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# New three-dimensional inorganic frameworks based on the uranophane-type sheet in monoamine templated uranyl-vanadates

Laurent Jouffret, Zhenmian Shao, Murielle Rivenet\*, Francis Abraham

Univ. Lille Nord de France, Unité de Catalyse et de Chimie du Solide, Equipe Chimie du Solide, UCCS UMR CNRS 8181, USTL/ENSCL, 59652 Villeneuve d'Ascq Cedex, France

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## ABSTRACT

Seven new uranyl vanadates with mono-protonated amine or tetramethylammonium used as structure directing cations,  $(C_2NH_8)_2\{[(UO_2)(H_2O)][(UO_2)(VO_4)]_4\} \cdot H_2O$  (*DMetU5V4*)  $(C_2NH_8)\{[(UO_2)(H_2O)_2][(UO_2)(VO_4)]_3\} \cdot H_2O$  (*DMetU4V3*),  $(C_5NH_6)_2\{[(UO_2)(H_2O)][(UO_2)(VO_4)]_4\} \cdot H_2O$  (*PyrU5V4*),  $(C_3NH_{10})\{[(UO_2)(H_2O)_2][(UO_2)(VO_4)]_3\} \cdot H_2O$  (*isoPrU4V3*),  $(N(CH_3)_4)\{[(UO_2)(H_2O)][(UO_2)(VO_4)]_3\} \cdot H_2O$  (*TMetU4V3*),  $(C_6NH_{14})\{[(UO_2)(H_2O)_2][(UO_2)(VO_4)]_3\} \cdot H_2O$  (*CHexU4V3*), and  $(C_4NH_{12})\{[(UO_2)(H_2O)][(UO_2)(VO_4)]_3\}$  (*TButU4V3*) were prepared from mild-hydrothermal reactions using dimethylamine, pyridine, isopropylamine, tetramethylammonium hydroxide, cyclohexylamine and tertbutylamine, respectively, with uranyl nitrate and vanadium oxide in acidic medium. The structures were solved using single-crystal X-ray diffraction data. The compounds exhibit three-dimensional uranyl-vanadate inorganic frameworks built from uranophane-type uranyl-vanadate layers pillared by uranyl polyhedra with cavities in between occupied by protonated organic moieties. In the uranyl-vanadate layers the orientations of the vanadate tetrahedra give new geometrical isomers leading to unprecedented pillared systems and new inorganic frameworks with  $U/V=4/3$ . Crystallographic data: (*DMetU5V4*) orthorhombic,  $Cmc2_1$  space group,  $a=15.6276(4)$ ,  $b=14.1341(4)$ ,  $c=13.6040(4)$  Å; (*DMetU4V3*) monoclinic,  $P2_1/n$  space group,  $a=10.2312(4)$ ,  $b=13.5661(7)$ ,  $c=17.5291(7)$  Å,  $\beta=96.966(2)^\circ$ ; (*PyrU5V4*), triclinic,  $P1$  space group,  $a=9.6981(3)$ ,  $b=9.9966(2)$ ,  $c=10.5523(2)$  Å,  $\alpha=117.194(1)^\circ$ ,  $\beta=113.551(1)^\circ$ ,  $\gamma=92.216(1)^\circ$ ; (*isoPrU4V3*) monoclinic,  $P2_1/n$  space group,  $a=10.3507(1)$ ,  $b=13.6500(2)$ ,  $c=17.3035(2)$  Å,  $\beta=97.551(1)^\circ$ ; (*TMetU4V3*) orthorhombic,  $Pbca$  space group,  $a=17.1819(2)$ ,  $b=13.6931(1)$ ,  $c=21.4826(2)$  Å; (*CHexU4V3*), triclinic  $P-1$  space group,  $a=9.8273(6)$ ,  $b=11.0294(7)$ ,  $c=12.7506(8)$  Å,  $\alpha=98.461(3)^\circ$ ,  $\beta=96.437(3)^\circ$ ,  $\gamma=105.955(3)^\circ$ ; (*TButU4V3*), monoclinic,  $P2_1/m$  space group,  $a=9.8048(4)$ ,  $b=17.4567(8)$ ,  $c=15.4820(6)$  Å,  $\beta=106.103(2)^\circ$ .

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## 1. Introduction

Hydrothermal synthesis and crystallization from aqueous solution in the presence of amine templating agents have demonstrated that for the various main groups and transition metals, high coordination environments can be reached giving birth to complex architected structures. The interest in uranium-oxoanion chemistry has exploded in the past 10 years. In particular, uranyl containing compounds were synthesized by using amine and a stunning number of tetrahedral oxoanions such as silicates [1], phosphates [2–7], arsenates [6,8], sulfates [9–16], selenates [17–24], molybdates [25–29], or chromates [30]. The dimensionality of the inorganic arrangement in these compounds varies from isolated anionic units (0-D) to chains (1-D), to nanotubes (1-D), to layers (2-D), and to three dimensional (3-D) frameworks. Since the connection of uranyl polyhedra occurs generally through the equatorial oxygen atoms

tendency to form layers predominates, however three-dimensional framework structures can also be by linkage of uranyl-oxoanion layers through non-uranyl or sometimes uranyl polyhedra.

The chemistry of compounds containing vanadate ions is often compared to that of phosphates and arsenates; however, pentavalent vanadium can be coordinated by either four or five oxygen atoms forming a tetrahedron or a square pyramid, respectively, leading to a more diversified and, sometimes, to a different crystal chemistry. For example, for  $U/X$  ratio = 1 ( $X=P, As, V$ ), the structure of natural uranyl-phosphates, arsenates, and vanadates are based on  $[(UO_2)(XO_4)]^-$  layers. These layers are built from corner-sharing uranium octahedra and  $XO_4$  tetrahedra in an autunite-type topology for phosphates and arsenates and from edge-sharing uranium pentagonal bipyramids and  $XO_5$  square pyramids with carnotite-type topology for vanadates [31,32]. As part of the studies of our group on the alkaline metals uranyl-vanadates we showed the key role of the alkaline ionic radius on the structure dimensionality, while only 2-D arrangements have been obtained for various compositions using K, Rb, and Cs [33–37], both 2-D and 3-D frameworks can be created with the smallest ions  $Li^+$  and  $Na^+$  [38–40]. Recently, we extended our

\* Corresponding author.

