

U(IV)/Ln(III) mixed site in polymetallic oxalato complexes. Part III: Structure of $\text{Na}[\text{Yb}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ and the derived quadratic series $(\text{NH}_4^+)_{1-x}[\text{Ln}_{1-x}\text{U}_x(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})] \cdot (3+x)\text{H}_2\text{O}$, $\text{Ln} = \text{Y}, \text{Pr}–\text{Sm}, \text{Gd}, \text{Tb}$

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Abstract

Single crystals of a new sodium ytterbium oxalate $\text{Na}[\text{Yb}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ (**1**) and six mixed lanthanide (III)–uranium (IV) oxalates $(\text{NH}_4^+)_{1-x}[\text{Ln}_{1-x}\text{U}_x(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})] \cdot (3+x)\text{H}_2\text{O}$, $\text{Ln} = \text{Y}$, $x = 0.47$ (**2**), $\text{Ln} = \text{Pr}$, $x = 0.42$ (**3**), $\text{Ln} = \text{Nd}$, $x = 0.60$ (**4**), $\text{Ln} = \text{Sm}$, $x = 0.55$ (**5**), $\text{Ln} = \text{Gd}$, $x = 0.25$ (**6**) and $\text{Ln} = \text{Tb}$, $x = 0.52$ (**7**) have been grown using slow diffusion through silica gels. The crystal structures of all the compounds have been determined by single-crystal X-ray diffraction. For compound **1** the symmetry is monoclinic, space group Pc , cell dimensions $a = 8.559(2)\text{Å}$, $b = 8.564(2)\text{Å}$, $c = 14.938(3)\text{Å}$, $\beta = 103.062(3)^\circ$, $Z = 4$. The structure of **1** is isotypic with $\text{Na}[\text{Y}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ and consists of layers formed by four-membered rings of Yb connected through oxalate ions. The ytterbium atom is nine-coordinated by oxygen from four bis-bidentate oxalate ligands and one water molecule which alternate up and down the layer. Na^+ ions and supplementary water molecules are located between the layers. The six mixed lanthanide (III)–uranium (IV) oxalates, **2–7**, are isotypic, the symmetry is tetragonal, space group $P4/n$, the unit cell parameters are in the range $8.7239(12)–8.9116(6)$ and $7.854(2)–7.9487(9)\text{Å}$ for a and c , respectively, $Z = 2$. The structure of the six compounds is built from the same two-dimensional arrangement of alternating metallic and oxalate ions forming four-membered rings. The layers are similar to that observed in **1** and the mixed Ln(III)/U(IV) oxalate layers are obtained by partial substitution of Ln(III) by U(IV) in a nine-coordinated site, the charge surplus being compensated by removal of monovalent cations in the interlayer space. The ammonium ions and the water molecules are disordered in the same crystallographic site. Thus these compounds form the third series of mixed lanthanide (III)–uranium (IV) oxalates, the tetragonal one, that completes the two others previously reported, the hexagonal and the triclinic series.
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1. Introduction

With the aim of identifying the different compounds which can appear during the treatment by oxalic acid of various nuclear streams (e.g. effluents), we undertook the synthesis and the characterization of all the uranium and/or lanthanide oxalates which are formed according to experimental conditions. Indeed, lanthanides are significantly present among the nuclear fission products and

lanthanide (III) ions can also be used to simulate trivalent actinides. Our strategy consists in establishing the structures of all the oxalates from single-crystal X-ray diffraction, then to identify, using the database thus made up, the phases which are formed during precipitation in the industrial conditions. In some processes using oxalic acid, tetravalent uranium is used preferentially to hexavalent uranium because of the lowest solubility of uranium oxalate. In this case, hydrazinium nitrate (N_2H_5^+ , NO_3^-) is added to the solution to stabilize tetravalent uranium. In general, lanthanide and actinide oxalates are not very soluble and the growth of single-crystals is not easy.

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Recently, we have demonstrated the efficiency of crystal growth of oxalate compounds by using the slow diffusion of ions through silica gel impregnated with oxalic acid [1,2].

The use of this crystal growth method from gel for several M^I -U^{IV}-Ln^{III} systems (M^I = Na, NH₄, N₂H₅, Ln^{III} = Ce, Nd, Sm) enabled us to isolate crystals of a new uranium(IV) oxalate (NH₄)₂U₂^{IV}(C₂O₄)₅·0.7H₂O (**225** compound) and of double U(IV)-Ln(III) oxalates resulting from the partial substitution of U^{IV} by Ln^{III} up to $M_3ULn(C_2O_4)_5 \cdot 10.4H_2O$ (**325** compound) obtained for M = Na and Ln = Ce [3]. The honeycomb-like structure of these oxalates is built from a three-dimensional arrangement of metallic and oxalate ions. Hexagonal rings of alternating metallic and oxalate ions form layers that are pillared by other oxalate ions. The monovalent cations and the water molecules occupy the created hexagonal tunnels. The charge deficit due to the U(IV)/Ln(III) substitution is compensated by addition of supplementary monovalent ions within the tunnels. The unit cell for this **225** series with formula $(M^I)_{2+x}U_{2-x}^{IV}Ln_x^{III}(C_2O_4)_5 \cdot nH_2O$ ($0 \leq x \leq 1$) is hexagonal or orthorhombic (pseudo-hexagonal) and the series is called hereafter the *hexagonal series*.

