

Hydrothermal Synthesis and Characterization of $(\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3)[\text{V}_6\text{O}_{14}]$

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A new layered vanadium oxide $(\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3)(\text{V}_6\text{O}_{14})$ was synthesized hydrothermally under autogenous pressure at 180°C for 48 h from a mixture of $\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2$ and V_2O_5 in aqueous solution. Its structure was determined from single-crystal X-ray diffraction at room temperature with final $R = 0.0774$ and $R_w = 0.0893$. It crystallizes in the monoclinic system (space group $P2_1/n$ with $a = 9.74(2)$ Å, $b = 6.776(5)$ Å, $c = 12.60(2)$ Å, $\beta = 96.1(1)^\circ$, $V = 827(2)$ Å³ and $Z = 2$). This compound contains mixed-valence $\text{V}^{5+}/\text{V}^{4+}$ vanadium oxide layers built from $[\text{V}^{\text{V}}\text{O}_4]$ tetrahedra and pairs of edge-sharing $[\text{V}^{\text{IV}}\text{O}_5]$ square pyramids with protonated organic amines occupying the interlayer space. © 2002 Elsevier Science (USA)

Key Words: vanadium oxides; 1,4-diaminobutane; hydrothermal synthesis; X-ray diffraction.

INTRODUCTION

The hydrothermal process in combination with organic templates has been used to synthesize a large family of layered vanadium oxides (1, 2). The crystalline V_2O_5 is currently used as a precursor and several vanadium oxides have been recently synthesized using amines, ammonium cations ($\text{N}(\text{CH}_3)_4^+$, CH_3NH_2) or diamines $\text{H}_2\text{N}-(\text{CH}_2)_n-\text{NH}_2$ ($n = 2, 3, 4$) as organic templates (3–5). They all exhibit a layered structure in which protonated amines are inserted between negatively charged vanadium oxide planes. It has been shown that the structure of the layers and particularly the coordination of vanadium centers are strongly dependent on the pH of the aqueous solution (1, 6). At a pH close to 7, vanadium oxide layers are currently built of $[\text{VO}_4]$ tetrahedra and $[\text{VO}_5]$ square pyramids and vanadium may exhibit both V^{IV} and V^{V} oxidation states. With ethylenediamine, it is possible to obtain the layered vanadium oxide $(\text{H}_3\text{N}-(\text{CH}_2)_2-\text{NH}_3)[\text{V}_4\text{O}_{10}]$ which is built from $[\text{V}^{\text{IV}}\text{O}_5]$ square pyramids

pairs sharing edges that are linked to six $[\text{V}^{\text{V}}\text{O}_4]$ tetrahedra (5, 4(a)). A diaminopropane analog was synthesized under slightly more acidic conditions (final pH 5). The inorganic framework of this vanadium oxide is the same that of $(\text{H}_3\text{N}-(\text{CH}_2)_2-\text{NH}_3)[\text{V}_4\text{O}_{10}]$ except that it differs in the way the layers are packed (7). Another vanadium oxide with a similar inorganic framework was also prepared with piperazine $\text{HN}(\text{C}_2\text{H}_4)_2\text{NH}$ at a pH close to 7. The only structural difference is the larger interlayer spacing due to the larger piperazine cations (5).

This paper deals with the synthesis and structure determination of a new mixed valence polyvanadate $(\text{H}_3\text{N}(\text{CH}_2)_4-\text{NH}_3)[\text{V}_6\text{O}_{14}]$ obtained via the hydrothermal treatment of V_2O_5 in the presence of 1,4-diaminobutane. With this diamine, the vanadium oxide $(\text{H}_3\text{N}-(\text{CH}_2)_4-\text{NH}_3)[\text{VO}_3]_2$ with a different structure was already reported (8). An effort is made to discuss the reaction conditions which are significant in the vanadium oxides formation.

EXPERIMENTAL

Hydrothermal Synthesis

The title compound $(\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3)[\text{V}_6\text{O}_{14}]$ was prepared from V_2O_5 (0.207 g, Aldrich 99%), 1,4-diaminobutane (0.1 g, Aldrich 99.6%) and distilled H_2O (5 mL) in a molar ratio of 1:1:245. The mixture was heated under hydrothermal conditions (48 h, 180°C) in a Parr Teflon-lined digestion bomb. Before and after the hydrothermal process, the pH of the solution was constant ($\text{pH} \approx 9$). Black plate-like crystals are precipitated from the solution. The precipitate is filtered, washed with acetone and dried in air at 60°C .

