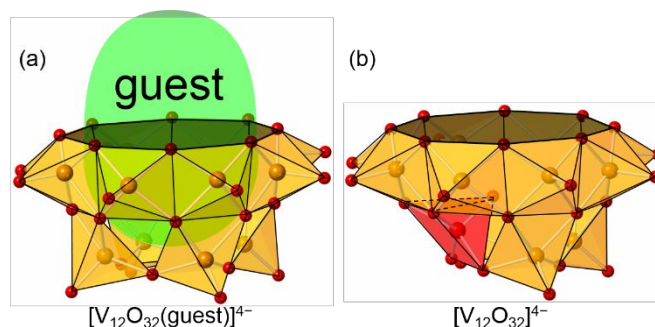


Figure 1. Host anion structures of (a) **V12(guest)** and (b) **V12-free**. Orange and red spheres and orange and red square pyramids represent vanadium and oxygen atoms and VO₅ units with their bases directed to the centre of the bowl, and the flipped VO₅ unit, respectively. Guest moiety can be inserted into the cavity of the bowl.

polyoxometalates are reported so far and they attract researchers as great functionalized materials in broad field of science. Their chemical property and stability are different by changing constituent elements, structures, valences, and counter ions. In particular, vanadium-based polyoxometalates show structure versatility due to the adoptable coordination geometry such as VO₄ tetrahedral, VO₅ square-pyramidal, and VO₆ octahedral units.⁶ We focused on the polyoxometalates based on VO₅ square-pyramidal units. The VO₅ units condensed with directing the base of the pyramid units to the centre of the cluster to form sphere type structures, and at the centre, various anion fragments are stabilized, even if the polyoxometalates themselves possess large anion charges.⁷ Usually, it is difficult to remove or exchange a centred fragment because the whole sphere cages have no exits for the centred fragment to pass. On the other hand, half sphere structure [V₁₂O₃₂]⁴⁻ (**V12**) has the 4.4 Å cavity entrance and through the

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entrance, some guest exchange reactions from a neutral guest to an anionic guest were achieved.⁸⁻¹⁰ Although the previous study revealed the guest exchange reaction rate, the affinity was not fully investigated. The equilibrium study of the host-guest ability of **V12** is urgent necessity because a host complex without any organic ligands in a molecular entity is still not fully understood. However, the study indicated some issues during the previous guest exchange system. Once anions are captured in the cavity of **V12**, the dissociation of the guest was hardly observed because the anion guest sat in the relatively positively charged cavity. In addition, some anions were causing a minor hydrolysis of **V12** to give $[V_5O_{14}]^{3-}$ due to the basicity of the ionic compounds, such as $\{Et_4N\}[NO_2]$, $\{Et_4N\}[OCN]$, $\{Et_4N\}[HCO_2]$, and $\{Et_4N\}[CH_3CO_2]$.¹⁰ Alternatively a multi atomic neutral guest may have better interaction because it is easier to dissociate to allow us to study an equilibrium of the host-guest system. Its less basicity also causes no hydrolysis. However, the previous guest exchange system prevented the equilibrium study in the solution state, because ^{51}V NMR spectra of each **V12** with a neutral guest give three peaks at the same chemical shifts. In theory, the guest exchange through 4.4 Å cavity entrance of **V12** is a two-step process of guest removal and guest accommodation. Recently, we have discovered that a bottom VO_5 unit of **V12** was flipped to form a unique flipping bowl structure when the guest was removed, and that it retrieved the cavity when it accommodated a guest gas (Figure 1).¹¹ They were investigated in the solid state and the guest affinity was not fully investigated. The molecular symmetry of the host of the guest-inserted type of **V12** (**V12(guest)**) and the guest-free type of **V12** (**V12-free**) were different each other, and the structures were distinguished by IR and ^{51}V NMR spectra. In this work, we evaluated systematic quantitative affinity between **V12** host and a guest by monitoring guest-insertion reactions causing structure transformation of **V12-free** and **V12(guest)**.

Results and discussion

Structure of dodecavanadate in the solution state.