E-mail address: [Murielle.rivenet@ensc-lille.fr](mailto:Murielle.rivenet@ensc-lille.fr) (M. Rivenet).

studies on the ability of various diamines to act as structure-directing agents for obtaining new uranyl vanadate architectures. By using 1,2-ethylenediamine and 1-methylpiperazine, carnotite-type layered compounds with new geometrical isomers have been obtained [41]; with piperazine and 1,4-diazabicyclo[2,2,2]octane, the layers are of the uranophane-type never evidenced for uranyl-vanadates [41]. Finally, a series of isotypic compounds  $(C_nN_2H_{2n+6})\{[(UO_2)(H_2O)]\{[(UO_2)(VO_4)]_4\} \cdot xH_2O$  denoted hereafter  $C_nU5V4$ , where  $C_n$  are di-protonated linear alkyl diamines  $C_nN_2H_{2n+6}^+$  with  $n=3-7$  has been reported [42]. Their three-dimensional inorganic framework is built from uranophane-type uranyl-vanadate layers pillared by  $[UO_6(H_2O)]$  pentagonal bipyramids. To study the role of the charge of the structure-directing organic cation and its distribution, hydrothermal synthesis of uranyl-vanadates using six related monoamines, dimethylamine (*DMet*), pyridine (*Pyr*), isopropylamine (*isoPr*), tetramethylamine (*TMet*) hydroxide, cyclohexylamine (*CHex*), and tertibutylamine (*TBut*) has been explored. The synthesis and structure of seven new uranyl-vanadates are reported in this paper. Among them, two (*DMetU5V4* and *PyrU5V4*) possess a three-dimensional uranyl-vanadate framework with  $U/V=5/4$  already reported for uranyl-containing compounds [42], but the five others display new geometrical isomers of the uranophane-type sheets and new organizations of the uranyl polyhedra pillars related to the geometry of the organic moiety leading to compounds with a  $U/V$  ratio of  $4/3$  not reported before.

## 2. Experimental

### 2.1. Materials

Uranyl nitrate  $UO_2(NO_3)_2 \cdot 6H_2O$  (Prolabo, R.P. normapur) and vanadium oxide  $V_2O_5$  (Merck, Extra pure) were used as received. A 0.40 mol/L solution of hydrochloric acid was prepared from concentrated acid (Carlo Erba, 37%,  $d=1.186$ ) and deionized water. 0.20 mol/L solutions of dimethylamine  $((CH_3)_2NH$ , 40 wt% ACROS), pyridine ( $C_5H_5N$ , 99% ACROS), isopropylamine  $((CH_3)_2CH-NH_2$ , 99% ACROS), tetramethylammonium hydroxide  $((CH_3)_4N^+ OH^-$ , 98+% ACROS), cyclohexylamine  $((C_6H_{11})NH_2$ , 98+% ALFA AERSAR), and tertibutylamine  $((CH_3)_3C-NH_2$ , 99% ACROS) were prepared by dissolution of the solid (tetramethylammonium hydroxide) or dilution of the liquid for the five amines in deionized water.

### 2.2. Synthesis

For each studied amine, 100.4 mg of uranyl nitrate ( $1.99 \times 10^{-4}$  mol), 18.1 mg of  $V_2O_5$  ( $0.99 \times 10^{-4}$  mol), 5 ml of a 0.40 mol/L solution of HCl ( $2 \times 10^{-3}$  mol), and 5 ml of the 0.20 mol/L solution of amine ( $1 \times 10^{-3}$  mol) were introduced in a 23 mL Teflon-lined Parr steel autoclave and, then, heated for 48 h at 180 °C. After cooling to ambient temperature at 5 °C/h, the collected crystalline samples were filtrated and washed with deionized water. The resulting samples were constituted of a yellow powder and crystals of the same color. With dimethylamine two types of single crystals in the form of needles and plates were obtained: they correspond to *DMetU5V4* and *DMetU4V3*, respectively. With the other amines, the single crystals and powder were separated by submitting the bulk samples diluted in deionized water to ultrasounds. In each case, the X-ray powder diffraction patterns of the powder and the crushed single crystal are identical and correspond to the pattern calculated from the single crystal X-ray structure results attesting the purity of the final samples. Reaction yields were not quantitatively determined.

### 2.3. Crystal structure determination

For every compound, a single crystal was isolated under an optical microscope for X-ray diffraction experiments. The selected crystals were mounted on a glass fibre and aligned on a Bruker SMART CCD X-ray diffractometer. Intensities were collected using  $MoK\alpha$  radiation selected by a graphite monochromator. The individual frames were measured using a  $\Omega$ -scan technique. Omega rotation and acquisition time were fixed for every compound, whose values range from 20 to 60 s/frame. The intensities were collected at 100 K using an OXFORD Cryosystem CRYOSTREAM 700 and between 2718 and 4240 frames were collected. The BRUKER program SAINT [43] was used for intensity data integration and correction for Lorentz, polarisation and background effects. After data processing, absorption corrections were performed using a semi-empirical method based on redundancy with the SADABS program [44]. The crystal structures were solved in the non-centrosymmetric space groups  $Cmc_21$  and  $P1$  for *DMetU5V4* and *PyrU5V4*, respectively, and in the centrosymmetric space groups  $P2_1/n$  for *DMetU4V3* and *isoPrU4V3*,  $Pbca$  for *TMetU4V3*,  $P-1$  for *CHexU4V3* and finally  $P2_1/m$  for *TButU4V3*. For *DMetU5V4* and *PyrU5V4* the good enantiomer was distinguished from another by taking into account anomalous scattering. No higher symmetry was found by checking the refined solutions with the ADDSYM algorithm in the program PLATON [45–47]. Details of the data collection and refinement are given in Table 1. The heavy atoms (U, V) positions were established by direct methods using the SIR97 program [48]. The oxygen, nitrogen, and carbon atoms were localized from difference Fourier maps. The positions of the hydrogen atoms could not be determined due to the low quality of crystals and due to the presence of very heavy U atoms. The latter also contribute significantly to the Fourier truncation effect yielding significant residual peaks. The last cycles of refinement included atomic positions and anisotropic displacement parameters ADP for heavy atoms (U and V) and isotropic ones for the other atoms. Full-matrix least squares structure refinements against F were carried out using the JANA2000 program [49]. For all the compounds except *TButU4V3*, the organic moieties have been localized from the crystal structure determination. In the case of *TButU4V3*, only one organic molecule on two was localized. In fact, numerous very weak intensity reflections indicate that *TButU4V3* crystallises in a monoclinic super lattice structure of parameters  $a'=20.4753(6)$ ,  $b'=17.4323(5)$ ,  $c'=21.3150(6)$  Å and  $\beta=90.659(1)^\circ$  with  $\vec{a}' = \vec{a} - \vec{c}$  and  $\vec{c}' = 2\vec{a} + \vec{c}$  leading to  $R_{int}$  and  $R_{sig}$  parameters with similar values (0.0698 and 0.0697, respectively). In spite of numerous efforts, attempts to solve the structure in the super lattice failed due to very low intensity superstructure reflections. Therefore, for this compound, only the average crystal structure obtained in the small lattice is reported. However, this mean structure, with satisfactory uranyl-vanadate framework refinement, allowed us to describe a new interesting inorganic arrangement, the first containing two types of pillars.

