

# Phase Transitions in Metavanadates. Polymerization of Tetrakis(*tert*-Butylammonium)-*cyclo*-Tetrametavanadate

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The compound tetrakis(*tert*-butylammonium)-*cyclo*-tetrametavanadate(V), the first oxovanadate salt isolated from aqueous solution which contains a discrete unprotonated  $[\text{V}_4\text{O}_{12}]^{4-}$  anion, undergoes an irreversible, reconstructive, continuous, and heterogeneous phase transition in the solid state by means of a nucleation and growth mechanism. This transformation yields a polymeric metavanadate of *tert*-butylammonium and it has been followed by X-ray powder diffraction and FTIR techniques. The polymeric compound has also been isolated from aqueous solution and its crystal structure resolved by single-crystal X-ray diffraction methods, this compound crystallizes in the monoclinic space group  $P2_1$ ,  $a = 10.397(2)$  Å,  $b = 5.873(1)$  Å,  $c = 13.879(4)$  Å,  $\beta = 111.02(3)^\circ$ ,  $V = 791.1(3)$  Å<sup>3</sup>,  $Z = 4$ , and  $R = 0.026$  for 1926 observed reflections with  $I \geq 3\sigma(I)$ . Comparison of the polymeric and cyclic metavanadate structures reveals several structural similarities such as V···V contacts and V–O–V angles. A possible transformation mechanism has been suggested on the basis of these structural analogies.

## Introduction

The solution and solid-state chemistries of some early transition metals (V, Mo, W, Nb, and Ta) are both characterized by a tremendous variety of polyoxoanions species ranging from monomers to high-nuclearity clusters which are formed by the assembling of  $\text{MO}_x$  units.<sup>1</sup> Due to the structural richness, the varied physical properties, and the successful uses of these inorganic metal–oxygen clusters, polyoxometalate chemistry is an active and renewed area of research which not only is of interest in inorganic chemistry but also has numerous applications in many fields such as catalysis, biology, medicine, and material science.<sup>2</sup> The understanding of the driving force for the formation of the oxometalates cages is still a challenge, but it is well-known that in solution there are quick and complex equilibria between polyoxospecies with different nuclearity which are strongly dependent on the media conditions such as pH value, ionic strength, temperature, and features counterion.<sup>3–7</sup> One of the best studied groups in polyoxometalate chemistry is the oxovanadium(V) compounds.<sup>1–3,8,9</sup> Single oxovanadates present in aque-

ous solution include monomer ( $\text{H}_2\text{VO}_4^-$ ,  $\text{HVO}_4^{2-}$ ,  $\text{VO}_4^{3-}$ ), dimer ( $\text{H}_2\text{V}_2\text{O}_7^{2-}$ ,  $\text{HV}_2\text{O}_7^{3-}$ ,  $\text{V}_2\text{O}_7^{4-}$ ), trimer ( $\text{V}_3\text{O}_{10}^{5-}$ ), tetramer ( $\text{V}_4\text{O}_{12}^{4-}$ ), pentamer ( $\text{V}_5\text{O}_{15}^{5-}$ ), and decamer ( $\text{H}_3\text{V}_{10}\text{O}_{28}^{3-}$ ,  $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ ,  $\text{HV}_{10}\text{O}_{28}^{5-}$ ,  $\text{V}_{10}\text{O}_{28}^{6-}$ ) species.<sup>5,8–10</sup> Although the existence of these vanadate oxoanions have been well-established by a combination of precise EMF, potentiometric, and NMR measurements,<sup>4–7</sup> not all of them have been characterized by X-ray crystallography. For example, the major constituents of so-called “metavanadate” aqueous solutions (pH 6.5–8) are the cyclic tetramer and pentamer, but the only salts that had been crystallized from such solutions contain polymeric anions with two structural types: (a) infinite chains of corner-shared  $\text{VO}_4$  tetrahedra<sup>11</sup> and (b) chains of edge-shared distorted  $\text{VO}_5$  trigonal bipyramids.<sup>12</sup> A protonated cyclic tetrameric anion,  $[\text{HV}_4\text{O}_{12}]^{3-}$ , was structurally characterized in the compound  $(n\text{-Bu}_4\text{N})_3[\text{HV}_4\text{O}_{12}]$ , but it was prepared in alcoholic solution.<sup>13</sup> Also the  $\{\text{V}_4\text{O}_{12}\}$  core stabilized by coordinating of its oxygen atoms to one or two ( $\eta$ -

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$C_8H_{12}Ir$  moities have been described in the complex anions  $[(\eta-C_8H_{12})Ir(V_4O_{12})]^{3-}$  and  $\{[(\eta-C_8H_{12})Ir]_2(V_4O_{12})\}^{2-}$  which were obtained as tetra-*n*-butylammonium salts from acetonitrile solutions.<sup>14</sup>