Characterization

Structure determination. Measurements were collected at room temperature on a Enraf-Nonius KAPPA

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automatic four-circle diffractometer using MoK α radiation ($\lambda = 0.71069 \text{ \AA}$) and graphite monochromator.

Details concerning the crystallographic data collection and structure determination for compound (1) are given in Table 1.

Cell dimensions were determined from 25 reflections dispersed in reciprocal space. Two standard reflections were monitored every 2 h during data collection to check crystal orientation and the absence of decomposition. The space group $P2_1/n$ was established by systematic absences. Intensities were corrected for Lorentz and polarization factors and an empirical absorption correction was applied

TABLE 1
Crystal Data and Structure Refinement
for $(\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3)[\text{V}_6\text{O}_{14}]$

Chemical formula	$(\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3)[\text{V}_6\text{O}_{14}]$
M (g mol^{-1})	613.76
Crystal system	monoclinic
Space group	$P2_1/n$
Z	2
Description	Black plate-like crystal
Size (mm)	$2 \times 0.4 \times 0.05$
Temperature (K)	295
<i>a</i> (\AA)	9.74(2)
<i>b</i> (\AA)	6.776(5)
<i>c</i> (\AA)	12.60(2)
α ($^\circ$)	90
β ($^\circ$)	96.1(1)
γ ($^\circ$)	90
<i>V</i> (\AA^3)	827(2)
<i>F</i> (000)	595.40
<i>D_c</i> (g cm^{-3})	2.49
μ (cm^{-1})	33.25
Diffractometer type	KAPPA
Radiation type	MoK α
Wavelength (\AA)	0.710690
Scan type	$2\Theta/\Omega$
Reflections measured	1675
Independent reflections	1440
Reflections used	810 ($I > 3\sigma(I)$)
<i>R_{int}</i>	0.10
Θ_{\min} , Θ_{\max}	1–25.00
<i>H_{min}</i> , <i>H_{max}</i>	0–11
<i>K_{min}</i> , <i>K_{max}</i>	0–8
<i>L_{min}</i> , <i>L_{max}</i>	–14–14
Refinement	On <i>F</i>
<i>R</i> -factor ^a	0.0774
Weighted <i>R</i> -factor ^b	0.0893
$\Delta\rho_{\min}$	–1.48
$\Delta\rho_{\max}$	1.33
No. of parameters	85
Goodness of fit	1.039
Abs correction	DIFABS (min:0.91; max : 1.05)

Note. Weighting scheme of the form $w = w'[1 - ((|F_o| - |F_c|)/6\sigma(F_o))^2]$ with $w' = 1/\sum_r A_r T_r(X)$ with coefficients 1.47, 0.776 and 0.795 for a Chebychev series for which $X = F_c/F_c(\max)$.

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b R_w = [\sum (w||F_o| - |F_c||)^2 / \sum wF_o^2]^{1/2}.$$

(9). The structure was solved using direct method with SHELXS program (10). Successive Fourier maps were used to locate the positions of all atoms. For the non-hydrogen atoms, full matrix least-squares refinement of atomic parameters and thermal parameters were carried out using CRYSTALS programs (11). Vanadium, carbon and nitrogen atoms were refined anisotropically, while oxygen atoms were refined isotropically. All hydrogen atoms were included in calculated positions with isotropic displacement parameters. The form factors were provided by CRYSTALS (11).

A ^{51}V NMR solution spectrum was recorded on a Bruker AC 300 spectrometer operating at 78 MHz, using a 90° pulse width of 11 μs , and a relaxation delay of 1 s. Pure VOCl_3 was used as an external reference for chemical shifts ($\delta = 0$ ppm). Four hundred FIDs were accumulated.

Thermogravimetric analyses were carried out under an oxygen flux of $5 \text{ cm}^3 \text{ min}^{-1}$ at a heating rate of 5°C min^{-1} using a Netsch STA 409 thermogravimetric analyser.

