

Synthesis and Characterization of Chloride-incorporated Dodecavanadate from Dicopper Complex of Macrocyclic Octadecavanadate

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A chloride-incorporated dodecavanadate, $[\text{V}_{12}\text{O}_{32}(\text{Cl})]^{5-}$ (**1**) has been synthesized from a dicopper macrocyclic complex, $[\text{Cu}_2\text{V}_8\text{O}_{24}]^{4-}$ (**2**). By using hydrogen cyanide with a chloride guest anion, two copper cations are removed and the presence of chloride anion template affords a new bowl-shaped dodecavanadate, **1**, with chloride anion at the center. The 1:1 mixture of **1** and $[\text{V}_{12}\text{O}_{32}(\text{CH}_3\text{CN})]^{4-}$ (**3**) in acetonitrile shows no ^{51}V NMR signal scrambling at room temperature suggesting the tight binding of the chloride anion inside the anionic bowl molecule. The dissociation of the chloride anion was only observed at higher temperatures.

The design and synthesis of host oxide-molecules is a current challenge in inorganic chemistry. A bowl-shaped dodecavanadate,¹ $[\text{V}_{12}\text{O}_{32}(\text{CH}_3\text{CN})]^{4-}$ (**3**), is an example of inorganic host molecules which incorporates a guest acetonitrile at the center of a cavity. The nitrile group is oriented inward to the host, and the dissociation of the acetonitrile is possible. Here, we report synthesis and characterization of a chloride-anion-incorporated dodecavanadate. The direct incorporation of a chloride to the dodecavanadate is difficult due to the electronic and steric factors. Thus, we develop a new ship-in-bottle-type synthesis by using an all-inorganic moiety. ^{51}V NMR spectra are then used to understand the binding preference of a chloride anion in the host.

The dodecavanadate host-guest bowl complex may be regarded as an electronically inverse system because of the electron-rich nitrile group pointing inside the anionic cage. The stabilization of the host-guest system was interpreted by ab initio modeling of electrostatic potential distribution.² The entrance of the cavity is nucleophilic as a result of the presence of bridging oxygen lone pairs. The electrophilic environment inside the cavity that is composed of twelve V^{5+} attracts the nitrile molecule at the center of the cage. Benzonitrile guest forms a key and keyhole complex with the dodecavanadate, and the binding preference of acetonitrile over benzonitrile has been reported.³ The incorporation of other guest molecules has not been reported except NO^- .⁴ Chloride incorporation has been studied in reduced polyoxovanadates with the larger spherical frameworks of pentadeca- and octadecavanadates.⁵ The chloride-incorporated polyoxovanadates with a V^{5+} lacunary core of a spherical structure have been reported recently, which is a trilacunary counter part of the reduced pentadecavanadate with a chloride incorporation.⁶

We have been studying new inorganic coordination chemistry between cyclic polyoxovanadates and metal species.⁷ The coordination chemistry of crown inorganic ligand, $(\text{VO}_3)_n^{n-}$, has been established with first row transition elements.⁸ The copper complex $[\text{Cu}_2\text{V}_8\text{O}_{24}]^{4-}$ has an octametallic ring, and the circular geometry of the polyoxovanadate ring is similar to the dodecavanadate bowl entrance. We tried the chloride incorporation reaction by self-condensation utilizing a crown V_8 ring as scaffolding for the synthesis of the dodecavanadate complex. The two separate units may be considered as building blocks of the dodecavanadate bowl: one is a cyclic $(\text{V}_8\text{O}_{24})^{8-}$ unit, which may constitute the rim of the dodecavanadate, and the other is a

$(\text{V}_4\text{O}_{12})^{4-}$ unit which is able to put a cap under the rim to form the bottom of the bowl by the condensation reaction. Hypothetically, the V_8 unit may be equilibrated with the V_4 unit. Thus, to synthesize bowl-type dodecavanadate with an incorporated chloride anion, the reaction condition with the simultaneous presence of the V_8 unit and chloride anion was investigated to drive the reaction to the self-assembly of the V_{12} bowl with chloride incorporation. We tried the in situ formation of the V_8 unit by a template-removing reaction from **2**.