Using Ln³⁺ solutions, free of U⁴⁺, two new hydrazinium-lanthanide double oxalates corresponding to **112** compounds (N₂H₅)Ln(C₂O₄)₂·nH₂O were obtained for Ln = Nd and Gd [4]. Alternating lanthanide and oxalate ions form distorted six-membered rings that delimit tunnels running along three directions and occupied by hydrazinium cations and water molecules. Starting from these lanthanide (III) compounds, isotopic hydrazinium or sodium-lanthanide(III)/uranium(IV) double oxalates with formula $(M^I)_{1-x}U_x^{IV}Ln_{1-x}^{III}(C_2O_4)_2 \cdot nH_2O$ ($0 \leq x \leq 1$) were obtained by partial substitution of Ln(III) by U(IV) in the nine-coordinated site, the charge excess being compensated by removal of monovalent ions from the tunnels. The unit cell for this **112** series is triclinic and the series is called hereafter the *triclinic series*. Compound where $x = 0$ could be obtained only for M^I = N₂H₅⁺. However, for M^I = Na⁺ and NH₄⁺, **112** oxalates have been reported with different arrangements of metal and oxalate ions. In these compounds, the lanthanide atoms are related by bis-chelating oxalate ligands to form a bi-dimensional arrangement of four-membered rings. In the anhydrous compound (NH₄)La(C₂O₄)₂, an oxalate ion assumes the connection of the layers to form a three-dimensional arrangement [5]. In (NH₄)Ln(C₂O₄)₂(H₂O), Ln = Eu–Yb [5] and $MLa(C_2O_4)_2(H_2O)_2 \cdot H_2O$, M = K, NH₄ [6], water molecules bonded to the Ln atoms preclude the connection in a third direction leading to bi-dimensional structures with K⁺ or NH₄⁺ ions localized into the interlayer space. The same type of metal-oxalate arrangement has been evidenced in Np(C₂O₄)₂·6H₂O [7], owing to the similarity of unit cell parameters [8], it can be expected for the corresponding U compound. The present paper reports the crystal growth and the crystal structure determination of the compound Na[Yb(C₂O₄)₂(H₂O)]·3H₂O ($x = 0$) and of double Ln(III)/U(IV)

oxalates isolated for Ln = Y, Pr, Nd, Sm, Gd, Tb, Yb and M = NH₄⁺ with structure built from the tetragonal arrangement of four-membered rings. These compounds contain U(IV)/Ln(III) mixed sites highlighted in the two first parts of this study and pertain to a new series called the *tetragonal series* formulated $M_{1-x}Ln_{1-x}U_x(C_2O_4)_2 \cdot nH_2O$ with M = Na⁺, NH₄⁺.

2. Experimental

2.1. Crystal synthesis

Single crystals of Na[Yb(C₂O₄)₂(H₂O)]·3H₂O (**1**) and (NH₄⁺)_{1-x}[Ln_{1-x}U_x(C₂O₄)₂(H₂O)]·(3+x)H₂O, Ln = Y, $x = 0.47$ (**2**), Ln = Pr, $x = 0.42$ (**3**), Ln = Nd, $x = 0.60$ (**4**), Ln = Sm, $x = 0.55$ (**5**), Ln = Gd, $x = 0.25$ (**6**) and Ln = Tb, $x = 0.52$ (**7**) were obtained by the slow diffusion of the cations U⁴⁺ and Ln³⁺ (Ln = Y, Pr, Nd, Sm, Gd, Tb or Yb) through silica gels impregnated with oxalic acid [9]. Two types of silica gels were prepared from sodium metasilicate and tetraethoxysilane (TEOS). The former was prepared by pouring 1 M sodium metasilicate solution into a mixture of 1 M oxalic acid and 3 M nitric acid so as to get a pH between 3.5 and 4. The resulting solution was then allowed to set in tubes of internal diameter 15 mm. To extend the scope of this mean of synthesis, substitution by other monovalent cations like ammonium or hydrazinium

Table 1
Crystal data and structure refinement for Na[Yb(C₂O₄)₂(H₂O)]·3H₂O, **1**

Compound	1
Empirical formula	YbNaC ₄ O ₁₂ H ₈
Formula weight (g mol ⁻¹)	444.13
Crystal system	Monoclinic
Space group	<i>Pc</i>
Crystal size (μm)	200 × 180 × 30
<i>a</i> (Å)	8.5591(16)
<i>b</i> (Å)	8.5640(17)
<i>c</i> (Å)	14.938(3)
β°	103.062(3)
Volume (Å ³)	1066.6(4)
<i>Z</i>	4
ρ_{calc} (Mg/m ³)	2.767
Abs. coef. (mm ⁻¹)	8.870
Absorption correction	Empirical
<i>F</i> (000)	836
Temperature (K)	293(2)
Wavelength (Å)	0.71073
θ range/°	2.38–28
Index ranges	–11 ≤ <i>h</i> ≤ 11, –11 ≤ <i>k</i> ≤ 11, –19 ≤ <i>l</i> ≤ 19
Reflections collected	7811
Independent reflections	4468
<i>R</i> (int)	0.0500
Data/restraints/parameters	4468/0/314
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0481, <i>wR</i> ₂ = 0.1255
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0524, <i>wR</i> ₂ = 0.1299
Extinction coefficient	0.0047(5)
Largest diff. peak/hole (e Å ⁻³)	2.406/–3.952

Table 2

Crystal data and structure refinement parameters for the U/Ln oxalates $(\text{NH}_4^+)_{1-x}[\text{Ln}_{1-x}\text{U}_x(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}] \cdot (3+x) \text{H}_2\text{O}$

