



Structural conversion from bowl- to ball-type polyoxovanadates: Synthesis of a spherical tetradecavanadate through a chloride-incorporated bowl-type dodecavanadate



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ABSTRACT

A spherical tetradecavanadate, $[V_{14}O_{38}(Cl)]^{7-}$, was synthesized from a chloride-incorporated bowl-type dodecavanadate, $[ClCV_{12}O_{32}]^{5-}$, which was prepared through a template switching reaction from $[Cu_2V_8O_{24}]^{4-}$ using the cation template removal reagent, hydrogen cyanide. X-ray structure analysis revealed a spherical V(V) polyoxovanadate framework, without V(IV) valence state. The two-step process, involving transformation of a disk to a bowl, then transformation from the bowl to a ball, enables the incorporation of a guest anion inside the ball. An alternative route from a hexadecavanadate, which avoids the use of hydrogen cyanide, is also described.

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1. Introduction

The design and synthesis of a host oxide-molecule is a current challenge in inorganic chemistry [1–4]. Super-molecular oxide molecules offer many potential applications, such as molecular recognition, transformation, and translocation. Some giant spherical polyoxomolybdates have been described, including spheres composed of hundreds of metal atoms that exhibited biological cell-like functions that restrict the ability of a guest molecule to move in and out of the cage [5–8]. For translocation, the development of a synthetic route to enable access to the cavity is necessary. The method reported here uses polyoxovanadate, $[ClCV_{12}O_{32}]^{5-}$ [9]. The approach demonstrates a synthetic pathway to spherical polyoxovanadates using a capping reaction on the half-spherical bowl-type molecule, which can complete the sphere after incorporation of a guest anion inside the bowl-type host molecule.

The dodecavanadate $[CH_3CN(CV_{12}O_{32})]^{4-}$ is a basket-shaped host molecule that incorporates an acetonitrile guest at the center of the cavity with the nitrile group and not the methyl group, which was oriented inward toward the anionic basket [10]. The benzonitrile guest complex $[C_6H_5CN(CV_{12}O_{32})]^{4-}$ also has been prepared, with a binding preference of acetonitrile over benzonitrile [11].

Incorporation of guest NO^- anions has also been reported [12]. In the “electronically inverse” host–guest system, which appears to be a seemingly contradictory phenomenon, an anionic guest is placed inside the anionic cage. The electrostatic balances of these clusters with the high-valent vanadium cation are studied by *ab initio* modeling [13,14]. The guest inside the bowl-shaped dodecavanadates are relatively free to dissociate due to their open frameworks.

Host polyoxovanadates with a ball-shaped structure were reported in a mixed valence state of V(V)/V(IV). The encapsulation of small anions, such as $X^-(Cl^-, Br^-, I^-)$, NO_3^- , CO_3^{2-} , N_3^- , ClO_4^- , or CN^- , in an anionic spherical cage were studied utilizing a template effect [15–19]. The electrostatic balance between an anionic template and a polyoxovanadate framework influenced the resulting structure of the sphere; *i.e.*, the combination of weak repulsion with the polyoxovanadate oxygen atoms and the attraction of the vanadium cationic center (the highest valence state of V(V)) controlled the architecture of the anion-templated polyoxovanadate cage. The reduced spherical polyoxovanadates produced a deep blue color due to intervalence transition bands. Instead of the reduced framework, the all-V(V) spherical polyoxovanadates exhibit decreased negative-negative repulsion between the guest anion and host cage, and it is our aim to develop an anion inside anion molecule by taking advantage of the favorable electrostatic balance. The spherical polyoxovanadates in an all-V(V) oxidation state was reported as a lacunary form, $[HV_{12}O_{32}(Cl)]^{4-}$ [20].

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Hybrid materials between organo-arsenate or phosphonate ligands with polyoxovanadates also have been reported through formation of a unique host system that can bind guest anions inside the hybrid cages. In those hybrid complexes, a square arrangement of vanadium atoms in a $[V_4O_8]^{4+}$ unit was used as a capping group in the host system; the square unit plays a fundamental role in anion binding [21–25].