However, the first discrete cyclic  $[V_4O_{12}]^{4-}$  have been recently described by us in the compound  $[(CH_3)_3CNH_3]_4[V_4O_{12}]$  which was isolated from aqueous solution containing a novel discrete anion based on a ring of four  $VO_4$  tetrahedra.<sup>15</sup> The tetrameric anion possesses rigorous crystallographic  $C_{4h}$  symmetry, and it is made up of four corner-linked  $VO_4$  tetrahedra forming a ring around the 4-fold axis. The vanadium and the bridging oxygen atoms are placed on the corners of two different squares rotated  $45^\circ$  one respect to the other forming a strictly planar  $V_4O_4$  ring. The terminal oxygen atoms lay at 1.287(2) Å above and below the ring plane. Crystals of cyclic compound after some time undergoes an irreversible phase transition to yield the polymeric metavanadate of *tert*-butylammonium  $[(CH_3)_3CNH_3][VO_3]$ . This phase transition takes place very slowly and the global process may last several months. By our knowledge, no information is presently available in the literature regarding this type of phase transition (polymerization) in the solid-state polyoxometalate chemistry. Polymerization process have been described for some nonmetal oxocompounds as  $SeO_3$ . In solid state its structure is built up from cyclic tetramers,  $Se_4O_{12}$ , but in the molten state it is polymeric like the isoelectronic polymetaphosphate ions.<sup>16</sup>

### Experimental Section

Vanadium pentoxide and *tert*-butylamine were purchased from Aldrich and Fluka, respectively, and used without further purification. Elemental analyses were performed on a Perkin Elmer 240 C-, H-, N-analyzer, and vanadium was determined thermogravimetrically as  $V_2O_5$  after thermal decomposition of the compound in an argon-oxygen atmosphere on a Setaram TAG 24 S 16 thermobalance. The density of the compounds were measured by flotation in acetone/ $CCl_4$ . The IR spectra were recorded on a Nicolet 740 FTIR spectrometer by KBr disk method. FTIR spectroscopy has allowed us to identify the white nuclei formed in the *cyclo*-tetrametavanadate original crystal as the polymeric *tert*-butylammonium metavanadate salt.

The phase transition has been followed by means of X-ray powder diffraction. All powder samples were analyzed using a Philips PW 1710 diffractometer with Cu K $\alpha$  radiation. The  $2\theta$  values have been corrected using the Guinier program<sup>17</sup> with an internal standard pattern of Si. The diffraction peaks have been indexed with the LSUCRE program<sup>18</sup> using the crystallographic parameters of tetrakis(*tert*-butylammonium)-*cyclo*-tetrametavanadate<sup>15</sup> and the ones of the polymeric metavanadate of *tert*-butylammonium, respectively. The homogeneity and purity of the bulk products for both compounds prepared here were confirmed by comparison of the observed and calculated X-ray powder diffraction patterns. The calculated patterns were produced using the LAZY-PULVERIX program<sup>19</sup> with the single-crystal coordinates.

**Synthesis of  $[(CH_3)_3CNH_3]_4[V_4O_{12}]$ .** To a stirred aqueous suspension (25 mL) of  $V_2O_5$  (5.82 g; 32 mmol), an excess of *tert*-butylamine (10.0 mL; 94 mmol) was added dropwise. The mixture was stirred at room temperature for 15 min. Then, the solution was filtered to remove insoluble black residues, and the resulting colorless solution was heated under reflux for 2 h. After 4 days, very nice prismatic colorless crystals of  $[(CH_3)_3CNH_3]_4[V_4O_{12}]$  were obtained. Anal. Calcd for  $C_{16}H_{48}N_4O_{12}V_4$ : C 27.76; H 6.99; N 8.09; V( $V_2O_5$ ) 52.54. Found: C 27.81; H 6.99; N 8.02; V( $V_2O_5$ ) 51.80.  $D_0 = 1.39(1)$ . IR ( $cm^{-1}$ ) 890 (s, br)  $[\nu_s(V(O)_2)]$ ; 810 (vs, br)  $[\nu_{as}(V(O)_2)]$ ; 500 (w)  $[\nu_{as}(V-O_b-V)]$ ; 460 (m)  $[\nu_s(V-O_b-V)]$ ; 375 (w)  $[\delta(VO_2)]$ .

**Synthesis of  $[(CH_3)_3CNH_3][VO_3]$ .** To a stirred aqueous suspension (25 mL) of  $V_2O_5$  (5.96 g; 33 mmol), an excess of *tert*-butylamine (11.0 mL; 104 mmol) was added dropwise. The mixture is stirred at room temperature until vanadium pentoxide dissolved. The resulting colorless solution was filtered off for removing any insoluble residues and then allowed to stand at room temperature. Overnight a white powder of  $[(CH_3)_3CNH_3][VO_3]$  appeared. Single crystals were obtained by recrystallization in water. Anal. Calcd for  $C_4H_{12}NO_3V$ : C 27.76; H 6.99; N 8.09; V( $V_2O_5$ ) 52.54. Found: C 27.68; H 6.95; N 8.01; V( $V_2O_5$ ) 53.51.  $D_0 = 1.43(1)$ . IR ( $cm^{-1}$ ) 970 (vs), 940 (vs)  $[\nu_s(V(O)_2)]$ ; 880 (vs), 810 (vs)  $[\nu_{as}(V(O)_2)]$ ; 645 (vs, br)  $[\nu_{as}(V-O_b-V)]$ ; 455 (m)  $[\nu_s(V-O_b-V)]$ ; 373 (w)  $[\delta(VO_2)]$ .