## 3. Results

### 3.1. Crystal structures description

The seven compounds contain  $(UO_2)^{2+}$  uranyl ions,  $VO_4^{3-}$  vanadate tetrahedra, mono-protonated amines, and water molecules. All the structures can be described as three-dimensional inorganic arrangements resulting from uranophane-type layers of edge and corner shared  $UO_7$  and  $VO_4$  polyhedra pillared by

**Table 1**  
Data of the refinements.

	DMetU5V4	PyrU5V4	DMetU4V3	isoPrU4V3	TMetU4V3	CHexU4V3	TButU4V3
<b>Crystal data</b>							
Chemical formula	C <sub>4</sub> H <sub>20</sub> N <sub>2</sub> O <sub>28</sub> U <sub>5</sub> V <sub>4</sub>	C <sub>10</sub> H <sub>16</sub> N <sub>2</sub> O <sub>28</sub> U <sub>5</sub> V <sub>4</sub>	C <sub>2</sub> H <sub>14</sub> N <sub>1</sub> O <sub>23</sub> U <sub>4</sub> V <sub>3</sub>	C <sub>3</sub> H <sub>16</sub> N <sub>1</sub> O <sub>23</sub> U <sub>4</sub> V <sub>3</sub>	C <sub>4</sub> H <sub>18</sub> N <sub>1</sub> O <sub>23</sub> U <sub>4</sub> V <sub>3</sub>	C <sub>6</sub> H <sub>20</sub> N <sub>1</sub> O <sub>23</sub> U <sub>4</sub> V <sub>3</sub>	C <sub>8</sub> H <sub>14</sub> N <sub>1</sub> O <sub>20</sub> U <sub>4</sub> V <sub>3</sub>
Formula weight (g mol <sup>-1</sup> )	1938.1	2006.1	1525.1	1539.1	1553.1	1579.1	1501.1
Crystal system	orthorhombic	Triclinic	monoclinic	monoclinic	orthorhombic	Triclinic	monoclinic
Space group	<i>Cmc</i> 21	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>Pbca</i>	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>m</i>
Unit-cell dimensions (Å)							
<i>a</i>	15.6276(4)	9.6981(3)	10.2312(4)	10.3507(1)	17.1819(2)	9.8273(6)	9.8048(4)
<i>b</i>	14.1341(4)	9.9966(2)	13.5661(7)	13.6500(2)	13.6931(1)	11.0294(7)	17.4567(8)
<i>c</i>	13.6040(4)	10.5523(2)	17.5291(7)	17.3035(2)	21.4826(2)	12.7506(8)	15.4820(6)
$\alpha$	90	117.194(1)	90	90	90	98.461(3)	90
$\beta$	90	113.551(1)	96.966(2)	97.5510(1)	90	96.437(3)	106.103(2)
$\gamma$	90	92.216(1)	90	90	90	105.955(3)	90
Cell volume (Å <sup>3</sup> )	3004.9(1)	802.85(4)	2415.04(18)	2423.56(5)	5054.29(8)	1297.31(14)	2545.9(2)
<i>Z</i>	4	1	4	4	8	2	4
Density, calculated (g cm <sup>-3</sup> )	4.28	4.14	4.19	4.23	4.08	4.04	3.91
<i>F</i> (0 0 0)	3255	866	2559	2583	5215	1328	2511
$\mu$ (MoK $\alpha$ ) (mm <sup>-1</sup> )	28.128	26.328	27.925	27.829	26.690	26.000	26.478
Crystal shape	Needle	Plate	Plate	Needle	Square	plate	rhombohedral
Crystal size ( $\mu$ m)	108 × 41 × 2	139 × 40 × 8	164 × 100 × 10	66 × 14 × 2	82 × 78 × 50	15 × 190 × 293	224 × 47 × 51
<b>Data collection</b>							
Diffractometer	Bruker smart CCD						
Temperature (K)	100						
Wavelength (Å)	0.71069 (MoK $\alpha$ )						
$\theta$ range (deg.)	1.94–29.46	2.38–33.81	1.90–33.96	1.91–25	1.90–32.03	1.64–38.33	1.80–25
Data collected	–21 ≤ <i>h</i> ≤ 21 –15 ≤ <i>k</i> ≤ 19 –16 ≤ <i>l</i> ≤ 18	–15 ≤ <i>h</i> ≤ 15 –15 ≤ <i>k</i> ≤ 15 –16 ≤ <i>l</i> ≤ 16	–14 ≤ <i>h</i> ≤ 15 –21 ≤ <i>k</i> ≤ 7 –27 ≤ <i>l</i> ≤ 24	–12 ≤ <i>h</i> ≤ 14 –19 ≤ <i>k</i> ≤ 17 –22 ≤ <i>l</i> ≤ 22	–18 ≤ <i>h</i> ≤ 23 –16 ≤ <i>k</i> ≤ 15 –31 ≤ <i>l</i> ≤ 32	–15 ≤ <i>h</i> ≤ 12 –19 ≤ <i>k</i> ≤ 18 –22 ≤ <i>l</i> ≤ 20	–15 <i>h</i> 15 –27 <i>k</i> 27 –24 <i>l</i> 24
No. of reflections measured	23217	33622	29217	25329	29857	51100	248100
No. of independent reflections used	4107	12300	9185	4189	6695	12083	4767
Redundancy	5.653	2.733	3.181	3.854	4.46	4.229	23.07
No. of unique reflections ( <i>I</i> > 3 $\sigma$ ( <i>I</i> )) used	3420	10211	6638	2999	4085	9191	4263
<i>R</i> ( <i>F</i> <sup>2</sup> ) <sub>int</sub>	0.0596	0.0476	0.0493	0.0727	0.0719	0.0604	0.0598
<i>R</i> <sub>sig</sub>	0.0490	0.0674	0.0570	0.0797	0.0729	0.0622	0.0285
<b>Absorption correction, refinement</b>							
<i>T</i> <sub>min</sub> / <i>T</i> <sub>max</sub>	0.112	0.482	0.380	0.629	0.646	0.346	0.360
<i>R</i> ( <i>F</i> ) obs	0.0284	0.0306	0.0346	0.0407	0.0394	0.0342	0.0547
w <i>R</i> ( <i>F</i> ) obs	0.0260	0.0265	0.0316	0.0396	0.0330	0.0355	0.0661
Max, min $\Delta\rho$ (e Å <sup>-3</sup> )	1.50/–1.20	1.17/–1.19	3.51/–2.14	5.41/–2.19	2.53/–3.07	2.16/–2.85	10.45/–5.18

uranium (VI) centred polyhedra. Various geometrical isomers were obtained according to the U:V ratio and the type of amine used. The geometrical difference lies in the orientation ordering of vanadium tetrahedra and the way the uranophane layers are linked to each other in the three dimensional framework either by the UO<sub>7</sub> pentagonal bipyramids or by both UO<sub>7</sub> pentagonal bipyramids and UO<sub>6</sub> square bipyramids. The average values of the U–O and V–O distances with the valence bond sums calculated using Burns parameters [50] for the U–O and Brese and O’Keeffe data [51] for the V–O bonds are reported in Table 2. Details of the U–O distances for the uranium pillars are given in Table 3.