New coordination chemistry involving inorganic ligands of cyclic polyoxovanadates has been developed [26]. Inorganic complexes between a crown-type polyoxovanadate, $(VO_3)_n^{n-}$, and a transition metal cation produced a type of inorganic coordination complexes with a vanadium ring size of $4 < n < 10$, depending on the type of metal cation used as a template [27–30]. To elucidate the reactivity of all-inorganic coordination complexes, a template-removal reaction was developed using the copper complex, $[Cu_2V_8O_{24}]^{4-}$ [31]. Here, the synthesis and structural studies of ball-shaped polyoxovanadate(V) are reported. The course of the synthesis is described in a stepwise manner: copper template removal from the disk-shaped macrocyclic copper complex $[Cu_2V_8O_{24}]^{4-}$ was performed to give bowl-shaped dodecavanadates with a chloride template, $[ClCV_{12}O_{32}]^{5-}$; then the bowl was capped to complete the ball using a Lewis acid to afford $[V_{14}O_{38}(Cl)]^{7-}$ with a structural rearrangement. The ^{51}V NMR spectra were then used to analyze the reaction and elucidate the structure of the complexes. An alternative route to synthesize $[ClCV_{12}O_{32}]^{5-}$ without using hydrogen cyanide also was explored.

2. Experimental

2.1. Materials and methods

All reactions and manipulations were conducted under a nitrogen atmosphere using Schlenk techniques. All reagent-grade chemicals were purchased and used without further purification. The starting complexes, $(n-Bu_4N)_4[Cu_2V_8O_{24}]$, $(Et_4N)_4[Cu_2V_8O_{24}]$ and $(Ph_4P)_2[V_6O_{13}(OCH_3)_6]$ were synthesized according to published procedures [31,32]. The purity of the crystals obtained was confirmed by FT-IR spectroscopy. Acetonitrile was distilled over P_2O_5 under a nitrogen atmosphere and stored in a sealed glass vessel. The UV-Vis spectra were recorded using a Hitachi U-3500 spectrophotometer. The C, H and N elemental analyses were performed at the Research Institute for Instrumental Analysis at Kanazawa University. Elemental analyses of Cl were performed by the Center for Organic Elemental Microanalysis Laboratory at Kyoto University. IR spectra were obtained on samples prepared as Nujol mulls between KBr plates on a Horiba FT-720 spectrophotometer. The ^{51}V NMR spectra were recorded on a JEOL JNM-LA400 spectrometer at 105.04 MHz in CH_3CN . Chemical shifts were externally referenced to neat $VOCl_3$ ($\delta = 0$ ppm). An ALS/CH Instruments electrochemical analyzer (Model 600A) was used for voltammetric experiments. The working electrode was glassy carbon, the counter electrode was Pt wire, and the reference electrode was Ag/Ag^+ . The redox potential ($E_{1/2}$ value) of ferrocene (Fc/Fc^+) versus the Ag/Ag^+ reference electrode was 28 mV with a 58 mV peak separation in our experiments. Electrospray mass spectra were recorded on a micromass LCT mass spectrometer. A 1.0 cm^3 aliquot of an acetonitrile solution was injected directly for ESI MS analysis. The tip of the capillary and the sampling cone were maintained at potentials of -1400 and -2 V, respectively. The source temperature was 25 °C. The m/z values refer to the highest peak of the ion clusters.

2.2. Synthesis of $(Et_4N)_5[ClCV_{12}O_{32}]$ (1)

Method (a). The template removal reaction was performed by bubbling HCN gas into 2 mL of an acetonitrile solution of the mix-

ture of $(n-Bu_4N)_4[Cu_2V_8O_{24}]$ (100 mg, 0.05 mmol) and Et_4NCl (350 mg, 2.1 mmol). A small excess amount of HCN gas was produced from the reaction of sulfuric acid and solid NaCN and bubbled through the mixture solution using a Teflon tube. The color of the solution changed from green to red-brown, and the mixture was stirred at 25 °C. After 1 h, a brown precipitate was produced and collected as a crude product. From the filtrate, colorless crystals of $(Et_4N)[Cu_2(CN)_3]$ were obtained after further crystallization of 1, and the complex was crystallographically identified [9,33]. The precipitate was redissolved in acetonitrile and recrystallized to give the product as brown crystals (30 mg, 33% based on V).