The molecular structures of **V12(guest)** and **V12-free** were previously determined by X-ray crystallographic analysis.^{8,10} During the structure conversion of the **V12** host, the overall features of IR spectra in the region of 1200–500 cm^{-1} were maintained. The only and crucial difference was the intensity of the peak at 850 cm^{-1} due to the $V-\mu_2-O$ stretching vibration of the bottom part of **V12** (Figure S1).¹¹ The solution state IR spectra of **V12(AN)** in AN and **V12-free** in acetone were identical to those in solid state, showing these structures are stable in the solution state (Figure S1). The symmetry of the host structure of **V12(guest)** (C_{4v}) was different from that of **V12-free** (Cs), showing three peaks in ^{51}V NMR spectrum at -590, -594, and -602 ppm for **V12(AN)** in AN with the intensity ratio of 1:1:1, and seven peaks at -498, -575, -580, -587, -595, -601, and -612 ppm for **V12-free** with intensity ratio of 1:2:1:2:1:2:3.[‡]

While acetone was suitable solvent to obtain the single crystals of **V12-free** for the x-ray crystallographic analysis, it was

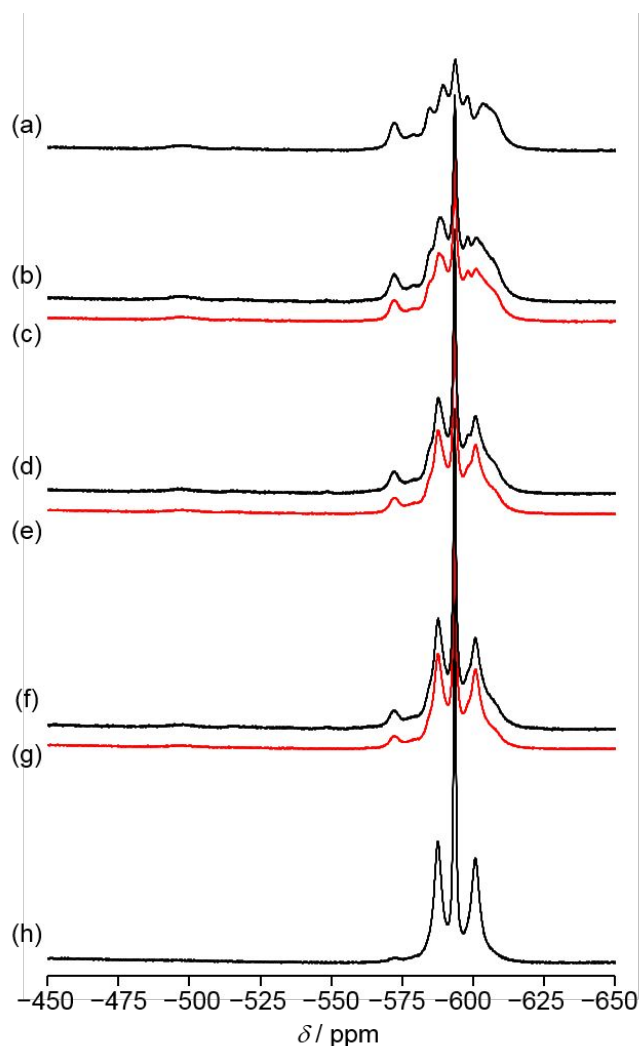


Figure 2. ^{51}V NMR spectra of DMF solution of **V12** in the presence of (a) 0, (b) 0.375, (d) 0.75, 1.13, and 5 equivalents of AN. Red lines represent the simulated spectra by using spectra (a) and (h). The ratio of **V12-free** were (c) 73%, (e) 50%, and (g) 35%, respectively.

insufficient to investigate the solution state chemistry due to the low solubility of **V12(guest)**. The tetra-*n*-butylammonium salt of **V12** showed high solubility in polar solvent. After the dissolution of **V12-free** into the solvent which acted as a guest into the cavity of **V12**, such as AN and NM, ^{51}V NMR spectrum showed three signals due to **V12(AN)** and **V12(NM)**. On the other hand, *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), have two methyl groups that hinder an electron-rich group from fitting into the cavity. ^{51}V NMR spectrum in DMF showed peaks at -497 (broad), -572, -578, -585, -589, -593, -598, -603, and -608 ppm (Figure 1). In addition to ^{51}V NMR and IR spectra in the solution state, the **V12-free** structure was maintained (Figure S1).

