

Synthesis and structure of $[\text{Ce}_2(\text{H}_2\text{O})_3](\text{C}_2\text{O}_4)_{2.5}(\text{H}_3\text{C}_2\text{O}_3)$ and $\text{Ce}_2(\text{C}_2\text{O}_4)(\text{H}_3\text{C}_2\text{O}_3)_4$: The latter structure presents an interesting new framework, with 2-fold interpenetration

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Abstract

Single crystals of two cerium complexes, with mixed-ligands oxalate and glycolate, have been prepared in a closed system, at 200 °C for one month: $[\text{Ce}_2(\text{H}_2\text{O})_3](\text{C}_2\text{O}_4)_{2.5}(\text{H}_3\text{C}_2\text{O}_3)$ **1** and $\text{Ce}_2(\text{C}_2\text{O}_4)(\text{H}_3\text{C}_2\text{O}_3)_4$ **2**. **1** crystallizes in the orthorhombic system, space group *Pbca*, with $a = 13.0090(13)$ Å, $b = 10.3870(8)$ Å, and $c = 22.102(3)$ Å while **2** crystallizes in the tetragonal system, space group *P4₂/nbc*, with $a = 11.7030(4)$ Å, $c = 13.2570(2)$ Å. For both complexes, the three-dimensional framework structure is built up by the linkages of the cerium and all the oxygen atoms of oxalate and glycolate ligands. For **2**, its structure presents a nice case of two 3D identical sub-lattices, with 2-fold interpenetration. The only link between these two sub-lattices is assumed by strong hydrogen bonds between the hydroxyl function of the glycolate and the oxygen atoms of the oxalate. The schematized framework of **2**, including only the cerium atoms, can be compared to that of cooperite (PtS).

For **1**, the two independent cerium have 9- or 10-fold coordination, forming a distorted monocapped or bicapped square antiprism polyhedron while for **2**, the two independent cerium present 8-fold coordination, forming an almost regular dodecahedron. A quite relevant feature of **2** is the complete absence of water. **2** has been extended to other lanthanides ($L_n = \text{Ce} \dots \text{Lu}$, yttrium included) leading to a family, which has been characterized by infra-red and thermal analysis.

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1. Introduction

The last few decades have witnessed considerable growth either in the synthesis of ceramic precursors or in the compounds with an open-framework. In these ways, lanthanide oxalates have received more or less attention:

- they are well known, as convenient precursors, for the thermal preparation of the corresponding oxides, or mixed oxides [1,2]. Our research about ceramic materials is currently focused on the development of a general technique, which employs chelating ligands to form polymeric precursors to favor the synthesis of

lanthanide sesquisulfides, at low temperatures, smaller than 1000 °C [3,4]. Lighter lanthanide oxalates give mainly rise to the β -phase [4]. On the opposite, such families as lanthanide oxalate-formate and oxalate-carbonate lead directly to the γ -phase [5], which in the case of cerium is used as a safe red pigment [6–9]. Thus, the final ceramic depends often on the nature of precursor. So, considerable interest is afforded to tailor the composition of precursor in order to obtain a given ceramic.

- lanthanide oxalates present generally a honey-comb layered structure in which the layers are separated by water molecules [10–14]. It will be interesting to bridge the layers by a dicarboxylic acid, like oxalic, without altering the open-feature of the layers. In that way, Vaidyanathan et al. isolate four three-dimensional

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lanthanide oxalates with an open-architecture, in presence of organic amines [15,16]. For our part, we have shown that some different protonated amines (e.g., guanidinium, tetramethylammonium, etc.) can be localized into the tunnels of the three-dimensional lanthanide oxalates [17–19].

However the carboxylate, bridging the layers, can be different from the oxalate. In particular, the family, $[Ln(H_2O)]_2(C_2O_4)(CO_3)_2$ with $Ln = Eu-Ho$, presents a relatively open-framework material, with two set of intersecting tunnels and whose $\sim 15\%$ of the unit-cell volume is empty [20,21]. Such lanthanide oxalate-carbonate and oxalate-formate families were prepared by hydrothermal technique by reacting the corresponding lanthanide oxalate and oxalic acid.

We have continued the preceding study by substituting glycolic acid, $HOCH_2COOH$, for oxalic acid, either alone or mixed with some amines (guanidinium, etc.). For the moment, we failed to incorporate the amines within these compounds, but we succeeded to isolate two new complexes of cerium oxalate-glycolate: $[Ce_2(H_2O)_3](C_2O_4)_{2.5}(H_3C_2O_3)$ **1** and $Ce_2(C_2O_4)(H_3C_2O_3)_4$ **2**. To our knowledge, these complexes are the first ones associating simultaneously these two ligands. The purpose of the present paper, is to describe the synthesis, the characterization and the structural determination of **1** and **2**. Complex **2** has been extended to the major part of the lanthanide series. Infrared spectra and thermal behavior of some pure complexes of the latter family will be presented.