Compound	2	3	4	5	6	7
Empirical formula	$\text{Y}_{0.53}\text{U}_{0.47}$ $\text{C}_4\text{O}_{12.47}\text{N}_{0.53}\text{H}_{11.06}$	$\text{Pr}_{0.58}\text{U}_{0.42}$ $\text{C}_4\text{O}_{12.42}\text{N}_{0.58}\text{H}_{11.16}$	$\text{Nd}_{0.4}\text{U}_{0.6}$ $\text{C}_4\text{O}_{12.6}\text{N}_{0.4}\text{H}_{10.8}$	$\text{Sm}_{0.45}\text{U}_{0.55}$ $\text{C}_4\text{O}_{12.55}\text{N}_{0.45}\text{H}_{10.9}$	$\text{Gd}_{0.75}\text{U}_{0.25}$ $\text{C}_4\text{O}_{12.25}\text{N}_{0.75}\text{H}_{11.5}$	$\text{Tb}_{0.48}\text{U}_{0.52}$ $\text{C}_4\text{O}_{12.52}\text{N}_{0.48}\text{H}_{10.96}$
Formula weight (g mol ⁻¹)	425.12	447.82	466.63	464.69	443.57	466.18
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	P4/n	P4/n	P4/n	P4/n	P4/n	P4/n
Crystal size (μm)	120 × 90 × 40	60 × 50 × 20	140 × 150 × 50	160 × 180 × 60	150 × 150 × 40	150 × 130 × 30
a (Å)	8.7365(4)	8.9116(6)	8.8875(8)	8.8161(14)	8.7686(3)	8.7239(12)
c (Å)	7.9487(9)	7.9326(13)	7.8962(14)	8.019(3)	7.9362(5)	7.854(2)
Volume (Å ³)	606.70(8)	629.98(12)	623.70(14)	623.3(2)	610.20(5)	597.7(2)
Z	2	2	2	2	2	2
ρ _{calc} (Mg/m ³)	2.335	2.386	2.223	2.436	2.507	2.564
Abs. coef. (mm ⁻¹)	9.157	8.438	5.989	8.930	9.432	9.813
Absorption correction	Empirical	Empirical	Empirical	Empirical	Empirical	Empirical
F(000)	394	414	387	417	419	420
Temperature (K)	273(2)	273(2)	273(2)	273(2)	273(2)	273(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
θ range /	2.56–38.95	2.57–36.20	2.58–29.07	2.31–27.97	2.57–32.54	3.30–28.48
Index ranges	–14 ≤ h ≤ 15, –15 ≤ k ≤ 11, –13 ≤ l ≤ 12	–13 ≤ h ≤ 12, –14 ≤ k ≤ 14, –13 ≤ l ≤ 12	–11 ≤ h ≤ 11, –11 ≤ k ≤ 12, –10 ≤ l ≤ 10	–11 ≤ h ≤ 11, –11 ≤ k ≤ 11, –10 ≤ l ≤ 10	–13 ≤ h ≤ 13, –13 ≤ k ≤ 13, –11 ≤ l ≤ 12	–11 ≤ h ≤ 11, –11 ≤ k ≤ 11, –10 ≤ l ≤ 10
Reflections collected	12887	29034	5145	4229	10860	4988
Independent reflections	1755	1532	791	723	1118	753
R(int)	0.0349]	0.0996]	0.0275]	0.0398]	0.0421]	0.0541]
Data/restraints/parameters	1755/0/44	1532/0/44	791/0/44	723/0/45	1118/0/44	753/0/46
Final R indices [I > 2σ(I)]	R1 = 0.0293, wR2 = 0.0697	R1 = 0.0398, wR2 = 0.0672	R1 = 0.0236, wR2 = 0.0653	R1 = 0.0341, wR2 = 0.0811	R1 = 0.0235, wR2 = 0.0604	R1 = 0.0392, wR2 = 0.0872
R indices (all data)	R1 = 0.0432, wR2 = 0.0736	R1 = 0.0733, wR2 = 0.0751	R1 = 0.0245, wR2 = 0.0658	R1 = 0.0369, wR2 = 0.0822	R1 = 0.0286, wR2 = 0.0628	R1 = 0.0455, wR2 = 0.0903
Extinction coefficient	—	0.0067(8)	—	0.0021(10)	0.005(8)	/
Largest diff. peak/hole (e Å ⁻³)	0.896/–0.895	1.070/–1.281	1.887/–0.673	4.054/–1.114	1.755/–0.664	5.007/–1.246

Table 3

Results of the structure refinements considering U and Ln on two sites for compounds 5 and 7

Atom	x	y	z	Ueq	U11	U22	U33
Compound 5 R1 = 0.0297, wR2 = 0.0705, R1 _{all} = 0.0325, wR2 _{all} = 0.0714							
U	1/4	1/4	0.0685(1)	0.018(1)	0.015(1)	0.015	0.022(1)
Sm	1/4	1/4	0.0688(5)	0.063(3)	0.031(2)	0.031	0.128(5)
Compound 7 R1 = 0.0319, wR2 = 0.0708, R1 _{all} = 0.0384, wR2 _{all} = 0.0737							
U	1/4	1/4	0.0690(2)	0.011(1)	0.011(1)	0.011	0.012(1)
Tb	1/4	1/4	0.0684(5)	0.039(2)	0.011(12)	0.011	0.094(4)

cations has been performed by ionic exchange between the silica gel and a nitric solution of oxalic acid 0.2 M and ammonium or hydrazinium nitrate 2 M added on the gel. For the TEOS gel preparation, exactly measured volumes of TEOS (2.5 mL) and ethanol (1.5 mL) were mixed. To the mixture was slowly added a solution of HNO₃, 3 M (1 mL), oxalic acid, 1 M (1.5 mL) and distilled water (1 mL). The heating of this mixture at 60 °C for 24 h resulted in a gel formation. For each silica gel, several crystal growths were tested for Y and Ln = La to Yb. One single crystal free of U, Na[Yb(C₂O₄)₂(H₂O)] · 3H₂O (**1**) and six single crystals containing both U⁴⁺ and Ln³⁺ in a mixed crystallographic

site and belonging to the family presented in this paper were obtained.

Crystal growth in silica gels is a quite particular method because ions diffusion rates, local concentrations and pH cannot be controlled, so the chemical composition of resulting crystals is not always in agreement with the starting stoichiometric ratios of the solutions and can display some variations depending on the position within the gel. The amount of crystals which can be isolated is always small, so, CHN compositional and TGA analysis cannot be performed. Furthermore, good enough crystals are not always obtained. For example, using Na⁺-gel and

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Na}[\text{Yb}(\text{C}_2\text{O}_4)_2(\text{OH}_2)] \cdot 3\text{H}_2\text{O}$, **1**