RESULTS AND DISCUSSION

Structure Description

The structure of the title compound was determined by single-crystal X-ray diffraction. Two polyhedral representations are shown in Figs. 1 and 2. Fractional coordinates for non-hydrogen atoms, as well as selected bond distances and angles are given in Tables 2 and 3, respectively.

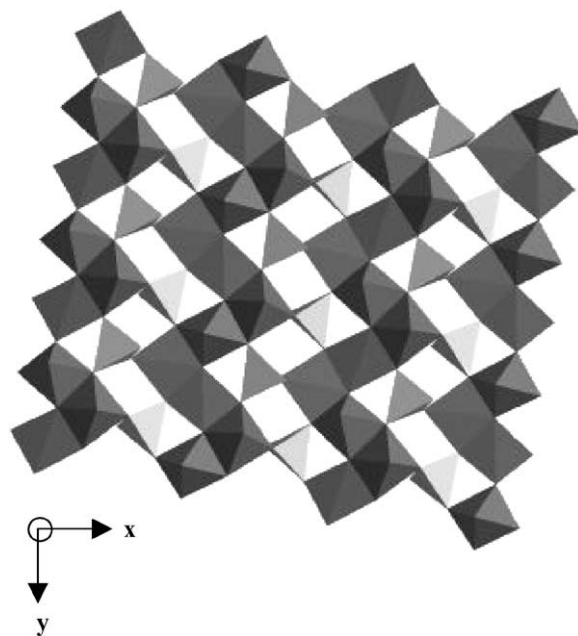


FIG. 1. Projection of the structure of $(\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3)[\text{V}_6\text{O}_{14}]$ along $[001]$.

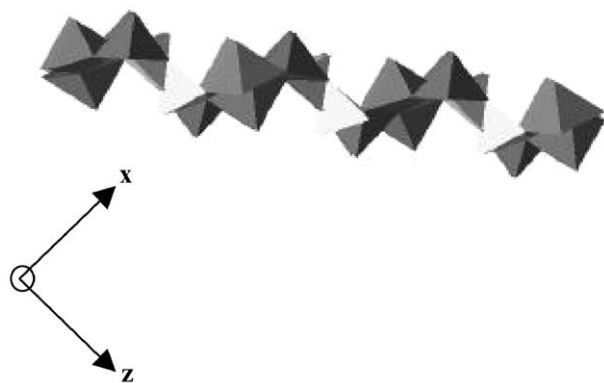


FIG. 2. Projection of the structure of (H₃N(CH₂)₄NH₃)[V₆O₁₄] along [010].

A similar structure was already described in several layered vanadium oxides as the V₃O₇ structure is one of the most prevalent of those found (6, 12–14). First described by Nazar *et al.* for the compound (DABCO)[V₆O₁₄]·H₂O (12), the structure is made of both [VO₅] square pyramids and [VO₄] tetrahedra. There are three non-equivalent vanadium sites in the structure of (H₃N(CH₂)₄NH₃)[V₆O₁₄]. V(1) and V(2) have a distorted square-pyramidal environment, while V(3) is in a tetrahedral coordination environment. V–O bond distances of VO₅ square pyramids are in the range 1.601(8)–2.03(1) Å and O–V–O bond angles in the range 76.8(4)–152.1(3)°. The V(3)O₄ tetrahedron has bond distances in the range 1.60(1)–1.821(9) and O–V–O bond angles in the range 107.4(5)–110.7(4)°. The oxidation state of vanadium is +4 in [VO₅] and +5 in [VO₄]. This assignment of oxidation state is consistent with

TABLE 2
Atomic Coordinates and Displacement Parameters (Å²)
for (H₃N(CH₂)₄NH₃)[V₆O₁₄]