The association constants of AN, benzonitrile (BN), DCE, NM, and DCM with **V12** were investigated (Table 1). By addition of 5 equivalents of AN to the DMF solution of **V12-free** (29 mM), ^{51}V NMR spectrum show three signals at -588, -594, and -602 ppm, showing the structure conversion from **V12-free** to **V12(AN)** in the solution state. Addition of molecular sieves 4A into this solution, **V12-free** was retrieved, suggesting that the structure conversion between **V12(AN)** and **V12-free** was reversible. In

Table 1. Association constants of **V12** with a various molecule guest in DMF solution at 25 °C^a

$\text{V12 - free} + \text{guest} \xrightleftharpoons{K_{\text{guest}}} \text{V12}(\text{guest})$			
entry	guest ^b	functional group	association constant $K_{\text{guest}} / \text{M}^{-1}$
1	DMF	amide	not inserted
2	DMSO	sulfoxide	not inserted
3	AN	nitrile	137±20
4	BN	nitrile	10±5
5	NM	nitro	0.13±0.1
6	DCE	chloro	35±5
7	DCM	chloro	0.25±0.1
8	DBE	bromo	114±5
9	DBM	bromo	0.23±0.1
10	DIE	iodo	2.1±0.5
11	DIM	iodo	< 0.030 ^c
12	chloroform	chloro	not inserted
13	DMC	carbonate	not inserted
14	EC	carbonate	0.56±0.1
15	EA	ester	not inserted
16	GBL	lactone	1.1±0.5
17	DVL	lactone	0.16±0.1
18	ECL	lactone	not inserted
19	acetone	ketone	not inserted
20	CP	ketone	not inserted
21	CB	ketone	0.17±0.1
22	BA	aldehyde	not inserted
23	HA	aldehyde	0.10±0.05
24	IBA	aldehyde	not inserted

a. Conditions: **V12-free** (29 mM), the required amount of additives, the total volume of the solution 0.5 mL. The equilibrium of **V12(guest)** and **v12-free** was monitored by ⁵¹V NMR. b. DMF = *N,N*-dimethylformamide, DMSO = dimethyl sulfoxide, AN = acetonitrile, BN = benzaldehyde, DCE = 1,2-dichloroethane, NM = nitromethane, DCM = dichloromethane, DBE = 1,2-dibromoethane, DBM = dibromomethane, DIE = 1,2-diiodoethane, DIM = diiodomethane, DMC = dimethyl carbonate, EC = ethylene carbonate, EA = ethyl acetate, GBL = γ -butyrolactone, DVL = δ -valerolactone, ECL = ϵ -caprolactone, CP = cyclopentanone, CB = cyclobutanone, BA = benzaldehyde, HA = hexanal, IBA = isobutanal. c. precipitates of **V12(DIM)** were formed by adding excess amount of DIM. The saturated condition ([DIM] = 3.7 M) gives signals due to **V12-free**. The values were calculated with the assumption that the structure conversion is less than 10%.

the presence of 0.38, 0.75, and 1. equivalents of AN, ⁵¹V NMR spectra showed the superposition of spectrum of **V12-free** and **V12(AN)** and the molar ratio of **V12(AN)** were 27, 50, and 65 %, respectively, showing the association constant K_{AN} of $137 \pm 10 \text{ M}^{-1}$ at 25°C. The strong affinity between **V12** and AN allowed to compare the electrochemical property between **V12-free** and **V12(AN)** in DMF by addition of small amount of AN. From the K_{AN} value, addition of 0.01 mL of AN per 1 mL of DMF with 1 mM of **V12** gives more than 95% of **V12(AN)**. The cyclic voltammograms of **V12-free** showed a reversible wave at -0.57 V and an irreversible reduction peak at -1.41 V vs Fc/Fc⁺ (Fc = ferrocene). In the presence of AN, a reversible wave was slightly shifted to -0.61 V, while an irreversible wave was not shifted (Figure S2).⁵ It is known that the structural isomers of polyoxometalates exhibit different redox properties.¹²

