U(IV)/LN(III) unexpected mixed site in polymetallic oxalato complexes: Part II— Substitution of U(IV) for Ln(III) in the new oxalates $(N_2H_5)Ln(C_2O_4)_2 \cdot nH_2O$ ($Ln = $ Nd, Gd)

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Abstract

Two new hydrazinium lanthanide(III) oxalates, $(N_2H_5)[Nd(C_2O_4)_2(H_2O)] \cdot 4H_2O$ (**1**) and $(N_2H_5)[Gd(C_2O_4)_2(H_2O)] \cdot 4.5H_2O$ (**2**) have been prepared and their crystal structures determined by single-crystal X-ray diffraction. The crystal structures were solved by the direct methods and Fourier difference techniques, and refined by a least-squares method on the basis of F^2 for all unique reflections. Crystallographic data: **1**, triclinic, space group $P\bar{1}$, $a = 8.507(3)$ Å, $b = 9.762(4)$, $c = 10.249(4)$ Å, $\alpha = 62.378(5)$, $\beta = 76.681(5)$, $\gamma = 73.858(5)$, $Z = 2$, $R_1 = 0.0335$ for 172 parameters with 3430 reflections with $I \geqslant 2\sigma(I)$; **2**, triclinic, space group $P\bar{1}$, $a = 8.52(3)$ Å, $b = 9.51(3)$, $c = 10.14(3)$ Å, $\alpha = 62.11(4)$, $\beta = 76.15(5)$, $\gamma = 73.73(5)$, $Z = 2$, $R_1 = 0.0325$ for 172 parameters with 1742 reflections with $I \geqslant 2\sigma(I)$. The two isotypic structures are built from a three-dimensional (3D) arrangement of lanthanide and oxalate ions. The lanthanide atom is coordinated by eight oxygen atoms from four tetradentate oxalate ions and one aqua oxygen. Alternating lanthanide and oxalate ions form six-membered rings that delimit tunnels running down three directions and occupied by hydrazinium and water molecules. Starting from these lanthanide(III) compounds two isotypic mixed Ln(III)/U(IV) oxalates, $(N_2H_5)_{0.75}[Nd_{0.75}U_{0.25}(C_2O_4)_2(H_2O)] \cdot 4.5H_2O$ (**3**) and $(N_2H_5)_{0.75}[Gd_{0.75}U_{0.25}(C_2O_4)_2(H_2O)] \cdot 4H_2O$ (**4**), are 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. Finally, using Na$^+$ gel, two mixed Ln(III)/U(IV) sodium oxalates, $Na_{0.5}[Nd_{0.5}U_{0.5}(C_2O_4)_2(H_2O)] \cdot 3H_2O$ (**5**) and $Na_{0.65}[Gd_{0.65}U_{0.35}(C_2O_4)_2(H_2O)] \cdot 4.5H_2O$ (**6**) have been obtained without any change in the 3D framework.
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1. Introduction

Oxalic acid is often used as precipitating agent—in the industrial plutonium conversion process or for waste decontamination purpose—or as complexing agent to adjust extracting characteristics of actinides and lanthanides or redox behavior of actinides. Thus chemical properties of actinide and lanthanide oxalates were often investigated in the past, but surprisingly enough, only

few crystallographic structures of these compounds have been determined. Simple hydrated lanthanide oxalates $[Ln(H_2O)_3]_2(C_2O_4)_3 \cdot nH_2O$ have been obtained for $Ln = $ La, Ce, Pr, Nd [1–3], Eu–Dy [4] and Er [5]. The lanthanide ion is coordinated by three bidentate oxalate ions and three water molecules. Structures of monovalent M ion—lanthanide double oxalates corresponding to the general formulae $MLn(C_2O_4)_2 \cdot nH_2O$ (called throughout this paper **112** compounds in relation to the $M/Ln/Ox = 1/1/2$ ratio) have also been established. Depending of the coordination modes of the oxalate ions and the number of water molecules that belongs to

the coordination of the lanthanide atom, various bi- and three-dimensional (2D and 3D) structures are obtained [6–9].

Recently we have demonstrated the efficiency of crystal growth of oxalate compounds by using the slow diffusion of the ions through silica gel impregnated with oxalic acid [10,11]. The use of this crystal growth method from gel for several M^{I}–U^{IV}–Ln^{III} systems (M^{I} = Na, NH$_4$, N$_2$H$_5$, Ln^{III} = Ce, Nd, Sm, Gd) enabled us to isolate crystals of a new U(IV) oxalate (NH$_4$)$_2$U$_2^{IV}$(C$_2$O$_4$)$_5 \cdot$ 2.5H$_2$O and of double U(IV)–Ln(III) oxalates resulting from the substitution of U^{IV} by Ln^{III} reported in Part 1 of this work. Using Ln^{3+} solutions, free of U^{4+}, two new hydrazinium-lanthanide double oxalates corresponding to **112** compounds (N$_2$H$_5$)Ln(C$_2$O$_4$)$_2 \cdot n$H$_2$O were obtained for Ln = Nd (n = 5) and for Ln = Gd (n = 5.5). Two hydrazinium-lanthanide/uranium(IV) double oxalates (N$_2$H$_5$)$_{0.75}$($Ln_{0.75}$U$_{0.25}$)(C$_2$O$_4$)$_2 \cdot n$H$_2$O were also obtained for Ln = Nd (n = 5.5) and for Ln = Gd (n = 5). Finally, similar compounds with sodium as monovalent ion but with higher U^{IV}/Ln^{III} substitution ratio, Na$_{0.5}$(Nd$_{0.5}$U$_{0.5}$)(C$_2$O$_4$)$_2 \cdot$ 4H$_2$O and Na$_{0.65}$(Gd$_{0.65}$U$_{0.35}$)(C$_2$O$_4$)$_2 \cdot$ 5.5H$_2$O were crystallized using Na$^+$ gels. Synthesis and X-ray crystal structure study of these new oxalates are reported in this second part of this work. The crystal structure of these oxalates are compared to that of lanthanide oxalates and other **112** compounds.

2. Experimental

2.1. Crystal synthesis

Single crystals of (N$_2$H$_5$)[Nd(C$_2$O$_4$)$_2$(H$_2$O)] $\cdot$ 4H$_2$O (**1**), (N$_2$H$_5$)[Gd(C$_2$O$_4$)$_2$(H$_2$O)] $\cdot$ 4.5H$_2$O (**2**), (N$_2$H$_5$)$_{0.75}$ [Nd$_{0.75}$U$_{0.25}$(C$_2$O$_4$)$_2$(H$_2$O)] $\cdot$ 4.5H$_2$O (**3**), (N$_2$H$_5$)$_{0.75}$ [Gd$_{0.75}$U$_{0.25}$(C$_2$O$_4$)$_2$(H$_2$O)] $\cdot$ 4H$_2$O (**4**), Na$_{0.5}$[Nd$_{0.5}$U$_{0.5}$ (C$_2$O$_4$)$_2$(H$_2$O)] $\cdot$ 3H$_2$O (**5**) and Na$_{0.65}$[Gd$_{0.65}$U$_{0.35}$ (C$_2$O$_4$)$_2$(H$_2$O)] $\cdot$ 4.5H$_2$O (**6**) were obtained by the slow diffusion of the cations through sodium silica gel or hydrazinium-exchanged silica gel impregnated with oxalic acid [12] and isolated after a 2–8 days crystallization process. The sodium silica gel is 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. Nitric acid is used to acidify the medium and oxalic acid as a source of anions. The resulting solution is then allowed to set in tubes of internal diameter 15 mm. The hydrazinium silica gel has been prepared by ionic exchange between the as-prepared silica gel and a nitric solution of oxalic acid 0.2 M and hydrazinium nitrate 2 M added on the gel. For each silica gel, several crystal growths were experimented for Ln = Ce, Nd, Sm and Gd. Single

crystals good enough for structure determination by X-ray diffraction were obtained for six compounds belonging to the family presented in this paper.

