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# Three New Organically Templated 1D, 2D, and 3D Vanadates: Synthesis, Crystal Structures, and Characterizations

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Three new vanadate compounds of the formulas $(C_2N_2H_{10})VO(OH)_4$ (**I**), $(NH_4)_3(C_3N_2H_5)V_4O_{10}$ (**II**), and $V(OH)_3 \cdot 0.97H_2O$ (**III**) have been synthesized by a solvothermal method and characterized by IR spectroscopy, elemental analysis, and thermogravimetric analysis. The crystal structures of the above three vanadates have been established by single-crystal X-ray diffraction. Compound **I** crystallizes as tetragonal, space group $P4/mmm$, with $a = 9.0465(11)$ Å, $c = 3.9897(10)$ Å, $V = 326.51(10)$ Å$^3$, and $Z = 2$. Compound **II** crystallizes as orthorhombic, space group $Immm$, with $a = 3.6012(10)$ Å, $b = 11.312(4)$ Å, $c = 15.050(4)$ Å, $V = 613.1(3)$ Å$^3$, and $Z = 2$. Compound **III** crystallizes as cubic, space group $Fd\bar{3}m$, with $a = 10.4252(17)$ Å, $V = 1133.1(3)$ Å$^3$, and $Z = 16$. Structural analyses reveal a one-dimensional beeline-chained structure, which consists of $VO_6$ octahedra in **I**. Compound **II** possesses a two-dimensional V–O-layered structure formed by $VO_5$ square pyramids; protonated imidazole and remaining $NH_4^+$ cations are inserted between the layers. The three-dimensional open framework of **III** with the pyrochlore type consists of $V_{12}$ and $V_4$ secondary building units by using $VO_6$ octahedra as building units.

## Introduction

There is considerable current interest in V−O cluster compounds because of their diverse properties, with applications to electrical chemistry, catalysis, sorption clathration, and photochemistry.[1−4] Structurally determined examples included discrete vanadates,[5−8] one-dimensional (1D) linear vanadates,[9,10] and two-dimensional (2D) layered vanadium compounds.[11−19] In the past few years, an important advance in vanadate chemistry has been the study of the assembly of V−O cluster anions and V−O layers with an inorganic or bridging transition-metal complex into extended three-dimensional (3D) frameworks,[20−25] because of the remarkable

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features of vanadium oxide surfaces and selective adsorption. Some reported open-framework materials such as $[M_3V_{18}O_{42}(H_2O)_{12}(XO_4)]\cdot 24H_2O$ (M = Fe, Co; X = V, S)[20] and $[\{Cu(1,2\text{-}pn)_2\}_7\{V_{16}O_{38}(H_2O)\}_2]\cdot 4H_2O$[21] have been structurally determined to have 3D structures constructed by V−O cluster anions and bridging transition-metal cations, while 3D frameworks for $[Co_2(ppca)_2(H_2O)(V_4O_{12})_{0.5}]$[26] and $[N(CH_3)_4]_2[Co(H_2O)_4V_{12}O_{28}]$[27] are built by V−O layers and bridging groups. One of the strategies used for the preparation of 3D vanadates is to employ a hydrothermal technique as a synthesis method. The reported successful examples included vanadosilicates[28,29] and vanadophosphites.[30,31] Although many porous silicate and germanate frameworks were determined to have only one type of $SiO_4$ and $GeO_x$ polyhedra, but no 3D vanadates constructed by one type of $VO_x$ polyhedra were reported until now because of the difficulty of controlling the connection of $VO_x$ polyhedra. Here, we present the synthesis and structural determinations of three new vanadates: $(C_2N_2H_{10})VO(OH)_4$ (**I**), $(NH_4)_3(C_3N_2H_5)V_4O_{10}$ (**II**), and $V(OH)_3\cdot 0.97H_2O$ (**III**). In **I**, the linear chains constructed from $VO_6$ octahedra are surrounded by organic amines, while **II** and **III** show 2D and 3D inorganic frameworks, respectively. In the first $VO_6$ octahedra building a 3D open pyrochlore structural framework[32−37] of **III**, the $H_2O$ molecule templates a $V_{12}$ cage and locates at the center of the cage.