With increasing the total amount of BN respective to **V12** from 5 to 25 equivalents, the peaks due to **V12(BN)** increased (Figure S3). The association constant K_{BN} was $10 \pm 5 \text{ M}^{-1}$ at 25°C. Previously, Klemperer investigated the equilibrium between **V12(AN)** and **V12(*p*-tolunitrile)** by addition of *p*-tolunitrile into the nitrobenzene solution of **V12(AN)** with giving the constant of 10 ± 3 at 8°C.⁹ This value showed the good agreement with the $K_{\text{AN}}/K_{\text{BN}}$ value of 14 in this work. By addition of 1, 2, and 3.8 equivalents of DCE with respect to **V12**, the molar ratio of **V12(DCE)** were 38, 58, and 75%, respectively, and the association constant K_{DCE} was 35 M^{-1} (Figure S4). For the insertion of NM and DCM, the structure conversion of **V12** require large amount of NM and DCM, and the association constants K_{NM} and K_{DCM} were 0.13 ± 0.1 and 0.25 ± 0.1 , respectively (Figures S5 and S6). In the case of NM and DCM, the repulsive interactions probably weaken the interaction. In the crystal structure, one of the oxygen atoms of nitro group was attractive in the cavity, and the other was repulsive from the entrance oxygen atoms of **V12**.¹⁰ One of the chlorine atoms of DCM located in the cavity and the other sat near the entrance oxygen atoms.¹¹ These results demonstrate relevance of the previous work; the anion insertion was carried out in NM solution, and guest removal was achieved by using **V12(DCM)**.

Stability comparison among alkyl halide.

In addition to DCE and DCM, the association of 1,2-dibromoethane (DBE), 1,2-diiodoethane (DIE), dibromomethane (DBM), and diiodomethane (DIM), were investigated (Figures S7-S10). Chloroform was not act as a guest for the cavity of **V12**.

The association constants of K_{DCE} , K_{DBE} , and K_{DIE} were 35 ± 5 , 114 ± 5 , and 2.1 ± 0.5 , respectively, showing the unusual order of the affinity. This is accountable for the size of the cavity and a halogen atom. Considering the van der Waals radii, **V12** possesses the 4.4 Å entrance and the size of chlorine, bromine, and iodine are 3.2, 3.9 and 4.3 Å, respectively. The previous work reveals that the size of the V8 ring of **V12** is comparable in the presence of chloride, bromide, and iodide.¹⁰ Therefore, the surface of the larger halogen atom is closer to the vanadium centres, arising the stronger attractive interaction. On the other hand, eight oxygen atoms of the cavity entrance work as the repulsive sites for halogen atom. The repulsive interaction between the oxygen atoms and the iodine atom weaken the affinity and the bromine atom is best fit to the cavity of **V12**. In the case of methylene halide, the stability constants of K_{DCM} and K_{DBM} were 0.25 ± 0.1 and 0.23 ± 0.1 , respectively. The value of $K_{\text{DBM}}/K_{\text{DBE}}$ was much smaller than that of $K_{\text{DCM}}/K_{\text{DCE}}$. Although the attractive interaction of the bromine atom with the cavity of **V12** is stronger than that of the chlorine atom, the steric hindrance between the external halogen atom and the cavity entrance is much effective. In the mixed solvent of DIM and DMF (v/v = 1:1) precipitates were formed. The strong peak at 850 cm^{-1} in IR spectrum of the precipitate, suggested the formation of **V12(DIM)**. On the other hand, IR spectrum of the filtrate show the weak peak at 850 cm^{-1} and ⁵¹V NMR spectrum of the filtrate show the peaks only due to **V12-free**. These results suggest that DIM is inserted into the cavity of **V12** to form **V12(DIM)** and the solubility of **V12(DIM)** is very low. The association

constant was evaluated from the saturated solution ($[DIM] = 3.7 \text{ M}$) with less than 10% structure conversion.

Steric effect of a dodecavanadate on the insertion of a carbonyl compounds.

Carbonyl is one of the typical electron-rich groups and the affinity of several types of carbonyl, such as carbonate, ester, ketone, and aldehyde were investigated.