Compounds **1** *and* **2:** When an aqueous solution of Nd^{3+} or Gd^{3+} (0.25 M, 2 mL) and hydrazinium cations (2 M, 4 mL), acidified by 3 M nitric acid (4 mL) is slowly added on the set hydrazinium-exchanged gel, octahedral crystals form slowly inside the gel. The crystals are dark rose and colorless for Nd and Gd, respectively.

Compounds **3** *and* **4:** Green-purple octahedral crystals of **3** and **4** were obtained when a mixture of U^{4+} (0.66 M, 2 mL), Nd^{3+} or Gd^{3+} (0.25 M, 2 mL), N$_2$H$_5^+$ (2 M, 2 mL), HNO$_3$ (3 M, 1 mL) was added on the hydrazinium-exchanged gel.

Compounds **5** *and* **6**: Parallelepipedic green single crystals of **5** and **6** were obtained when the sodium silica gel was covered with a mixture of U^{4+} (0.5 M, 1 mL), Nd^{3+} (0.25 M, 2 mL), HNO$_3$ (2.5 M, 5.5 mL) and U^{4+} (0.66 M, 0.5 mL), Gd^{3+} (0.25 M, 0.5 mL), HNO$_3$ (3 M, 2 mL), respectively.

2.2. Single-crystal data collection

The single-crystal diffraction intensities for each compound were measured on a AXS BRUKER SMART CCD-1K diffractometer system equipped with a fine-focus Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000 W power. The detector was placed at a distance of 5.41 cm from the crystal under the conditions given in Table 1 and extracted from the collected frames using the program SaintPlus 6.02 [13]. The structure resolutions and refinements were performed with the SHELXTL software package [14]. The lattice parameters were refined from the complete data set and an absorption correction, based on the faces indices for **5**, and empirical for other crystals, was performed [15]. The heavy atoms were located using the direct methods, while the remaining atoms were found from successive Fourier map analyses. The hydrogen atoms of water molecules could not be located because of the presence of heavy atoms and of the important thermal agitation of water molecules. The atomic positions for all atoms, the anisotropic displacement parameters for metal and oxalate ion atoms and isotropic displacement parameters for N and water O atoms were included in the last cycles of refinement. In the absence of TGA analysis, which cannot be performed on one single crystal, the water content can display some variations depending on the position within the gel, the ambient water pressure and temperature variations during the measurements, therefore the water contents were deduced for each single crystal from the structural study. However, the water content is a real

Table 1
Crystal data and structure refinement parameters

Compound	1	2	3	4	5	6
Empirical formula	$Nd_2C_8N_4O_{26}H_{30}$	$Gd_2C_8N_4O_{27}H_{32}$	$U_{0.5}Nd_{1.5}C_8N_3O_{27}H_{29.5}$	$U_{0.5}Gd_{1.5}C_8NO_{26}H_{27.5}$	$UNdNaC_8O_{24}H_{16}$	$U_{0.7}Gd_{1.3}Na_{1.3}C_8O_{27}H_{22}$
Formula weight (g/mol)	886.60	930.62	934.98	934	893.34	950.9
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Crystal size (μm)	$200 \times 200 \times 200$	$150 \times 150 \times 150$	$250 \times 250 \times 250$	$230 \times 230 \times 220$	$300 \times 100 \times 100$	$200 \times 150 \times 180$
a (Å)	8.507(3)	8.52(3)	8.417(2)	8.533(4)	8.673(8)	8.861(7)
b (Å)	9.762(4)	9.51(3)	9.716(3	9.370(4)	9.411(9)	9.352(8)
c (Å)	10.249(4)	10.14(3)	10.117(3)	10.003(4)	10.048(9)	10.124(8)
α (deg)	62.378(5)	62.11(4)	61.951(4)	63.283(6)	63.71(1)	64.11(1)
β (deg)	76.681(5)	76.15(5)	77.816(4)	75.905(6)	76.11(1).	75.00(1)
γ (deg)	73.858(5)	73.73(5)	74.279(4)	74.276(6)	75.45(1)	75.39(1)
Volume (Å^3)	719(1)	691(4)	700(1)	681(2)	704(1)	720(1)
Z	1	1	1	1	1	1
ρ_{calc} (Mg/m^3)	1.978	2.158	2.150	2.217	2.089	2.132
Abs. coef. (mm^{-1})	3.672	4.866	5.752	6.698	7.670	6.722
Absorption correction	Empirical	Empirical	Empirical	Empirical	Gaussian faces-indexed	Empirical
Max and min transmission	—	—	—	—	0.0767 and 0.218	—
$F(000)$	404	420	421	419	403	424
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Wavelength Å()	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
θ_{range} (deg)	3.57–29.38	2.29–22.49	3.01–28.24	2.30–28.09	2.45–27.81	2.27–27.29
Index ranges	$-11 \leqslant h \leqslant 11$, $-13 \leqslant k \leqslant 13$, $-13 \leqslant l \leqslant 13$	$-9 \leqslant h \leqslant 9$, $-10 \leqslant k \leqslant 10$, $-10 \leqslant l \leqslant 10$	$-10 \leqslant h \leqslant 10$, $-12 \leqslant k \leqslant 12$, $-13 \leqslant l \leqslant 13$	$-10 \leqslant h \leqslant 10$, $-12 \leqslant k \leqslant 12$, $-13 \leqslant l \leqslant 13$	$-11 \leqslant h \leqslant 11$, $-11 \leqslant k \leqslant 10$, $-13 \leqslant l \leqslant 9$	$-11 \leqslant h \leqslant 10$, $-11 \leqslant k \leqslant 11$ $-12 \leqslant l \leqslant 13$
Reflections collected	6181	3620	5261	5152	3793	4452
Independent reflections	3430	1742	2911	2824	2761	2407
$R_{(int)}$	0.0229	0.0254	0.0247	0.0288	0.0251	0.0531
Data/restraints/parameters	3430/2/172	1742/0/172	2911/0/170	2824/0/164	2761/0/193	2407/0/162
Final R indices $[I > 2\,\text{sigma}(I)]$	$R_1 = 0.0335$, $wR_2 = 0.0913$	$R_1 = 0.0325$, $wR_2 = 0.0879$	$R_1 = 0.0494$, $wR_2 = 0.1319$	$R_1 = 0.0352$, $wR_2 = 0.0882$	$R_1 = 0.0391$ $wR_2 = 0.1123$	$R_1 = 0.0560$ $wR_2 = 0.1337$
R indices (all data)	$R_1 = 0.0370$, $wR_2 = 0.0934$	$R_1 = 0.0339$, $wR_2 = 0.0901$	$R_1 = 0.0532$, $wR_2 = 0.1381$	$R_1 = 0.0391$, $wR_2 = 0.0897$	$R_1 = 0.0419$ $wR_2 = 0.1134$	$R_1 = 0.0608$ $wR_2 = 0.1360$
Extinction coefficient	—	0.0048(12)	—	0.0027(9)	0.0028(10)	—
Largest diff. peak/hole (e/Å^3)	0.954/−0.793	1.165/−0.761	2.610/−2.715	1.655/−1.644	1.387/−1.366	2.666/−2.927

feature of the compounds which needs further investigations from powder samples.

2.2.1. 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).

2.3. Structure refinement

The crystal structure of all these mixed oxalates (1–6) was solved in a triclinic system in space group $P\bar{1}$. The crystal data and the structure refinement parameters are gathered in Table 1.