## Experimental Section

**General Remarks.** All chemicals purchased were of reagent grade and were used without further purification. The crystalline product was characterized by thermal analysis, powder X-ray diffraction (XRD), single-crystal XRD, and IR spectrometry. The C, H, and N elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. As, V, and B were determined by a Leeman inductively coupled plasma (ICP) spectrometer. IR spectra were recorded from KBr pellets on a Nicolet 170SXFT/IR spectrometer. Thermogravimetric (TG) analyses were carried out on a Diamond TG/DTA instrument (Perkin-Elmer) thermal analyzer (50−1100 °C) under a $N_2$ atmosphere at a scan rate of 10 °C/min.

**Synthesis of $(C_2N_2H_{10})VO(OH)_4$ (I).** First, a mixture of $NH_4VO_3$ (0.23 g), ethylenediamine (0.15 g), and HF (0.2 mL, 40%) was dissolved in $H_2O$ (1.02 g) and glycol (4.31 g) in a molar ratio of 2:2.5:4:57:69. Then it was stirred for ca. 20 min in air and sealed in a 18-mL Teflon-lined reactor, which was heated at 160 °C for 6 days. Green prism crystals were isolated after being cooled to room temperature, filtered off, and washed with distilled $H_2O$ (0.13 g, yield 32.99% based on V). Elem anal. Calcd: C, 12.18; N, 14.21; H, 7.10; V, 25.89. Found: C, 12.14; N, 14.18; H, 7.05; V, 25.52. The IR spectrum of **I** exhibits intense bands at around 3007 $cm^{-1}$ that correspond to the O−H and N−H stretching vibrations, while the bending bands of $CH_2$ and $NH_2$ groups are present in the 1561−1325 $cm^{-1}$ region. The bands around 1060−1019 $cm^{-1}$ are attributed to the V−O−H bending mode, which can be compared with those in other vanadates.[9] The strong band at 522 $cm^{-1}$ is due to the $V^{IV}-O-V^{IV}$ stretching vibration.

**Synthesis of $(NH_4)_3(C_3N_2H_5)V_4O_{10}$ (II).** Typically, a mixture of $NH_4VO_3$ (0.23 g), imidazole (0.27 g), $H_3AsO_4$ (0.60 g, 66.87%), and $H_2O$ (2.50 g) in a molar ratio of 2:4:2.83:139 was stirred for ca. 20 min in air, and then it was transferred to and sealed in a 18-mL Teflon-lined reactor and kept at 160 °C for 5 days. After being cooled to room temperature, filtered off, and washed with distilled $H_2O$, black prism crystals were obtained (0.15 g, yield 61.60% based on V). Elem anal. Calcd: C, 7.39; N, 14.37; H, 3.49; V, 41.89. Found: C, 7.42; N, 14.41; H, 3.56; V, 42.06. The ICP analysis showed that As was not incorporated in the final product, and compound **II** cannot be obtained without $H_3AsO_4$. The IR spectrum of **II** exhibits bands at around 3163−3061 $cm^{-1}$ that are due to the N−H stretching mode, while the intense bands at 1578 and 1417 $cm^{-1}$ are attributed to the bending vibrations of the $CH_2$ and $NH_2$ groups. The strong band at 985 $cm^{-1}$ is due to the terminal V═O stretching, while the bands in the 865−559 $cm^{-1}$ region are attributed to $\nu$(V−O−V).

**Synthesis of Compound III.** First, a mixture of $V_2O_5$ (0.18 g), tetramethylammonium hydroxide (0.21 g, 25%), and HF (0.2 mL, 40%) was dissolved in $H_2O$ (0.49 g) and glycol (3.56 g) in a molar ratio of 1:0.6:4:27:57. Then it was stirred for 20 min in air and sealed in a 18-mL Teflon-lined reactor, which was heated at 160 °C for 5 days. The resulting dark-green hexagonal block crystals of **III** were isolated after being cooled to room temperature, filtered off, and washed with distilled $H_2O$ (0.07 g, yield 29.29% based on V). The IR spectrum of **III** reveals that the band at 3448 $cm^{-1}$ is characteristic of $OH^-$. The bands at around 845−560 $cm^{-1}$ are attributed to V−O stretching vibrations.