While dimethyl carbonate (DMC) showed no interaction with the cavity of **V12**, in the presence of cyclic carbonates such as ethylene carbonate gave **V12(EC)** with the association constant of 0.56 ± 0.1 (Figure S11). The IR spectra of the isolated samples in the region of $1200\text{--}500 \text{ cm}^{-1}$ were identical to the typical spectrum of **V12(guest)** (Figure S12). The stretching vibration bands of the C=O bond of free EC were observed at 1803 and 1773 cm^{-1} , and those of the inserted EC appeared at

lower wavenumbers at 1757 and 1742 cm^{-1} , suggesting that the carbonyl group of EC stabilized in the cavity of **V12** behave as if it is coordinated to Lewis acid centres.¹³

The insertion of ester and lactone showed unique size-selectivity. Ethyl acetate was not inserted into the **V12** cavity. γ -Butyrolactone (GBL) with a 5-membered ring was interacted with the cavity with $K_{\text{GBL}} = 1.1 \pm 0.5$, while ϵ -caprolactone (ECL) with 7-membered ring was not (Figures 3 and S13). In the case of δ -valerolactone (DVL) with 6-membered ring, **V12(DVL)** was observed in ^{51}V NMR spectrum (Figure 3), but the chemical equilibrium did not moved to give only **V12(DVL)**, even when **V12** was dissolved in only DVL. From ^{51}V NMR spectrum, the ratio of **V12-free** to **V12(DVL)** was 35:65 in DVL. On the other hand, **V12(DVL)** were able to be isolated by utilizing the difference of the solubility. Rapid addition of the DVL solution of **V12** into large excess amount of ethyl acetate, gave the mixture of **V12-free** and **V12(DVL)** with almost the same molar ratio as that observed in solution state (Figure 3). From the mixed solvent of DVL and ethyl acetate (2:3, v/v), the crystalline samples of **V12(DVL)** were obtained (Figure 3). The intensity of the peak at 850 cm^{-1} in IR spectrum suggested the chiefly presence of **V12(DVL)**. IR peaks due to carbonyl of **V12(GBL)** and **V12(DVL)** were observed at 1717 and 1685 cm^{-1} , respectively, while those of free GBL and DVL were at 1772 and 1728 , respectively (Figure 3).

In the case of acetone, two methyl groups that hinder an electron-rich carbonyl group from fitting into the cavity. While cyclopentanone (CP) with 5-membered ring was not inserted into the cavity of **V12**, cyclobutanone (CB) were inserted to give **V12(CB)** with K_{DBM} of 0.17 ± 0.1 (Figure S13). From IR spectrum, the peaks due to carbonyl group of the inserted CB (1740 cm^{-1}) was shifted from the free CB (1776 cm^{-1}) (Figure S14). Aldehydes are less bulky carbonyl compounds and hexanal (HA) was interacted with the cavity of **V12** with K_{HA} of 0.10 ± 0.05 (Figure S15), although benzaldehyde (BA) and isobutanol (IBA) showed no effect on the flip of VO_5 unit of **V12-free**.

Experimental

Measurements. NMR spectra were recorded with JEOL JNM-LA400. ^{51}V NMR spectra were measured at 105.15 MHz with the same gain level. All spectra were obtained in the solvent indicated at $25 \text{ }^\circ\text{C}$. IR spectra were measured on Jasco FT/IR-4100 using attenuated Total Reflection (ATR) method with ZnSe prism. Cyclic voltammetry was carried out with an ALS Model 600A instrument and Biologic SP-50 by using a standard three-electrode cell with a glassy carbon electrode, a Pt counter electrode, and an Ag/Ag^+ reference electrode, with scan rate of 200 mV/sec . The concentrations of **V12** and the supporting electrolyte $\{n\text{-Bu}_4\text{N}\}\text{PF}_6$ was 1 and 100 mM , respectively.

Materials. All reagents were obtained from commercial suppliers and were used without further purification. Tetra-*n*-butylammonium salts of **V12(AN)**, **V12(NM)**, **V12(DCM)** and **V12(DCE)** were synthesized following the literature method.¹⁰ Tetra-*n*-butylammonium salts of **V12-free** was prepared by dissolving **V12(DCM)** in acetone and addition of the solution to