Atom	Site	x	y	z	$U(\text{eq})^a$
Yb(1)	2a	0.00000	0.09691(5)	0.00000	14(1)
Yb(2)	2a	0.52993(5)	0.59763(5)	0.06913(3)	14(1)
Na(1)	2a	0.8910(7)	0.6245(6)	0.2851(4)	36(1)
Na(2)	2a	0.1973(9)	0.3149(8)	-0.2155(5)	49(2)
C(1)	2a	0.8274(16)	0.8269(14)	0.0812(8)	18(2)
C(2)	2a	0.7089(16)	0.8727(14)	-0.0076(8)	17(2)
O(1)	2a	0.5757(10)	0.8057(8)	-0.0266(6)	19(2)
O(2)	2a	0.7785(10)	0.7187(9)	0.1289(6)	22(2)
O(3)	2a	0.9588(12)	0.8944(8)	0.1016(7)	23(2)
O(4)	2a	0.7553(10)	0.9754(9)	-0.0559(6)	24(2)
C(3)	2a	0.2362(15)	0.3768(14)	0.0788(9)	18(2)
C(4)	2a	0.2865(16)	0.3227(14)	-0.0073(8)	19(2)
O(5)	2a	0.1247(11)	0.3029(9)	0.1028(6)	23(2)
O(6)	2a	0.4105(11)	0.381(1)	-0.0247(7)	23(2)
O(7)	2a	0.3144(10)	0.4871(10)	0.1217(6)	25(2)
O(8)	2a	0.1981(10)	0.2227(9)	-0.0561(6)	24(2)
C(5)	2a	-0.2229(15)	0.3929(13)	-0.0117(9)	16(2)
C(6)	2a	-0.2410(15)	0.3093(14)	0.0765(8)	18(2)
O(9)	2a	-0.1736(10)	0.1796(9)	0.0956(6)	20(2)
O(10)	2a	-0.1399(11)	0.3245(10)	-0.0584(6)	24(2)
O(11)	2a	-0.3006(11)	0.5172(10)	-0.0299(6)	24(2)
O(12)	2a	-0.3175(12)	0.3791(10)	0.1280(7)	26(2)
C(7)	2a	0.2204(14)	0.8038(13)	-0.0126(9)	18(2)
C(8)	2a	0.3083(17)	0.8873(13)	0.0746(9)	18(2)
O(13)	2a	0.4301(10)	0.8228(9)	0.1238(6)	22(2)
O(14)	2a	0.2475(10)	1.0145(10)	0.0935(6)	21(2)
O(15)	2a	0.0921(11)	0.8636(10)	-0.0560(6)	23(2)
O(16)	2a	0.2861(11)	0.6825(9)	-0.0350(6)	24(2)
O(17)	2a	-0.057(2)	0.0953(10)	-0.1708(11)	25(4)
O(18)	2a	0.6001(18)	0.5969(9)	0.2402(9)	17(3)
O(19)	2a	0.4857(13)	-0.3028(10)	-0.2098(7)	35(2)
O(20)	2a	-0.3460(13)	0.0474(13)	0.2209(7)	34(2)
O(21)	2a	0.4925(12)	0.8351(12)	0.3467(7)	34(2)
O(22)	2a	0.2075(13)	-0.0262(11)	-0.2231(7)	35(2)
O(23)	2a	0.9225(16)	0.3421(13)	0.3033(9)	45(3)
O(24)	2a	1.1643(17)	0.5999(13)	0.2671(10)	47(3)

^a $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

solutions of Ln^{3+} cations, crystals of sufficient quality for a complete structural determination were obtained only for $\text{Ln} = \text{Yb}$, using Na^+ -gel and mixtures of U^{4+} and Ln^{3+} cations, oxalates that belong to the two previously reported series have been obtained [3,4].

Compound 1: When an aqueous solution of Yb^{3+} (0.145 M, 2 mL) acidified by 6.7 M nitric acid (2 mL) is slowly added on a Na-silica gel, colorless plate-shaped crystals form slowly inside the gel.

Compounds 4 and 5: The addition of a nitric mixture (3 M, 1.5 mL) of uranium (IV) (0.5 M, 1 mL), neodymium (0.25 M, 2 mL) and ammonium (0.5 M, 6 mL) cations above the NH_4^+ -exchanged gel permitted the synthesis of **4**. The slow addition on the set hydrazinium-exchanged gel of a mixture of aqueous solutions of U^{4+} (0.66 M, 2 mL) and Sm^{3+} nitrate (0.125 M, 6 mL) acidified by 3 M nitric acid (1 mL) leads to the formation of prismatic green crystals of **5**.

Table 5

Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for the U/Ln oxalates $[(\text{NH}_4^+)_{1-x}(\text{H}_2\text{O})_{3+x}] [\text{Ln}_{1-x}\text{U}_x(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}]$

	Compound	Site	x	y	z	$U(\text{eq})$
U/Ln	2	2c	1/4	1/4	0.0667(1)	21(1)
	3	2c	1/4	1/4	0.0672(1)	25(1)
	4	2c	1/4	1/4	0.0666(1)	23(1)
	5	2c	1/4	1/4	0.0686(1)	26(1)
	6	2c	1/4	1/4	0.0676(1)	22(1)
	7	2c	1/4	1/4	0.0688(1)	18(1)
	C(1)	2	8g	0.4762(2)	0.5400(2)	0.0832(2)
3		8g	0.4770(4)	0.5382(4)	0.0833(4)	30(1)
4		8g	0.4773(4)	0.5391(4)	0.0836(4)	23(1)
5		8g	0.4763(8)	0.5411(8)	0.0801(7)	30(1)
6		8g	0.4766(4)	0.5401(4)	0.0816(4)	30(1)
7		8g	0.4754(1)	0.5404(9)	0.0817(9)	19(2)
O(1)		2	8g	0.3745(2)	0.4754(2)	0.1681(2)
	3	8g	0.3797(3)	0.4757(3)	0.1697(3)	39(1)
	4	8g	0.3792(3)	0.4752(3)	0.1711(3)	32(1)
	5	8g	0.3768(6)	0.4771(6)	0.1691(6)	39(1)
	6	8g	0.3770(3)	0.4758(3)	0.1696(4)	42(1)
	7	8g	0.3756(6)	0.4767(6)	0.1710(8)	22(1)
	O(2)	2	8g	0.5428(2)	0.6628(2)	0.1179(2)
3		8g	0.5428(3)	0.6595(3)	0.1179(3)	34(1)
4		8g	0.5430(3)	0.6594(3)	0.1189(4)	28(1)
5		8g	0.5420(6)	0.6633(6)	0.1138(7)	36(1)
6		8g	0.5423(3)	0.6633(3)	0.1158(4)	38(1)
7		8g	0.5420(7)	0.6653(6)	0.1174(8)	22(1)
O(3)		2	2c	1/4	1/4	0.3695(5)
	3	2c	1/4	1/4	0.3782(8)	45(1)
	4	2c	1/4	1/4	0.3824(8)	44(2)
	5	2c	1/4	1/4	0.3741(3)	42(2)
	6	2c	1/4	1/4	0.3707(8)	41(1)
	7	2c	1/4	1/4	0.3774(5)	34(2)
	N(1)	2	8g	0.2407(6)	0.5323(5)	0.5451(4)
3		8g	0.2375(7)	0.5345(6)	0.5434(5)	74(2)
4		8g	0.2383(9)	0.5332(8)	0.5441(6)	67(2)
5		8g	0.244(3)	0.5275(16)	0.5477(10)	100(4)
6		8g	0.2402(1)	0.5321(8)	0.5446(6)	86(2)
7		8g	0.235(3)	0.5348(12)	0.5447(8)	44(3)