**Single-Crystal Structure Determinations.** The single crystals of all three compounds were chosen and glued to a thin glass fiber by epoxy glue in air for data collection. The diffraction data were collected on a Bruker Apex2 CCD with Mo Kα radiation ($\lambda$ = 0.710 73 Å) at 293 K using the $\omega-2\theta$ scan method. An empirical absorption correction was applied. The structures were solved by direct methods and difference Fourier synthesis. The V atom is located directly, while the remaining O, C, and N atoms are found from difference Fourier synthesis for the three compounds. Crystal data collection, parameters, and refinement statistics for **I**−**III** are listed in Table 1. All of the non-H atoms were refined anisotropically, while the H atoms of organic amine molecules for **I** and **II** were refined in calculated positions, assigned isotropic thermal parameters, and allowed to ride their parent atoms. All calculations were performed using the *SHELXTL-97* program package.[38]

## Results and Discussion

**Compound I.** The asymmetric unit of **I** (Figure 1) contains two crystallographically independent V atoms, but both have

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**Table 1.** Crystal Data and Structure Refinement Parameters for **I**−**III**

| compound | **I** | **II** | **III** |
|---|---|---|---|
| empirical formula | $C_2H_{14}N_2O_5V$ | $C_3H_{17}N_5O_{10}V_4$ | $H_{4.94}O_{3.97}V$ |
| fw | 197.09 | 486.98 | 119.49 |
| $T$ (K) | 293(2) | 293(2) | 293(2) |
| wavelength (Å) | 0.710 73 | 0.710 73 | 0.710 73 |
| crystal system | tetragonal | orthorhombic | cubic |
| space group | $P4/mmm$ | $Immm$ | $Fd\bar{3}m$ |
| $a$ (Å) | 9.0465(11) | 3.6012(10) | 10.4252(17) |
| $b$ (Å) | 9.0465(11) | 11.312(4) | 10.4252(17) |
| $c$ (Å) | 3.9897(10) | 15.050(4) | 10.4252(17) |
| $V$ (Å$^3$) | 326.51(10) | 613.1(3) | 1133.1(3) |
| $Z$ | 2 | 2 | 16 |
| $\rho$ (g/cm$^3$) | 2.005 | 2.638 | 2.802 |
| $\mu$ (mm$^{-1}$) | 1.491 | 3.023 | 3.293 |
| $\theta$ range (deg) | 2.25−25.40 | 2.25−25.99 | 3.38−24.85 |
| $R$ [$I > 2\sigma(I)$] | R1 = 0.0569, wR2 = 0.1605 | R1 = 0.0370, wR2 = 0.1111 | R1 = 0.0669, wR2 = 0.1545 |
| $R$ (all data) | R1 = 0.0649, wR2 = 0.1692 | R1 = 0.0394, wR2 = 0.1125 | R1 = 0.0836, wR2 = 0.1669 |

the same chemical environment. Each V atom is coordinated by six O atoms, while $VO_6$ octahedra connect with each other by sharing the corners to generate a linear $[VO_2(OH)_4]_n$ chain, in which O(2) and O(4) act as two bridging O atoms and coordinate to adjacent V atoms. Interestingly, because the angles for V−$O_{2b}$−V are 180°, the $[-V-O-]_n$ chain is a beeline, which is very rare compared with other 1D chain vanadates.[9,10] The OH groups [O(3) and O(1)] are terminally bonded to V atoms with V−O distances of 1.876(9)−1.895(6) Å, which are much longer than the V−$O_t$ (terminal O) distances and similar to the V−$O_b$ distances in the reported vanadates. Fully protonated ethylenediamine cations adopt this high symmetry ($D_{4h}$) by using disorder. As shown in Figure 2, adjacent organic amines are involved in hydrogen-bonding inter-reaction with each other to make a soft organic framework. The $[VO_2(OH)_4]_n$ chains are ordered in the channels and separated by the organic amines. The shortest V⋯V distance from adjacent V−O chains is 6.40(2) Å. Compared with $(C_2N_2H_{10})V_4O_{10}$,[16] the same organic amine was used in the synthesis. However, the difference is that **I** has a very unusual linear $V^{IV}-O-V^{IV}$ chain, while $(C_2N_2H_{10})V_4O_{10}$ possesses a layered structure, with protonated ethylenediamine occupying the interlayer space. The bond distances for V−O vary from 1.876(9) to 1.9949(5) Å, which can be compared with those in $(C_2N_2H_{10})V_4O_{10}$. Bond-valence-sum (BVS) calculations[39] [V(1) = 3.88 and V(2) = 4.03] indicate the valence state of V to be 4+, which is in agreement with the charge balance in **I**.