**Determination of the Crystal Structure of  $[(CH_3)_3CNH_3][VO_3]$ .** A crystal of *tert*-butylammonium metavanadate compound suitable for structure analysis was mounted on an Enraf-Nonius CAD4 diffractometer. X-ray data were collected with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å) at room temperature using the  $\omega$ - $2\theta$  scan technique. Cell parameters and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range  $15^\circ < 2\theta < 30^\circ$ . A total of 2512 reflections were measured in the range  $2^\circ \leq 2\theta \leq 60^\circ$  ( $h = 0-14$ ,  $k = 0-8$ ,  $l = -19$  to 19), 1926 of which, with  $I > 3\sigma(I)$ , were used in the development and refinement of the structure. No significant decay of the intensity of two standard reflections recorded after every 100 reflections was observed. The intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction following the procedure DIFABS<sup>20</sup> with minimum and maximum correction coefficients 0.755 and 1.331, respectively, was applied. The atomic scattering factors and anomalous dispersion factors were taken from the literature.<sup>21</sup> Experimental details and crystal data for both compounds are given in Table 1.

The structure was solved using direct methods.<sup>22</sup> Non-hydrogen atoms were refined anisotropically by full-matrix least-squares analysis using the X-RAY76 System.<sup>23</sup> All hydrogen atoms were clearly visible in a difference Fourier synthesis and their positional coordinates were refined but their isotropic thermal parameters were fixed. The highest peak in the final Fourier difference map was 0.37 e/Å<sup>3</sup>. Since the polymeric compound crystallizes in an enantiomeric space group, its inversion was refined to discrepancy indices  $R/R_w$  of 0.030/0.032. The absolute structure of the compound corresponding to the reported atomic coordinates was also confirmed by the fact that a parameter that multiplies all  $\Delta f'$  values refined toward the value of +1.03(8).<sup>24</sup>

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**Table 1. Crystal Data and Data Collection Parameters for the Compounds**

compound	$[(\text{CH}_3)_3\text{CNH}_3][\text{VO}_3]$	$[(\text{CH}_3)_3\text{CNH}_3]_4[\text{V}_4\text{O}_{12}]^a$
mol wt	173.09	692.34
system	monoclinic	tetragonal
space group	$P2_1$ (No. 4)	$I4/m$ (No. 87)
$a$ (Å)	10.397(2)	15.000(2)
$b$ (Å)	5.873(1)	
$c$ (Å)	13.879(4)	7.379(2)
$\beta$ (deg)	111.02(3)	
$V$ (Å <sup>3</sup> )	791.1(3)	1660.3(6)
$Z$	4	2
$F(000)$	360	720
$D_o$ (Mg m <sup>-3</sup> )	1.43(1)	1.39(1)
$D_x$	1.453	1.385
$\mu$ (cm <sup>-1</sup> )	11.604	11.058
shape	prism	prism
size (mm)	$0.17 \times 0.40 \times 0.40$	$0.10 \times 0.20 \times 0.25$
color	colorless	colorless
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
temp (K)	295(1)	295(1)
radiation (Å)	0.710 69	0.710 69
monochromator	graphite	graphite
scan mode	$\omega/2\theta$	$\omega/2\theta$
$\theta$ range	1–30	2–35
$hkl$	0 → 14; 0 → 8; –19 → 19	–24 → 24; –24 → 24; 0 → 11
controls	intensity and orientation	intensity and orientation
reflins		
periodicity	3600 s; 100 reflins	7200 s; 100 reflins
measd reflns	2512	7570
independent reflns	2512	1941 ( $R_{\text{int}} = 0.029$ )
$[I \geq 3\sigma(I)]$		
obsd reflns	1926	1384
no. of variables	234	59
max ( $\Delta/\sigma$ )	0.40	1.11 [ $y$ of H(112)]
average ( $\Delta/\sigma$ )	0.033	0.10
( $\Delta\rho$ ) (e Å <sup>-3</sup> )	0.37	0.92
$R$	0.026	0.044
$R_w$	0.028	0.048

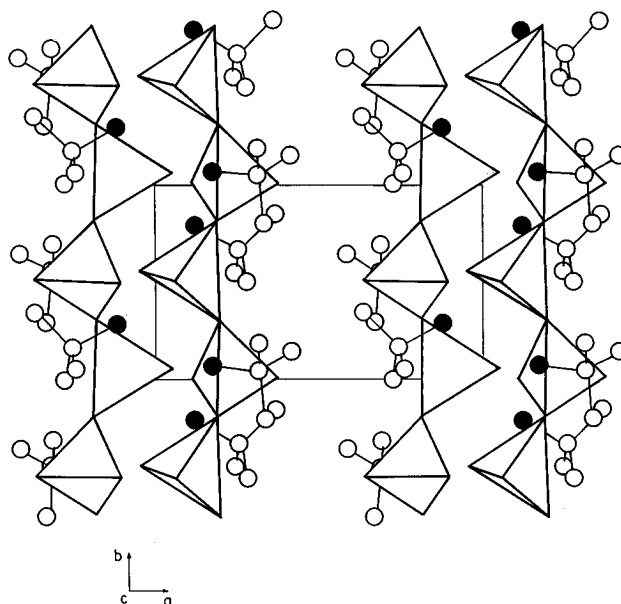
<sup>a</sup> Data are taken from ref 15.