### 3.2. The uranophane type two-dimensional uranyl-vanadate layers

In DMetU5V4 and PyrU5V4, the VO<sub>4</sub> tetrahedra sharing edges with one side of a uranyl chain alternatively point down (*d*) and up (*u*) which corresponds to the geometrical isomer *a/a* previously described by Locock and Burns [52]. However, two arrangements are observed: in DMetU5V4 two successive tetrahedra that share an edge or a vertex with the same UO<sub>7</sub> polyhedron point, alternatively, in the same or in the opposite direction leading to the *a<sub>du</sub>a<sub>du</sub>/a<sub>ud</sub>a<sub>ud</sub>* isomer (Fig. 1a) whilst for

PyrU5V4 the two tetrahedra sharing an edge or a vertex with the same UO<sub>7</sub> polyhedron point systematically in opposite direction giving the *a<sub>du</sub>a<sub>du</sub>/a<sub>ud</sub>a<sub>ud</sub>* isomer (Fig. 1b). In the first case, the tetrahedra that point up (and the tetrahedra that point down) form parallel broken lines, although in the second case the lines are straightforward. The *a<sub>du</sub>a<sub>du</sub>/a<sub>ud</sub>a<sub>ud</sub>* geometrical isomer was previously found in the C<sub>n</sub>U5V4 compounds [42] and in the caesium uranyl phosphate [53] and arsenate [54], Cs<sub>2</sub>(UO<sub>2</sub>)[(UO<sub>2</sub>)(XO<sub>4</sub>)<sub>4</sub> · nH<sub>2</sub>O. The *a<sub>du</sub>a<sub>du</sub>/a<sub>ud</sub>a<sub>ud</sub>* isomer exists in 3D uranyl-phosphates A<sub>2</sub><sup>BP</sup>(UO<sub>2</sub>)[(UO<sub>2</sub>)(PO<sub>4</sub>)<sub>4</sub> · nH<sub>2</sub>O, where A is a monovalent cation A = K<sup>+</sup>, Rb<sup>+</sup> [53], Tl<sup>+</sup> [55], Et<sub>2</sub>NH<sub>2</sub><sup>+</sup> [3], or the divalent piperazinium cation (N<sub>2</sub>C<sub>6</sub>H<sub>14</sub>)<sup>2+</sup> [6], in the 3D uranyl arsenates Rb<sub>2</sub>(UO<sub>2</sub>)[(UO<sub>2</sub>)(PO<sub>4</sub>)<sub>4</sub> · 2H<sub>2</sub>O [54] and in 2D compounds (Et<sub>3</sub>NH)[(UO<sub>2</sub>)<sub>2</sub>(XO<sub>4</sub>)(XO<sub>3</sub>OH)]<sub>4</sub> with X = P [2] and As [6], but this isomer is herein observed in uranyl-vanadates for the first time.

In the U4V3 compounds three different geometrical isomers can be distinguished considering the succession of tetrahedra that point up or down in a direction parallel to the diagonals of the layers (Fig. 1c–e). The same geometrical isomer is observed in the three compounds DMetU4V3, isoPrU4V3 and TMetU4V3 in which tetrahedra that point down (or up) form broken lines of four tetrahedra length segments (Fig. 1c). In CHexU4V3 and TButU4V3, three types of diagonal lines succeed one another in

**Table 2**Average U–O and V–O distances and bond valence for U and V atoms in the compounds *PyrU5V4*, *DMetU5V4*, *DMetU4V3*, *IsoprU4V3*, *TMetU4V3*, *CHexU4V3* and *TbutU4V3*.

	<i>PyrU5V4</i>	<i>DMetU5V4</i>	<i>DMetU4V3</i>	<i>IsoprU4V3</i>	<i>TMetU4V3</i>	<i>CHexU4V3</i>	<i>TbutU4V3</i>
U–O <sub>uranyl</sub>							
U1	1.7755(6)	1.784(1)	1.7775(5)	1.756(9)	1.786(7)	1.780(4)	1.731(5)
U2	1.778(6)	1.771(1)	1.779(5)	1.765(9)	1.770(7)	1.775(5)	1.777(5)
U3	1.781(6)	1.761(2)	1.7655(5)	1.775(9)	1.785(7)	1.789(4)	1.768(5)
U4	1.7705(8)		1.762(4)	1.783(5)	1.761(7)	1.773(5)	1.789(2)
U5	1.7765(6)						1.760(2)
U–O <sub>equatorial</sub>							
U1	2.397(6)	2.3934(1)	2.3686(4)	2.363(7)	2.381(7)	2.386(6)	2.380(5)
U2	2.397(6)	2.3718(1)	2.388(4)	2.392(7)	2.379(7)	2.377(6)	2.394(7)
U3	2.3672(6)	2.4102(3)	2.387(6)	2.370(4)	2.371(5)	2.441(6)	2.376(6)
U4	2.3984(6)		2.3994(5)	2.401(3)	2.409(7)	2.402(5)	2.392(4)
U5	2.3918(6)						2.289(1)
V–O							
V1	1.706(7)	1.702(2)	1.705(5)	1.715(7)	1.709(7)	1.711(5)	1.697(9)
V2	1.715(7)	1.722(2)	1.708(5)	1.712(7)	1.709(7)	1.708(5)	1.705(5)
V3	1.706(7)		1.707(5)	1.707(5)	1.707(7)	1.709(4)	1.719(5)
V4	1.716(7)						
Bond valence							
U1	5.99(3)	5.96(6)	6.12(2)	6.30(5)	6.00(3)	6.01(2)	6.38(5)
U2	5.98(3)	6.12(6)	6.00(2)	6.08(5)	6.12(4)	6.08(2)	6.00(5)
U3	5.99(3)	6.2(1)	6.09(2)	5.98(5)	6.01(4)	6.00(2)	6.15(5)
U4	6.03(4)		6.10(2)	5.95(5)	6.06(4)	5.99(2)	5.93(9)
U5	6.01(3)						6.03(8)
V1	5.20(5)	5.29(9)	5.24(3)	5.11(6)	5.18(5)	5.16(3)	5.36(7)
V2	5.10(4)	5.04(9)	5.18(3)	5.15(6)	5.19(5)	5.20(3)	5.25(8)
V3	5.21(5)		5.20(3)	5.20(7)	5.21(5)	5.18(3)	5.03(7)
V4	5.09(5)						

**Table 3**U–O distances for the uranium pillars in the compounds *PyrU5V4*, *DMetU5V4*, *DMetU4V3*, *IsoprU4V3*, *TMetU4V3*, *CHexU4V3* and *TbutU4V3*.