Compounds 2, 3, 6 and 7: Prismatic green crystals of mixed uranium–yttrium (**2**),–praseodymium (**3**),–gadolinium (**6**) and–terbium (**7**) oxalates were obtained when the TEOS gel was covered with a mixture of aqueous solutions of U^{4+} (0.065 M, 4 mL), Ln^{3+} (0.25 M, 1 mL) and NH_4^+ (0.05 M, 4 mL) nitrates, acidified by 3 M nitric acid (3 mL).

For all compounds single crystals were isolated after a 2–8 day crystallization period.

2.2. Single-crystal data collection

A suitable single crystal of each compound was carefully selected for the X-ray studies. The single crystal diffraction intensities were measured on an AXS BRUKER SMART CCD-1 K diffractometer system for compounds **1, 4, 5**

and 7 and on a AXS BRUKER X8 CCD-1 K diffractometer for the other compounds. The diffractometers were equipped with a fine-focus Mo-target X-ray tube ($\lambda = 0.71073 \text{ \AA}$) operated at 2000 W power. The detectors

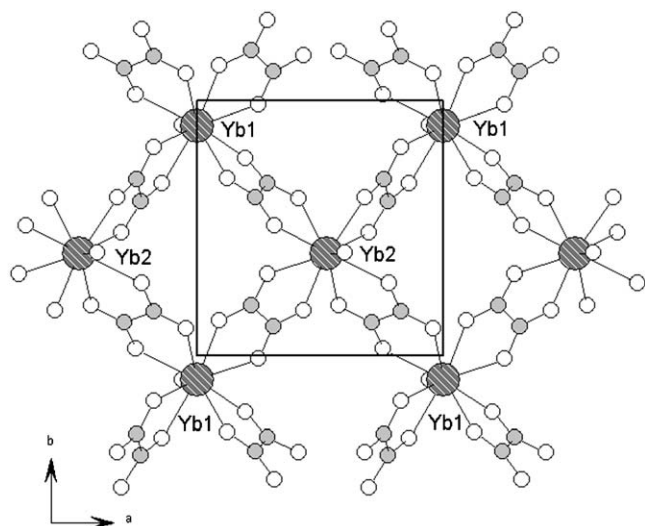


Fig. 1. Two-dimensional arrangement parallel to (001) of oxalate-bridged ytterbium polyhedra in $\text{Na}[\text{Yb}(\text{C}_2\text{O}_4)_2(\text{OH}_2)] \cdot 3\text{H}_2\text{O}$.

were placed at a distance of 5.41 cm from the crystal. The intensities were extracted from the collected frames using the program SaintPlus 6.02 [10]. The structure resolutions and refinements were performed with the SHELXTL software package [11]. The lattice parameters were refined from the complete data set and an empirical absorption correction was performed for all compounds [12]. The heavy atoms were located using the direct methods, while the remaining atoms were found from successive Fourier map analyses. The location of the H atoms of ammonium ions and water molecules was not determined because of the presence of very heavy atoms and important thermal agitation of water molecules. Excepted for **1**, where isotropic atomic displacement parameters of the water oxygen atoms O(17) and O(18) were used, for the other studied crystals the atomic positions and the anisotropic displacement parameters for all atoms were included in the last cycles of refinement.

2.3. Chemical composition analysis

Chemical composition analysis was performed by Energy Dispersive Spectroscopy (EDS) on a JSM 5300 Scanning Electronic Microscope (SEM) equipped with a PGT X-ray microanalysis system (IMIX).