## Results and Discussion

The crystal structure of the  $[(\text{CH}_3)_3\text{CNH}_3]_4[\text{V}_4\text{O}_{12}]$  compound consists of discrete cyclic anions,  $[\text{V}_4\text{O}_{12}]^{4-}$ , and *tert*-butylammonium cations,  $[(\text{CH}_3)_3\text{CNH}_3]^+$ , linked together by means of electrostatic interactions and an extensive network of hydrogen bonds.<sup>15</sup> The cyclic anions are located on the symmetry centers (000) and  $(1/2, 1/2, 1/2)$ . The *tert*-butylammonium cations are placed between the anions with its N atoms directed towards the O<sub>t</sub> atoms forming an extensive network of hydrogen contacts.

Figure 1 shows a projection of the crystal structure of the polymeric compound onto the plane (001). The crystal structure of this compound is made up of polymeric metavanadate anions and *tert*-butylammonium cations linked together by means of electrostatic interactions, hydrogen bonds and van der Waals contacts. The metavanadate anion,  $[\text{VO}_3]^-$ , consists of  $\text{VO}_4$  tetrahedra that are joined by vertices O(5) and O(6) in zigzag chains which sweep along in the direction [010] and have a repeat unit of two tetrahedra. The cations are located between these chains with their N atoms directed toward the oxygen atoms of the anion whereas their hydrophobic groups are directed towards the region  $x = 1/2$ .

Positional coordinates are included in Table 2, while selected bond distances and angles are listed in Table 3. An extensive network of hydrogen bonds of the types

**Figure 1.** Projection of the crystal structure of the compound  $[(\text{CH}_3)_3\text{CNH}_3][\text{VO}_3]$  onto the plane (001).**Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for  $[(\text{CH}_3)_3\text{CNH}_3][\text{VO}_3]$** 

atom	$x$	$y$	$z$	$U_{\text{eq}}^a$
V(1)	0.21387(5)	0.03482(–)	0.25113(4)	187(1)
V(2)	0.09319(5)	0.5460(2)	0.31747(4)	207(2)
O(1)	0.1054(3)	0.0031(6)	0.1297(2)	32(1)
O(2)	–0.0510(3)	0.5615(9)	0.2181(2)	39(1)
O(3)	0.3682(3)	0.0085(8)	0.2524(2)	38(1)
O(4)	0.0571(3)	0.4994(6)	0.4233(2)	33(1)
O(5)	0.1839(3)	–0.1856(5)	0.3337(2)	26(1)
O(6)	0.1928(3)	0.3106(6)	0.3019(2)	33(1)
N(11)	0.1706(3)	0.0654(9)	0.5133(2)	27(1)
C(12)	0.3124(3)	0.0479(13)	0.5973(2)	31(1)
C(13)	0.3329(8)	–0.2038(12)	0.6242(5)	65(3)
C(14)	0.3111(7)	0.1878(12)	0.6898(5)	53(2)
C(15)	0.4156(5)	0.1429(13)	0.5523(4)	57(2)
N(21)	0.8799(3)	0.2872(7)	0.0432(3)	27(1)
C(22)	0.7456(4)	0.1675(7)	0.0251(3)	27(1)
C(23)	0.7568(5)	0.0520(17)	0.1268(3)	48(2)
C(24)	0.6333(5)	0.3449(11)	–0.0068(4)	47(2)
C(25)	0.7237(6)	–0.0039(10)	–0.0617(4)	52(2)

<sup>a</sup>  $U_{\text{eq}} = [(\text{Å}^2 \times 10^4) \text{ for V and } (\text{Å}^2 \times 10^3) \text{ for C, N and O}]$ .**Table 3. Bond Lengths V–O (Å), Distances O...O (Å) and Angles O–V–O (deg) for the Compound  $[(\text{CH}_3)_3\text{CNH}_3][\text{VO}_3]$** 

	V(1)	O(1)	O(3)	O(5)	O(6)
O(1)	1.668(2)		108.1(2)	110.4(2)	111.1(2)
O(3)	1.605(3)	2.651(3)		108.6(2)	110.0(2)
O(5)	1.829(3)	2.873(4)	2.792(5)		108.5(2)
O(6)	1.810(4)	2.870(4)	2.800(5)	2.953(5)	
	V(2)	O(2)	O(4)	O(5) <sup>a</sup>	O(6)
O(2)	1.636(2)		109.9(2)	109.6(2)	109.7(2)
O(4)	1.664(3)	2.685(4)		107.8(2)	107.7(2)
O(5) <sup>a</sup>	1.809(3)	2.819(5)	2.807(5)		113.0(2)
O(6)	1.787(4)	2.799(5)	2.786(5)	2.999(5)	

<sup>a</sup> Symmetry code:  $x, y + 1, z$ .

