



A new series of pillared uranyl-vanadates based on uranophane-type sheets in the uranium-vanadium-linear alkyl diamine systems

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ABSTRACT

A new family of three-dimensional (3D) uranyl vanadates ($C_3N_2H_{12}\{[(UO_2)(H_2O)][(UO_2)(VO_4)]_4\} \cdot 1H_2O$ (C3UV), ($C_4N_2H_{14}\{[(UO_2)(H_2O)][(UO_2)(VO_4)]_4\} \cdot 2H_2O$ (C4UV), ($C_5N_2H_{16}\{[(UO_2)(H_2O)][(UO_2)(VO_4)]_4\}$ (C5UV), ($C_6N_2H_{20}\{[(UO_2)(H_2O)][(UO_2)(VO_4)]_4\}$ (C6UV) and ($C_7N_2H_{22}\{[(UO_2)(H_2O)][(UO_2)(VO_4)]_4\}$ (C7UV) was prepared from mild-hydrothermal reactions using 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane and 1,7-diaminoheptane as structure directing agents. The five compounds are orthorhombic, space group $Cmc2_1$, with $a \approx 15.6$, $b \approx 14.1$, $c \approx 13.6$ Å. The structures were solved using single-crystal X-ray diffraction data. The compounds contain the same three-dimensional inorganic framework built from uranyl-vanadate layers of uranophane-type anion topology pillared by $[UO_6(H_2O)]$ pentagonal bipyramids. The doubly protonated diamines reside in the cavities created by the inorganic framework and are linked to the inorganic framework through hydrogen bonds involving one nitrogen atom. The structure is compared with that of uranyl-phosphates and uranyl-arsenates containing alkaline metals. The use of alkaline metals for the synthesis of uranyl-vanadates leads to carnotite-type compounds.

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1. Introduction

The large number of published papers focusing on the solid state chemistry of uranyl-containing inorganic compounds enlightens diversity in this subject. Most of the reported compounds put forward hexavalent uranium polyhedra associated to various oxoanions such as phosphate, vanadate, molybdate... The great diversity of structural arrangements of these compounds can be explained by the manifold polyhedral building units of both uranium (VI) and oxoanions. Generally, the uranyl ions coordination is completed in the equatorial plane by oxygen atoms shared with the oxoanions to build two-dimensional arrangements. Most often, the presence of the uranyl ions precludes the linkage in the third direction, so layered compounds are obtained [1,2]. However, in some cases, three-dimensional rigid open-frameworks are built from sheets pillared by uranium (VI) polyhedra through the oxygen atoms of the oxoanions not involved in the sheets, or, rarely, through cation–anion interactions. The first framework based on uranophane-type sheets pillared by $(UO_2)O_2(H_2O)_3$ pentagonal bipyramids has been evidenced in the uranyl-vanadate $(UO_2)\{[(UO_2)(VO_4)]_2\} \cdot 5H_2O$ [3]. The neutral framework creates perpendicular channels occupied by water molecules. The phosphate and arsenate $(UO_2)\{[(UO_2)(XO_4)]_2\} \cdot 4H_2O$ ($X=P$ [4] and

$X=As$ [5]) possess homeotypic frameworks. Similar anionic frameworks but with less pillars $[(UO_2)\{(UO_2)(XO_4)\}_4]^{2-}$ have been obtained using alkali metals K ($X=P$) [6], Rb and Cs ($X=P, As$) [7], thallium ($X=P$) [8] or the piperazinium cation ($N_2C_4H_{12}^{2+}$) ($X=P$) [9]. Finally $(Et_2NH_2)_2\{(UO_2)\{(UO_2)(PO_4)\}_4\}$ [10] contains a similar framework but with uranium octahedra acting as pillars.

As part of our ongoing study on the crystal chemistry of uranyl-vanadates [11–19] we are exploring the role of various amines as template or structure directing agent for the hydrothermal synthesis of compounds with novel structural topologies. There are numerous recent studies dedicated to the chemistry of organically templated uranium (VI) molybdates [20–24], chromates [25], silicates [26], sulfates [27–33], selenates [34–41], phosphates [9,10,42–45] and arsenates [9,46], which shows the diversity of the inorganic arrangement according to the organic molecule used, but the chemistry of organically templated uranium vanadates remains unexplored so far. Recently, we reported six new diamine templated layered uranyl-vanadate compounds [47]. The investigations were herein extended to the study of the effect of linear alkyl diamine chains on the structure of the uranyl-vanadates. A series of compounds with the formula $(C_nN_2H_{2n+6})\{[(UO_2)(H_2O)][(UO_2)(VO_4)]_4\} \cdot xH_2O$ was synthesized using 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane and 1,7-diaminoheptane. The obtained compounds are designated hereafter C_nUV , where C_n are di-protonated alkyl diamines $C_nN_2H_{2n+6}^{2+}$ with $n=3-7$. Their crystal structures are reported in the present paper.

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Table 1
Details of the data collection and refinement.

	C3UV	C4UV	C5UV	C6UV	C7UV
Crystallographic data					
Crystal system			orthorhombic		
Space group			<i>Cmc</i> ₂₁		
Unit-cell dimensions (Å)					
<i>a</i>	15.2754(2)	15.558(1)	15.7246(7)	15.6926(5)	15.9505(6)
<i>b</i>	14.1374(2)	14.1876(9)	14.1208(5)	14.2108(3)	14.1889(6)
<i>c</i>	13.6609(2)	13.6903(9)	13.5697(5)	13.7003(3)	13.7168(5)
Cell volume (Å ³)	2950.13(7)	3022.0(3)	3013.1(2)	3055.23(2)	3104.4(2)
<i>Z</i>	4	4	4	4	4
Density, calculated (g cm ⁻³)	4.2449(7)	4.2778(5)	4.2975(3)	4.2687(2)	4.1969(3)
<i>F</i> (000)	3231	3287	3247	3271	3099
Intensity collection					
Wavelength (Å)	0.71069 (MoK α) for all				
θ range (deg)	1.96–31.05	2.45–29.05	1.94–28.51	1.93–24.62	1.92–32.19
	–21 $\leq h \leq$ 22	–20 $\leq h \leq$ 21	–20 $\leq h \leq$ 21	–18 $\leq h \leq$ 17	–23 $\leq h \leq$ 20
Data collected	–20 $\leq k \leq$ 19	–18 $\leq k \leq$ 19	–18 $\leq k \leq$ 18	–16 $\leq k \leq$ 16	–19 $\leq k \leq$ 18
	–18 $\leq l \leq$ 19	–18 $\leq l \leq$ 18	–18 $\leq l \leq$ 13	–16 $\leq l \leq$ 16	–20 $\leq l \leq$ 20
No. of reflections measured	27 953	12 699	15 711	13 005	15 105
No. of independent reflections	4556	3852	3269	2618	5194
Redundancy	6.137	3.297	4.808	4.969	2.908
No. of unique reflections	3806	3461	2714	2112	3438
μ (MoK α) (mm ⁻¹)	28.649	27.974	28.049	27.664	27.227
<i>R</i> (<i>F</i> ²) _{int}	0.0891	0.0536	0.0662	0.0803	0.0740
Refinement					
No. of parameters	117	126	120	123	102
Weighting scheme	1/ σ^2	1/ σ^2	1/ σ^2	1/ σ^2	1/ σ^2
<i>R</i> (<i>F</i>) obs/all	0.0358/0.0469	0.0340/0.0401	0.0488/0.0615	0.0533/0.0677	0.0465/0.0882
w <i>R</i> (<i>F</i>) obs/all	0.0337/0.0351	0.0385/0.0401	0.0471/0.0483	0.0563/0.0578	0.0497/0.0537
Max, min $\Delta\rho$ (e. Å ⁻³)	4.04/–4.64 ^a	1.84/–1.81	2.89/–2.74	1.68/–1.54	4.69/–3.37 ^a

^a Close to U.**Tables 2**Atomic coordinates ($\times 10^5$ for U, $\times 10^4$ for V) and displacement parameters (in Å² $\times 10^4$) for U and V atoms in the compounds C*n*UV, *n*=3–7.