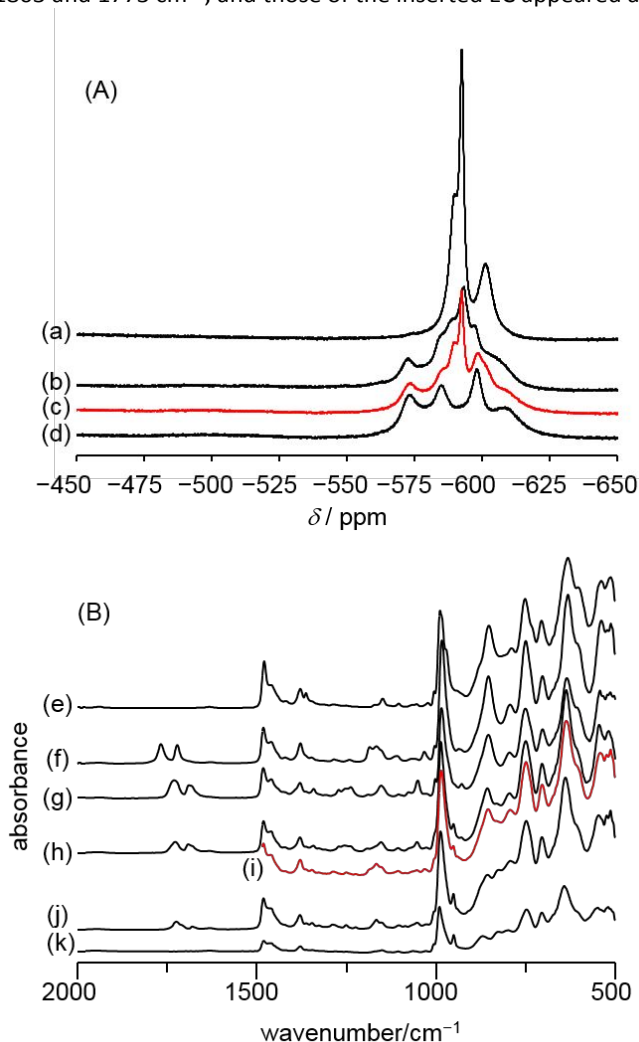


Figure 3. (A) ^{51}V NMR spectra of the **V12-free** dissolved in (a) GBL, (b) DVL, and (d) ECL. The red line represents the simulated spectrum with using spectra (a) and (d) with the ratio of 35:65. (B) IR spectra of (e) **V12(AN)**, the precipitates formed by the rapid addition of diethyl ether to (f) GBL, (h) DVL, and (j) ECL solution of **V12** to the excess amount of EA, (g) the crystalline samples of **V12(DVL)**, (i) the simulated spectrum with using spectra (f) and (j) with the ratio of 35:65, and (k) **V12(AN)**.

excess amount of diethyl ether with vigorous stirring followed by filtration and dryness under inert condition.

Structure conversion from V12-free to V12(guest). V12-free 30 mg (0.014 mmol) was dissolved in 0.5 mL of DMF solution with the required amount of additives (guest molecules). The molar ratio of V12-free and V12(guest) were determined by ⁵¹V NMR spectra with intensity ratio and/or simulated spectra by using the spectrum of the authentic V12-free and that of the samples after the structure conversion.

Conclusions

Into the cavity of half spherical structure composed of VO₅, several electron-rich functional groups are stabilized, even if the cluster possess high anion charge. By monitoring the structure conversion caused by the presence or absence of the guest moiety, the host-guest interaction was evaluated. The V12 host showed the unique affinity with a bromine atom due to the appropriate size to the cavity. The steric structures around the functional groups were affected on the interaction with the cavity. For the insertion of carbonyl group into the cavity, the absence of α -carbon atoms and/or the direction of α -hydrogen atoms is important to fit the cavity.

Complexation of a metal-oxide hole with a single molecule and activation of the functional groups at the cavity entrance was demonstrated here. This molecular level observation helps understanding the inorganic host materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

‡ The peak position was shifted when the solvent system was changed.

§ The cyclic voltammograms of V12(AN) in AN showed two reversible waves at -0.41 and -1.14 V. That of V12-free in acetone showed one reversible wave at -0.57 V and an irreversible reduction peak at -1.37 V. Since the potential was shifted when the solvent system was changed, the comparison in the same solvent system is important (Figure S2).

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Chemo- and Size-Selective Molecule Association of a Bowl-Type Dodecavanadate Cage

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The affinity between a guest molecule and a dodecavanadate host was evaluated by monitoring the structure transformation caused by the presence of a guest molecule or not.