For compounds 1 and 2, whereas the localization of metals and oxalate ions that form the framework of the structure is straightforward, the localization of hydrazinium ions and water molecules inside the channels is more laborious. The distinction of N and O atoms results from interatomic distance considerations, which allow the identification of N_2H_5 entities. Moreover, in the two cases, some water molecules exhibited high displacement parameters and are located much too close to nitrogen atoms, so the occupancy rate of their site was fixed to 1/2 in the last cycles of refinement. It should be noted that, as usually found in related materials, the water molecules inside the large channels are weakly bonded and have a "zeolitic" character [16–18]. However it is noteworthy that, in spite of disorder and water content variability, the hydrazinium and water all occupy equivalent positions in the two structures.

The structure determination of 3 and 4 was carried out using 1 and 2 results. A mixed lanthanide–uranium site was introduced. The refinement of the U/Ln ratio considering a full occupancy of the site gave a value close to 0.75/0.25 in accordance with the EDS analysis results, which was finally fixed for the two compounds. The mixed site in this series was confirmed by the study of Na-containing compounds 5 and 6.

For 5, the first structural refinement led to the formula $U_2(C_2O_4)_4 \cdot 13H_2O$. This solution was satisfactory both on crystallographic and chemical terms ($R_1 = 4.6\%$) but was not in agreement with the chemical composition as determined by EDS. Indeed, the synthesized compound is a mixed oxalate of U(IV), neodymium(III) and sodium and the quantitative analysis indicated that the U(IV), neodymium(III) and sodium(I) ratio are close to 1:1:1. Finally, the structure determination was performed introducing sodium and neodymium atoms in the formula, the U(IV) on neodymium(III) ratio and the crystallographic coordinates of the two elements were refined. The better solution was obtained for uranium and neodymium atoms in the same crystallographic position and for U(IV) on neodymium(III) ratio fixed to unity in

accordance with the EDS results. The isotropic displacement parameters of the water molecule O(w14) was high so its crystallographic position has to be split into two close sites O(w14) and O(w14A). The other non-bonded water molecules O(w10), O(w11), O(w12), O(w13) exhibited also high anisotropic displacement parameters so the occupancy of their sites was fixed to 0.5 and the resulting chemical formula is then $Na_{0.5}[U_{0.5}Nd_{0.5}(C_2O_4)_2(H_2O)] \cdot 3H_2O$.

For 6 the Gd occupancy of the mixed site was refined to 0.65(2) in agreement with the EDS analysis results. The occupancy of the Na site was constrained to be the same as that of Gd.

3. Results and discussion

Atomic coordinates are given in Tables 2, 4 and 6 and selected bond lengths and angles in Tables 3, 5 and 7 for 1 and 2, 3 and 4, 5 and 6, respectively. The six compounds are isotypic. The four independent oxalate anions possess an inversion center at the middle of the C–C bond.

The building unit of 1 is shown in Fig. 1a. The structure of $(N_2H_5)[Nd(C_2O_4)_2(H_2O)] \cdot 4H_2O$ (1) and $(N_2H_5)[Gd(C_2O_4)_2(H_2O)] \cdot 4.5H_2O$ (2) is built from polyhedra of lanthanide atoms connected by oxalate groups to form a 3D anionic framework $[Ln(C_2O_4)_2(H_2O)]^-$ ($Ln = $ Nd, Gd), which displays tunnels with elliptic cross-sections (Fig. 2) in three directions forming cavities at their intersections. The $N_2H_5^+$ ions and all the water molecules, except O(w11), occupy the same positions in the two lanthanide oxalates structures and almost all half occupy positions related by an inversion center, so they are disordered in the largest elliptic tunnels running down the a-axis and centered on the inversion center (Fig. 3). The N–N distances for the hydrazinium ions in 1 are in agreement with values generally reported whereas in 2 they are abnormally short; however, there is great disorder between the water molecules and the hydrazinium cations, so nitrogen and oxygen atoms are very difficult to localize precisely.

In the 3D network the Ln atoms are connected by tetradentate oxalate groups. The Ln atom is surrounded by nine oxygen atoms from four oxalate ions and one aqua ligand, O(w9), with bond lengths varying in a narrow range 2.470(3)–2.514(4) and 2.424 (8)—2.474(8) Å, for $Ln = $ Nd and Gd, respectively. The coordination polyhedron around Ln can be described as a tri-capped trigonal prism (Fig. 1b). The decrease of the mean Ln–O bond length from Nd, 2.495(3) Å, to Gd, 2.449(8) Å, is in agreement with the ionic radius variation from 1.163 Å for Nd to 1.107 Å for Gd for coordination number nine [19]. Bond-valence sums calculation using the Brese and O'Keefe bond-valence parameters [20] with $b = 0.37$ Å indicates that the two

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $(N_2H_5)[Nd(C_2O_4)_2(H_2O)] \cdot 4H_2O$ (normal types) and $(N_2H_5)[Gd(C_2O_4)_2(H_2O)] \cdot 4.5H_2O$ (italic types)

Atom	Site	Occup	x	y	z	$U_{(eq)}$
Nd	2i	1	0.33386(3)	0.36924(3)	0.83930(2)	0.031(1)
Gd	*2i*	*1*	*0.33294(4)*	*0.371970(4)*	*0.84010(4)*	*0.027(1)*
O(1)	2i	1	−0.0757(4)	0.6895(4)	0.9889(4)	0.043(1)
O(1)	*2i*	*1*	*−0.0811(7)*	*0.6959(7)*	*0.9844(7)*	*0.038(1)*
O(2)	2i	1	0.3142(4)	0.0909(4)	0.9246(4)	0.042(1)
O(2)	*2i*	*1*	*0.3173(7)*	*0.0920(7)*	*0.9217(7)*	*0.037(1)*
O(3)	2i	1	0.5313(5)	0.3111(4)	0.6447(4)	0.045(1)
O(3)	*2i*	*1*	*0.5277(7)*	*0.3066(7)*	*0.6497(6)*	*0.037(1)*
O(4)	2i	1	0.5417(5)	0.5155(5)	0.8200(4)	0.043(1)
O(4)	*2i*	*1*	*0.5374(8)*	*0.5199(7)*	*0.8150(6)*	*0.039(1)*
O(5)	2i	1	0.5735(4)	0.1656(4)	0.9626(4)	0.045(1)
O(5)	*2i*	*1*	*0.5672(7)*	*0.1710(6)*	*0.9682(7)*	*0.040(2)*
O(6)	2i	1	0.1302(4)	0.6037(4)	0.8481(4)	0.045(1)
O(6)	*2i*	*1*	*0.1331(7)*	*0.6079(7)*	*0.8473(6)*	*0.039(1)*
O(7)	2i	1	0.3466(5)	0.3894(5)	1.0719(4)	0.045(1)
O(7)	*2i*	*1*	*0.3409(7)*	*0.3911(8)*	*1.0734(6)*	*0.040(1)*
O(8)	2i	1	0.3475(4)	0.5985(4)	0.5892(4)	0.042(1)
O(8)	*2i*	*1*	*0.3482(7)*	*0.6038(7)*	*0.5887(6)*	*0.038(1)*
O(w9)	2i	1	0.1322(5)	0.3717(6)	0.6930(5)	0.058(1)
O(w9)	*2i*	*1*	*0.1343(8)*	*0.3790(8)*	*0.6963(7)*	*0.048(2)*
C(1)	2i	1	0.0158(6)	0.5846(5)	0.9528(5)	0.036(1)
C(1)	*2i*	*1*	*0.0134(10)*	*0.5873(10)*	*0.9517(9)*	*0.031(2)*
C(2)	2i	1	0.4255(5)	−0.0216(5)	0.9891(5)	0.033(1)
C(2)	*2i*	*1*	*0.4268(10)*	*−0.0231(10)*	*0.9855(9)*	*0.029(2)*
C(3)	2i	1	0.4469(5)	0.5829(5)	0.4842(5)	0.033(1)
C(3)	*2i*	*1*	*0.4477(10)*	*0.5868(10)*	*0.4831(9)*	*0.031(2)*
C(4)	2i	1	0.5571(6)	0.5375(5)	0.9266(5)	0.035(1)
C(4)	*2i*	*1*	*0.5579(10)*	*0.5377(10)*	*0.9250(9)*	*0.033(2)*
N(1)	2i	½	−0.1430(20)	0.1281(19)	0.7108(19)	0.096(4)
N(1)	*2i*	*½*	*−0.126(7)*	*0.133(7)*	*0.730(7)*	*0.23(2)*
N(2)	2i	½	−0.099(3)	0.191(2)	0.793(2)	0.125(6)
N(2)	*2i*	*½*	*−0.099(2)*	*0.191(2)*	*0.812(2)*	*0.066(5)*
N(3)	2i	½	0.614(4)	−0.029(4)	0.696(4)	0.203(13)
N(3)	*2i*	*½*	*0.529(5)*	*0.990(5)*	*0.647(5)*	*0.145(12)*
N(4)	2i	½	0.484(3)	0.024(3)	0.605(3)	0.152(9)
N(4)	*2i*	*½*	*0.525(6)*	*0.073(6)*	*0.502(6)*	*0.186(18)*
O(w10)	2i	½	−0.021(2)	0.8095(19)	0.565(2)	0.107(5)
O(w10)	*2i*	*1*	*0.025(2)*	*0.818(2)*	*0.5176(19)*	*0.161(6)*
O(w11)	2i	½	0.045(3)	0.833(3)	0.495(3)	0.156(8)
O(w11)	*2i*	*½*	*0.291(7)*	*0.040(6)*	*1.293(6)*	*0.203(19)*
O(w12)	2i	½	0.766(3)	−0.101(3)	0.696(3)	0.182(9)
O(w12)	*2i*	*½*	*−0.227(7)*	*0.890(7)*	*0.670(7)*	*0.25(3)*
O(w13)	2i	1	0.2224(14)	0.8929(12)	0.7715(12)	0.160(4)
O(w13)	*2i*	*1*	*0.2320(20)*	*0.9018(19)*	*0.7615(18)*	*0.153(5)*
O(w14)	2i	½	−0.0286(17)	0.0692(14)	0.9785(15)	0.095(4)
O(w14)	*2i*	*½*	*−0.025(4)*	*0.052(4)*	*0.952(3)*	*0.152(11)*
O(w15)	2i	½	−0.1755(12)	0.5738(12)	0.6090(11)	0.064(2)
O(w15)	*2i*	*½*	*−0.182(2)*	*0.586(2)*	*0.597(2)*	*0.074(5)*
O(w16)	2i	½	0.2595(17)	0.3246(16)	0.4446(16)	0.095(4)
O(w16)	*2i*	*½*	*0.256(2)*	*0.316(2)*	*0.4514(18)*	*0.066(4)*