Atom	Wyck.	compound	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
U1	8 <i>b</i>	C3UV	22183(2)	49207(2)	43733	69.4(9)	116(2)	41(2)	52(2)	–2(2)	–3(2)	2(2)
		C4UV	22448(2)	49199(3)	43733	88.5(12)	91(2)	103(2)	64(2)	–3(2)	2(2)	–32(17)
		C5UV	23362(4)	49281(4)	43733	105.5(18)	217(4)	45(3)	50(3)	–4(3)	1(3)	1(2)
		C6UV	22869(8)	49290(8)	43733	76(4)	131(6)	57(7)	41(6)	–17(6)	1(7)	8(5)
		C7UV	22923(5)	49184(4)	43733	138.6(17)	302(3)	80(3)	34(2)	–17(3)	–4(3)	0(2)
U2	8 <i>b</i>	C3UV	27336(2)	74046(3)	55971(4)	70.1(9)	118(2)	41(2)	52(2)	–2(2)	6(2)	4(2)
		C4UV	27007(3)	74013(3)	55944(4)	90.5(12)	104(2)	107(2)	62(2)	30(2)	5(2)	2(2)
		C5UV	27805(4)	74032(4)	56121(7)	93.2(18)	188(4)	34(3)	51(3)	5(3)	3(3)	0(2)
		C6UV	27310(7)	74032(8)	55976(11)	73(4)	123(6)	60(7)	36(5)	–1(6)	21(7)	1(5)
		C7UV	27020(4)	74017(4)	56012(5)	124.8(16)	257(3)	77(3)	40(2)	16(3)	3(3)	–3(2)
U3	4 <i>a</i>	C3UV	5000	59591(4)	22832(5)	82.8(13)	99(2)	78(2)	71(2)	0	0	–7(2)
		C4UV	5000	59595(4)	23270(6)	91.5(14)	77(2)	97(3)	101(2)	0	0	–6(2)
		C5UV	5000	60891(7)	23007(9)	143(3)	179(6)	125(5)	121(4)	0	0	–25(4)
		C6UV	5000	60559(11)	23221(16)	93(5)	113(2)	103(9)	65(8)	0	0	–18(8)
		C7UV	5000	59844(6)	23175(8)	179(3)	220(5)	205(5)	111(3)	0	0	–50(3)
V1	8 <i>b</i>	C3UV	2552(1)	5129(1)	1699(1)	71(5)	113(8)	47(8)	54(8)	0(6)	–2(5)	0(6)
		C4UV	2603(1)	5134(1)	1698(1)	82(5)	89(8)	108(10)	50(10)	–12(7)	–5(6)	7(7)
		C5UV	2671(2)	5151(2)	1669(2)	128(10)	234(17)	95(17)	56(17)	9(14)	12(12)	–25(10)
		C6UV	2653(4)	5144(4)	1684(4)	150(20)	180(3)	14(4)	14(4)	0(3)	20(3)	–10(3)
		C7UV	2666(2)	5147(2)	16812(17)	147(8)	294(16)	118(15)	28(11)	–28(13)	–11(10)	–4(9)
V2	8 <i>b</i>	C3UV	3065(1)	7376(1)	3265(1)	76(4)	126(8)	44(8)	57(7)	–8(6)	5(7)	3(6)
		C4UV	3065(1)	7362(1)	3277(1)	91(5)	117(10)	94(9)	63(8)	13(7)	6(8)	–4(7)
		C5UV	3092(2)	7419(2)	3208(2)	106(9)	213(19)	72(15)	37(13)	25(14)	10(12)	1(10)
		C6UV	3071(4)	7390(4)	3256(4)	120(19)	220(4)	9(3)	4(3)	1(3)	–2(3)	–10(2)
		C7UV	3082(2)	73587(19)	32853(18)	133(8)	286(17)	76(13)	37(9)	31(12)	–1(11)	10(9)

2. Experimental

2.1. Synthesis

The five compounds were prepared in acidic medium (pH \approx 2) by means of using the same hydrothermal conditions and

a U/V/amine ratio of 1/2/2.5. For each considered linear diamine, 1,2-diaminoethane (Alfa Aesar 99%, *d*=0.899), 1,3-diaminopropane (Acros 99%, *d*=0.888), 1,4-diaminobutane (Aldrich 99%, *d*=0.877), 1,5-diaminopentane (Acros 98%, *d*=0.87), 1,6-diaminohexane (Acros 99.5%), 1,7-diaminoheptane (Acros 98%), a mixture of uranyl nitrate (UO₂(NO₃)₂·6H₂O Prolabo, R.P.

Tables 3Atomic coordinates ($\times 10^4$) and displacement parameters (in $\text{\AA}^2 \times 10^4$) for the oxygen atoms of the uranyl-vanadate framework in the compounds CrUV, $n=3-7$.

Atom	Wyck.		x	y	z	U_{iso}
O1	8b	C3UV	3332(4)	4611(5)	4262(5)	012(1)
		C4UV	3340(5)	4609(5)	4260(6)	014(2)
		C5UV	3393(8)	4539(8)	4180(9)	018(3)
		C6UV	3393(12)	4578(13)	4244(15)	014(5)
		C7UV	3353(7)	4602(7)	4287(8)	016(2)
O2	8b	C3UV	1113(4)	5217(5)	4498(5)	015(2)
		C4UV	1144(5)	5230(5)	4532(6)	016(2)
		C5UV	1267(8)	5311(8)	4508(9)	019(3)
		C6UV	1203(12)	5265(13)	4481(16)	015(5)
		C7UV	1213(7)	5215(7)	4506(8)	018(2)
O3	8b	C3UV	1605(4)	7579(5)	5405(4)	009(1)
		C4UV	1599(5)	7564(5)	5413(6)	014(2)
		C5UV	1662(9)	7457(9)	537(1)	027(4)
		C6UV	1591(13)	7530(14)	5402(15)	022(6)
		C7UV	1601(7)	7520(7)	5400(7)	019(3)
O4	8b	C3UV	3868(4)	7209(5)	5754(5)	012(1)
		C4UV	3828(5)	7194(5)	5739(6)	016(2)
		C5UV	3891(7)	7302(8)	5715(9)	014(3)
		C6UV	3838(12)	7233(12)	5713(15)	011(5)
		C7UV	3797(7)	7246(7)	5761(8)	017(2)
O5	4a	C3UV	5000	6594(8)	1158(7)	016(2)
		C4UV	5000	6636(8)	1239(8)	012(2)
		C5UV	5000	6648(13)	1026(14)	021(4)
		C6UV	5000	673(2)	118(2)	025(9)
		C7UV	5000	6675(13)	1247(12)	031(4)
O6	4a	C3UV	5000	5314(7)	3403(7)	012(2)
		C4UV	5000	5311(7)	3421(8)	014(2)
		C5UV	5000	5551(12)	3417(13)	016(4)
		C6UV	5000	5438(19)	343(2)	014(7)
		C7UV	5000	5280(11)	3378(11)	020(4)
O7	8b	C3UV	3068(4)	8305(5)	4114(4)	010(1)
		C4UV	3053(5)	8296(5)	4112(5)	012(2)
		C5UV	3038(7)	8313(8)	4053(8)	010(3)
		C6UV	3041(12)	8307(13)	4085(12)	009(5)
		C7UV	3049(7)	8305(7)	4086(6)	013(2)
O8	8b	C3UV	2117(4)	5967(5)	0919(5)	011(1)
		C4UV	2153(5)	5979(5)	0917(6)	012(2)
		C5UV	2213(8)	5958(8)	0865(8)	013(3)
		C6UV	2217(11)	5971(13)	0889(12)	003(4)
		C7UV	2217(6)	5977(7)	0896(6)	008(2)
O9	8b	C3UV	2525(5)	4204(5)	0871(5)	011(1)
		C4UV	2542(5)	4196(5)	0870(6)	014(2)
		C5UV	2726(8)	4230(8)	0827(8)	015(3)
		C6UV	2631(13)	4226(14)	0863(14)	020(6)
		C7UV	2602(7)	4219(8)	0884(7)	018(3)
O10	8b	C3UV	2652(4)	6496(5)	4055(5)	009(1)
		C4UV	2636(5)	6508(6)	4045(6)	013(2)
		C5UV	2790(8)	6501(9)	3983(9)	014(3)
		C6UV	2699(13)	6526(15)	4056(14)	017(5)
		C7UV	2664(7)	6500(8)	4069(7)	016(2)
O11	8b	C3UV	1945(5)	4956(5)	2719(5)	011(1)
		C4UV	2010(5)	4957(6)	2722(6)	015(2)
		C5UV	2066(9)	4919(9)	2657(10)	022(3)
		C6UV	2105(13)	4955(13)	2679(14)	010(5)
		C7UV	2126(7)	4973(8)	2703(8)	016(2)
O12	8b	C3UV	2411(4)	7565(4)	2292(6)	011(1)
		C4UV	2444(5)	7547(5)	2271(7)	011(2)
		C5UV	2415(8)	7558(7)	2258(10)	014(3)
		C6UV	2459(12)	7560(12)	2259(15)	010(5)
		C7UV	2495(7)	7546(7)	2272(9)	017(2)
O13	8b	C3UV	4083(5)	7118(5)	2905(5)	013(2)
		C4UV	4074(6)	7097(6)	2983(5)	017(2)
		C5UV	4090(9)	7283(9)	2769(10)	019(3)
		C6UV	4079(14)	7162(14)	2907(13)	013(5)
		C7UV	4070(8)	7120(9)	2991(7)	020(3)
O14	8b	C3UV	3577(5)	5399(5)	1995(5)	016(2)
		C4UV	3611(5)	5407(5)	1977(6)	014(2)
		C5UV	3643(8)	5490(9)	1983(9)	022(3)