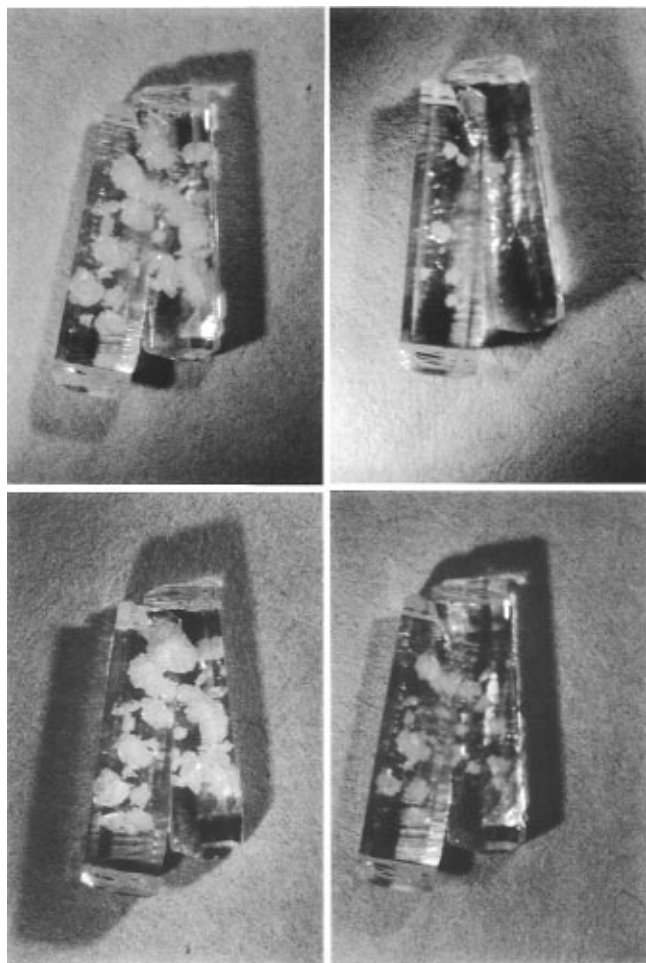
N–H...O [ $\text{N} \cdots \text{O} = 2.767(5) - 2.940(5) \text{ Å}$ ]<sup>25</sup> and C–H...O [ $\text{C} \cdots \text{O} = 3.461(9) \text{ Å}$ ]<sup>26</sup> between *tert*-butylammonium cations and polyanion oxygen atoms is established. Only, the bridge oxygen atom, O(5), forms hydrogen contacts, whereas all the terminal oxygen atoms, except the O(3)

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**Table 4. Hydrogen Contacts (Å, deg) for the Compound  $[(CH_3)_3CNH_3][VO_3]$** 

bond type	X-H	X...O	H...O	$\angle X-H...O$
N(11)-H(111)...O(4) <sup>a</sup>	1.01(6)	2.833(5)	1.84(5)	168(5)
N(11)-H(112)...O(5)	0.84(6)	2.940(5)	2.12(7)	166(6)
N(11)-H(113)...O(4)	0.84(6)	2.897(6)	2.07(6)	171(7)
N(21)-H(211)...O(1) <sup>b</sup>	0.99(7)	2.775(4)	1.78(7)	179(6)
N(21)-H(212)...O(2) <sup>c</sup>	0.76(8)	2.784(5)	2.04(7)	165(8)
N(21)-H(213)...O(1) <sup>d</sup>	0.93(8)	2.767(5)	1.86(8)	167(7)
C(14)-H(141)...O(2) <sup>a</sup>	1.11(7)	3.461(9)	2.41(7)	159(6)

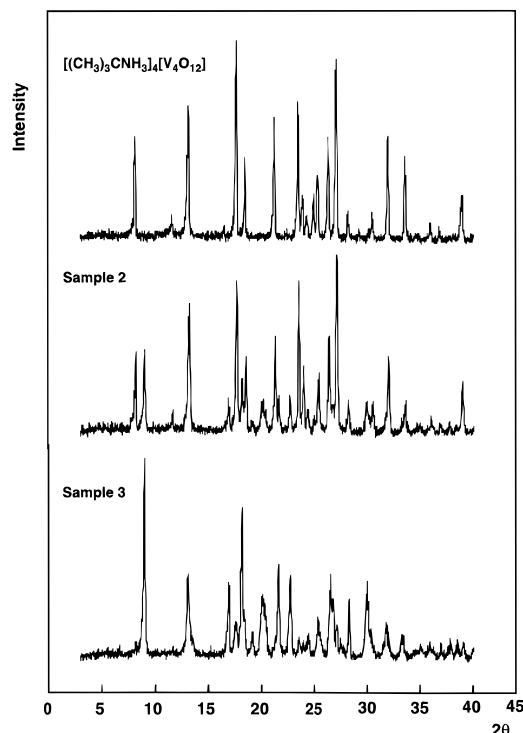
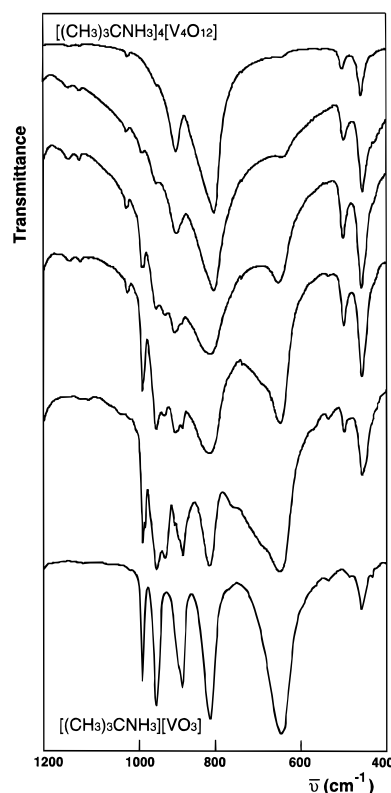
Symmetry codes: <sup>a</sup>  $-x, y - 1/2, -z + 1$ . <sup>b</sup>  $x + 1, y, z$ . <sup>c</sup>  $-x + 1, y + 1/2, -z$ . <sup>d</sup>  $-x + 1, y, z$ .