Atom	x	y	z	U_{eq}/U_{iso}^a
V(1)	0.52273(19)	−0.2441(3)	0.17502(15)	0.0186
V(2)	0.71523(19)	0.0134(3)	0.29455(15)	0.0185
V(3)	0.9887(2)	−0.2456(4)	0.40557(16)	0.0201
C(1)	1.1132(15)	−0.148(2)	0.1022(12)	0.0348
C(2)	1.0243(15)	−0.104(3)	0.0008(15)	0.0394
N(1)	1.1530(12)	−0.363(2)	0.113(1)	0.0353
O(1)	0.4007(8)	−0.2654(14)	0.2500(6)	0.0241(19)
O(2)	0.6390(9)	0.0384(15)	0.4008(7)	0.029(2)
O(3)	1.153(1)	−0.2228(17)	0.4120(8)	0.039(2)
O(12)	0.5653(8)	0.0431(13)	0.1779(6)	0.0235(19)
O(13)	0.4385(9)	−0.2258(15)	0.0306(7)	0.028(2)
O(21)	0.7021(9)	−0.2543(14)	0.2533(7)	0.0253(19)
O(23)	0.9149(8)	−0.0241(15)	0.3494(6)	0.0254(19)

Note. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

^a U_{eq} for the V, N, and C atoms and U_{iso} for the O atoms.

TABLE 3
Selected Bond Distances (Å) and Angles (deg)
for (H₃N(CH₂)₄NH₃)[V₆O₁₄]

V(1)–O(1)	1.601(8)	V(1)–O(12)	1.989(9)
V(1)–O(13)	1.920(9)	V(1)–O(21)	1.914(9)
V(1)–O(23)	2.03(1)	V(2)–O(2)	1.607(9)
V(2)–O(12)	1.970(8)	V(2)–O(21)	1.89(1)
V(2)–O(21)	1.895(9)	V(2)–O(23)	2.009(8)
V(3)–O(3)	1.60(1)	V(3)–O(12)	1.821(9)
V(3)–O(13)	1.710(9)	V(3)–O(23)	1.78(1)
C(1)–C(2)	1.50(2)	C(1)–N(1)	1.51(2)
C(2)–C(2)	1.48(3)		
O(1)–V(1)–O(12)	104.1(4)	O(1)–V(1)–O(13)	107.2(4)
O(12)–V(1)–O(13)	91.2(4)	O(1)–V(1)–O(21)	112.7(4)
O(12)–V(1)–O(21)	81.3(4)	O(13)–V(1)–O(21)	140.0(4)
O(1)–V(1)–O(23)	105.0(4)	O(12)–V(1)–O(23)	148.6(3)
O(13)–V(1)–O(23)	91.2(4)	O(21)–V(1)–O(23)	76.8(4)
O(2)–V(2)–O(12)	103.9(4)	O(2)–V(2)–O(21)	107.9(4)
O(12)–V(2)–O(21)	82.5(4)	O(2)–V(2)–O(23)	115.3(5)
O(12)–V(2)–O(23)	89.1(4)	O(21)–V(2)–O(23)	136.81(15)
O(2)–V(2)–O(23)	104.0(4)	O(12)–V(2)–O(23)	152.1(3)
O(21)–V(2)–O(23)	90.5(4)	O(21)–V(2)–O(23)	77.7(4)
O(3)–V(3)–O(12)	109.3(5)	O(3)–V(3)–O(13)	110.2(5)
O(12)–V(3)–O(13)	110.5(4)	O(3)–V(3)–O(23)	107.4(5)
O(12)–V(3)–O(23)	110.7(4)	O(13)–V(3)–O(23)	108.6(4)
C(2)–C(1)–N(1)	113.0(13)	C(1)–C(2)–C(2)	110.9(19)
V(1)–O(12)–V(2)	92.9(4)	V(1)–O(12)–V(3)	135.4(5)
V(2)–O(12)–V(3)	131.1(5)	V(1)–O(13)–V(3)	137.0(5)
V(1)–O(21)–V(2)	98.0(4)	V(1)–O(21)–V(2)	105.2(4)
V(2)–O(21)–V(2)	150.1(5)	V(1)–O(23)–V(2)	97.1(4)
V(1)–O(23)–V(3)	137.4(5)	V(2)–O(23)–V(3)	125.4(5)

the overall charge balance of the compound and confirmed by the bond strength calculations around vanadium atoms using the following equation proposed by Brown for vanadium oxide compounds: $s = (d/R_1)^{-N}$, where s is the bond valence and d is the bond distance (15). Considering the empirical parameters R_1 and N ($R_1 = 1.791$; $N = 5.1$ for V⁵⁺ and $R_1 = 1.770$; $N = 5.2$ for V⁴⁺ (16)), the valence sum calculations give a value of 4.0 for V(1), 4.1 for V(2) and 5.0 for V(3).