Tables 3 (continued)

Atom	Wyck.		x	y	z	U_{iso}
Ow1	4a	C6UV	3644(13)	5437(14)	1943(14)	022(6)
		C7UV	3642(8)	5409(8)	1938(8)	022(3)
		C3UV	5000	4460(8)	1227(7)	018(2)
		C4UV	5000	4439(8)	1293(8)	019(3)
		C5UV	5000	4409(17)	1448(17)	045(6)
		C6UV	5000	455(2)	115(2)	024(8)
		C7UV	5000	4505(13)	1229(12)	031(4)

Table 4

Atomic coordinates (in Å) and isotropic displacement parameters (in Å²) for the interlayer molecules in the compounds C_nUV, n=3–7.

Atom	Wyck.	Comp	Occ.	x	y	z	U_{iso}
N1	4a	C3UV	0.5	0.6569(9)	−0.0829(8)	0.016(3)	
		C4UV	0.5	0.650(1)	−0.074(1)	0.018(3)	
		C5UV	0.5	0.658(2)	−0.114(2)	0.042(7)	
		C6UV	0.5	0.631(3)	−0.071(3)	0.040(12)	
		C7UV	0.5	0.655(3)	−0.082(3)	0.119(15)	
C1	4a	C3UV	0.5	0.706(1)	−0.178(1)	0.033(4)	
		C4UV	0.5	0.809(2)	−0.150(2)	0.045(6)	
		C5UV	0.5	0.753(4)	−0.129(6)	0.12(2)	
		C6UV	0.5	0.679(5)	0.830(5)	0.06(2)	
C2	4a	C3UV	0.5	0.810(1)	0.839(1)	0.031(4)	
		C4UV	0.5	0.870(3)	0.688(3)	0.05(1)	
		C5UV	0.5	0.793(4)	0.781(4)	0.079(14)	
		C6UV	0.5	0.784(3)	0.840(3)	0.023(12)	
C3	4a	C3UV	0.5	0.871(1)	0.748(1)	0.037(4)	
		C4UV	0.5	0.528(2)	0.696(2)	−0.163(2)	0.040(8)
		C5UV	0.5	0.897(3)	0.764(3)	0.053(11)	
		C6UV	0.5	0.833(4)	0.751(5)	0.059(19)	
C4	8b	C4UV	0.5	0.532(3)	0.879(3)	0.774(3)	0.06(1)
		C5UV	0.5	−0.047(4)	0.673(4)	0.090(16)	
		C6UV	0.5	−0.066(3)	0.751(4)	0.028(14)	
C5	4a	C5UV	0.5	0.068(3)	0.689(4)	0.081(15)	
		C6UV	0.5	0.018(4)	0.148(3)	0.031(14)	
C6	4a	C6UV	0.5	0.912(5)	0.162(4)	0.06(2)	
		C3UV	0.5	−0.027(1)	0.768(1)	0.028(3)	
N2	4a	C4UV	0.5	0.943(2)	0.607(2)	0.096(9)	
		C5UV	0.5	0.117(3)	0.588(3)	0.087(13)	
		C6UV	0.5	0.868(3)	0.067(3)	0.040(12)	
Ow2	4a	C3UV	0.5	0.104(2)	0.627(1)	0.086(6)	
		C4UV	0.5	0.858(1)	0.415(1)	0.071(6)	
Ow3	4a	C4UV	0.5	0.874(2)	0.161(2)	0.14(1)	

normapur-100.4 mg, 0.2 mmol), vanadium oxide (V₂O₅ Merck, Extra pur-36.4 mg, 0.2 mmol) and linear alkyl diamine (NH₂(CH₂)_nNH₂)

with 3 ≤ n ≤ 7 (2.5 ml of a 0.2 mol/L solution, 0.5 mmol) was dissolved in deionised water (2.5 ml, 138 mmol) added with hydrochloric acid (HCl, Carlo Erba, 37%, d=1.186–2.5 ml of a 0.4 mol/L solution, 1 mmol). The solutions were heated to 180 °C, in 23 mL Teflon-lined Parr steel autoclaves, for 48 h. The resulting solids were collected after cooling to ambient temperature, filtration and washing with deionised water in 60–75% yields for n=3–6 and a low 16% yield for n=7. They consist of powders with color evolving from yellow (n=3, 4) to green (n=5–7) accompanied by some crystals. For each experiment, X-ray diffraction patterns of the crushed crystals and of the powder are identical. They match the X-ray diffraction patterns calculated from the single crystal results, indicating that both powder and crystals belong to the same compound.

Table 5

Principal interatomic distances (in Å) and uranyl angles in the compounds C_nUV, n=3–7.

	C3UV	C4UV	C5UV	C6UV	C7UV
U1–O1	1.763(6)	1.767(8)	1.770(12)	1.815(19)	1.754(11)
U1–O2	1.750(8)	1.780(8)	1.776(12)	1.773(19)	1.782(11)
O1–U–O2	174.62(49)	177.98(35)	177.34(57)	179.10(85)	177.71(51)
U1–O7	2.353(7)	2.376(7)	2.395(11)	2.395(18)	2.386(10)
U1–O8	2.460(7)	2.474(8)	2.388(11)	2.441(17)	2.448(9)
U1–O9	2.436(7)	2.447(8)	2.383(11)	2.429(19)	2.457(10)
U1–O10	2.364(7)	2.377(8)	2.392(13)	2.400(21)	2.359(11)
U1–O11	2.297(7)	2.292(8)	2.367(14)	2.339(19)	2.308(11)
U2–O3	1.761(6)	1.747(8)	1.791(14)	1.818(20)	1.786(11)
U2–O4	1.768(6)	1.791(8)	1.758(11)	1.761(19)	1.774(11)
O3–U–O4	176.85(49)	177.43(36)	173.60(58)	176.03(82)	177.51(51)
U2–O7	2.446(6)	2.456(7)	2.508(11)	2.486(17)	2.504(9)
U2–O8	2.355(7)	2.351(7)	2.339(11)	2.346(18)	2.339(10)
U2–O9	2.327(7)	2.311(7)	2.326(11)	2.349(20)	2.338(11)
U2–O10	2.470(7)	2.473(8)	2.552(12)	2.453(20)	2.462(10)
U2–O12	2.327(8)	2.307(10)	2.255(14)	2.296(21)	2.314(12)
U3–O5	1.778(10)	1.771(11)	1.901(19)	1.835(28)	1.765(17)
U3–O6	1.781(10)	1.757(11)	1.695(18)	1.754(27)	1.765(15)
O5–U–O6	178.30(76)	178.72(50)	177.89(82)	178.57(12)	179.22(74)
U3–O13	2.317(7)	2.342(9)	2.301(13)	2.281(21)	2.377(12)
U3–O13	2.317(7)	2.342(9)	2.301(13)	2.281(21)	2.377(12)
U3–O14	2.347(8)	2.349(8)	2.336(13)	2.36(2)	2.373(13)
U3–O14	2.347(8)	2.349(8)	2.336(13)	2.36(2)	2.373(13)
U3–Ow1	2.563(11)	2.581(11)	2.640(24)	2.675(28)	2.576(18)
V1–O8	1.728(7)	1.752(8)	1.734(12)	1.742(18)	1.749(10)
V1–O9	1.730(7)	1.751(8)	1.733(11)	1.723(20)	1.715(11)
V1–O11	1.692(7)	1.696(8)	1.676(14)	1.634(20)	1.663(11)
V1–O14	1.661(8)	1.659(8)	1.657(13)	1.649(21)	1.639(13)
V2–O7	1.752(7)	1.752(7)	1.708(11)	1.729(18)	1.735(10)
V2–O10	1.764(7)	1.737(9)	1.735(13)	1.746(21)	1.755(11)
V2–O12	1.684(8)	1.703(9)	1.683(13)	1.687(21)	1.697(12)
V2–O13	1.671(8)	1.663(9)	1.690(14)	1.684(22)	1.662(13)

No precipitate was obtained by using 1,2-diaminoethane in the same conditions: alone a green solution results from the hydrothermal treatment. Two-dimensional compounds (C_nN₂H_{2n+6}) [(UO₂)₂(V₂O₈)] with structure based on carnotite-type layers were obtained for n=2 and 3 starting from a U/V/amine ratio of 1/1/2.5 obtained by using twice less vanadium oxide [47]. Using this U/V/amine ratio and longer 1,n-diaminoalkanes with n=4–7 leads to C_nUV compounds and crystals of less good quality than a U/V/amine ratio equal to 1/2/2.5.