**Compound II.** The asymmetric unit of **II** contains nine non-H atoms, of which four belong to the 2D inorganic framework with one crystallographically distinct V atom and three O atoms. There are three types of O atoms: terminal, two-bridging, and three-bridging. As shown in Figure 3, each V atom is coordinated by five O atoms that include one terminal, one two-bridging, and three three-bridging, while adjacent $VO_5$ square pyramids connect with each other by sharing the edges to make a V−O layer, which are similar to the reported 2D vanadates.[11−19] The V−O distances vary from 1.611(4) to 1.978(4) Å, while the distance between the layers is about 7.5 Å. Interestingly, the $NH_4^+$ cation involves hydrogen bonding with the terminal O atoms from the inorganic framework to template a soft double four-membered (D4R) ring, as shown in Figure 4. The N⋯O distances are 2.92(2) Å. Adjacent V−O layers are connected through the D4R rings to generate a zeolite-like inorganic framework with eight-membered ring channels along the

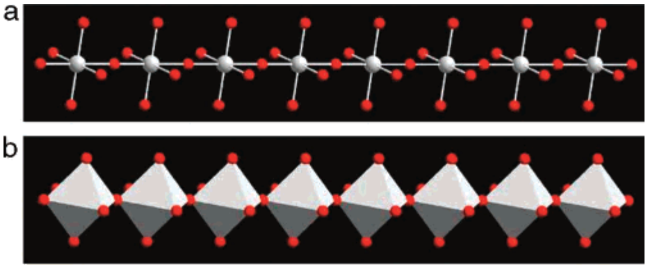

**Figure 1.** (a) 1D beeline-chained structure of **I**, in which O(2) and O(4) act as two-bridging O atoms and coordinate to adjacent V atoms to form a linear $[VO_2(OH)_4]_n$ chain (H atoms are omitted). (b) Polyhedral view of the 1D chained structure of **I**, showing the $VO_6$ octahedra connected with each other by sharing corners to generate a chained structure of **I**.

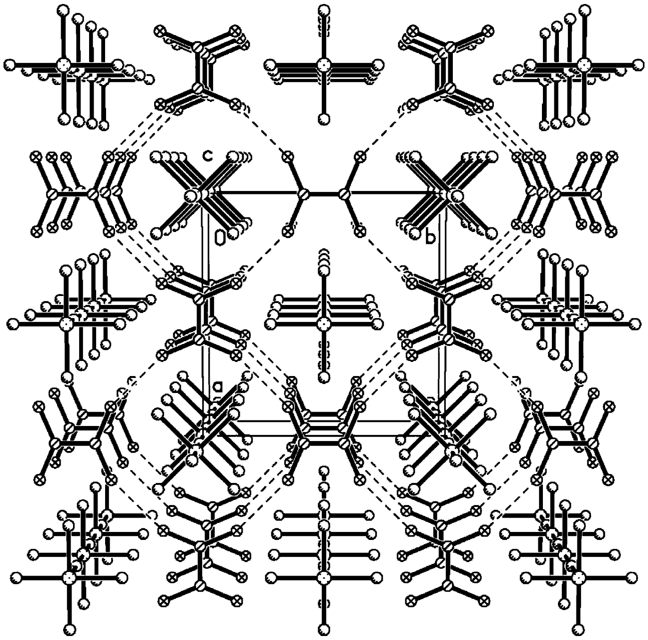

**Figure 2.** Packing view of **I** along the $c$ axis showing the adjacent organic amines involved in a hydrogen-bonding inter-reaction with each other to make a soft organic framework. The $[VO_2(OH)_4]_n$ chains are inserted in the channels and separated by the organic amines (all H atoms are omitted for clarity).