2. Experimental part

All syntheses were carried out in Teflon-lined steel reactor under autogeneous pressure. XRD patterns were recorded on a Seifert Diffractometer, XRD 3000, using $CuK\alpha$ radiation. Thermogravimetric analyses were performed in the temperature range 20–1000 °C at a heating rate of 5 °C min^{-1} under O_2 atmosphere, using a Setaram apparatus. IR spectra were recorded between 4000 and 400 cm^{-1} on a Perkin-Elmer 1725X FT-IR spectrometer. Samples were run as KBr pellets.

2.1. Synthesis

An aqueous suspension (50 mL) of cerium oxalate ‘decahydrate’ (1 mmol) was reacted with a variable amount of glycolic acid (3, 5 and 10 mmol), at 200 °C for one month. After cooling, the final products were filtered, washed with distilled water and dried at 20 °C. In all the proportions of glycolic acid used, single crystals were obtained.

By using the larger proportion of glycolic acid (10 mmol), the X-ray powder diffraction pattern showed

the presence of only a single phase that is in agreement with the theoretical diagram for **2**. By using the intermediate proportion, the X-ray powder diffraction pattern evidenced the presence of two phases: complex **2** as the major one but also complex **1**. Decreasing again the previous ratio resulted in a mixture of phases: complex **1** and the starting oxalate.

By varying the lanthanide element, with 10 mmol of glycolic acid per 1 mmol of lanthanide oxalate in the same conditions, some compounds isostructural with the corresponding cerium complexes were obtained. Smaller elements than cerium, Pr...Lu, crystallized into complex **2**, as pure phase (cf. results). On the opposite, bulkier element than cerium, lanthanum, gave a mixture of phases: single crystal of the complex **1** ($a = 10.433(1) \text{ \AA}$, $b = a = 13.084(1) \text{ \AA}$, and $c = a = 22.150(2) \text{ \AA}$) and dilanthanum sesquioxalate pentahydrate, for which the structure is yet unknown [5].

2.2. Crystal structure determination

A suitable single crystal for each compound was carefully selected under a binocular. The diffraction data were collected using an Enraf Kappa-CCD automatic X-ray single crystal diffractometer ($MoK\alpha$ radiation). The refined cell constants and additional relevant crystal data are given in Table 1.

For both compounds SIR92 [22] was used to determine the structure by direct methods and refinements were performed using SHELX-97 [23]. The heavy Ce atoms were easily localized and subsequent difference Fourier syntheses revealed the location of the other atoms (O, C and H). Hydrogen atoms were introduced as riding at their relevant parent atoms. The intensity data were corrected for absorption using Gaussian integration [24] and a ‘‘multi-scan’’ technique [25] for **1** and **2**, respectively. The refinements were carried out using anisotropic thermal displacements for all the non-hydrogen atoms. The final atomic coordinates, equivalent displacement parameters and selected bond distances and angles for **1** are listed in Tables 2 and 3 and for **2** in Tables 4 and 5.

3. Results

3.1. Description of the structures

Both structures present some similarities and dissimilarities, which will be described now. In both cases, the structure is built up from oxalate and glycolate ligands sharing all their oxygen atoms with cerium atoms leading to a three-dimensional network. However, the relative amount of these two ligands and their packing differ.

Table 1
Crystallographic data and structure refinement for $[\text{Ce}_2(\text{H}_2\text{O})_3](\text{C}_2\text{O}_4)_{2.5}(\text{H}_3\text{C}_2\text{O}_3)$ **1** and $\text{Ce}_2(\text{C}_2\text{O}_4)(\text{H}_3\text{C}_2\text{O}_3)_4$ **2**