Anal. Calc. for $C_{42}H_{103}N_6ClO_{32}V_{12}$: 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, 1000–500 cm^{-1}): 997(s), 979(s), 968(s), 848(m), 750(m), 721(m), 624(sh), 590(sh). ^{51}V NMR (CH_3CN): $\delta = -579$ (4V), -587 (4V), -597 (4V).

Method (b). To avoid the use of poisonous HCN gas, a coupling reaction of hexamethoxy-hexavanadate was performed. A $(Ph_4P)_2[V_6O_{13}(OMe)_6]$ (500 mg, 0.363 mmol) solution in dichloromethane (12.0 mL) was added to a stock solution of *i*-propanol (4.0 mL) with six equivalents of water and the solution was stirred for several minutes until an orange homogeneous solution was obtained. Complete evaporation of the solvents under reduced pressure gave orange solids. The dried powder was dissolved in dichloromethane (5 mL) followed by addition of Et_4NCl (300 mg, 1.81 mmol). The mixture was stirred for ten minutes followed by addition of diethyl ether, which caused a brown powder to precipitate. The brown powder was collected and washed with dichloromethane, then diethyl ether, and was dissolved in nitromethane (8.0 mL). The addition of diethyl ether was carefully controlled to avoid immediate formation of precipitates and left to allow recrystallization. After one day, 92.9 mg of brown crystals were obtained in a 28% yield based on V. The IR and ^{51}V NMR spectra were identical to the complex synthesized in method (a).

2.3. Synthesis of $(Et_4N)_2(Ph_4P)_3[H_2V_{14}O_{38}(Cl)]$ (2)

A mixture of $(Et_4N)_5[ClCV_{12}O_{32}]$ (80 mg, 0.05 mmol), $n-Bu_4NCl$ (400 mg, 1.4 mmol), and $Co(NO_3)_2 \cdot 6H_2O$ (15 mg, 0.05 mmol) in 2 mL acetonitrile was allowed to stand for 2 days at 25 °C. The addition of Et_4NCl (350 mg, 2.1 mmol) to the mixture produced a brown precipitate after 1 h. The crude product was collected and washed with acetonitrile three times. After suspending the precipitate in acetonitrile, Ph_4PBr (210 mg, 0.5 mmol) was added and stirred to give a red-brown solution. After filtering any undissolved material, brown crystals of $(Et_4N)_2(Ph_4P)_3[H_2V_{14}O_{38}Cl]$ were obtained (10 mg, 9% based on V). **Anal. Calc.** for $C_{88}H_{102}N_2ClO_{38}P_3V_{14}$: C, 40.08; H, 3.90; N, 1.06; Cl, 1.34. Found: C, 39.76; H, 3.93; N, 1.10; Cl, 1.28%. IR (Nujol, 1000–500 cm^{-1}): 978(s), 914(w), 842(s), 787(w), 750(m), 721(s), 688(w), 647(m), 522(w). ^{51}V NMR (CH_3CN): $\delta = -547$ (2V), -567 (2V), -579 (6V), -592 (4V).

2.4. Synthesis of $(Et_4N)_5[H_2V_{14}O_{38}(Cl)]$ (2a)

The addition of $ZrOCl_2 \cdot 8H_2O$ (58 mg, 0.181 mmol) in 1.0 mL methanol to a 10 mL dichloromethane solution of $(Ph_4P)_2[V_6O_{13}(OMe)_6]$ (500 mg, 0.363 mmol) gave a homogeneous solution that was stirred overnight. After filtering pale-yellow material, brown crystals were obtained by adding 40 mL of diethyl ether with diffusion of ethyl acetate into the solution. Yields: 72.5 mg, 23% based on V.

Anal. Calc. for $C_{40}H_{102}N_5ClO_{38}V_{14}$: C, 23.90; H, 5.12; N, 3.48. Found: C, 23.89; H, 5.02; N, 3.48%. IR (KBr, 1000–500 cm^{-1}): 984(s), 849(s), 789(w), 760(m), 660(m), 592(w). ^{51}V NMR (CH_3CN): $\delta = -545$ (2V), -566 (2V), -579 (6V), -589 (4V).

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