**Figure 2.** Cyclo to polymeric metavanadate phase transition. Process of nucleation growth. (1) top right, (2) bottom right, (3) top left, and (4) bottom left.

atom, are involved in this network of hydrogen contacts (Table 4).

Crystals of cyclic compound are quite stable, but after some time it is observed that some crystalline white nuclei are formed. The size of these nuclei increases with the time. This process has been followed taking photographs of crystals of the original compound, weekly (Figure 2). These white nuclei have been identified as the polymeric *tert*-butylammonium metavanadate by means of X-ray powder diffraction and infrared spectroscopy.

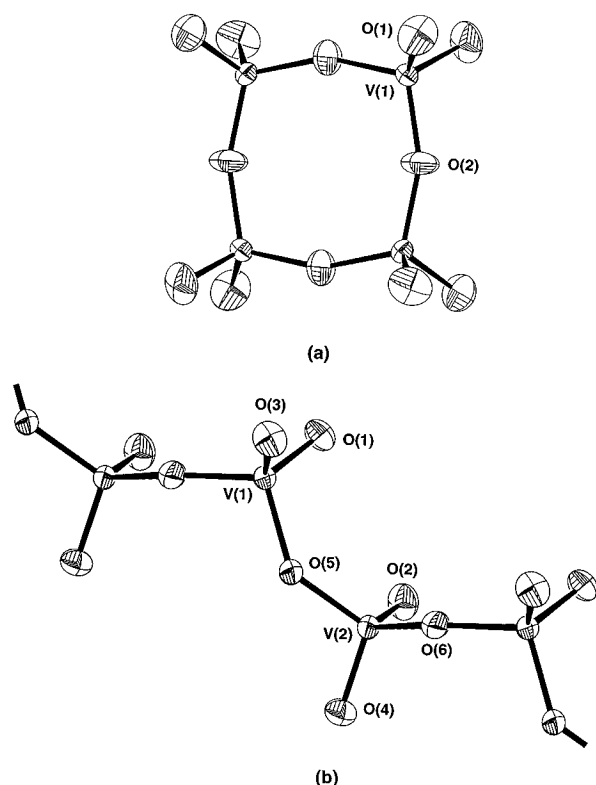
The X-ray powder diffraction experiments indicate that some peaks corresponding to the polymeric metavanadate (final product) are observed whereas some peaks of the *cyclo*-tetrametavanadate are missed. Figure 3 shows the X-ray powder diffraction patterns obtained for the original *cyclo*-tetrametavanadate, for

**Figure 3.** Sequence of X-ray powder diffraction pattern from  $[(CH_3)_3CNH_3]_4[V_4O_{12}]$  to  $[(CH_3)_3CNH_3][VO_3]$ .**Figure 4.** Sequence of FTIR spectra from  $[(CH_3)_3CNH_3]_4[V_4O_{12}]$  to  $[(CH_3)_3CNH_3][VO_3]$ .

a sample in which the existence of some nuclei of the final phase are observed and for another sample that is found in a more advanced point of the transformation. It is observed the appearance of the characteristic peak of the polymer at 9.70 Å, corresponding to the (100) reflection, with an intensity that increases up to be 100%; besides of other peaks of the polymeric metavanadate, so that, in the last diffraction pattern, all the