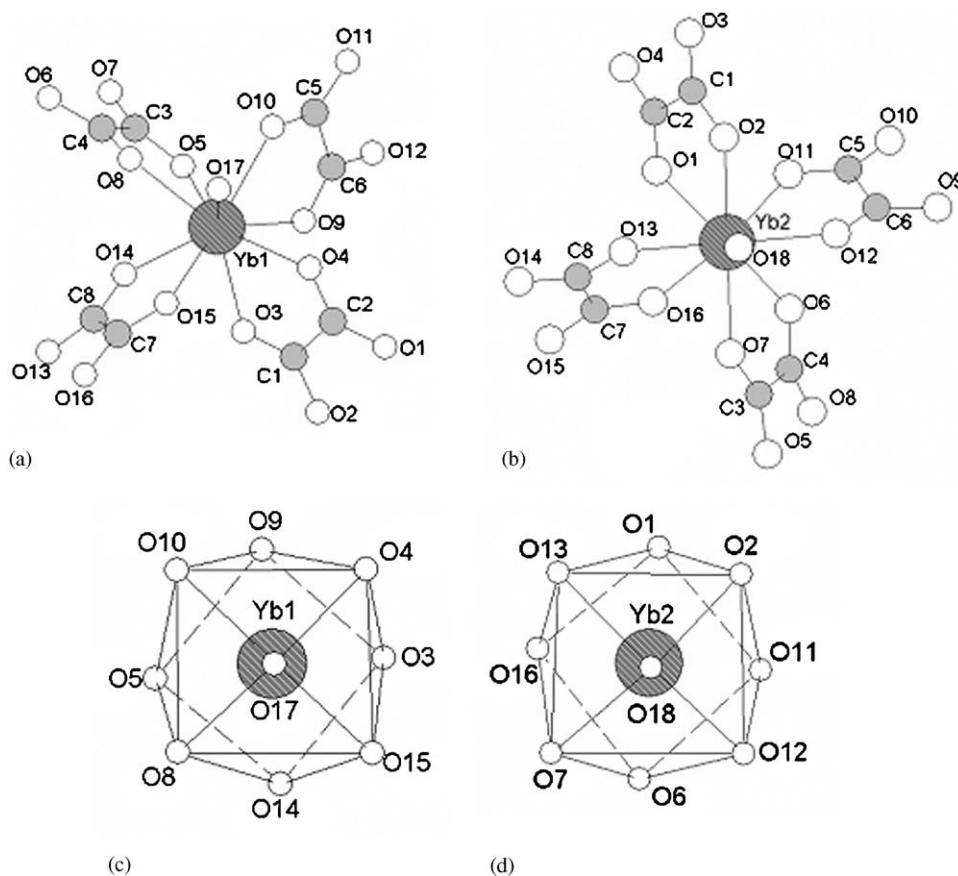


Fig. 2. Building units in $\text{Na}[\text{Yb}(\text{C}_2\text{O}_4)_2(\text{OH}_2)] \cdot 3\text{H}_2\text{O}$ showing the atom labelling scheme and formed by ytterbium (III) ion, four oxalate anions and one aqua oxygen (a) and (b for Yb(1) and Yb(2), respectively). Polyhedron around Yb(1) (c) and Yb(2) (d) described as a mono-capped square antiprism.

Table 6
Bond lengths and average values [Å] for the Yb and Na polyhedra in $\text{Na}[\text{Yb}(\text{C}_2\text{O}_4)_2(\text{OH}_2)] \cdot 3\text{H}_2\text{O}$, **1**

Yb environments			
Yb(1)–O(3)	2.382(8)	Yb(2)–O(1)	2.372(7)
Yb(1)–O(4)	2.319(8)	Yb(2)–O(2)	2.354(8)
Yb(1)–O(5)	2.422(8)	Yb(2)–O(6)	2.409(9)
Yb(1)–O(8)	2.319(8)	Yb(2)–O(7)	2.360(9)
Yb(1)–O(9)	2.389(8)	Yb(2)–O(11)	2.395(9)
Yb(1)–O(10))	2.350(8)	Yb(2)–O(12)	2.337(9)
Yb(1)–O(14)	2.367(8)	Yb(2)–O(13)	2.331(8)
Yb(1)–O(15)	2.369(9)	Yb(2)–O(16)	2.416(9)
Yb(1)–O(17)	2.487(15)	Yb(2)–O(18)	2.489(14)
<Yb(1)–O>	2.378(9)	<Yb(2)–O>	2.385(9)
Na environments			
Na(1)–O(2)	2.451(10)	Na(2)–O(5)	2.647(11)
Na(1)–O(10)	2.450(11)	Na(2)–O(16)	2.630(11)
Na(1)–O(17)	2.501(11)	Na(2)–O(19)	2.453(13)
Na(1)–O(18)	2.440(16)	Na(2)–O(22)	2.477(11)
Na(1)–O(23)	2.442(12)	Na(2)–O(23)	2.442(16)
Na(1)–O(24)	2.424(15)	Na(2)–O(24)	2.464(12)
<Na(1)–O>	2.434(12)	<Na(2)–O>	2.518(12)

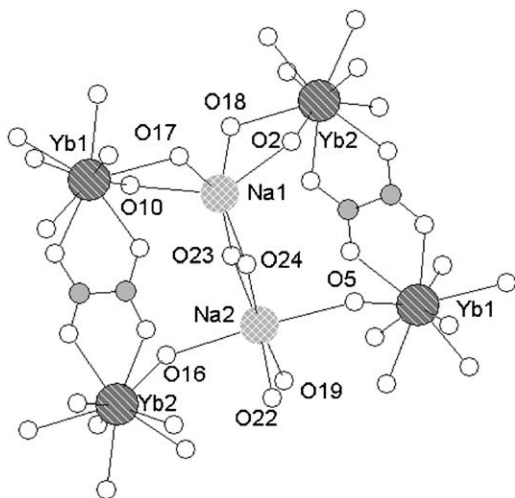


Fig. 3. In $\text{Na}[\text{Yb}(\text{C}_2\text{O}_4)_2(\text{OH}_2)] \cdot 3\text{H}_2\text{O}$, the connection between parallel oxalate-ytterbium sheets is assumed by dimeric units of edge-shared NaO_6 polyhedra.

3. Structure solution and refinement

The crystal structure of **1** was solved in the non-centrosymmetric *Pc* space group. The crystal structure of all the mixed oxalates (**2–7**) was solved in the tetragonal system in space group *P4/n*. The crystal data, the experimental details for the structure determinations and the structure refinement parameters are gathered in Table 1 for **1** and Table 2 for **2–7**.

For compounds **2–7**, the EDS analysis unambiguously indicates the presence of both U and *Ln*, so a mixed lanthanide–uranium site was introduced. As U and *Ln* are not accurately distinguished by crystal refinement from

X-ray data, the U/*Ln* ratio were fixed to the values obtained from the EDS analyses considering a full occupancy of the crystallographic position.

For the compounds **2–7**, the NH_4^+ ions and the non-bonded water molecules are disordered on the same crystallographic site labeled N(1) and considered totally occupied. For compound **5**, hydrazinium ion is not evidenced from difference syntheses, the initial hydrazinium ion is probably partially oxidized, which induces the formation of ammonium ions [13] as already observed for other compounds.