The all-inorganic macrocyclic compound, **2**, was reacted with hydrogen cyanide to remove the template copper atoms. Three equivalents of hydrogen cyanide react in an acetonitrile solution of **2** in the presence of chloride anion.⁹ Two Cu^{2+} ions were removed and the self-condensation allows the chloride anion to be trapped inside the dodecavanadate bowl framework. The colorless crystals of $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Cu}_2(\text{CN})_3]$ were obtained after crystallization of **1** from the filtrate, and the structure of the copper complex was crystallographically identified.¹⁰ The bromide- and iodide-incorporated products were thermally unstable and could not be isolated. For the reaction, the presence of excess chloride anion is essential, while the reaction with stoichiometric amount of chloride anion produces **3**.

To find the template-removing reagent for **2**, the survey experiments were performed by using hydrogen cyanide, sodium cyanide, and ethylenediamine. The best template-removing reagent for **2** was hydrogen cyanide gas to synthesize **1**. When sodium cyanide was used as a template-removing reagent, precipitates were immediately formed and could not be identified. The employment of ethylenediamine as a template-removing reagent leads to an appearance of characteristic blue color which is indicative of the formation of Cu^{2+} complex. However, $\text{V}_4\text{O}_{12}^{4-}$ was formed instead of the bowl molecule because of the basicity of ethylenediamine which forces equilibrium shift to degrade the cyclic species into $\text{V}_4\text{O}_{12}^{4-}$ which was characterized by IR and X-ray crystallography.

Crystal structure determination¹¹ of **1** reveals the chloride-incorporated dodecavanadate framework which is composed of twelve VO_5 square-pyramids as shown in Figure 1, exhibiting an anion inside the polyoxo-anion framework.¹² The framework of dodecavanadate is the same as that of the acetonitrile-incorporated **3**.

In our case, the octametallic entrance of the cage formed by V2, V3, V4, V6, V7, V9, V11, and V10, is distorted in an oval shape by the chloride anion incorporation. In contrast, the acetonitrile-templated dodecavanadate, **3**, has a relatively circular entrance. The position of the chloride anion is completely buried inside the bowl cage, and the distance from the least-squares plane defined by the octametallic entrance is 0.607(2) Å inside the bowl. The $\mu^2\text{-O}$ oxygens at the rim of the bowl entrance provide a nucleophilic environment, which may prevent the dissociation of the chloride anion. The electronic attraction between the chloride anion and the vanadium cations also plays a role to keep the anion inside the anionic cage. The closest contacts of the chloride with

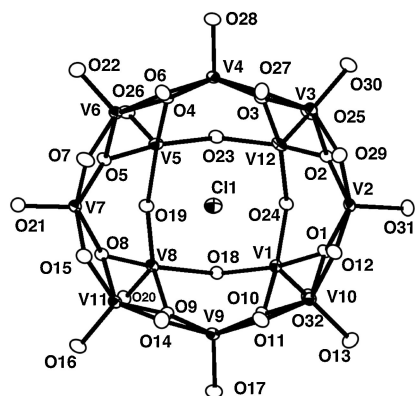


Figure 1. ORTEP view of host-guest anion **1**. Selected distances (Å) are as follows: V–O₁, 1.594(2)–1.608(2); V–μ²-O, 1.750(2)–1.860(2); V–μ³-O, 1.882(2)–1.985(2); V...Cl, 3.1104(7)–3.8690(8), V2...V7, 7.5556(6), V4...V9, 7.1137(6).

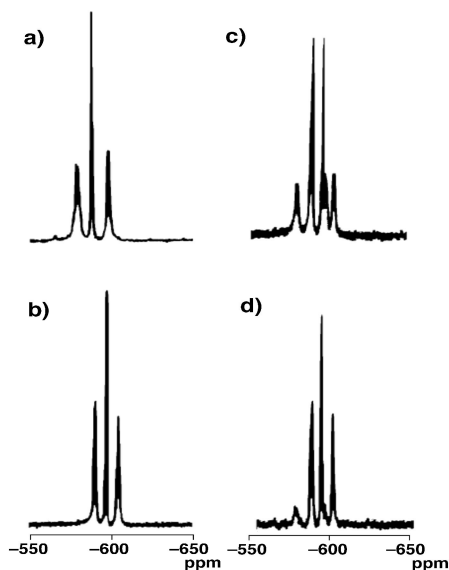


Figure 2. ⁵¹V NMR spectra of a) complex **1**, b) complex **3**, c) 1:1 mixture of complex **1** and **3**, d) after refluxing the mixture c) in acetonitrile.

the bottom of the cage are observed at four vanadiums on V1, V5, V8, and V12 (3.1104(7)–3.1893(8) Å).