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

Table 3
Significant bond lengths (Å) and angles (deg) for $(N_2H_5)[Nd(C_2O_4)_2(H_2O)] \cdot 4H_2O$ (first column) and $(N_2H_5)[Gd(C_2O_4)_2(H_2O)] \cdot 4.5H_2O$ (second column)

LnO_9 polyhedron	$Ln = Nd$	$Ln = Gd$
Ln–O(1)	2.497(3)	2.462(8)
Ln–O(2)	2.482(4)	2.425(10)
Ln–O(3)	2.470(3)	2.424(8)
Ln–O(4)	2.487(4)	2.430(8)
Ln–O(5)	2.511(3)	2.471(8)
Ln–O(6)	2.482(3)	2.428(8)
Ln–O(7)	2.510(3)	2.474(9)
Ln–O(8)	2.506(3)	2.474(8)
Ln–O(w9)	2.514(4)	2.454(8)

Hydrazinium cations	$Ln = Nd$	$Ln = Gd$
N(1)–N(2)	1.409(16)	1.30(6)
N(3)–N(4)	1.448(18)	1.31(5)

Oxalate groups	$Ln = Nd$	$Ln = Gd$		$Ln = Nd$	$Ln = Gd$
C(1)–C(1)	1.543(9)	1.535(17)	O(6)–C(1)–O(1)	126.4(4)	125.5(8)
C(1)–O(1)	1.252(6)	1.245(10)	O(6)–C(1)–C(1)	117.1(5)	116.7(9)
C(1)–O(6)	1.252(5)	1.265(10)	O(1)–C(1)–C(1)	116.6(5)	117.7(9)
C(2)–C(2)	1.532(9)	1.564(16)	O(5)–C(2)–O(2)	126.3(4)	128.2(7)
C(2)–O(5)	1.254(6)	1.247(11)	O(5)–C(2)–C(2)	116.9(5)	115.9(9)
C(2)–O(2)	1.256(6)	1.241(10)	O(2)–C(2)–C(2)	116.7(5)	115.8(9)
C(3)–C(3)	1.542(8)	1.560(17)	O(8)–C(3)–O(3)	126.4(4)	127.5(8)
C(3)–O(3)	1.255(6)	1.262(11)	O(8)–C(3)–C(3)	116.8(5)	116.5(9)
C(3)–O(8)	1.248(5)	1.242(10)	O(3)–C(3)–C(3)	116.8(5)	115.9(9)
C(4)–C(4)	1.564(9)	1.568(17)	O(7)–C(4)–O(4)	126.8(4)	127.0(7)
C(4)–O(4)	1.247(6)	1.260(11)	O(7)–C(4)–C(4)	117.2(5)	117.0(10)
C(4)–O(7)	1.234(6)	1.244(11)	O(4)–C(4)–C(4)	116.0(5)	116.0(10)

lanthanide(III) ions are slightly over-bonded with calculated valences of 3.24 and 3.19 v.u. for Nd and Gd, respectively. The nine-coordination is the more commonly adopted by Ln(III) ions in oxalates. In the **313** compounds $K_3[Ln(H_2O)](C_2O_4)_3 \cdot 2H_2O$ (Ln = Nd, Sm, Eu, Gd, Tb) [21], the geometry of the four oxalates around the Ln(III) ion is different, chains of Ln^{3+} alternating with bis-bidentate oxalate ions are formed, the coordination of the lanthanide ion is completed by two non-bridging bidentate oxalates and one water molecules. Many other **112** lanthanide-based oxalates have been described and are reported in Table 8. In $(NH_4)[Gd(H_2O)](C_2O_4)_2$ [8], the lanthanide ion is also coordinated by four bidentate oxalates and one aqua oxygen, but the geometry of the coordination is still different with the four oxalates nearly in a plane containing Ln forming four-membered rings and the $Ln–OH_2$ bond nearly perpendicular to this plane leading to a layered structure. The layers formed in $M[La(H_2O)_2](C_2O_4)_2 \cdot H_2O$ (M = K, NH$_4$) [7] are very similar, however the coordination of the La atom is completed by a second aqua oxygen opposite to the other to form a ten-coordination polyhedron. In $(NH_4)La(C_2O_4)_2$ the water molecule is replaced by an

Table 4
Atomic coordinates and equivalent isotropic displacement parameters for $(N_2H_5)_{0.75}[Nd_{0.75}U_{0.25}(C_2O_4)_2(H_2O)] \cdot 4.5H_2O$ (normal types) and $(N_2H_5)_{0.75}[Gd_{0.75}U_{0.25}(C_2O_4)_2(H_2O)]$ $4H_2O$ (italic types)