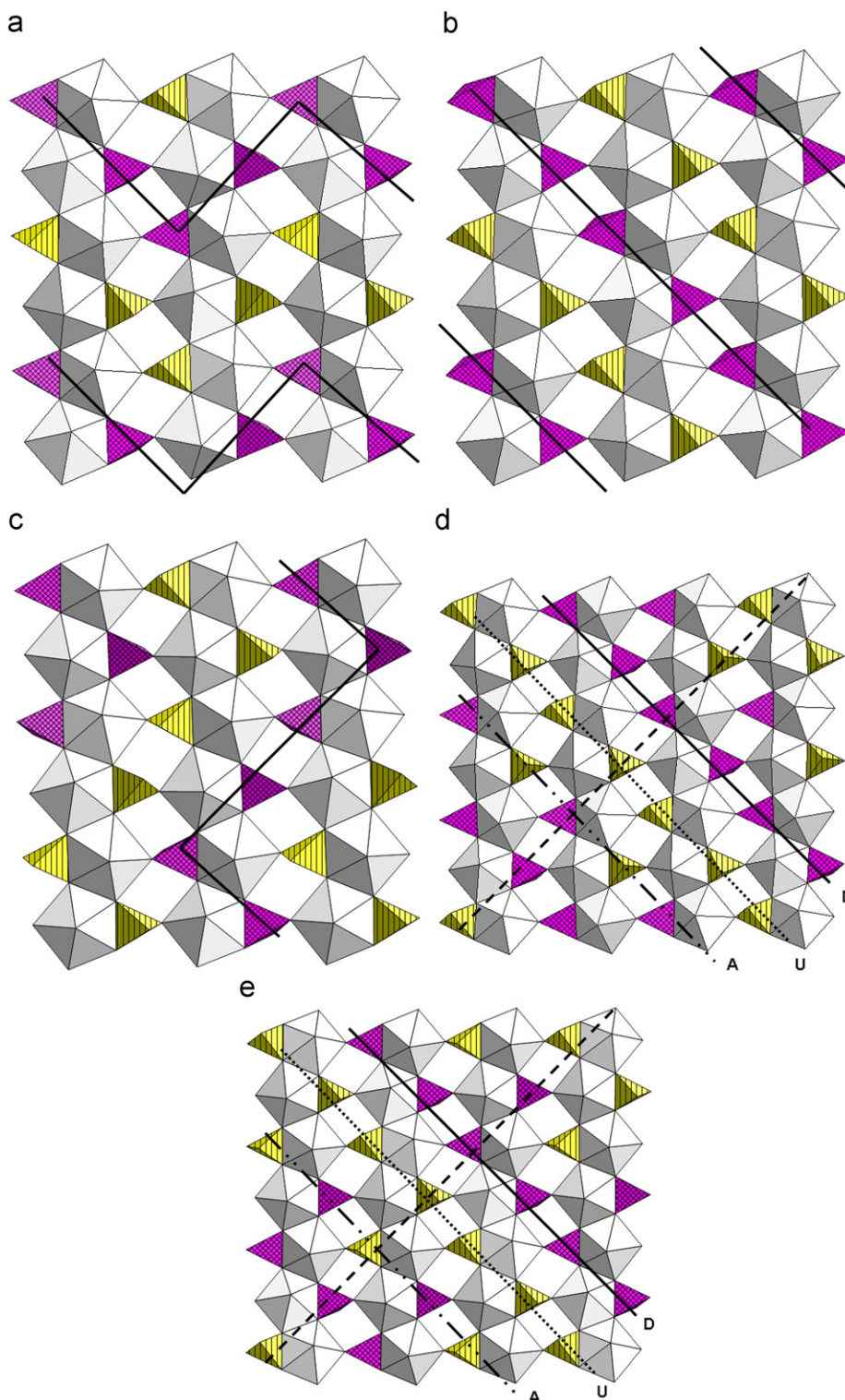
<i>DMetU5V4</i>		<i>PyrU5V4</i>		<i>DMetU4V3</i> and <i>isoPrU4V3</i>	
U3–O5	1.696(20)	U5–O5	2.453(7)	U4–O16	1.772(4)
U3–O6	1.82(2)	U5–O6	2.333(6)	U4–O17	1.752(4)
U3–O13	2.363(13)	U5–O15	2.340(6)	U4–O18	2.346(5)
U3–O13	2.363(13)	U5–O16	2.507(6)	U4–O19	2.321(5)
U3–O14	2.342(14)	U5–O20	1.784(7)	U4–O20	2.282(5)
U3–O14	2.342(14)	U5–O21	1.769(7)	U4–O21	2.455(5)
U3–Ow1	2.561(26)	U5–O22	2.326(7)	U4–Ow1	2.594(6)
					2.570(11)
<i>TMetU4V3</i>		<i>CHexU4V3</i>		<i>TbutU4V3</i>	
U4–O16	1.773(7)	U4–O16	1.771(5)	U4–O16	1.820(21)
U4–O17	1.748(7)	U4–O17	1.776(5)	U4–O17	1.771(21)
U4–O18	2.343(7)	U4–O18	2.351(5)	U4–O18	2.284(12)
U4–O19	2.434(7)	U4–O19	2.338(6)	U4–O18	2.284(12)
U4–O20	2.317(7)	U4–O20	2.322(5)	U4–O19	2.430(19)
U4–O21	2.346(7)	U4–O21	2.464(5)	U–O19	2.430(19)
U4–Ow1	2.605(8)	U4–Ow1	2.537(5)	U4–Ow1	2.557(19)
					1.769(22)
					1.784(20)
					2.265(16)
					2.265(16)
					2.299(18)
					2.299(18)
					1.769(22)

which all the tetrahedra point up (line U), or down (line D), or alternately up and down (line A). The two geometrical isomers *CHexU4V3* and *TbutU4V3* can be differentiated by considering the way the pairs of tetrahedra located on each side of the empty squares of the uranophane topology alternate along the direction perpendicular to lines U, D, and A. The difference between the sequences *dd/ud/uu* (Fig. 1d) and *du/ud* (Fig. 1e) found for *CHexU4V3* and *TbutU4V3*, respectively, can be explained by the translation of line A. These three new geometrical isomers are evidenced for the first time in uranyl–vanadate systems. The last one is also found in the two-dimensional uranyl–phosphate ( $\text{Pr}_4\text{NH}[(\text{UO}_2)_3(\text{PO}_4)(\text{HPO}_4)_2]$ ) obtained with tetrapropylammonium [2].