The square pyramids share edges to form zigzag chains, connected by corner-sharing tetrahedra (see Fig. 1). Two adjacent square pyramids have their short V=O up and the next two down. Each tetrahedron shares two corners with one chain of square pyramids, one corner with the neighboring chain and the fourth corner is a non-bonding vanadyl group.

While the structure of the V₃O₇ layer was already found in different vanadium oxides, Whittingham *et al.* reported structural differences among those oxides concerning mainly the planarity of the V₃O₇ sheet and the relative orientation of the neighboring chains (1). In the case of (H₃N(CH₂)₄NH₃)[V₆O₁₄], there is a puckering of the vanadium oxide layer (see Fig. 2). Actually, the planarity

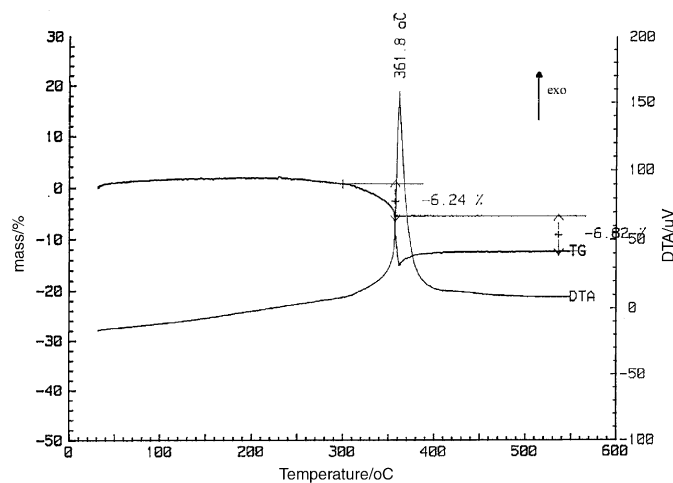


FIG. 3. Thermal analysis of $(\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3)[\text{V}_6\text{O}_{14}]$.

of the V_3O_7 layer strongly depends on the nature of the VO_4 tetrahedron oxygens that are bonded to the chains. The V_3O_7 layer may be almost planar as in $(\text{TMA})[\text{V}_3\text{O}_7]$ or puckered as in $(\text{DABCO})[\text{V}_6\text{O}_{14}] \cdot \text{H}_2\text{O}$ (1).

The transformation between the chains in $(\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3)[\text{V}_6\text{O}_{14}]$ compound is a little complex and proceeds through a glide plane perpendicular to the chain. Such a feature was already observed in the case of $(\text{CH}_3\text{NH}_3)[\text{V}_3\text{O}_7]$ (1). But a more simple symmetry relation between the chains was also reported for $(\text{TMA})[\text{V}_3\text{O}_7]$ compound as the chains are transformed by a simple translation in the direction perpendicular to the chain (1).

Thermal Analysis

A single mass loss corresponding to an exothermic DTA peak occurs around 360°C (Fig. 3). It should be due to the combustion of organic compounds. It is followed by a slight increase in weight that could be assigned to the oxidation of vanadium into V_2O_5 . The total weight loss ($\approx 18\%$) corresponds to a stoichiometry close to 0.5 mol of diamine per $[\text{V}_3\text{O}_7]$.

^{51}V NMR of the Solution

The ^{51}V NMR solution spectrum of the pale-yellow supernatant solution recorded at room temperature exhibits two peaks (Fig. 4). According to literature, the first one at -577 ppm can be assigned to cyclic metavanadates $[\text{V}_4\text{O}_{12}]^{4-}$, whereas the second one at -585 ppm should be due to cyclic pentamers $[\text{V}_5\text{O}_{15}]^{5-}$ (17). No peak corresponding to decavanadate species can be seen on this spectrum. The title compound has been synthesized at a pH close to 9 which is consistent with the presence of metavanadates in solution.