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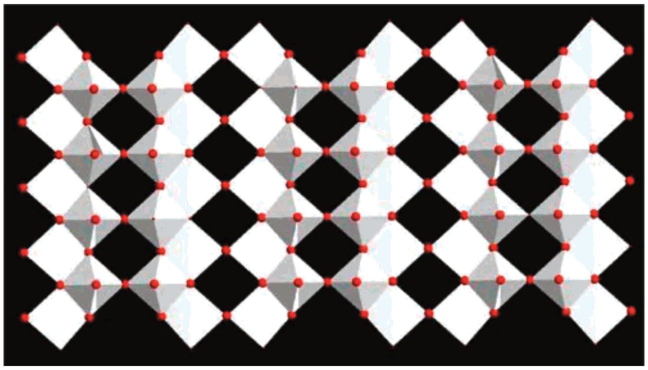

**Figure 3.** Polyhedral view of the V−O layer in **II** formed by $VO_5$ square pyramids connecting with each other by sharing edges.

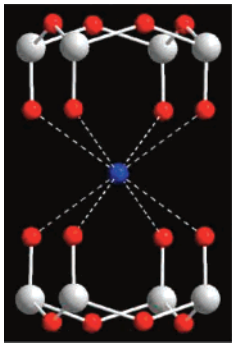

**Figure 4.** Double four-membered (D4R) ring found in **II**.

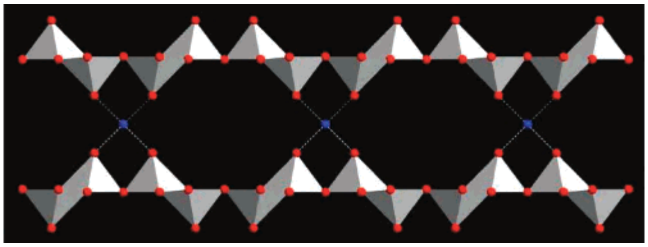

**Figure 5.** 2D inorganic framework of **II** with eight-membered-ring channels along the (1, 0, 0) direction generated by the adjacent V−O layers through hydrogen bonding.

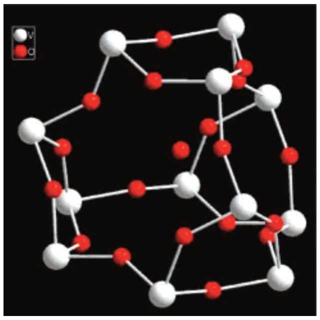

**Figure 6.** Building unit of the $V_{12}$ cage in **III**. The $H_2O$ molecule is located at the center of the $V_{12}$ cage.

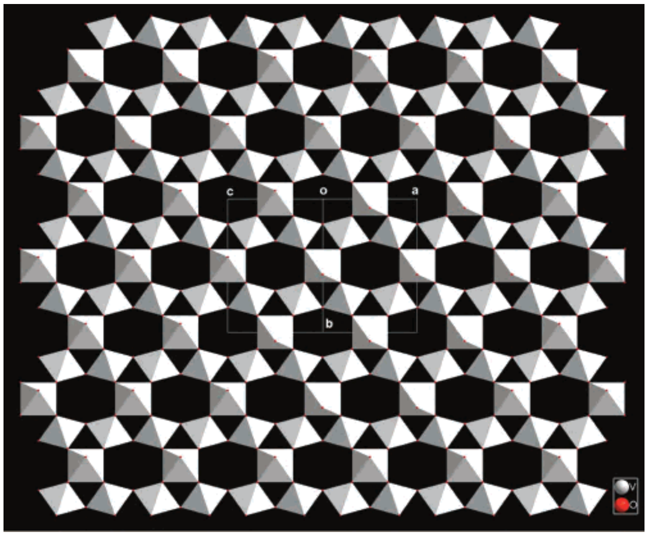

**Figure 7.** Polyhedral view of the framework of **III** with interesting six-membered-ring channels (all H atoms are omitted for clarity).

crystallographic (1, 0, 0) direction (Figure 5). As the second structure-directing agent (SDA), protonated imidazole molecule and the remaining $NH_4^+$ cations occupy the eight-membered channels. The oxide state for V is confirmed by BVS calculations [V(1) = 4.38], which indicate the valence state of V to be 4+.