### 3.3. The uranyl polyhedra pillars and the three-dimensional uranyl–vanadate frameworks

In all the studied compounds uranyl ions are localized in the interlayer space and stand parallel to the layers. In *DMetU5V4* and *PyrU5V4*, a pair of tetrahedra that point down is above a pair of tetrahedra that point up giving four oxygen atoms directed to the interlayer space with an O–O distance compatible with the equatorial edge of an interlayer uranyl ion. These oxygen atoms are used to coordinate the interlayer uranyls whose equatorial plane is further completed by an oxygen atom belonging to a water molecule to form an  $[(\text{UO}_2)\text{O}_4(\text{H}_2\text{O})]$  pentagonal bipyramid (PBP). The  $[(\text{UO}_2)\text{O}_4(\text{H}_2\text{O})]$  PBP (Fig. 2a), denoted as P4 hereafter, act as



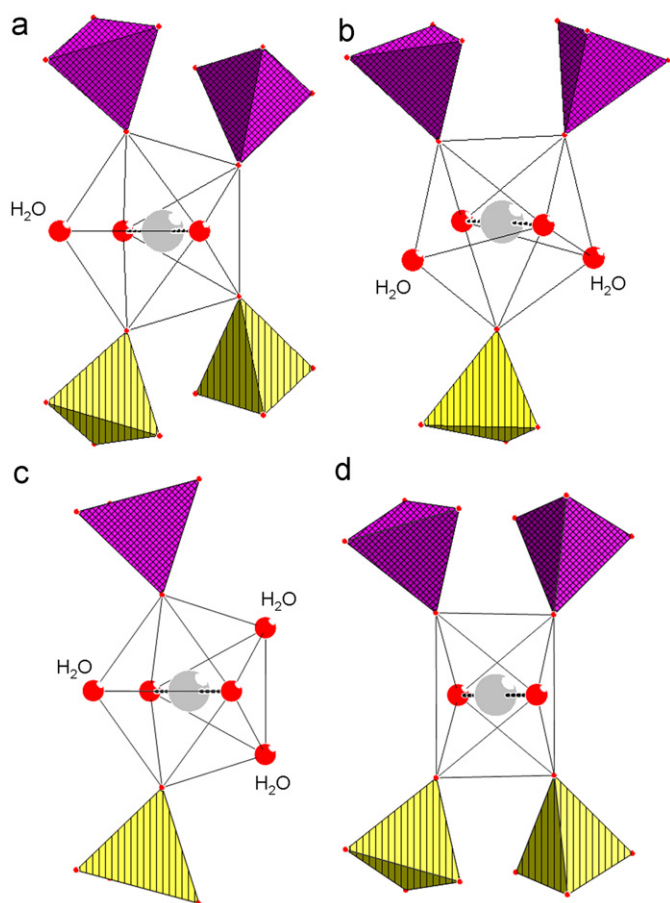


**Fig. 1.** The uranophane-type sheet in (a) *DMetU5V4*, (b) *PyrU5V4*, (c) *DMetU4V3* and *isoPrU4V3* and *TMetU4V3*, (d) *CHexU4V3*, and (e) *TButU4V3* (uranyl polyhedra are shown in grey,  $\text{VO}_4$  tetrahedra that point up in yellow, and  $\text{VO}_4$  tetrahedra that point down in purple). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

pillars between the two layers. There is one P4 pillar for four tetrahedra leading to inorganic three dimensional arrangements of formula  $\{[(\text{UO}_2)(\text{H}_2\text{O})][(\text{UO}_2)(\text{VO}_4)_4]^{2-}\}$ . It is interesting to note that in *PyrU5V4* the  $\text{UO}_2$  ions of the pillars are all parallel (“ferro-type” alignment) (Fig. 3a) whereas in *DMetU5V4* they are parallel in a

(001) plane but approximately perpendicular in two successive planes (“antiferro”-type alignment).

In the geometrical isomers of the other compounds there are again pairs of tetrahedra that point up but also “isolated” tetrahedra that point up. The compounds *DMetU4V3*, *isoPrU4V3*,



**Fig. 2.**  $[(\text{UO}_2)\text{O}_4(\text{H}_2\text{O})]$  PBP pillar (P4) linked to four tetrahedra (a).  $[(\text{UO}_2)\text{O}_3(-\text{H}_2\text{O})_2]$  PBP pillar (P3) linked to three tetrahedra (b).  $[(\text{UO}_2)\text{O}_2(\text{H}_2\text{O})_3]$  PBP pillar (P2) linked to two tetrahedra (c).  $[\text{UO}_6]$  octahedral pillar linked to four tetrahedra (P4') (d).

and *TMetU4V3* are based on the same geometrical isomer of the uranophane-type sheets that are pillared on the same way to give the same type of inorganic three-dimensional framework. In opposite to a pair of tetrahedra that point up the adjacent layer put a tetrahedron that points down. The three corresponding oxygen atoms belong to the equatorial plane of an interlayer uranyl ion that completes its coordination with two oxygen atoms of water molecules to create a  $[(\text{UO}_2)\text{O}_3(\text{H}_2\text{O})_2]$  PBP acting as a pillar between the two layers. This type of pillar is denoted hereafter P3 (Fig. 2b). There is one P3 pillar for three tetrahedra leading to inorganic three dimensional arrangements  $\{[(\text{UO}_2)(\text{H}_2\text{O})_2][(\text{UO}_2)(\text{VO}_4)]_3\}^-$  (Fig. 3b) never evidenced till date.

In *CHexU4V3*, two adjacent layers are related by an inversion centre so, above a succession of lines D/U/A, there is a succession U/A/D leading also to pillars P3 (between U and A and between A and D) (Fig. 3c) and to a three-dimensional arrangement with the formula  $\{[(\text{UO}_2)(\text{H}_2\text{O})_2][(\text{UO}_2)(\text{VO}_4)]_3\}^-$ . The uranyl ions of the pillars are all parallel (Fig. 4a).