2.2. Crystal structure determination

Single crystals were isolated under an optical microscope. The selected crystals were mounted on a glass fibre and aligned on a 3 circles Bruker SMART diffractometer equipped with a CCD detector (BRUKER SMART CCD 1 K or APEX II) for single-crystal

X-ray diffraction experiments. The intensities were collected at 100 K using an OXFORD Cryosystem CRYOSTREAM 700 and MoK α radiation selected by a graphite monochromator. Between 2500 and 3900 frames were collected in order to cover the full sphere. The individual frames of the single crystals of C₄UV, C₆UV and C₇UV were measured using a Ω -scan technique while those of the single crystals of C₃UV and C₅UV were measured using an optimised Φ and Ω -scan collection strategy (COSMO BRUKER program [48]). Acquisition time was fixed at 25 s/frame for C₃UV and at 20 s/frame for C₄UV–C₇UV.

The BRUKER program SAINT [49] 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 [50]. Details of the data collection and refinement are given in Table 1.

The obtained compounds all exhibit orthorhombic symmetry with parameters close to 15.5, 14.1 and 13.6 Å for *a*, *b* and *c*, respectively. The crystal structures were solved in the non-centrosymmetric space group *Cmc*2₁. The heavy atoms (U, V) positions were established by direct methods using the SIR97 program [51]. The oxygen, nitrogen and carbon atoms were localized from difference Fourier maps. Since refining anisotropic

temperature factors for all atoms resulted in some non-positive definite values for some oxygen atoms of the structure, the last cycles of refinement included atomic positions and anisotropic displacement parameters for the heaviest atoms U and V but isotropic displacement parameters for C, N and O. Hydrogen atoms could not be located as often the case in heavy uranium atoms containing phases. Full-matrix least squares structure refinements against F were carried out using the JANA2000 program [52]. The atomic positional parameters and displacement parameters are given in Tables 2 to 4. Selected interatomic distances and uranyl angles are reported in Table 5. The data reported for each of the C_nUV compound were differentiated one from another by using specific fonts: bold for C3UV; standard typesetting for C4UV; bold and italic for C5UV; italic for C6UV and standard typesetting for C7UV.

2.3. Powder X-ray diffraction

The X-ray diffraction patterns of the solids were recorded with a Bruker AXS D8 ADVANCE diffractometer with the parafocusing Bragg–Brentano geometry, using CuK α ₁, α ₂ radiation ($\lambda_{k\alpha 1} = 1.54051$ Å, $\lambda_{k\alpha 2} = 1.54433$ Å) and an energy dispersive detector (sol-X). The patterns were recorded under air over the angular range 5–90° (2 θ), with a step length of 0.02° (2 θ) and a counting time of 15 s.step⁻¹. Purity of the solids was systematically checked applying the “pattern matching” option of the FullProf program [53] to the whole diagram. The peak shape was fitted by a pseudo-Voigt function. In order to describe the angular dependence of the peak full-width at half-maximum (H), the formula of Caglioti et al. [54] was used, where *U*, *V* and *W* are parameters refined in the process. The calculations involved the refinement of 2 θ zeropoint, cell parameters and background level by a polynomial function. The fit of calculated data in regard to the observed data was indicated by the reliability factors and by the plot of observed and calculated patterns as represented for C5UV in Fig. 1.

2.4. FTIR Microspectrometry

The FT-IR spectra were recorded in air using a Bruker IFS 88 spectrometer coupled with a Bruker IR II microscope. The FT-IR spectra were collected using single crystals in transmission mode applying a resolution of 4 cm⁻¹ and 200 scans. The single crystals were put on a BaF₂ window which is transparent in the studied wave-numbers range (4000–800 cm⁻¹).

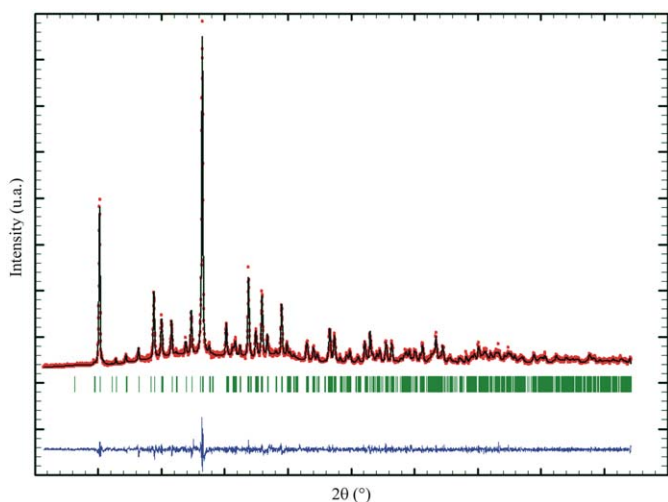


Fig. 1. Observed (red), calculated (black) XRD patterns and their difference (blue) for (C₅N₂H₁₆)(UO₂)(H₂O)(VO₄)₄. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

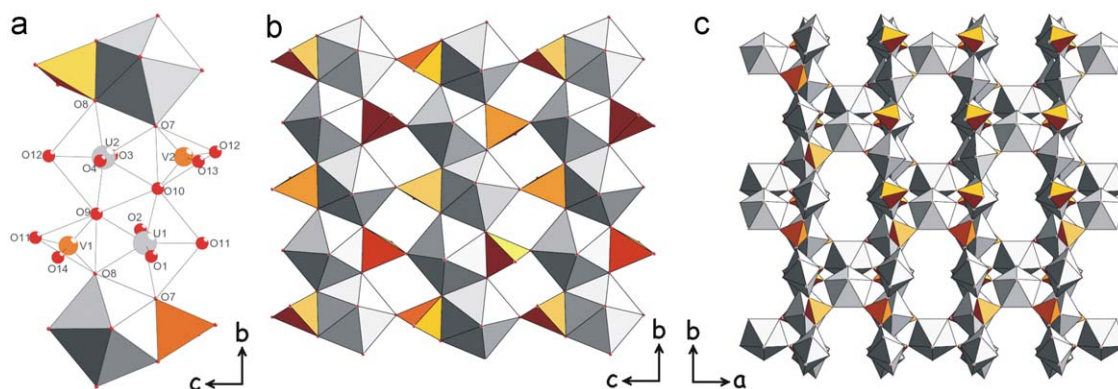


Fig. 2. The uranyl-vanadate framework is built from five primary units, three uranium-centered pentagonal bipyramids (PBP) U(1)O₇, U(2)O₇ and U(3)O₆(H₂O) and two VO₄ tetrahedra. a) U(1) and U(2) PBPs share the O(7)–O(8) edge between them and the O(8)–O(9) and O(7)–O(10) edges with V(1)O₄ and V(2)O₄ tetrahedra, respectively, to build a secondary building unit [U(1)V(1)U(2)V(2)O₁₆] further connected by O(9)–O(10) edges to form a [U(1)V(1)U(2)V(2)O₁₂] chain running down [0 1 0]. b) Consecutive chains are connected through O(11) and O(12) atoms into a uranophane-type layer. c) The layers are stacked along [1 0 0] and pillared by U(3)O₆(H₂O) PBPs sharing two O(13)–O(14) edges with two consecutive layers.