**Compound III.** The single-crystal X-ray structural analysis reveals a pyrochlore structural 3D open framework[32−37] of **III**, which consists of $V_{12}$ and $V_4$ SBUs sharing faces. As shown in Figure 6, three $VO_6$ octahedra share corners to make a three-membered ring, while six $VO_6$ octahedra share corners to make a six-membered ring. Furthermore, three six-membered rings and three three-membered rings are connected by sharing edges to generate a $V_{12}$ cage. A $V_4$ SBU is also found in the framework of **III**, which is generated by connecting the three three-membered rings through the sharing of common edges. Two neighboring $V_{12}$ and $V_4$ SBUs are linked by bridging O atoms to yield an open framework with interesting six-membered-ring channels (Figure 7). Each $V_{12}$ cage is surrounded by six $V_4$ SBUs, and each $V_4$ unit is further surrounded by three $V_{12}$ cages along the (1, 1, 1) direction. The diameter of each six-membered ring is 5.0 Å, approximately. Because vanadate **III** crystallizes in high-symmetry cubic $Fd\bar{3}m$, there is only one crystallographically independent V atom, which is coordinated by six O (OH) atoms. The V−O bond distance is 1.9630(18) Å and O−V−O angles vary from 89.1(2) to 180.0(3)°, which are in agreement with those found in reported $V^{III}$ compounds.[9] The shortest distance of V−V is 3.6 Å in both SBUs, while angles of V−V−V are 120° in three-membered rings. The oxide state for V is confirmed by BVS calculations [V(1) = 3.30], which show the valence state of V is 3+. Although tetramethylammonium hydroxide is not included in the final product, it is necessary to reduce $V^V$ to $V^{III}$. The same reaction of $V^V$ ($V_2O_5$) → $V^{III}$ has been found in the formation of $(C_2N_2H_{10})[V^{III}(OH)(SO_4)_2]\cdot H_2O$ under similar synthesis conditions.[9]

As the SDA, the $H_2O$ molecule is located at the center of the $V_{12}$ cage (Figure 6). The $H_2O$ molecule exerts SDA effects by using $O-H\cdots O_w$-type hydrogen bonding. The shortest distance between the $H_2O$ molecule and the O atom from the framework is 2.93(2) Å, while the angle of $O-H\cdots O_w$ is 166.9(3)°. The $H_2O$ molecules have been adapted to high symmetry by using disorder with an occupied factor of 0.487(13).

**TG Analyses. Compound I.** TG analysis of **I** reveals that the total weight loss is 58.29% in the temperature range 50−1100 °C, which is attributed to the release of $C_2N_2H_8$ (ethylenediamine) and structural $H_2O$. Because the TG analysis was carried out under a $N_2$ atmosphere, the final product is $VO_2$. The calculated value (57.84%) for $C_2N_2H_8$ (30.44%) and structural $H_2O$ (27.40%) is in good agreement with the observed value.

**Compound II.** The TG curve indicates that the total weight loss of **II** is 32.35% from 50 to 900 °C, which is attributed to the release of $NH_3$, $C_3N_2H_4$ (imidazole), and structural $H_2O$. The final product is $VO_2$ in a $N_2$ atmosphere. This is in good agreement with the calculated value (31.82%) for $NH_3$ (10.47%), $C_3N_2H_4$ (13.96%), and structural $H_2O$ (7.39%).

**Compound III.** The TG curve of **III** shows two stages for the lost weight. The first stage occurs between 50 and 325 °C with a weight loss of 12.50%. The second weight loss is 22.20% from 325 to 900 °C. These are in agreement with the calculated values for guest $H_2O$ (14.61%) and structural $H_2O$ (22.60%). The open framework of **III** is unstable to remove $H_2O$ molecules, while the final product is $V_2O_3$ (TG analysis was carried out under a $N_2$ atmosphere).

## Conclusions

In conclusion, three new vanadates of 1D, 2D, and 3D have been synthesized under solvothermal conditions, in which **I** and **II** are organically templated by ethylenediamine and imidazole, respectively. Furthermore, this work demonstrates that a solvothermal method is another route to obtaining new vanadate frameworks. The formation of $V_{12}$ and $V_4$ SBUs in **III** suggests that there will be many potential implications of vanadates as new candidates for the model of zeolites and catalysis.

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**Supporting Information Available:** Molecule structures, TG curves, and selected bond lengths and angles of **I**−**III**, the smallest $V_4$ cage in **III**, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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