Atom	Site	Occup	x	y	z	$U_{(eq)}$
U/Nd	2i	$\frac{1}{4}/\frac{3}{4}$	0.32863(4)	0.36995(4)	0.83849(4)	0.029(1)
U/Gd	*2i*		*0.33250(3)*	*0.36823(3)*	*0.84050(3)*	*0.029(1)*
O(1)	2i	1	−0.0740(7)	0.6917(7)	0.9863(7)	0.037(1)
O(1)	*2i*	*1*	*−0.0832(6)*	*0.6977(5)*	*0.9830(5)*	*0.041(1)*
O(2)	2i	1	0.3119(6)	0.0919(7)	0.9224(6)	0.034(1)
O(2)	*2i*	*1*	*0.3204(6)*	*0.866(5)*	*0.9190(6)*	*0.042(1)*
O(3)	2i	1	0.5267(7)	0.3084(6)	0.6472(6)	0.032(1)
O(3)	*2i*	*1*	*0.5299(6)*	*0.3070(5)*	*0.6465(5)*	*0.044(1)*
O(4)	2i	1	0.5383(7)	0.5182(8)	0.8166(6)	0.035(1)
O(4)	*2i*	*1*	*0.5331(6)*	*0.5233(6)*	*0.8133(5)*	*0.040(1)*
O(5)	2i	1	0.5700(7)	0.1682(7)	0.9669(8)	0.043(2)
O(5)	*2i*	*1*	*0.5686(6)*	*0.1755(5)*	*0.9606(5)*	*0.042(1)*
O(6)	2i	1	0.1263(7)	0.6062(7)	0.8424(6)	0.034(1)
O(6)	*2i*	*1*	*0.1371(6)*	*0.6052(5)*	*0.8502(5)*	*0.044(1)*
O(7)	2i	1	0.3440(7)	0.3903(9)	1.0725(6)	0.042(2)
O(7)	*2i*	*1*	*0.3419(6)*	*0.3916(6)*	*1.0745(5)*	*0.045(1)*
O(8)	2i	1	0.3402(6)	0.5985(6)	0.5845(5)	0.025(1)
O(8)	*2i*	*1*	*0.3427(6)*	*0.6001(5)*	*0.5918(5)*	*0.044(1)*
O(w9)	2i	1	0.1212(6)	0.3718(7)	0.6930(6)	0.033(1)
O(w9)	*2i*	*1*	*0.1378(7)*	*0.3662(7)*	*0.7015(6)*	*0.059(1)*
C(1)	2i	1	0.0143(8)	0.5870(9)	0.9510(8)	0.027(1)
C(1)	*2i*	*1*	*0.0153(7)*	*0.5869(7)*	*0.9516(6)*	*0.033(1)*
C(2)	2i	1	0.4254(8)	−0.0234(9)	0.9886(8)	0.029(2)
C(2)	*2i*	*1*	*0.4287(7)*	*−0.0266(7)*	*0.9881(7)*	*0.035(1)*
C(3)	2i	1	0.4465(8)	0.5842(7)	0.4826(7)	0.021(1)
C(3)	*2i*	*1*	*0.4452(8)*	*0.5850(7)*	*0.4843(7)*	*0.034(1)*
C(4)	2i	1	0.5572(9)	0.5367(11)	0.9266(8)	0.034(2)
C(4)	*2i*	*1*	*0.5563(8)*	*0.5390(7)*	*0.9241(7)*	*0.035(1)*
N(1)	2i	$\frac{1}{2}$	−0.1547(18)	0.1119(16)	0.7220(16)	0.035(3)
N(2)	2i	$\frac{1}{2}$	−0.097(3)	0.179(2)	0.790(2)	0.063(5)
N(3)	2i	$\frac{1}{2}$	−0.0326(17)	0.0789(15)	0.9565(15)	0.031(3)
O(w10)	2i	$\frac{1}{2}$	−0.0329(19)	0.8213(17)	0.5579(17)	0.048(3)
O(w11)	2i	$\frac{1}{2}$	0.063(3)	0.869(2)	0.476(2)	0.071(5)
O(w12)	2i	1	0.497(3)	0.002(3)	0.617(3)	0.206(16)
O(w13)	2i	1	0.7862(16)	0.1105(15)	1.2158(14)	0.099(5)
O(w14)	2i	$\frac{1}{2}$	−0.200(3)	0.862(3)	0.654(3)	0.100(7)
O(w15)	2i	$\frac{1}{2}$	0.1777(13)	0.4176(12)	0.3872(12)	0.028(2)
O(w16)	2i	$\frac{1}{2}$	0.2773(18)	0.3085(17)	0.4582(16)	0.049(3)
N(1)	*2i*		*0.720(3)*	*−0.031(2)*	*0.725(2)*	*0.151(7)*
N(2)	*2i*		*0.592(6)*	*0.969(5)*	*0.656(6)*	*0.24(3)*
O(w10)	*2i*		*−0.190(4)*	*0.079(4)*	*0.241(4)*	*0.195(12)*
O(w11)	*2i*		*−0.010(5)*	*−0.015(4)*	*0.140(4)*	*0.213(14)*
O(w12)	*2i*	*1*	*0.017(2)*	*0.8318(19)*	*0.5196(19)*	*0.202(6)*
O(w13)	*2i*		*0.311(3)*	*0.909(3)*	*0.688(3)*	*0.147(8)*
O(w14)	*2i*		*−0.074(2)*	*0.156(2)*	*0.8204(19)*	*0.098(5)*
O(w15)	*2i*		*0.177(2)*	*0.426(2)*	*0.4065(18)*	*0.091(4)*
O(w16)	*2i*		*0.242(3)*	*0.307(3)*	*0.449(3)*	*0.125(7)*

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

Table 5
Significant bond lengths (Å) and angles (deg) for $(N_2H_5)_{0.75}[Nd_{0.75}U_{0.25}(C_2O_4)_2(H_2O)] \cdot 4.5H_2O$ (first column) and $(N_2H_5)_{0.75}[Gd_{0.75}U_{0.25}(C_2O_4)_2(H_2O)]$ $4H_2O$ (second column)

$(U,Ln)O_9$ polyhedra	$Ln = Nd$	$Ln = Gd$
U/Ln–O(1)	2.487(5)	2.434(4)
U/Ln–O(2)	2.457(6)	2.416(5)
U/Ln–O(3)	2.462(5)	2.412(4)
U/Ln–O(4)	2.480(6)	2.425(5)
U/Ln–O(5)	2.494(5)	2.453(5)
U/Ln–O(6)	2.471(6)	2.414(4)
U/Ln–O(7)	2.499(5)	2.469(5)
U/Ln–O(8)	2.487(5)	2.461(4)
U/Ln–O(w9)	2.502(5)	2.421(6)

Hydrazinium cations	$Ln = Nd$	$Ln = Gd$
N(3)–N(3)	1.38(3)	
N(1)–N(2)	1.37(2)	1.43(5)

Oxalate groups	$Ln = Nd$	$Ln = Gd$		$Ln = Nd$	$Ln = Gd$
C(1)–C(1)	1.564(15)	1.533(12)	O(1)–C(1)–O(6)	126.7(7)	126.0(6)
C(1)–O(6)	1.264(8)	1.251(7)	O(1)–C(1)–C(1)	117.5(7)	116.8(6)
C(1)–O(1)	1.238(9)	1.254(7)	O(6)–C(1)–C(1)	115.8(8)	117.2(6)
C(2)–C(2)	1.535(13)	1.538(12)	O(5)–C(2)–O(2)	127.0(7)	127.0(6)
C(2)–O(2)	1.264(9)	1.256(8)	O(5)–C(2)–C(2)	117.6(8)	117.4(7)
C(2)–O(5)	1.253(10)	1.246(7)	O(2)–C(2)–C(2)	115.1(8)	115.6(7)
C(3)–C(3)	1.548(12)	1.548(12)	O(8)–C(3)–O(3)	126.6(6)	126.8(6)
C(3)–O(8)	1.250(8)	1.246(7)	O(8)–C(3)–C(3)	117.1(7)	116.6(6)
C(3)–O(3)	1.257(8)	1.254(7)	O(3)–C(3)–C(3)	116.2(7)	116.4(6)
C(4)–C(4)	1.555(14)	1.560(11)	O(7)–C(4)–O(4)	126.0(7)	126.7(5)
C(4)–O(4)	1.252(9)	1.248(8)	O(7)–C(4)–C(4)	117.5(8)	117.3(7)
C(4)–O(7)	1.235(10)	1.223(8)	O(4)–C(4)–C(4)	116.5(9)	116.1(7)

number of water molecules and of the nature of the monovalent counter-ion on the environment of the lanthanide ion and on the connectivity leading to various 2D or 3D networks.