For compound **1** residual electron density is observed in the vicinity of Yb atom, at 0.99 Å from Yb(1) and 1.04 Å from Yb(2), the largest hole is also near Yb(1), at 0.93 Å. For some mixed compounds, particularly for **5** and **7**, high residual electron density is also observed in the vicinity of the heavy atom, at 0.88 and 0.86 Å from U/Sm and U/Tb, respectively. Splitting of the two heavy atoms (U and *Ln*) on two sites allows a weak reduction in the reliability factors and the disappearance of the residual electron density taken into account by a high thermal displacement of one of the two atoms, however these two atoms are not refined in significantly different positions (Table 3). The other atom coordinates are not modified by this splitting. So, the results considering the splitting were not considered as significant.

The atomic positional parameters and equivalent isotropic displacement parameters are given in Table 4 for compound **1** and in Table 5 for compounds **2–7**.

4. Results and discussion

The compound $\text{Na}[\text{Yb}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ (**1**) is isostructural with the yttrium oxalate $\text{Na}[\text{Y}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ [14] and exhibits a two-dimensional arrangement of Yb-centered polyhedra linked through bis-bidentate oxalate groups forming four-membered rings where the two independent Yb atoms alternate (Fig. 1). The two independent Yb atoms are nine-fold coordinated with oxygen atoms from four bidentate oxalate groups and one water molecule and the polyhedra can be described as mono-capped square antiprisms, with water oxygen at the longest distance as a cap (Fig. 2). The water molecules O(17) and O(18), that belong to the coordination of Yb(1) and Yb(2) respectively, point alternately up and down the layer.

The layer is similar to that obtained in homeotypic **112** compounds with yttrium such as $\text{NH}_4[\text{Y}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]$ [15] and $\text{Cs}[\text{Y}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]$ [16] and with lanthanide metals such as $\text{NH}_4[\text{Ln}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]$ (*Ln* = Eu–Yb) [5], $\text{CN}_3\text{H}_6[\text{La}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]$ and $(\text{NH}_4)_{0.5}(\text{CN}_3\text{H}_6)_{0.5}[\text{Nd}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]$ [17].

The principal bond lengths in the coordination polyhedra around Yb and Na are reported in Table 6. The average Yb–O are the same, 2.378 and 2.385 Å for Yb(1) and Yb(2), respectively, slightly lower than the average Y–O distances in the isotopic yttrium compound, in

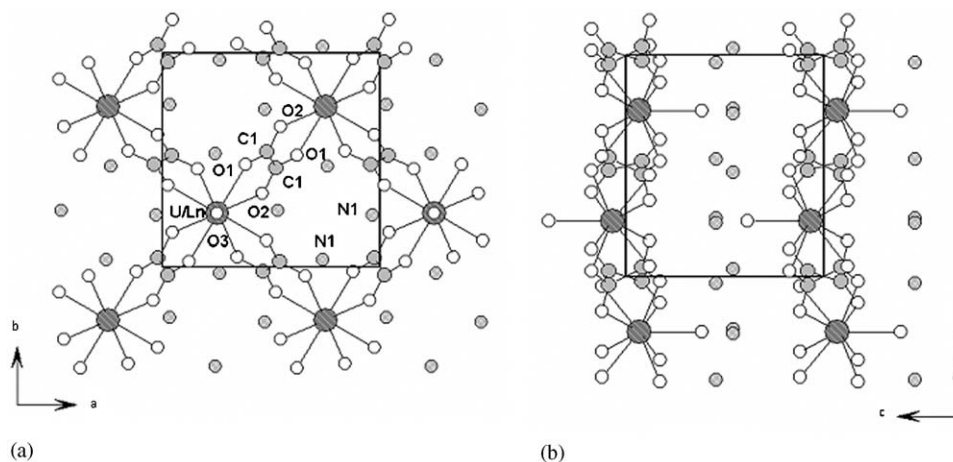


Fig. 4. Projections of the crystal structure of the $[(\text{NH}_4^+)_{1-x}(\text{H}_2\text{O})_{3+x}][\text{Ln}_{1-x}\text{U}_x(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}]$ compounds along $[001]$ and $[100]$ showing (a) the two-dimensional arrangement of U/Ln polyhedra connected through bis-bidentate oxalate ions and (b) the interleaved NH_4^+ and H_2O entities.

Table 7

U/Ln-O bond lengths and average values [\AA] for the U/Ln oxalates $[(\text{NH}_4^+)_{1-x}(\text{H}_2\text{O})_{3+x}][\text{Ln}_{1-x}\text{U}_x(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}]$

Compound	y	Pr	Nd	Sm	Gd	Tb
$\text{U/Ln-O}(1)$ (4x)	2.390(1)	2.458(2)	2.451(3)	2.431(5)	2.411(3)	2.399(5)
$\text{U/Ln-O}(2)$ (4x)	2.451(1)	2.493(3)	2.485(3)	2.467(5)	2.452(3)	2.445(6)
$\text{U/Ln-O}(3)$	2.407(4)	2.467(6)	2.494(7)	2.450(1)	2.406(6)	2.423(2)
$\langle \text{U/Ln-O} \rangle$	2.419(2)	2.475(4)	2.471(5)	2.449(4)	2.429(4)	2.422(5)

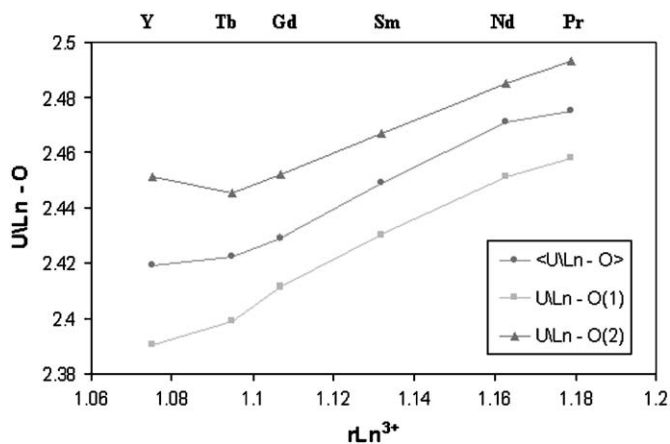


Fig. 5. Variation of the average Ln/U-O (●), $\text{Ln/U-O}(1)$ (■) and $\text{Ln/U-O}(2)$ (▲) distances versus the ionic radius of the Ln^{3+} ion.

agreement with the decrease of the ionic radius from Y to Yb in nine-fold coordination [18]. The two independent Na^+ ions located in the interlayer space are both six-coordinated, however their coordination polyhedra differ. The distorted octahedron around $\text{Na}(2)$ is formed by two oxygen atoms that belong to two oxalate ions from two parallel layers and by four water molecules. For $\text{Na}(1)$, the polyhedron is more distorted, with an oxalate oxygen atom and a water oxygen atoms that belong to the same $\text{Yb}(1)\text{O}_9$ polyhedron, an oxalate and a water oxygen atom that belong to the same $\text{Yb}(2)\text{O}_9$ polyhedron of a parallel layer

and two water molecules (Fig. 3). Finally the two NaO_6 polyhedra share an $\text{O}(23)\text{--O}(24)$ edge to form a dimeric unit.