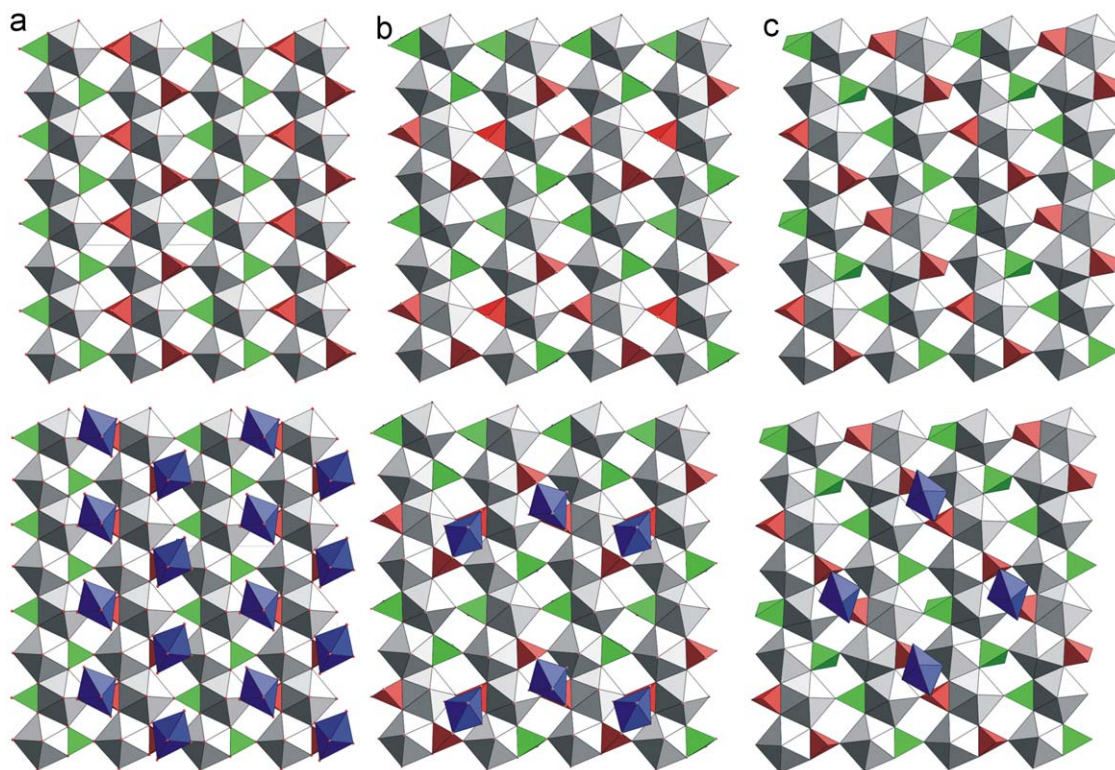


Fig. 3. a) For the *dd/uu* geometrical isomer of the uraniumophane-type sheet each oxygen atom of the VO_4 tetrahedra not involved in the sheet formation belongs to independent U(3) PBPs leading to $[\text{UO}_4(\text{H}_2\text{O})_3]$ pillars and to neutral three-dimensional frameworks $[\text{UO}_2(\text{H}_2\text{O})_3][(\text{UO}_2)(\text{XO}_4)]_2$ ($\text{X}=\text{P}$ [4], As [5] and V [3]). For the $a_{4u}a_{4d}/a_{4u}a_{4d}$ (b) and $a_{4u}a_{4d}/a_{4u}a_{4d}$ (c) geometrical isomers two oxygen atoms of two VO_4 tetrahedra not involved in the sheet formation belong to the same U(3) PBP leading to $[\text{UO}_6(\text{H}_2\text{O})]$ pillars and the creation of $[\text{UO}_2(\text{H}_2\text{O})][(\text{UO}_2)(\text{XO}_4)]_4^-$ ($\text{X}=\text{P}$ [6], As [7] and V (present work) anionic frameworks.

3. Results and discussion

The structure of the five compounds is based on the same three-dimensional arrangement of U(VI) pentagonal bipyramids (PBP) and vanadate tetrahedra. The channels of this open-framework structure are filled by the di-protonated $\text{C}_n\text{N}_2\text{H}_{2n+6}^{2+}$ ions and extra water molecules.

3.1. Cation coordination polyhedra

For the five compounds, each of the three independent uranium atoms, U(1), U(2) and U(3), is strongly bonded to two oxygen atoms forming nearly linear uranyl cation $(\text{UO}_2)^{2+}$. The $\text{O}=\text{U}=\text{O}$ bond angles range from $173.6(6)^\circ$ to $179.2(8)^\circ$ and the $\text{U}=\text{O}$ bond lengths range from $1.750(8)$ to $1.90(2)\text{Å}$. The uranyl cations are coordinated by five oxygen atoms that form the equatorial planes of the $[\text{UO}_7]$ pentagonal bipyramids. The equatorial U–O bond lengths values vary from $2.26(2)$ to $2.67(3)\text{Å}$. Their average value, $2.39(2)\text{Å}$, corresponds to the mean value found for a great number of well-refined structures [2].

The VO_4 tetrahedra are strongly distorted for the two symmetrically independent vanadium atoms (V(1) and V(2)) with two long V–O distances in the range from $1.71(2)$ to $1.764(7)\text{Å}$ when the oxygen atoms belong to an edge shared with a $[\text{UO}_7]$ PBP and two slightly shorter V–O bond lengths lying in the range from $1.63(2)$ to $1.703(9)\text{Å}$ when the O atoms are corners shared with different $[\text{UO}_7]$ PBPs. Furthermore, the O–O edges shared between VO_4 and $[\text{UO}_7]$ polyhedra are shorter than the other non-shared O–O edges, so the corresponding O–V–O angles are significantly lower than 109.7° (average value = $96.5(1)^\circ$).

3.2. Bond valence sums calculations

Using Burns parameters for uranium atoms [55], the U–O bond distances can be used to calculate the bond valence sums for U(1) to U(3) atoms in the five compounds. The obtained values, 5.83 to 6.18 valence units (*vu*), are consistent with hexavalent uranium. The bond valence sums calculated using Brese and O’Keeffe data for the V–O bonds [56] are in the range 5.06–5.47 *vu* in agreement with the +5 formal charge of vanadium atoms. Three types of oxygen atoms exist in the compounds. (i) The terminal oxygen (O(1) to O(6)) of the uranyl ions are strongly bonded to the uranium atoms and their valence practically satisfied by the $\text{U}=\text{O}$ bond, the valence for these bonds varying from 1.32 to 1.98 *vu*. (ii) The oxygen atoms O(7) to O(10), which are shared between two $[\text{UO}_7]$ polyhedra and one VO_4 tetrahedron (Fig. 2a), with valence bond sums in the range 2.10–2.33 *vu* and (iii) the oxygen atoms O(11) to O(14), which pertain to one VO_4 tetrahedron and one $[\text{UO}_7]$ polyhedron, with intermediate bond valence sums (1.92–2.10 *vu*).

3.3. The three-dimensional inorganic open-framework

For U(1) and U(2) the five equatorial oxygen belong to vanadate tetrahedra (Fig. 2a). U(1) and U(2) PBPs share O(7)–O(8) and O(9)–O(10) equatorial edges to form ${}^\infty[\text{UO}_5]$ chains in which U(1) and U(2) alternate along the axis $[010]$ (Fig. 2a). The V(1) O_4 tetrahedra are linked to one side of a ${}^\infty[\text{U}(1)\text{U}(2)\text{O}_{10}]$ chain by sharing the O(8)–O(9) edges with the $[\text{U}(1)\text{O}_7]$ polyhedra and the V(2) O_4 tetrahedra are linked to the other side by sharing the O(7)–O(10) edges with the $[\text{U}(2)\text{O}_7]$ PBPs to form ${}^\infty[\text{U}(1)\text{V}(1)\text{U}(2)\text{V}(2)\text{O}_{12}]$ uranyle–vanadate chains. Finally, the $[\text{U}(1)\text{O}_7]$