Although the Ln/Ox ratio is different it is instructional to compare the structure of **1** and **2** with that of the simple lanthanide(III) oxalates. The Ln(III) oxalates $[Ln(H_2O)_3]_2(C_2O_4)_3 \cdot nH_2O$ [1–5] are tris-chelated oxalate complexes, the coordination of Ln(III) is completed by three aqua oxygen atoms, the three bis-bidentate oxalates are nearly in a plane containing Ln with two water molecules on one side of the plane and the third on the other side, the bridging of metal atoms by oxalate ions leads to the formation of 2D honeycomb layers (Fig. 4a) which are held together by hydrogen bonds via water molecules situated between the layers. In the new Ln(III) oxalates **1** and **2**, the same type of honeycomb layers are found, two couples of aqua oxygen atoms, which were in opposite, are replaced by an oxalate ion to form a 3D structure (Fig. 4b). If one imagines the

oxalate O atom of an other layer, so double layers are formed [8]. Finally in $M[Ce(H_2O)](C_2O_4)_2 \cdot H_2O$ (M = Li, Na), the coexistence of bi- and monodentate oxalate ions leads to the formation of a 3D framework [9]. The **112** oxalates show the directing role of the

Table 6
Atomic coordinates and equivalent isotropic displacement parameters for $Na_{0.5}[Nd_{0.5}U_{0.5}(C_2O_4)_2(H_2O)]$ $3H_2O$ (normal types) and $Na_{0.65}$ $[Gd_{0.65}U_{0.35}(C_2O_4)_2(H_2O)] \cdot 4.5H_2O$ (italic types)

Atom	Site	Occup	x	y	z	$U_{(eq)}$
U/Nd	2i	$\frac{1}{2}/\frac{1}{2}$	0.32980(4)	0.36454(4)	0.84235(4)	0.029(1)
U/Gd	*2i*	*0.35(2)/0.65*	*0.33139(6)*	*0.36576(7)*	*0.84394(6)*	*0.031(1)*
O(1)	2i	1	−0.0808(7)	0.6976(7)	0.9783(7)	0.036(1)
O(1)	*2i*	*1*	*−0.0841(10)*	*0.7018(10)*	*0.9747(10)*	*0.040(2)*
O(2)	2i	1	0.3262(7)	0.0794(7)	0.9176(7)	0.040(1)
O(2)	*2i*	*1*	*0.3279(10)*	*0.0806(10)*	*0.9171(10)*	*0.040(2)*
O(3)	2i	1	0.5281(8)	0.3094(7)	0.6436(7)	0.038(1)
O(3)	*2i*	*1*	*0.5271(11)*	*0.3085(10)*	*0.6438(9)*	*0.041(2)*
O(4)	2i	1	0.5297(8)	0.5244(7)	0.8123(6)	0.038(1)
O(4)	*2i*	*1*	*0.5254(11)*	*0.5290(10)*	*0.8113(9)*	*0.041(2)*
O(5)	2i	1	0.5645(8)	0.1772(7)	0.9629(7)	0.039(1)
O(5)	*2i*	*1*	*0.5653(10)*	*0.1799(10)*	*0.9608(10)*	*0.039(2)*
O(6)	2i	1	0.1382(8)	0.6028(7)	0.8501(7)	0.040(2)
O(6)	*2i*	*1*	*0.1409(10)*	*0.6044(10)*	*0.8554(10)*	*0.045(2)*
O(7)	2i	1	0.3404(8)	0.3927(8)	1.0745(7)	0.040(1)
O(7)	*2i*	*1*	*0.3388(11)*	*0.3913(11)*	*1.0770(10)*	*0.044(2)*
O(8)	2i	1	0.3380(7)	0.5929(7)	0.5921(6)	0.038(1)
O(8)	*2i*	*1*	*0.3408(10)*	*0.5968(10)*	*0.5929(9)*	*0.039(2)*
O(w9)	2i	1	0.1351(9)	0.3543(9)	0.7050(8)	0.051(2)
O(w9)	*2i*	*1*	*0.1424(12)*	*0.3551(12)*	*0.7102(11)*	*0.054(3)*
C(1)	2i	1	0.0160(10)	0.5891(9)	0.9500(8)	0.029(2)
C(1)	*2i*	*1*	*0.0174(14)*	*0.5888(14)*	*0.9506(13)*	*0.031(3)*
C(2)	2i	1	0.4299(10)	−0.0263(10)	0.9861(9)	0.030(2)
C(2)	*2i*	*1*	*0.4321(15)*	*−0.0296(15)*	*0.9876(13)*	*0.033(3)*
C(3)	2i	1	0.4445(10)	0.5817(10)	0.4852(9)	0.031(2)
C(3)	*2i*	*1*	*0.4465(14)*	*0.5832(14)*	*0.4852(12)*	*0.032(3)*
C(4)	2i	1	0.5552(10)	0.5387(9)	0.9238(8)	0.030(2)
C(4)	*2i*	*1*	*0.5535(15)*	*0.5404(14)*	*0.9244(13)*	*0.036(3)*
Na(1)	2i	$\frac{1}{2}$	0.0260(16)	0.0452(14)	0.2875(13)	0.081(3)
Na(1)	*2i*	*0.65(2)*	*0.0322(16)*	*0.0382(15)*	*0.2892(14)*	*0.089(5)*
O(w10)	2i	$\frac{1}{2}$	0.0170(18)	0.8110(15)	0.5397(17)	0.053(4)
O(w10)	*2i*	*1*	*0.024(2)*	*0.811(2)*	*0.537(2)*	*0.116(8)*
O(w11)	2i	$\frac{1}{2}$	0.700(2)	−0.0226(17)	0.7271(17)	0.059(4)
O(w11)	*2i*	*0.93(4)*	*0.701(2)*	*−0.021(2)*	*0.721(2)*	*0.112(8)*
O(w12)	2i	$\frac{1}{2}$	−0.061(2)	0.117(2)	0.8575(19)	0.069(5)
O(w12)	*2i*	*0.78(4)*	*−0.072(3)*	*0.135(3)*	*0.853(3)*	*0.123(11)*
O(w13)	2i	$\frac{1}{2}$	0.254(2)	0.918(2)	0.730(2)	0.073(5)
O(w13)	*2i*	*0.96(4)*	*0.251(3)*	*0.930(2)*	*0.721(2)*	*0.144(11)*
O(w14)	2i	0.71(2)	0.174(4)	0.417(5)	0.403(3)	0.118(14)
O(w14A)	2i	0.29(2)	0.260(5)	0.301(6)	0.448(3)	0.060(15)
O(w14)	*2i*	*0.83(5)*	*0.200(3)*	*0.394(3)*	*0.419(3)*	*0.170(16)*

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

additional replacement of two remaining oxygen atoms which point one towards the other between two honeycomb layers by an oxalate ion a structure related with that of the oxalates described in Part I of this work is obtained (Fig. 4c). This structural relationship well illustrates the possibility to transform a 2D to a 3D network of Ln–oxalates arrangement by exploiting the Ln/Ox ratio.