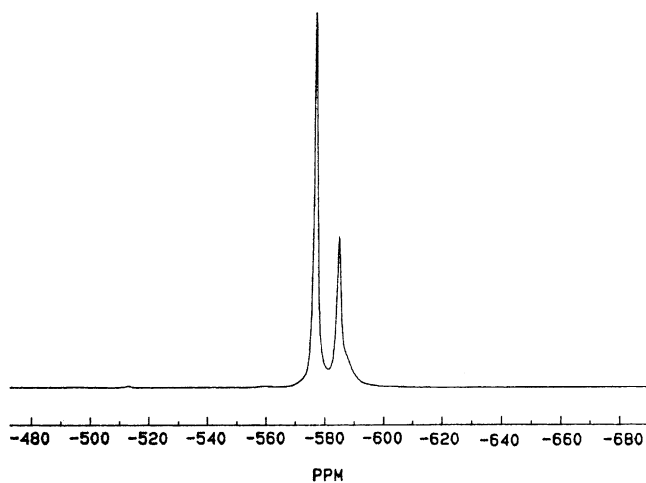


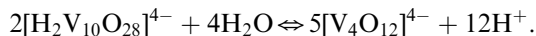
FIG. 4. ^{51}V NMR spectrum of the supernatant solution ($\text{pH} \approx 9$).

DISCUSSION

The $(\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3)[\text{V}_6\text{O}_{14}]$ compound reported in this paper exhibits the $[\text{V}_3\text{O}_7]$ structure already described in several layered vanadium oxide compounds (6, 12-14). Several parameters are important in the synthesis, the pH of the aqueous solution, the ratio of the reactants, the nature of the ions and the temperature. In particular, Whittingham *et al.* pointed out the importance of the pH on vanadium coordination and consequently on the structure of the inorganic framework [1,6]. At high pH values, vanadium is only four-fold coordinated in the oxide. However, as the pH decreases, the vanadium coordination increases to five (square pyramids) at $\text{pH} \approx 7$ until six (octahedra) at $\text{pH} < 2$ (6). The title compound has been synthesized at a pH close to nine which is consistent with the presence of $[\text{VO}_5]$ square pyramids and $[\text{VO}_4]$ tetrahedra in the structure.

A similar synthesis was published by Riou and Férey a few years ago (8). However, a completely different compound, $(\text{H}_3\text{N}-(\text{CH}_2)_4-\text{NH}_3)(\text{VO}_3)_2$, was obtained. The structure consists of metavanadate chains made of corner-sharing $[\text{V}^{\text{V}}\text{O}_4]$ tetrahedra. As a consequence, in contrast to the $(\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3)[\text{V}_6\text{O}_{14}]$ compound reported here, $(\text{H}_3\text{N}-(\text{CH}_2)_4-\text{NH}_3)(\text{VO}_3)_2$ does not contain any V^{4+} ions. The heating temperature (180°C) was about the same for both syntheses. But for the synthesis of $(\text{H}_3\text{N}-(\text{CH}_2)_4-\text{NH}_3)(\text{VO}_3)_2$, HF was added in addition to V_2O_5 , the 1,4 diaminobutane and H_2O . F^- ions were not involved in the structure of this compound, but the final pH was much lower, around 5 instead of 9. We may assume that V^{5+} is not reduced by diamines at such a low pH and light yellow crystals were formed that contain only V^{5+} ions. Actually, decavanadates $[\text{V}_{10}\text{O}_{28}]^{6-}$ rather than metavanadates are the most stable species at $\text{pH} \approx 5$. However, as we

have shown earlier by in situ ⁵¹V NMR studies, decavanadates are transformed into metavanadates as the temperature increases and only metavanadate tetramers were observed around 180°C (18).



Therefore, solid metavanadates made of corner-sharing [V^VO₄] tetrahedra are precipitated from the solution under hydrothermal conditions.

In our case, at pH ≈ 9, we may assume that V⁵⁺ is partly reduced by organic templates under hydrothermal conditions. Such a reduction has already been observed in the synthesis of layered vanadium oxide (3–5) or polyoxovanadates clusters (19, 20). V⁴⁺ ions are too large to be four-fold coordinated and coordination expansion then occurs upon reduction leading to the formation of [V^{IV}O₅] square pyramids. Condensed phases are then formed via oxolation reactions leading to the formation of edge-sharing [V^{IV}O₅] chains. Non-reduced V⁵⁺ ions remain tetrahedrally coordinated and link square pyramids chains together via corners.

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