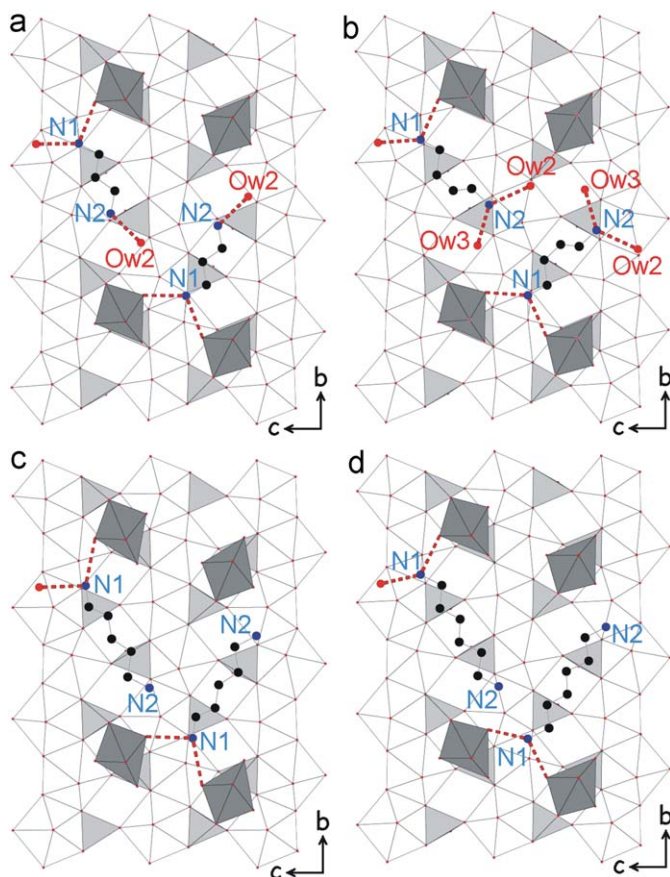


Fig. 4. Projection in the (100) plane showing the amine position and its linkage to the inorganic framework by hydrogen bonds through the N(1) atom in C3UV (a), C4UV (b), C5UV (c), and C6UV (d).

Table 6
Hydrogen bonds characteristics involving the N(1) atom in the C_nUV compounds.

Compound	N(1)–O(5) (Å)	N(1)–O(6) (Å)	O(5)–N(1)–O(6) (°)
C3UV	2.71(1)	2.86(2)	112.03(4)
C4UV	2.71(2)	2.82(2)	118.0(6)
C5UV	2.92(3)	3.04(3)	104.0(8)
C6UV	2.61(5)	2.76(5)	128.9(9)
C7UV	2.84(5)	2.82(4)	116.5(2)

and [U(2)O₇] PBPs of one chain share their remaining O(11) and O(12) oxygen atoms, respectively, with the V(1)O₄ and V(2)O₄ tetrahedra of an adjacent chain to form an uranophane-type sheet ${}^2_{\infty}[(\text{UO}_2)_2(\text{VO}_4)_2]^{2-}$ parallel to the (100) plane (Fig. 2b).

These sheets, stacked along [100], are linked into a rigid 3D framework by [U(3)O₇] PBPs acting as pillars (Fig. 2c). The O(5)=U(3)=O(6)²⁺ uranyl ions are parallel to the sheets and their equatorial environment is built by four vanadate oxygens from two adjacent ${}^2_{\infty}[(\text{UO}_2)_2(\text{VO}_4)_2]^{2-}$ layers at distances ranging from 2.28(3) to 2.38(2) Å and one water oxygen (Ow1) at longer distance (from 2.56(2) to 2.68(8) Å for C3UV and C6UV, respectively). The layers are connected through the pillars by means of the O(13) and O(14) atoms, which pertain, each, to one VO₄ tetrahedron belonging to the layers and to [U(3)O₇] acting as pillars.

3.4. Pillar study according to the geometrical isomer

In the sheets, alternating VO₄ tetrahedra sharing edges with one side of a uranyl chain alternatively point down (d) and up (u)

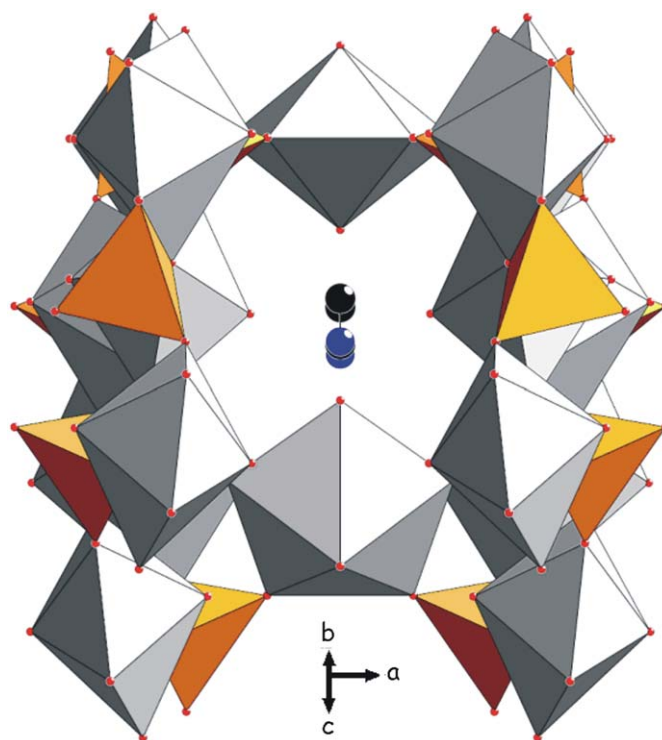


Fig. 5. Projection along the [021] direction showing the position of the amine molecule (for C3UV as an example).

which corresponds to the geometrical isomer *a/a* as defined by Locock et al. [5]. Up to now, among the six different geometrical isomers reported by Locock et al. [5], only two lead to the formation of pillars and three-dimensional frameworks. The *dd/uu* geometrical isomer puts in opposite two oxygen atoms from two consecutive layers. These two opposite oxygen atoms anchor the uranyl pillars meanwhile the three remaining equatorial oxygen atoms are part of water molecules. That allows the formation of [UO₄(H₂O)₃] pillars, hung on each of the consecutive layers only by one oxygen atom. In Fig. 3a, the oxygen atom points up as found in the compounds [UO₂(H₂O)₃][(UO₂)(XO₄)₂ · nH₂O (X=P, n=1 [4], X=As, n=1 [5], X=V, n=2 [3]), which adopt different space groups however. The *aa/aa* geometrical isomer puts in opposite two pairs of oxygen atoms leading to the formation of twice less pillars [UO₆(H₂O)] and the creation of [UO₂(H₂O)][(UO₂)(XO₄)₄]²⁻ frameworks. However for this geometrical isomer two possibilities occur, i) *a_{du}a_{du}/a_{du}a_{ud}* when the two tetrahedra that share an edge or a vertex with the same [UO₇] polyhedron point, alternatively, in the same direction and in opposite direction along the ${}^1_{\infty}[\text{UO}_5]$ chains direction and ii) *a_{du}a_{du}/a_{ud}a_{ud}* when the tetrahedra sharing an edge with an [UO₇] polyhedron points down and the tetrahedra sharing a vertex with the same [UO₇] polyhedron points down all along the ${}^1_{\infty}[\text{UO}_5]$ chains direction. The first case is found in the C_nUV compounds and in the caesium uranyl-phosphate [6] and arsenate [7], the guest molecules or ions are distributed along a broken line (Fig. 3b). The second one is found in A₂[UO₂(H₂O)][(UO₂)(XO₄)₄ · H₂O, X=P, A=K, Rb [6], Tl [8], X=As, A=Rb [7] in which the alkaline ions are located between two tetrahedra along a straight line (Fig. 3c). As evidenced from Fig. 3a, the uranophane layer for the *dd/uu* geometrical isomer has an inversion centre at the middle of the empty square that corresponds to the inversion centre of the various centrosymmetric space groups adopted by the corresponding compounds. For the *a_{du}a_{du}/a_{ud}a_{ud}* geometrical isomer such an inversion centre exists (Fig. 3c) and the structure can be centrosymmetric as, for