	1	2
System	Orthorhombic	Tetragonal
Space group	<i>Pbca</i>	<i>P4₂/nbc</i>
<i>a</i> (Å)	13.0090(13)	11.7030(4)
<i>b</i> (Å)	10.3870(8)	
<i>c</i> (Å)	22.102(3)	13.2570(2)
<i>V</i> (Å ³)	2986.5(5)	1815.68(9)
Z/formula	8	4
Formula weight	629.38	668.44
$\rho_{\text{calc.}}$ (g cm ⁻³)	2.800	2.445
Color	Colorless	Colorless
Crystal habit	Parallelepipedic	Parallelepipedic
Dimension mm	0.35 * 0.16 * 0.14	0.50 * 0.19 * 0.13
$\lambda(\text{MoK}\alpha)$ (Å)	0.71073	0.71073
$\mu_{\text{MoK}\alpha}$ (cm ⁻¹)	61.09	50.32
Min./max. transmission	0.175/0.348	0.097/0.187
Max. Bragg angle	30°	30°
Collected data/unique data	18642/3803	12480/1318
Observed data (<i>I</i> > 2σ(<i>I</i>))	3344	713
Restraints/parameters	0/227	0/67
Final <i>R</i> factor (<i>I</i> > 2σ(<i>I</i>)) (%)	<i>R</i> = 3.05, <i>wR</i> = 6.57	<i>R</i> = 2.27, <i>wR</i> = 6.01
Final <i>R</i> factor (all data) (%)	<i>R</i> = 3.69, <i>wR</i> = 6.86	<i>R</i> = 4.95, <i>wR</i> = 8.16
Goodness of fit on <i>F</i> ²	1.139	1.078
Weighting scheme	0.0136/18.4436	0.0319/1.8725
Large diff. peak and hole (e Å ⁻³)	0.947/-1.108	1.366/-0.581

$$R = \sum |F_o| - |F_c| / \sum F_o, \quad wR = \{ \sum w[F_o^2 - F_c^2]^2 / \sum wF_o^2 \}^{1/2}.$$

3.1.1. $[\text{Ce}_2(\text{H}_2\text{O})_3](\text{C}_2\text{O}_4)_{2.5}(\text{H}_3\text{C}_2\text{O}_3)$ **1**

This compound crystallizes in the orthorhombic system, space group *Pbca*. There are two independent cerium atoms, 2.5 oxalate ligands abbreviated as Ox1, Ox2 and Ox3, one glycolate group and three water molecules, per asymmetric unit. Ox1 is centrosymmetric. The linkages between Ce atoms and all the oxygen atoms of oxalate or glycolate groups build up the three-dimensional structure of **1**.

The projection, along [100] direction, shows that only Ox1 and Ox2 ligands are involved (Fig. 1). It is worthwhile to note the role of Ox2 that relates four cerium atoms and thus acts as the main building unit of this structure. This ligand is bischelating towards Ce1 and Ce2, in a usual way, but it is one time more chelating to Ce2^{vii} at longer distances, via O5 and O6 and it is also monodentate to Ce1ⁱⁱⁱ via O3 (the symmetry codes are listed in Table 3). Through Ox2, the distances Ce1–Ce1ⁱⁱⁱ, Ce1–Ce2^{vii}, Ce2–Ce2^{vii}, and Ce1–Ce2 are equal to 4.3776(5), 5.2578(6), 5.2956(4), and 6.6408(6) Å respectively. In the *y* direction, two Ce1

Table 2
Final least-squares atomic parameters with estimated standard deviations for $[\text{Ce}_2(\text{H}_2\text{O})_3](\text{C}_2\text{O}_4)_{2.5}(\text{H}_3\text{C}_2\text{O}_3)$ **1**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)
Ce1	0.54841(2)	0.30309(2)	0.47921(1)	0.01343(8)
Ce2	0.46111(2)	0.71417(2)	0.25491(1)	0.01330(8)
O1	0.5433(3)	0.0821(3)	0.4366(1)	0.0235(7)
O2	0.5326(3)	−0.1292(3)	0.4539(1)	0.0261(8)
O3	0.5291(2)	0.5304(3)	0.4421(1)	0.0175(6)
O4	0.4912(3)	0.6605(3)	0.3659(1)	0.0258(7)
O5	0.5228(2)	0.3273(3)	0.3638(1)	0.0184(6)
O6	0.5021(3)	0.4642(3)	0.2871(1)	0.0217(7)
O7	0.1240(2)	0.6306(3)	0.2954(1)	0.0201(6)
O8	0.2958(2)	0.6217(3)	0.2960(1)	0.0220(7)
O9	0.1285(2)	0.8083(3)	0.2090(1)	0.0235(7)
O10	0.2998(2)	0.8140(3)	0.2127(1)	0.0212(7)
O11	0.6767(3)	0.4310(3)	0.5372(2)	0.0276(8)
O12	0.6904(3)	0.1843(3)	0.5317(2)	0.0306(8)
O13	0.8598(3)	0.1827(3)	0.5440(2)	0.0260(7)
Ow1	0.7172(3)	0.3202(5)	0.41459(2)	0.047(1)
Ow2	0.3997(3)	0.8787(3)	0.3304(15)	0.0295(8)
Ow3	0.3911(3)	0.5622(3)	0.1788(1)	0.0239(7)
C1	0.5218(4)	−0.0148(4)	0.4682(2)	0.0168(8)
C2	0.5111(3)	0.5536(4)	0.3863(2)	0.0155(8)
C3	0.5118(3)	0.4388(4)	0.3424(2)	0.0151(8)
C4	0.2119(3)	0.6646(4)	0.2783(2)	0.0161(8)
C5	0.2140(3)	0.7725(4)	0.2297(2)	0.0160(8)
C6	0.7717(3)	0.3817(5)	0.5568(2)	0.0222(9)
C7	0.7739(3)	0.2400(4)	0.5428(2)	0.0186(8)
H11	0.6735	0.5261	0.5330	0.033
H1a	0.7797	0.2832	0.4253	0.057
H1b	0.7026	0.3440	0.3735	0.057
H2a	0.3996	0.9677	0.3226	0.035
H2b	0.4002	0.8715	0.3728	0.035
H3a	0.3923	0.5830	0.1371	0.029
H3b	0.3963	0.4702	0.1819	0.029
H6a	0.8249	0.4250	0.5375	0.027
H6b	0.7791	0.4012	0.5962	0.027