The compounds $(N_2H_5)_{0.75}[Ln_{0.75}U_{0.25}(C_2O_4)_2$ $(H_2O)] \cdot nH_2O$ obtained for Ln = Nd (3) and Ln = Gd (4) are characterized by the same 3D arrangement of Ln-centered polyhedra linked through bis-bidentate oxalate groups but, astonishingly Ln(III) is partially substituted

by U(IV) in the same crystallographic site, the excess of charge being compensated by the reduction of the hydrazinium ion content. The substitution on the metallic site does not involve significant deformation of the environment. As in the parent compounds **1** and **2** the decrease of the mean Ln–O bond length from Nd, 2.482(3) Å, to Gd, 2.434(8) Å, is in agreement with the ionic radius variation from Nd to Gd [16]. Moreover, the weak reduction of the mean Ln/U–O bond length from the parent to the corresponding substituted compound is in agreement with the diminution of the ionic radii from Ln^{3+} to U^{4+}, 1.05 Å in nine-coordination [16]. The hydrazinium ions and the water molecules

Table 7
Significant bond lengths (Å) and angles (deg) for $Na_{0.5}[U_{0.5}Nd_{0.5}(C_2O_4)_2(H_2O)] \cdot 3H_2O$ (first column) and $Na_{0.65}[Gd_{0.65}U_{0.35}(C_2O_4)_2(H_2O)] \cdot 4.5H_2O$ (second column)

$(U,Ln)O_9$ polyhedra	Ln = Nd	Ln = Gd		Ln = Nd	Ln = Gd
U/Ln–O(1)	2.467(6)	2.485(8)			
U/Ln–O(2)	2.451(6)	2.443(9)			
U/Ln–O(3)	2.457(6)	2.462(8)			
U/Ln–O(4)	2.453(6)	2.446(9)			
U/Ln–O(5)	2.492(6)	2.524(9)			
U/Ln–O(6)	2.453(6)	2.463(9)			
U/Ln–O(7)	2.487(6)	2.492(9)			
U/Ln–O(8)	2.480(6)	2.514(9)			
U/Ln–O(w9)	2.467(7)	2.454(10)			
Na(1)O_6 polyhedra	*Ln = Nd*	*Ln = Gd*			
Na(1)–O(w11)	2.31(2)	2.30(2)			
Na(1)–O(w13)	2.40(2)	2.47(2)			
Na(1)–O(w12)	2.47(2)	2.51(3)			
Na(1)–O(w10)	2.516(17)	2.48(2)			
Na(1)–O(w10)	2.55(2)	2.59(2)			
Na(1)–O(1)	2.731(12)	2.741(15)			
Oxalate groups	*Ln = Nd*	*Ln = Gd*		*Ln = Nd*	*Ln = Gd*
C(1)–C(1)^I	1.582(15)	1.58(2)	O(1)–C(1)–O(6)	127.9(7)	126.4(11)
C(1)–O(1)	1.241(10)	1.272(14)	O(1)–C(1)–C(1)	116.9(8)	116.8(12)
C(1)–O(6)	1.262(10)	1.249(14)	O(6)–C(1)–C(1)	115.2(8)	116.8(12)
C(2)–C(2)	1.545(15)	1.56(2)	O(2)–C(2)–O(5)	126.8(8)	126.5(11)
C(2)–O(5)	1.271(10)	1.264(15)	O(2)–C(2)–C(2)	118.0(9)	116.1(13)
C(2)–O(2)	1.230(10)	1.281(15)	O(5)–C(2)–C(2)	115.3(9)	117.4(14)
C(3)–C(3)	1.539(17)	1.55(2)	O(3)–C(3)–O(8)	127.1(8)	126.5(11)
C(3)–O(3)	1.257(10)	1.262(14)	O(3)–C(3)–C(3)	115.8(9)	116.6(12)
C(3)–O(8)	1.262(10)	1.270(13)	O(8)–C(3)–C(3)	117.1(8)	116.8(12)
C(4)–C(4)	1.566(14)	1.55(2)	O(7)–C(4)–O(4)	126.8(7)	125.8(11)
C(4)–O(7)	1.244(10)	1.269(15)	O(7)–C(4)–C(4)	116.5(9)	118.2(14)
C(4)–O(4)	1.261(10)	1.286(15)	O(4)–C(4)–C(4)	116.7(9)	115.9(14)
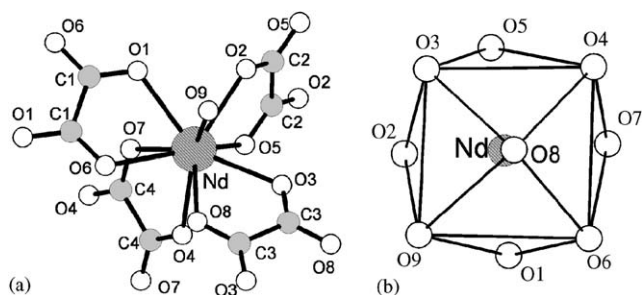
Fig. 1. Building unit in $(N_2H_5)[Nd(C_2O_4)_2(H_2O)] \cdot 4H_2O$ showing the atom labelling scheme and formed by neodymium(III) ion, four oxalate anions and one aqua oxygen (a), polyhedron around Nd described as a tri-capped trigonal prism (b).

are also disordered within the spacious channels of the structure. However, whereas the N(1)N(2) hydrazinium ion occupy the same position in **3** than in **1** and **2**, the N(3)N(4) hydrazinium ion is replaced by N(3)N(3) in **3**. In **4** only one hydrazinium ion occupies another

position. The N–N distances for the hydrazinium ions are in agreement with values generally reported.

Compounds **5** and **6** contain Na as monovalent ion. In **5**, half the Nd(III) is substituted by U(IV), all the Nd/U–O distances, and of course the mean Nd/U–O distance are lower than in **1** and **3** in agreement with the ionic radius diminution from Nd^{3+} to U^{4+} [16]. On the contrary, the results concerning compound **6** are surprising; firstly, replacement of Nd by Gd is accompanied by a decrease of the unit cell volume from **1** to **2** and from **3** to **4**, when it is accompanied by an equivalent increase from **5** to **6**; secondly, all the Ln/U–O distances, and of course the mean Ln/U–O distance, slightly increase from **4** to **6** in disagreement with the substitution rate variation. In the two compounds the Na atom is octahedrally coordinated by five aqua oxygen atoms and by one O(1) oxygen atom that belong to an oxalate ion, in **6**, two positions related by an inversion center are sometimes simultaneously occupied leading to the formation of
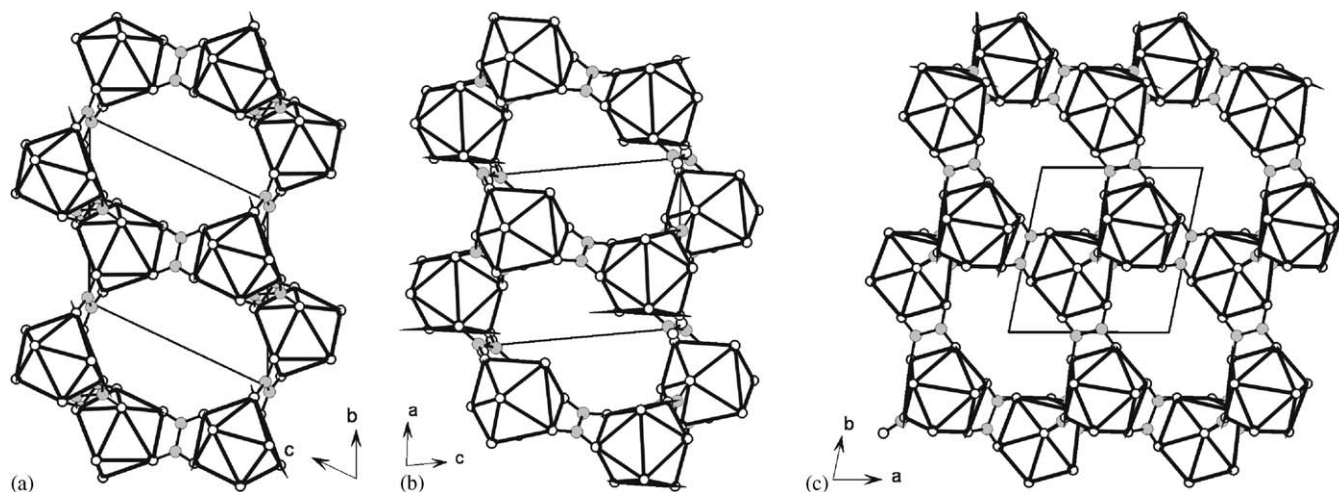
Fig. 2. Framework of oxalate-bridge neodymium polyhedra in $(N_2H_5)[Nd(C_2O_4)_2(H_2O)] \cdot 4H_2O$ showing elliptic channels running down (a) [1 0 0], (b) [0 1 0] and (c) [0 0 1] directions.
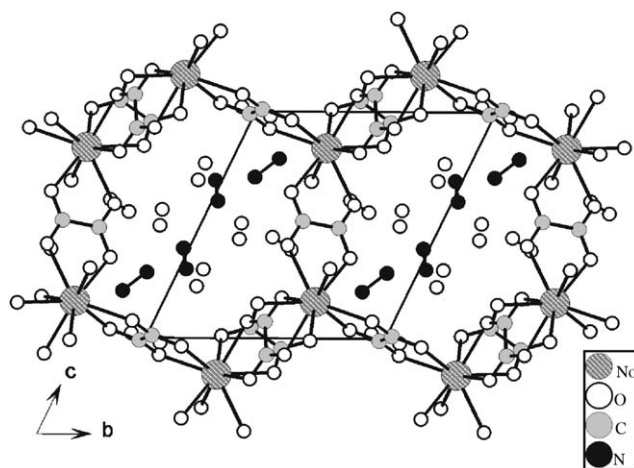