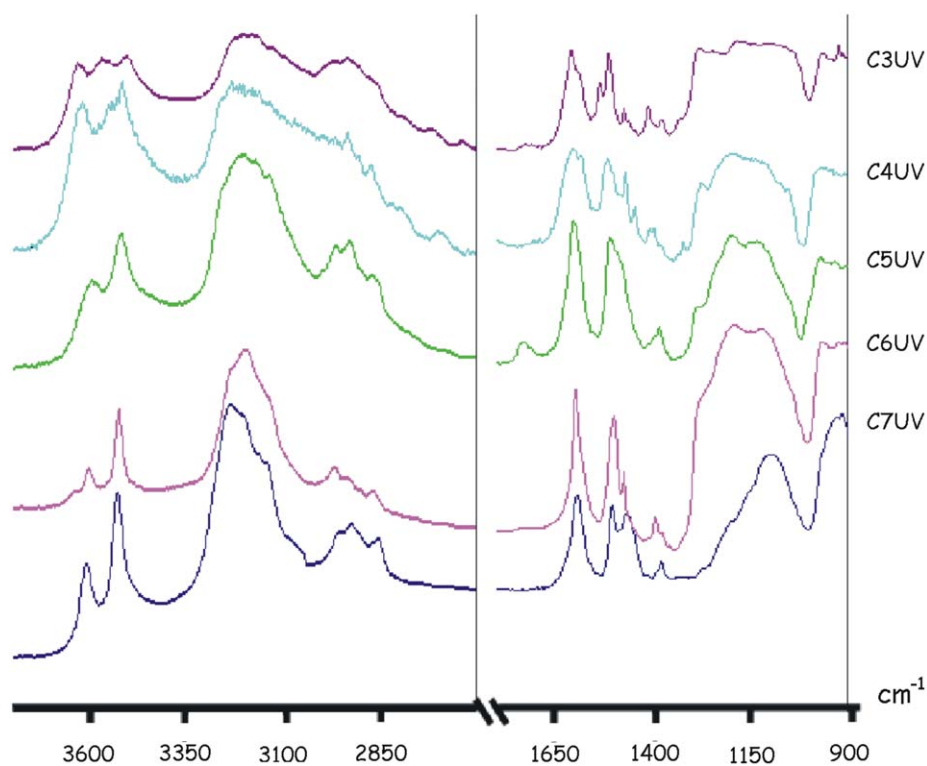


Fig. 6. FTIR spectra of C_nUV compounds collected on single crystals.

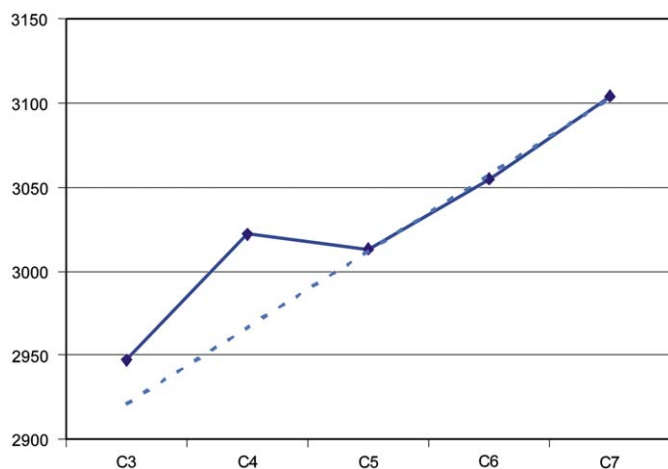


Fig. 7. Variation of the unit cell volume versus n in the C_nUV three-dimensional compounds.

example, in $Rb_2(UO_2)[(UO_2)(AsO_4)]_4(H_2O)_2$ [7]. On the contrary, for the $a_{du}a_{du}/a_{du}a_{du}$ arrangement adopted by the present compounds there cannot be an inversion centre (Fig. 3b) and the structures are non-centrosymmetric.

3.5. Interlayer space occupation

The uranyl-vanadate framework displays tunnels in which the doubly protonated amines balancing the charge of the anionic inorganic framework reside. In the compounds C3UV, C5UV and C6UV the diamine molecules adopt the same planar conformation: the N–C_n–N chains are in the m mirror parallel to (011) at $x=1/2$ and are located above the VO_4 tetrahedra of the $[(UO_2)_2(VO_4)_2]^{2-}$ uranophane layers that point down (Fig. 4).

The butanediamine in C4UV compounds adopts a different conformation and is disordered over two positions related by the mirror. The $N(1)$, $C(1)$ and $N(2)$ sites, located at $x=1/2$ are fully occupied. Placing $C(2)$, $C(3)$ and $C(4)$ in the m mirror led to high isotropic displacement parameters, U_{iso} , equal to 0.09, 0.10 and 0.18 for $C(2)$, $C(3)$ and $C(4)$, respectively. Moreover, when these atoms were located at $x=1/2$, they could not be refined overall: $C(2)$, $C(3)$ and $C(4)$ were therefore placed in general positions half occupied. In C7UV, the diamine could not be located during the X-ray structure determination: only the $N(1)$ atom could be located. In C3UV–C7UV, the amines are tied to the inorganic framework by the $N(1)$ atom, which occupies nearly the same position in the five compounds and is linked to two $[UO_7]$ pillars through hydrogen bonds with the corresponding uranyl oxygens (Table 6). Starting from the $N(1)$ atom the amines run along approximately $[0\bar{2}1]$ and $[021]$ directions (Fig. 5). For C3UV and C4UV, the channels also contain water molecules that are hydrogen bonded to $N(2)$.

The presence of the organic guest molecule in the five compounds was confirmed using infrared spectroscopy. The five compounds exhibit similar infrared spectra (Fig. 6) with the bending vibrations of C–H and N–H at around 1600 and 1500 cm^{-1} , respectively, while the stretching vibrations of C–N, C–H and N–H are observed in the domains 1020–1380, 2800–3000 and $3100\text{--}3570\text{ cm}^{-1}$, respectively.

The b and c unit cell parameters that correspond to the uranophane-type sheet dimensions do not vary significantly for the C_nUV series. In fact in the uranophane-type sheet these dimensions correspond to the ${}^1_{\infty}[UO_5]$ chain direction and to the perpendicular one and are correlated to the tetrahedra dimension: they strongly increase from phosphate ($b=13.8\text{ \AA}$, $c=13.0\text{ \AA}$) to arsenate ($b'=14.0\text{ \AA}$, $c'=13.4\text{ \AA}$) and slightly from arsenate to vanadate ($b=14.1\text{ \AA}$, $c=13.6\text{ \AA}$) in agreement with the variation of the X^{5+} ionic radius [57]. On the contrary, the a parameter corresponding to the interlayer distance, and thus the unit cell

volume (Fig. 7), increases with n and the water content. The decrease observed between C4UV and C5UV is due to the decrease of the water content from 2 to 0.

The inorganic framework in the C n UV compounds is isotypic to that of caesium uranyl-phosphate and uranyl-arsenate $A_2[VO_2(H_2O)][(VO_2)(XO_4)]_4 \cdot H_2O$, $X=P, As, A=Cs$ [6–7] and homeotypic to that of $A_2[VO_2(H_2O)][(VO_2)(XO_4)]_4 \cdot H_2O$, $X=P, A=K, Rb$ [6], Tl [8], $X=As, A=Rb$ [7]. Attempts to synthesize similar K, Rb or Cs uranyl-vanadates systematically led to the preparation of $A_2[(VO_2)_2(VO_4)_2]_4$ compounds with carnotite-type structure [58–60] that are very stable. Furthermore the “exchange” experiments which were carried out in order to replace diamines in C n UV compounds by caesium or ammonium ions by means of using caesium or ammonium solutions led to the formation of the corresponding carnotite-type compounds with dissolution of a part of uranium giving yellow solutions.

4. Conclusion

Using linear alkyl diamine $C_nN_2H_{2n+4}$ with $3 \leq n \leq 7$, five new isotypic uranyl-vanadates were hydrothermally synthesized in which the di-protonated amines occupy the sites created by a three-dimensional framework built from uranophane-type uranyl-vanadate layers pillared by $[UO_6(H_2O)]$ pentagonal bipyramids. The compounds are isotypic to $Cs_2[UO_2(H_2O)][(VO_2)(PO_4)]_4 \cdot H_2O$ and $Cs_2[UO_2(H_2O)][(VO_2)(AsO_4)]_4 \cdot H_2O$ with $[(VO_2)(XO_4)]_4^{4-}$ layers corresponding to the $a_{du}a_{du}/a_{ud}a_{ud}$ geometrical isomer. This type of isomer allows the pillars to be distributed along a broken line. In the geometrical isomers $a_{du}a_{du}/a_{ud}a_{ud}$ previously found, $A_2[UO_2(H_2O)][(VO_2)(XO_4)]_4 \cdot H_2O$, $X=P, A=K, Rb, Tl, X=As, A=Rb$, the pillars are located along a straight line. Further experiments using other amines to build three-dimensional uranyl-vanadate frameworks are in progress so as to evidence the relationship between the geometrical isomer and the three-dimensional uranyl-vanadate frameworks.

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The crystallographic data can be obtained through the FIZ data bank by quoting the CSD numbers 421126 (C3UV), 421127 (C4UV), 421128 (C5UV), 421129 (C6UV) and 421125 (C7UV).

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2009.10.020.