The ⁵¹V NMR of **1** in acetonitrile is shown in Figure 2. Three kinds of vanadium environments are distinguished as three signals with 1:1:1 intensity ratio according to the three kinds of chemical environments of vanadium atoms. The signal assignments¹³ are the same as that of **3** (–589, –596, and –604 ppm) with downfield shifts due to the chloride incorporation. The signal at –579 ppm that was assigned as the signal from the bottom of the host (V1, V5, V8, and V12) was broader than the signal of **3** due to the interaction with the chloride anion. ⁵¹V NMR of **1** shows no sign of chloride dissociation for at least for a week at room temperature. To elucidate intermolecular exchange of the chloride anion, ⁵¹V NMR observation of a mixture of 1:1 molar ratio of chloride complex **1** and acetonitrile complex **3** was performed. Overlapping of the signals was observed, and no exchange reaction between those species took place at room temperature. The dissociation of the chloride anion from the cage was observed gradually in

refluxing acetonitrile solution. After the dissociation, rebinding of the chloride anion was not observed, and acetonitrile complex **3** was accumulated in the solution. The irreversible dissociation suggests complex **3** may be the thermodynamically stable form. The experiment in other solvent was not possible due to the poor solubility of complex **1**.

In conclusion, we could successfully trap chloride anion inside a negatively charged dodecavanadate core by ship-in-bottle-type synthesis, and the anion inside the polyoxo-anion is stabilized by a Coulombic interaction between chloride anion and V⁵⁺ centers. The chloride anion is tightly trapped inside the cage, and dissociation is not observed at room temperature. The ability of the host oxide molecules to deliberately open and close the cavity is an interesting feature and may be tailored to functional materials with specific translocation properties.

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- A mixture of **2** (180 mg, 0.1 mmol) and [(C₂H₅)₄N]Cl (400 mg, 2.4 mmol) in acetonitrile (2 cm³) was bubbled with three equivalents of HCN gas. The color of the solution changed to brown, and the mixture was stirred for 1 h at 25 °C to afford the brown precipitation of crude products. The precipitate was dissolved in acetonitrile to give the product as brown crystals (12 mg, 20% based on V). Calcd for C₄₂H₁₀₃N₆ClO₃₂V₁₂: C, 27.25; H, 5.61; N, 4.54; Cl, 1.92%. Found: C, 27.18; H, 5.73; N, 4.50; Cl, 2.07%. IR (Nujol, 500–1000 cm⁻¹): 997(s), 979(s), 968(s), 848(m), 750(m), 721(m), 624(sh), 590(sh). ⁵¹V NMR (CH₃CN, VOCl₃): δ –579 (4V), –587 (4V), –597 (4V).
- Crystal data for [(C₂H₅)₄N][Cu₂(CN)₃]: M_r = 335.4, Orthorhombic, space group *Ibam*, a = 14.892(8), b = 8.110(4), c = 12.180(7) Å, V = 1471(1) Å³, Z = 4, Mo Kα radiation (λ = 0.7107 Å), T = –150 °C, R(R_w) = 0.0295(0.0623), S = 1.02. CCDC: 773453.
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- Crystal data for ((C₂H₅)₄N)₅[V₁₂O₃₂(Cl)]·CH₃CN: M_r = 1851.0, Orthorhombic, space group *Pca2₁*, a = 24.8213(7), b = 14.1901(4), c = 19.7157(5) Å, V = 6944.2(3) Å³, Z = 4, Mo Kα radiation (λ = 0.7107 Å), T = –150 °C, R(R_w) = 0.0200(0.0538), S = 1.08. CCDC: 773452.
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