The structural arrangement of *TButU4V3* is quite original. In this compound two adjacent layers are related by a mirror so, above the succession D/U/A is U/D/A and two types of pillars are formed. The first type of pillars lies in between the U and D lines where in front of a pairs of tetrahedra that point up the adjacent layer puts a pair of tetrahedra that point down. In this case no water molecule completes the equatorial plane of uranyl leading to a  $[(\text{UO}_2)\text{O}_4]$  square bipyramid and pillars denoted P4' (Fig. 2d). Additionally, the two lines A from adjacent layers put in opposite

to an "isolated" tetrahedron pointing up an "isolated" tetrahedron pointing down. The equatorial plane of the corresponding uranyl ion is completed by three water oxygen atoms giving a new pillar  $[(\text{UO}_2)\text{O}_2(\text{H}_2\text{O})_3]$  PBP denoted P2 (Fig. 2c). There is one pillar P4' for four tetrahedra and one pillar P2 for two tetrahedra giving a three-dimensional open framework  $\{[(\text{UO}_2)][(\text{UO}_2)(\text{H}_2\text{O})_3][(\text{UO}_2)(\text{VO}_4)]_6\}^{2-}$  (Fig. 3d). All the  $\text{UO}_2$  belonging to the same type of pillars (P2 or P4') are parallel in planes (001). They succeed in the sequence P4'P4'P2P2 in a way such as they are perpendicular to each other (Fig. 4b). Pillars P4' exist in the previously reported uranyl phosphate  $(\text{Et}_2\text{NH}_2)_2\{[(\text{UO}_2)][(\text{UO}_2)(\text{PO}_4)]_4\}$  [3]. A three dimensional uranyl-vanadate framework based on uranophane-type layers connected by only P2 pillars has been described in  $[(\text{UO}_2)(\text{H}_2\text{O})_3][(\text{UO}_2)(\text{VO}_4)]_2 \cdot 2\text{H}_2\text{O}$  [56]. Isotypic uranyl phosphate and uranyl vanadate have been reported [57,52] but it is the first time that both of the pillars P4' and P2 are found in a same structural arrangement.

### 3.4. Interstitial amines and water oxygen

The channels or holes created by the open uranyl-vanadate three-dimensional frameworks are occupied by protonated amines and occluded water molecules.

In *DMetU5V4*, the dimethyl ammonium ions are located approximately above all the  $\text{VO}_4$  tetrahedra of the  $[(\text{UO}_2)_2(\text{VO}_4)_2]^{2-}$  uranophane layers that point down, in positions similar to the caesium ions in the isotypic compounds  $\text{Cs}_2(\text{UO}_2)[(\text{UO}_2)(\text{XO}_4)]_4 \cdot n\text{H}_2\text{O}$ ,  $X = \text{P}$  [53],  $\text{As}$  [54]. They are alternately parallel and perpendicular to the uranophane layers.

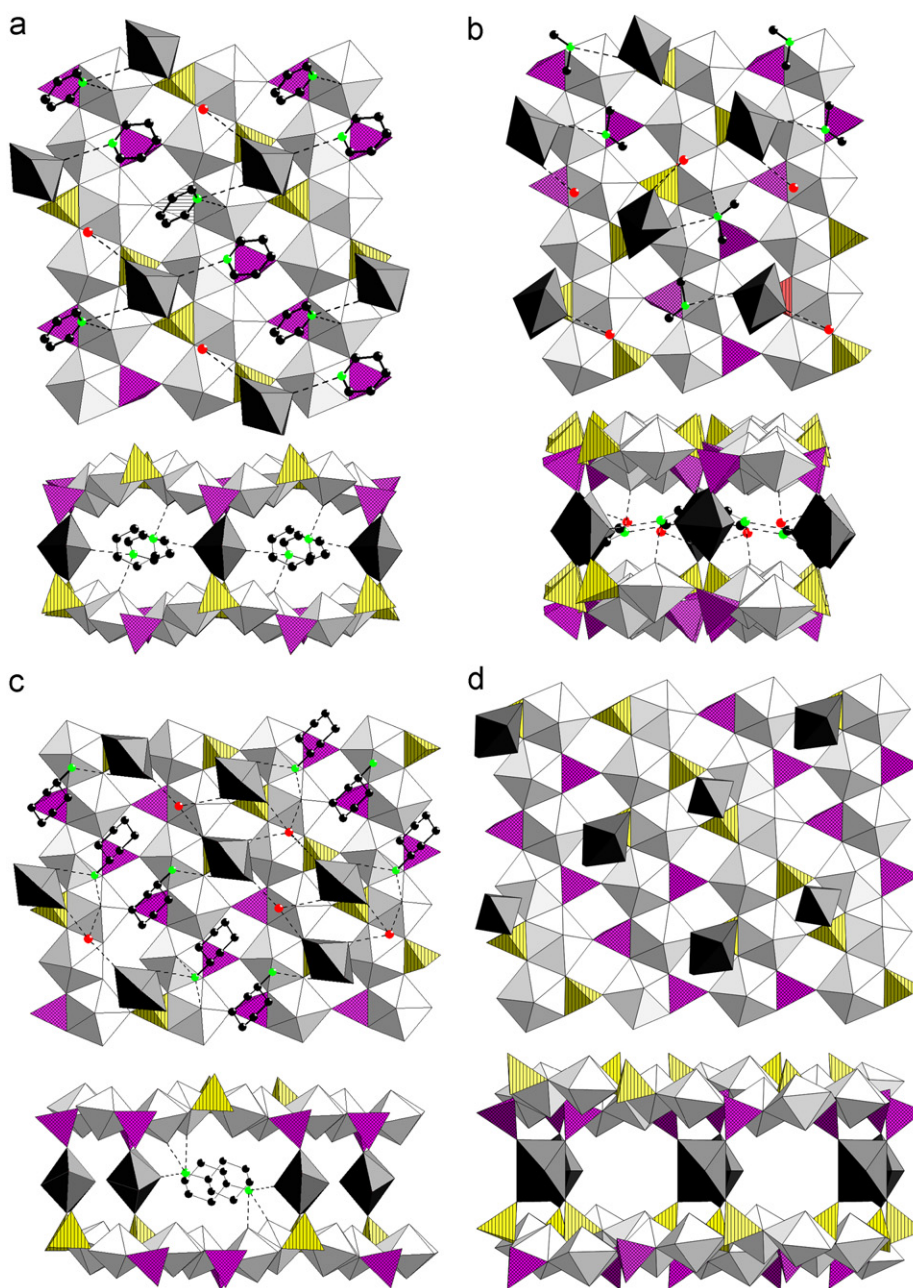
In *PyrU5V4*, there are two crystallographically independent pyridinium ions that occupy the channels running down the [100] direction and alternate above the tetrahedra that point down. They are connected to the inorganic framework through hydrogen bonds between the N atoms and uranyl oxygen atoms of both the pillars and the layers. The oxygen atoms of the occluded water molecules Ow2 are localized between P4 pillars and are connected to the water oxygen Ow1 of P4 through a hydrogen bond ( $\text{Ow}2-\text{Ow}1 = 2.74(1) \text{ \AA}$ ) (Fig. 3a).