Fig. 3. Occupation of the tunnels running down the a-axis by disordered $N_2H_5^+$ ions and free H_2O molecules in $(N_2H_5)[Nd(C_2O_4)_2(H_2O)] \cdot 4H_2O$.

edge-shared octahedra dimers with intra-dimer Na–Na distance of 3.92(2) Å. The formation of these dimers and the higher water contents should be responsible of the abnormal variations discussed above. However, further investigations are necessary to explain these features. The valence bond sums for Na^+ ions are, respectively, 0.97 and 0.93 v.u. for **5** and **6**.

In the six compounds, the bond lengths and bond angles in the oxalate ligands (C–O in the range 1.230(10)–1.271(10) Å, C–C in the range 1.532(9)–1.582(15) Å, O–C–O = 126.0(7)–128.2(7)°, O–C–C = 115.1(8)–118.0(9)°) are in agreement with the mean values reported by Hahn for oxalate compounds, C–O = 1.24 Å, C–C = 1.55 Å, O–C–O = 125°, O–C–C = 117° [22].

4. Conclusion

Single crystals of two new hydrazinium lanthanide oxalates $(N_2H_5)[Ln(C_2O_4)_2.H_2O] \cdot nH_2O$ have been obtained using a gel method for $Ln = $ Nd, $n = 4$ and $Ln = $ Gd, $n = 4.5$. They are 3D framework materials composed of a linked network of Ln-centered polyhedra, constructed via coordinating tetradentate oxalate ions, the hydrazinium ions and water molecules being disordered in the created tunnels. Two U(IV) containing oxalates have been obtained from these two compounds by the replacement of one-quarter of the Ln(III) by U(IV) ion and by the removal of one-quarter of the hydrazinium cation according to the substitution scheme Ln(III) $+ A^+ \rightarrow$ U(IV). Astonishingly in the mixed Ln(III)/U(IV) oxalates, Ln(III) and U(IV) are disordered on the same crystallographic site and are nine-coordinated by oxygen atoms from four bidentate oxalate ions and one aqua oxygen. What is more, the partial substitution of Ln(III) ($Ln = $ Nd or Gd) by U(IV) in the same crystallographic site, does not generate any modification of the crystal structure. Thus, solid solutions of the type $A_{1-x}^+Ln_{1-x}^{III}U_x^{IV}(C_2O_4)_2 \cdot nH_2O$ can be expected for $A^+ = Na^+$ and $N_2H_5^+$. The studied single crystals belong to the $0 \leqslant x \leqslant 0.5$ domain. The $x = 1$ compound corresponds to the U(IV) oxalate $U(C_2O_4)_2 \cdot nH_2O$, already reported but with a layered structure of U(IV) atoms connected by four tetradentate oxalate groups. Changing crystal growth conditions other structural families of lanthanide–actinide oxalates can be formed and are under investigation. Preparation of powder samples is in progress and should allow the determination of the solid solution domains for the different A^+–Ln(III)–U(IV)–$C_2O_4^{2-}$ systems and chemical compositional analysis together with TGA to

Table 8
Coordination number and structure dimensionality of lanthanide oxalates

Compound	C.N.	Structure		Reference
$[Ln(H_2O)_3]_2(C_2O_4)_3\ nH_2O$	9	2D		[1–5]
$K_3[Ln(H_2O)](C_2O_4)_3\ 2H_2O$	9	1D		[18]
$(NH_4)[Gd(H_2O)](C_2O_4)_2$	9	2D		[8]
$M[La(H_2O)_2](C_2O_4)_2\ H_2O$	10	2D		[7]
$(NH_4)La(C_2O_4)_2$	9	2D		[8]
$M[Ce(H_2O)](C_2O_4)_2\ H_2O$	9	3D		[9]
$(N_2H_5)[Nd(H_2O)](C_2O_4)_2\ 4H_2O$	9	3D		This work

The schemes coordination of the lanthanide ion together with the different chelating modes of the oxalate ligands.
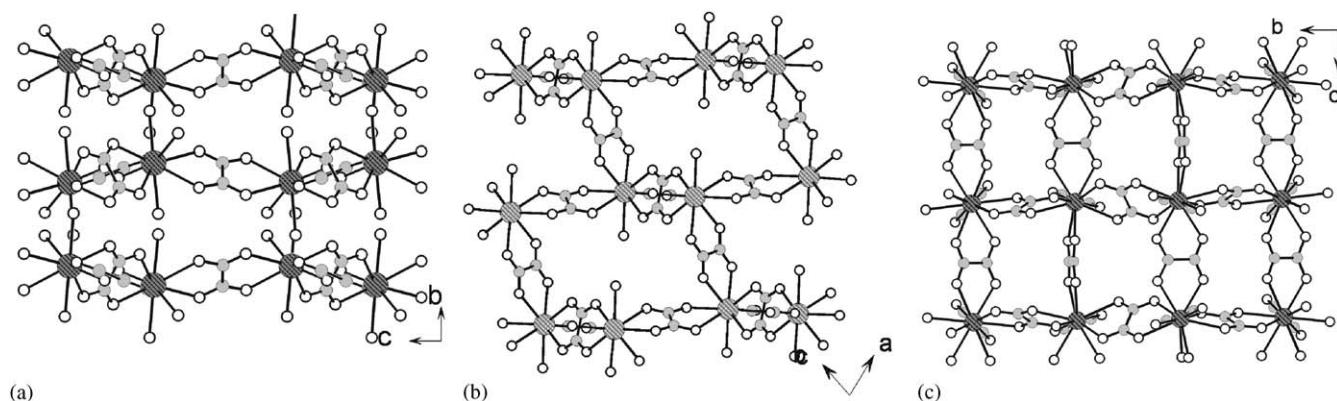
Fig. 4. From 2D to 3D networks in lanthanide–actinide oxalates: stacking of honeycomb-type layers held together by (a) hydrogen bonds (not represented for clarity) via water molecules in $[La(H_2O)_3]_2(C_2O_4)_3 \cdot 10H_2O$, (b) oxalate bridges and hydrogen bonds via water molecules in $(N_2H_5)[Nd(C_2O_4)_2(H_2O)] \cdot 4H_2O$, (c) oxalate bridges in $(NH_4)_2[U_2(C_2O_4)_5] \cdot 2.5H_2O$.

determine the water content for each composition. The results will be presented in a forthcoming paper.

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