References

- [1] P.C. Burns, M.L. Miller, R.C. Ewing, F. Hawthorne, *Can. Miner.* 34 (1996) 845.
- [2] P.C. Burns, *Can. Miner.* 43 (2005) 1839.
- [3] M. Saadi, C. Dion, F. Abraham, *J. Solid State Chem.* 150 (2000) 72.
- [4] A.J. Locock, P.C. Burns, *J. Solid State Chem.* 163 (2002) 275.
- [5] A.J. Locock, P.C. Burns, *J. Solid State Chem.* 176 (2003) 18.
- [6] A.J. Locock, P.C. Burns, *J. Solid State Chem.* 167 (2002) 226.
- [7] A.J. Locock, P.C. Burns, *J. Solid State Chem.* 175 (2003) 372.
- [8] A.J. Locock, P.C. Burns, *Z. Kristallogr.* 219 (2004) 259.
- [9] A.J. Locock, P.C. Burns, *J. Solid State Chem.* 177 (2004) 2675.
- [10] J.A. Danis, W.H. Runde, B. Scott, J. Fetting, B. Eichhorn, *Chem. Commun.* 22 (2001) 2378.
- [11] F. Abraham, C. Dion, N. Tancret, M. Saadi, *Adv. Mater. Res.* (1994) 511.
- [12] I. Duribreux, C. Dion, M. Saadi, F. Abraham, *J. Solid State Chem.* 146 (1999) 258.
- [13] C. Dion, S. Obbade, E. Raekelboom, M. Saadi, F. Abraham, *J. Solid State Chem.* 155 (2000) 342.
- [14] S. Obbade, C. Dion, L. Duvieubourg, M. Saadi, F. Abraham, *J. Solid State Chem.* 173 (2003) 1.
- [15] I. Duribreux, M. Saadi, S. Obbade, C. Dion, F. Abraham, *J. Solid State Chem.* 172 (2003) 351.
- [16] S. Obbade, C. Dion, M. Saadi, F. Abraham, *J. Solid State Chem.* 177 (2004) 1567.
- [17] S. Obbade, C. Dion, M. Rivenet, M. Saadi, F. Abraham, *J. Solid State Chem.* 177 (2004) 2058.
- [18] S. Obbade, L. Duvieubourg, C. Dion, F. Abraham, *J. Solid State Chem.* 180 (2007) 866.
- [19] S. Obbade, C. Renard, F. Abraham, *J. Solid State Chem.* 182 (2009) 1377.
- [20] P.S. Halasyamani, R.J. Francis, S.M. Walker, D. O’Hare, *Inorg. Chem.* 38 (1999) 271.
- [21] S.V. Krivovichev, P.C. Burns, *J. Solid State Chem.* 170 (2003) 106.
- [22] S.V. Krivovichev, C.L. Cahill, E.V. Nazarchuk, P.C. Burns, Th. Armbruster, W. Depmeier, *Microporous and Mesoporous Mater.* 78 (2005) 209.
- [23] S.V. Krivovichev, C.L. Cahill, E.V. Nazarchuk, P.C. Burns, Th. Armbruster, W. Depmeier, *Microporous and Mesoporous Mater.* 78 (2005) 217.
- [24] S.V. Krivovichev, C.L. Cahill, E.V. Nazarchuk, P.C. Burns, Th. Armbruster, W. Depmeier, *Microporous and Mesoporous Mater.* 78 (2005) 225.
- [25] S.V. Krivovichev, I.G. Tananaev, V. Kahlenberg, B.F. Myasoedov, *Radiochemistry* 48 (2006) 213.
- [26] X. Wang, J. Huang, A.J. Jacobson, *J. Am. Chem. Soc.* 124 (2002) 15190.
- [27] A.J. Norquist, P.M. Thomas, M.B. Doran, D. O’Hare, *Chem. Mater.* 14 (2002) 5179.
- [28] M.B. Doran, A.J. Norquist, D. O’Hare, *Chem. Commun.* 24 (2002) 2946.
- [29] P.M. Thomas, A.J. Norquist, M.B. Doran, D. O’Hare, *J. Mater. Chem.* 13 (2003) 88.
- [30] A.J. Norquist, M.B. Doran, D. O’Hare, *Solid State Sci.* 5 (2003) 1149.
- [31] A.J. Norquist, M.B. Doran, P.M. Thomas, D. O’Hare, *Dalton Trans.* 6 (2003) 1168.
- [32] A.J. Norquist, M.B. Doran, P.M. Thomas, D. O’Hare, *Inorg. Chem.* 42 (2003) 5949.
- [33] A.J. Norquist, M.B. Doran, D. O’Hare, *Inorg. Chem.* 44 (2005) 3837.
- [34] S.V. Krivovichev, V. Kahlenberg, *Z. Anorg. Allg. Chem.* 631 (2005) 2352.
- [35] S.V. Krivovichev, V. Kahlenberg, I.G. Tananaev, B.F. Myasoedov, *Z. Anorg. Allg. Chem.* 631 (2005) 2358.
- [36] S.V. Krivovichev, V. Kahlenberg, E.Yu. Avdontseva, E. Mersdorf, R. Kaindl, *Eur. J. Inorg. Chem.* (2005) 1653.
- [37] S.V. Krivovichev, V. Kahlenberg, I.G. Tananaev, B.F. Myasoedov, *Dokl. Phys. Chem.* 403 (2005) 124.
- [38] S.V. Krivovichev, I.G. Tananaev, B.F. Myasoedov, *Radiochemistry* 48 (2006) 552.
- [39] S.V. Krivovichev, V. Kahlenberg, I.G. Tananaev, R. Kainhard, E. Mersdorf, B.F. Myasoedov, *J. Am. Chem. Soc.* 127 (2005) 1072.
- [40] S.V. Krivovichev, V.V. Gurzhii, I.G. Tananaev, B.F. Myasoedov, *Dokl. Phys. Chem.* 409 (2006) 228.
- [41] J. Ling, G.E. Sigmon, P.C. Burns, *J. Solid State Chem.* 182 (2009) 402.
- [42] R.B. Francis, M.J. Drewitt, P.S. Halasyamani, C. Ranganatchachar, D. O’Hare, W. Clegg, S.J. Teat, *Chem. Commun.* (1998) 279.
- [43] M.B. Doran, C.L. Stuart, A.J. Norquist, D. O’Hare, *Chem. Mater.* 16 (2004) 565.
- [44] Y.L. Lai, R.K. Chiang, K.H. Lii, S.L. Wang, *Chem. Mater.* 20 (2008) 523.
- [45] T.H. Bray, J.D. Gorden, T.E. Albrecht-Schitt, *J. Solid State Chem.* 181 (2008) 2199.
- [46] E.V. Alekseev, V. Krivovichev, W. Depmeier, *Radiochemistry* 50 (2008) 445.
- [47] M. Rivenet, N. Vigier, P. Roussel, F. Abraham, *J. Solid State Chem.* 180 (2007) 713.
- [48] COSMO Bruker program V1.56 copyright 1999–2006, Bruker AXS, inc.
- [49] SAINT Plus Version 6.22, Bruker Analytical X-ray Systems, Madison, WI, 2001.
- [50] SADABS Version 2.03: Bruker Analytical X-ray Systems, Madison, WI, 2001.
- [51] A. Altomare, G. Cascaro, G. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Gamalli, *J. Appl. Crystallogr.* 27 (1994) 135.
- [52] V. Petricek, M. Dusek, L. Palatinus, *JANA 2000*, Institute of Physics, Praha Czech Republic, 2005.
- [53] J. Rodriguez-Carvajal, *Physica B* 192 (1993) 55.
- [54] G. Caglioti, A. Paoletti, F. Ricci, *Nucl. Instrum. Methods* 3 (1958) 223.
- [55] P.C. Burns, R.C. Ewing, F.C. Hawthorne, *Can. Miner.* 35 (1997) 1551.
- [56] N.E. Brese, M. O’Keeffe, *Acta Crystallogr. B* 47 (1991) 192.
- [57] R.D. Shannon, *Acta Crystallogr. A* 32 (1976) 751.
- [58] P.B. Barton, *Am. Miner.* 43 (1958) 799.
- [59] F. Abraham, C. Dion, M. Saadi, *J. Mater. Chem.* 3 (1993) 459.
- [60] P.G. Dickens, G.P. Stuttard, R.G.J. Ball, A.V. Powell, S. Hull, S. Patat, *J. Mater. Chem.* 3 (1992) 161.