In *DMetU4V3*, *isoPrU4V3*, and *TMetU4V3* (Fig. 3b), the organic cations occupy the two thirds of the holes between two tetrahedra that point away the interlayer space, the last third being occupied by water oxygen atoms Ow3 which are, in the three compounds, connected through a hydrogen bond to a water oxygen of the P3 pillar. In *DMetU4V3* and *isoPrU4V3* the cations are hydrogen bonded to one uranyl oxygen of the pillar P3 and one uranyl oxygen of U(3) that pertains to the uranophane-type sheet.

In *CHexU4V3*, the protonated cyclohexylamines are located in the channels created by all the pairs of tetrahedra that point away the interlayer space (Fig. 3c). They are connected through a strong hydrogen bond to one uranyl oxygen of the P3 pillars and through weaker bonds to two uranyl oxygens of the layers PBP. The occluded water oxygen (Ow3) is localized between P3 pillars to which it is connected through a hydrogen bonds network involving the equatorial water oxygens. It is also connected through weak bonds to the uranyl oxygen atoms of the third P3 pillar and of a layer PBP.

## 4. Conclusions

Many different organic templates can be used to hydrothermally synthesize hybrid organic-inorganic uranium vanadate materials in which the structure directing organic species is incorporated into a di- or tri-dimensional inorganic framework based on uranophane-type sheets while, in contrast, the natural uranyl vanadates are built from carnotite-type layers. In most of the compounds the



**Fig. 3.** Polyhedral representation of the three-dimensional uranyl-vanadate open frameworks  $\{[(\text{UO}_2)(\text{H}_2\text{O})] [(\text{UO}_2)(\text{VO}_4)_4]^{2-}$  in *PyrU5V4* (a);  $\{[(\text{UO}_2)(\text{H}_2\text{O})_2][(\text{UO}_2)(\text{VO}_4)_3]^{-}$  in *DMetU4V3*, *isoPrU4V3*, *TMetU4V3* (b) and *CHexU4V3* (c);  $\{[(\text{UO}_2)] [(\text{UO}_2)(\text{H}_2\text{O})_3][(\text{UO}_2)(\text{VO}_4)]_6\}^{2-}$  in *TButU4V3* (d) (uranyl polyhedra of the uranophane-type sheets are shown in grey, uranyl polyhedra that act as pillar in black.  $\text{VO}_4$  tetrahedra in hatched yellow and purple). Interstitial amine ions are shown in the channels. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

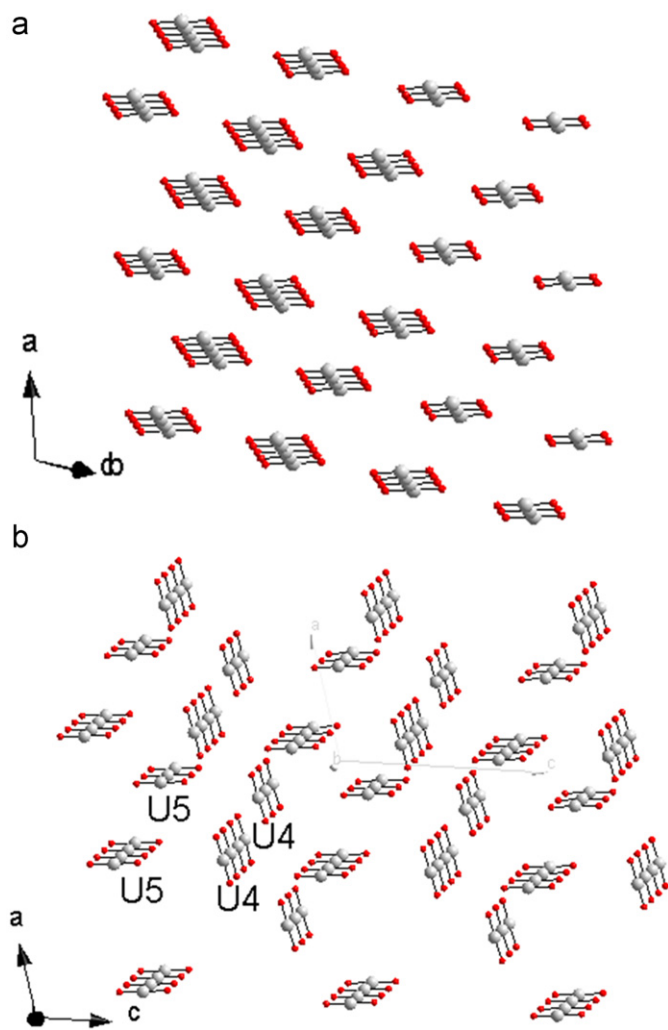
uranophane-type layers are pillared by uranium polyhedra. The materials reported in [42] and in this paper show that the composition (number of pillars and thus U/V ratio) and the detailed structure of the inorganic layers are influenced by the precise nature of the organic template used under similar reaction conditions.

The series of three-dimensional uranyl vanadates can be formulated  $A_{(N-2)/n}^{n+} \{ \text{PN} [ (\text{UO}_2)(\text{VO}_4)_N ] \}$  with  $\text{PN} = (\text{UO}_2)(\text{H}_2\text{O})_{5-N}$  and  $N = 2, 3, 4$ . The term  $N = 4$  ( $U/V = 5/4$ ) is obtained by using both di-protonated ( $n = 2$ ) [42] and mono-protonated ( $n = 1$ ) amines (this work), the term  $N = 3$  ( $U/V = 4/3$ ), reported for the first time in this work, is obtained only for  $n = 1$ , the term  $N = 2$  ( $U/V = 3/2$ ) is stabilized without organic template [56].

Compounds corresponding to the terms  $N = 4$  and  $N = 2$  have been obtained in uranyl-phosphate and uranyl-arsenate systems; synthesis of the term  $N = 3$  is planned.

No other term can be expected for this series; however, *TButU4V3* reveals the possibility of (i) new pillars  $\text{PN}'$  with  $\text{PN}' = (\text{UO}_2)(\text{H}_2\text{O})_{4-N}$  and (ii) simultaneous presence of two different pillars  $\text{P2}$  and  $\text{P4}'$  in the same inorganic arrangement. While, in this case, the average composition of the uranyl vanadate framework corresponds to that of  $N = 3$ , new series such as  $A_{(N_1+N_2-4)/n}^{n+} \{ \text{PN}_1 \text{PN}_2 [ (\text{UO}_2)(\text{VO}_4) ]_{N_1+N_2} \}$  can be foreseen leading to new compositions, as for example,  $U/V = 7/5$  ( $N_1 = 2, N_2 = 3$ ) or  $U/V = 9/7$  ( $N_1 = 3, N_2 = 4$ ).





**Fig. 4.** Orientation of the uranyl ions forming the pillars in *CHexU4V3* (a) and *TButU4V3* (b).

## Appendix. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2010.07.035.

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