Table 5. Similarities Observed between Both Structures

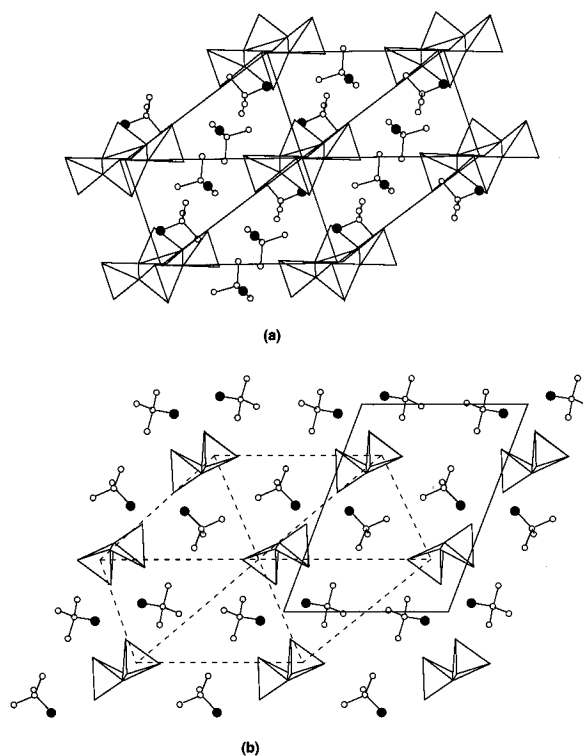
$[(\text{CH}_3)_3\text{CNH}_3]_4[\text{V}_4\text{O}_{12}]$	$[(\text{CH}_3)_3\text{CNH}_3][\text{VO}_3]$
angle $\text{V}-\text{O}-\text{V} = 158.3(2)^\circ$	angle $\text{V}(1)-\text{O}(6)-\text{V}(2) = 153.6(2)^\circ$ .
distance $\text{V}\cdots\text{V}_{\text{cis}} = 3.4734(6) \text{ \AA}$	distance $\text{V}(1)\cdots\text{V}(2) = 3.502(1) \text{ \AA}$
hydrogen contacts: The $\text{O}_b$ atom does not receive hydrogen contacts.	hydrogen contacts: the bridge oxygen atom $\text{O}(6)$ , does not receive hydrogen contacts
some hydrogen contacts: $\text{N}(1)-\text{H}(11)\cdots\text{O}(1)\text{N}\cdots\text{O} = 2.771(2) \text{ \AA}$	some hydrogen contacts: $\text{N}(21)-\text{H}(211)\cdots\text{O}(1)\text{N}\cdots\text{O} = 2.775(4) \text{ \AA}$ $\text{N}(21)-\text{H}(212)\cdots\text{O}(2)\text{N}\cdots\text{O} = 2.784(5) \text{ \AA}$ $\text{N}(21)-\text{H}(213)\cdots\text{O}(1)\text{N}\cdots\text{O} = 2.767(5) \text{ \AA}$
the V and $\text{O}_b$ atoms are located in the same plane ( $z = 0$ ), being the distance between two parallel cyclic units of $7.379(2) \text{ \AA}$ (parameter $c$ )	the V atoms of a same chain are located in a plane ( $-0.4767x - 0.8791y = -3.3241$ ), and the bridge oxygen atoms are in the plane $-0.855x - 0.519y = -2.458$ being the angle between planes of $30.3(4)^\circ$ . The distance between 2 V atoms of different parallel chains is $7.376(3) \text{ \AA}$ . $4b = 23.492 \text{ \AA}$
(main diagonal) $= \sqrt{2a^2 + c^2} = 22.460 \text{ \AA}$	



**Figure 5.** ORTEP views of (a)  $[\text{V}_4\text{O}_{12}]^{4-}$  and (b)  $[\text{VO}_3]^\infty$  anions.

important peaks for  $d \geq 3.88$  ( $2\theta \leq 22.91^\circ$ ) correspond to the polymeric metavanadate (final phase). On the other hand, the peaks at 10.61, 4.14, 3.75, and  $2.30 \text{ \AA}$ , characteristic of the *cyclo*-tetrametavanadate are not observed.

The sequence of IR spectra from *cyclo*-tetrametavanadate to polymeric metavanadate is shown in Figure 4. At the beginning, there are only two broad bands centered at  $890$  and  $800 \text{ cm}^{-1}$ , corresponding to the symmetrical and antisymmetrical stretching  $\text{V}-\text{O}_t$  vibrations and two bands of less intensity at  $500$  and  $460 \text{ cm}^{-1}$ , that are attributable to the symmetrical and antisymmetrical stretching vibrations for the bond  $\text{V}-\text{O}_b$  of the tetrakis(*tert*-butylammonium)-*cyclo*-tetrametavanadate. When the phase transition advances, a splitting of the stretching  $\text{V}-\text{O}_t$  bands takes place, observing the appearance of new bands, initially shoulders, at  $970$ ,  $935$ , and  $890 \text{ cm}^{-1}$  and a displacement of the band centered at  $800\text{--}810 \text{ cm}^{-1}$ , the first two are assigned to the symmetrical stretching  $\text{V}-\text{O}_t$  vibrations and the ones at  $890$  and  $810 \text{ cm}^{-1}$  correspond to the antisymmetrical stretching  $\text{V}-\text{O}_t$  of the polymeric meta-