The bond lengths and bond angles in the four independent oxalate ligands (distances C-O range from 1.240(16) to 1.295(16) \AA and C-C from 1.518(19) to 1.538(18) \AA , average angle O-C-O is $126(1)^\circ$ and O-C-C is $117(1)^\circ$ are in good agreement with the mean values reported by Hahn for oxalate compounds, $\text{C-O} = 1.24 \text{\AA}$, $\text{C-C} = 1.55 \text{\AA}$, $\text{O-C-O} = 125^\circ$, $\text{O-C-C} = 117^\circ$ [19].

The isotopic compounds $(\text{NH}_4^+)_{1-x}[\text{Ln}_{1-x}\text{U}_x(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}] \cdot (3+x)\text{H}_2\text{O}$, 2–7, are characterized by the same two-dimensional arrangement of Ln -centered polyhedra linked through bis-bidentate oxalate groups but, astonishingly $\text{Ln}(\text{III})$ is partially substituted by $\text{U}(\text{IV})$ in the same crystallographic site, the surplus of charge being compensated by the removal of monovalent ions. The arrangement is more symmetric and the unit cell contains only one independent Ln/U atom and one independent oxalate entity (Fig. 4a). The Ln/U environment is also more symmetric with the Ln/U and $\text{O}(3)$ atoms on the four-fold axis. The Ln/U-O distances and the average values are reported in Table 7. For the lanthanide-containing compounds, compared to the average Ln-O distances in homeotypic compounds, the introduction of U atom in the site, is accompanied by a reduction of the average Ln/U-O distance in agreement with the smaller radius of U^{4+} in nine-coordination [18] and with the increased bond valence demand of the tetravalent cation, for example, from

2.497 Å for Nd in $(\text{NH}_4)_{0.5}(\text{CN}_3\text{H}_6)_{0.5}[\text{Nd}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]$ [17] to 2.471 Å in **4** and from 2.436 Å for Gd in $\text{NH}_4[\text{Gd}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]$ [5] to 2.429 Å in **6**. The average U/Ln–O distance is influenced by the largest metal as shown in Fig. 5 which reveals a monotonic variation of the average distance with the ionic radius of the Ln^{3+} cation in nine-coordination [18]. Note that the U/Ln atom is displaced from the center of the Archimedian antiprism toward the O(1)₄ square giving systematically shorter Ln–O(1) distances and greater O(1)–O(1) distances compared to the corresponding distances involving O(2) atoms. The U/Ln–O(1) and Ln/U–O(2) (excepted for Y that is not actually a lanthanide metal) also vary regularly with the ionic radius of the Ln^{3+} cation. The NH_4^+ ions and non-bonded H_2O molecules occupy the same site labelled N(1) and located in the interlayer space (Fig. 4b). A N(1) atom is hydrogen bonded to two oxygen atoms O(2) and O(3) with distances in the range 2.80(1)–2.87(1) and 2.814(2)–2.856(6) Å for O(2) and O(3), respectively. The N(1)–N(1) distance varying in the range 2.75(3)–2.88(3) Å is compatible with a full occupancy of the corresponding site by both NH_4^+ and H_2O .

5. Conclusion

This series constitutes the third example of mixed Ln(III)/U(IV) oxalates in which U(IV) and Ln(III) are disordered on the same crystallographic site. These mixed oxalates can be derived from the $(\text{NH}_4)\text{Ln}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})$, $\text{Ln} = \text{Eu}–\text{Yb}$ [5] compounds by the partial substitution of Ln(III) by U(IV) and the removal of NH_4^+ for charge compensation according to the scheme $\text{Ln(III)} + \text{NH}_4^+ \rightarrow \text{U(IV)}$. This series of compounds corresponds to the same formula as the previously reported triclinic series [4]. Whereas in both these series the metallic cation Ln(III)/U(IV) is nine-coordinated by oxygen atoms from four bidentate oxalate ions and one water molecule, the arrangement of the Ln/ UO_9 polyhedra is totally different leading to a three-dimensional framework of six-membered rings in the triclinic series and to a two-dimensional network of four-membered rings in the present series. As already reported [3,4], only a few crystals of various composition are obtained from the gel crystal growth method used, so a sufficient quantity of crystals of homogeneous composition can not be isolated to allow a total and unambiguous characterization of, for example, the water content. From the single crystal studies it is also impossible to define the role of the various factors influencing the type of structure obtained: Ln/U ratio, monovalent ion nature, (Ln+U)/oxalate ratio, temperature... At most, one can note that single crystals of the hexagonal series were obtained for the three studied monovalent cations (Na^+ , NH_4^+ , N_2H_5^+), those of the

triclinic series for $M^+ = \text{N}_2\text{H}_5^+$ and Na^+ and the tetragonal series for $M^+ = \text{NH}_4^+$ and Na^+ . Single crystals of the hexagonal series correspond to compounds rather rich in uranium. Owing to these difficulties and to the importance of these compounds in the nuclear industry, we have planned the preparation of powder samples in various synthesis conditions to define the role of each experimental parameter, to determine the solid solution domain for the different systems and to carry chemical compositional analysis together with TGA to determine the water content for each composition. The results of this extended study will be reported in a forthcoming paper.

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