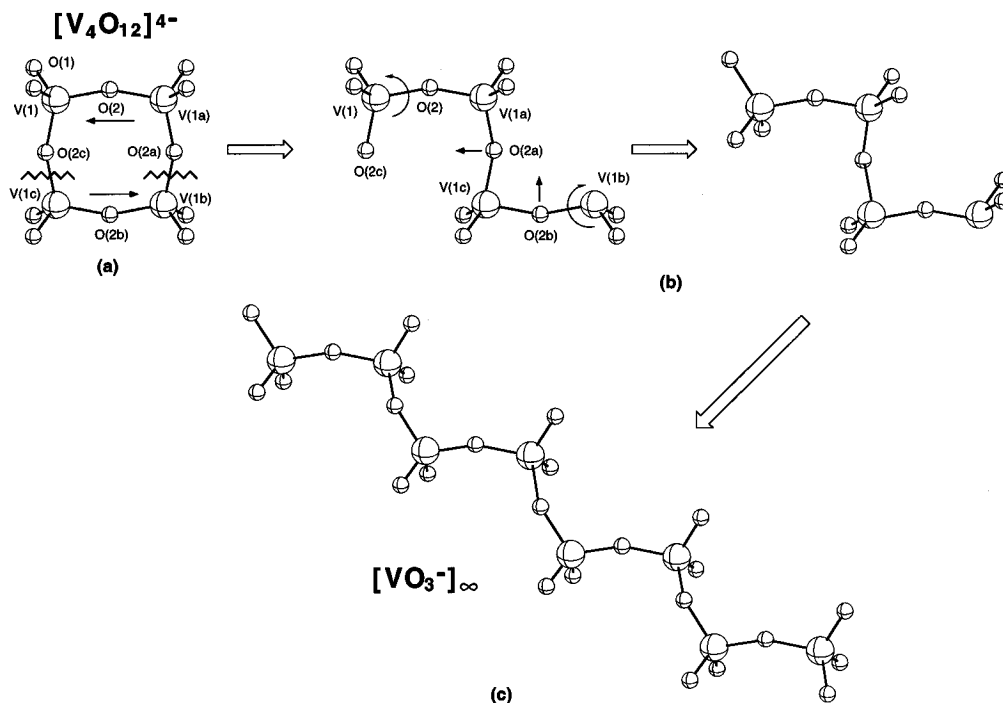


**Figure 6.** View of the crystal structure of the compound  $[(\text{CH}_3)_3\text{CNH}_3]_4[\text{V}_4\text{O}_{12}]$  along the direction  $[111]$ : (a) Projection onto the plane  $(010)$  of the crystal structure of  $[(\text{CH}_3)_3\text{CNH}_3][\text{VO}_3]$ . (b) Relation with the crystal structure of the compound  $[(\text{CH}_3)_3\text{CNH}_3]_4[\text{V}_4\text{O}_{12}]$ .

vanadate. Also observed is a new broad band at  $645 \text{ cm}^{-1}$ , characteristic of the polymeric metavanadate that is due to the antisymmetrical stretching  $\text{V}-\text{O}_b$  vibrations.

So, for all these data, we can suggest that the compound tetrakis(*tert*-butylammonium)-*cyclo*-tetrametavanadate(V) undergoes an irreversible, reconstructive, continuous, and heterogeneous phase transition by means of a nucleation and growth mechanism to yield the polymeric metavanadate of *tert*-butylammonium. This phase transition, like most of the reconstructive ones takes place very slowly. The global process may last several months, and the conversion rate varies from crystal to crystal. On the other hand, if the crystals contain some impurities, mainly Fe and V(IV) from the  $\text{V}_2\text{O}_5$  used as starting material, these ones act delaying the transformation from *cyclo*-tetrametavanadate to polymeric metavanadate.

Besides, it is worthwhile noting that some structural characteristics of the *cyclo*-tetrametavanadate are not



**Figure 7.** Mechanism for the cyclic  $\rightarrow$  polymeric phase transition.

significantly changed in the polymeric metavanadate. The Figure 5, represents the  $[V_4O_{12}]^{4-}$  and  $[VO_3]^-_\infty$  anions, showing the bond distances and angles. The V(1)-O(6)-V(2) of the polymeric metavanadate is similar to the V-O-V angle of the *cyclo*-tetrametavanadate. Another structural similarities between both compounds are summarized in Table 5.

If we observe the unit cell of the *cyclo*-tetrametavanadate along the diagonal [111] (Figure 6a), seen is a hexagonal disposition of the tetramers that coincides with that one of the metavanadate chains in the projection onto the plane (010) of the crystal structure of the polymeric metavanadate. Figure 6b represents this projection of the *tert*-butylammonium metavanadate showing the relation with the structure of the *cyclo*-tetrametavanadate. In this case, the distance between the metavanadate chains are slightly shorter than the ones between different  $[V_4O_{12}]^{4-}$  rings in the structure of the cyclic compound, as it corresponds to a denser structure.

Taking into account all these similarities, it has been proposed that a mechanism of heterolitic breaking of the  $[V_4O_{12}]^{4-}$  cyclic units through the bonds V(1b)-O(2a) and V(1c)-O(2c) (Figure 7a), yielding the fragments  $\{V_2O_5\}$  and  $\{V_2O_7\}^{4-}$ , displacement of approximately 1.75 Å, and formation of a new bond V(1c)-O(2a) between units  $\{V_2O_5\}$  and  $\{V_2O_7\}^{4-}$  originating a new open unit  $[V_4O_{12}]^{4-}$  (Figure 7b). Every open unit must rotate  $\sim 19^\circ$  around the axis that connect the V(1a)-V(1c) atoms to permit the formation of new V-O bonds with another open units generated from the corresponding rings located at different *z* levels, forming a chain

$[VO_3]^-_\infty$  (Figure 7c), being the polymerization direction parallel to the main diagonal of the *cyclo*-tetrametavanadate cell.

On the other hand, based on volumes determined from the X-ray structure, the *t*-BuNH<sub>3</sub>[VO<sub>3</sub>] formula units in the cyclic and polymeric compounds possess volumes of 197.78 and 207.53 Å<sup>3</sup>, respectively, suggesting that the polymeric compound would be more stable at higher pressures. Besides, the thermal study of compound under an argon and oxygen atmosphere and also under an inert atmosphere of argon by means of TG, DTA, and DSC techniques from room temperature until the compound begins its decomposition around 140 °C, does not reveal the existence of any phase transition. So, this transformation could be a pressure-induced phase transition.<sup>27</sup>

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**Supporting Information Available:** Tables giving crystal data and details of structure determination, anisotropic thermal parameters for non-hydrogen atoms, hydrogen atom locations, and a full list of bond length and angles, inter- and intramolecular contact distances including hydrogen contacts (22 pages). Ordering information is given on any current masthead page.

CM950342H

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