atoms are bridged either by Ox1 or by sharing an edge, O3–O3ⁱⁱⁱ, alternatively. The packing of Ox1 and Ox2 leads to puckered (100) layer in which narrow cavities are developed. Two water molecules, Ow2 and Ow3 bound to the Ce2, are localized in these cavities.

Successive (100) layers are bridged by Ox3, which is bischelating to two Ce2 atoms and the glycolate connecting two Ce1 atoms (Fig. 2). This gives rise to small tunnels in which the water molecule Ow1, bound to Ce1, is localized. The three water molecules and the hydroxyl group of the glycolate are hydrogen bonded to some oxygen atoms, thus strengthening the cohesion of the framework (Table 3). The strongest hydrogen bond is the one given by the hydroxyl of the glycolate (distance O11–O13^{vi} = 2.661(5) Å and the corresponding angle O11–H11–O13^{vi} = 161.5°).

Ce1 is 9-fold coordinated (8 oxygen atoms plus one water molecule) with distances ranging from 2.481(3) to 2.651(3) Å (average 2.547 Å, Table 3). The coordination geometry of the Ce1 atom may be described as a

Table 3
Interatomic distances (Å) and angles (deg) for Ce₂(H₂O)₃(C₂O₄)_{2.5}(H₃C₂O₃) **1**

Around the cerium atoms			
Ce1–O1	2.481(3)	Ce2–Ow3	2.480(3)
Ce1–O11	2.489(3)	Ce2–O9 ^{iv}	2.516(3)
Ce1–O12	2.506(4)	Ce2–Ow2	2.519(3)
Ce1–O13 ⁱ	2.511(3)	Ce2–O10	2.520(3)
Ce1–O3	2.512(3)	Ce2–O8	2.525(3)
Ce1–O2 ⁱⁱ	2.561(3)	Ce2–O4	2.543(3)
Ce1–O5	2.585(3)	Ce2–O7 ^{iv}	2.546(3)
Ce1–Ow1	2.626(4)	Ce2–O6	2.745(3)
Ce1–O3 ⁱⁱⁱ	2.651(3)	Ce2–O6 ^v	2.799(3)
		Ce2–O5 ^v	2.883(3)
Around the ligands			
O1–C1	1.256(5)	O1–C1–O2	127.0(4)
O2–C2	1.237(5)	O1–C1–C1 ⁱⁱ	115.3(5)
C1–C1 ⁱⁱ	1.547(8)	O2–C1–C1 ⁱⁱ	117.7(5)
			Ox1
O3–C2	1.278(5)	O3–C2–O4	124.5(4)
O4–C2	1.228(5)	O3–C2–C3	117.6(4)
O5–C3	1.260(5)	O4–C2–C3	117.9(4)
O6–C3	1.257(5)	O5–C3–O6	124.7(4)
C2–C3	1.538(6)	O5–C3–C2	118.4(3)
		O6–C3–C2	116.9(4)
			Ox2
O7–C4	1.256(5)	O7–C4–O8	127.1(4)
O8–C4	1.242(5)	O7–C4–C5	115.3(4)
O9–C5	1.259(5)	O8–C4–C5	117.5(4)
O10–C5	1.254(5)	O9–C5–O10	125.2(4)
C4–C5	1.552(6)	O9–C5–C4	116.7(4)
		O10–C5–C4	118.1(4)
			Ox3
O11–C6	1.406(5)	O11–C6–C7	108.1(4)
C6–C7	1.504(7)	C6–O11–H11	115.4
O12–C7	1.254(6)	O12–C7–O13	123.5(4)
O13–C7	1.266(5)	O12–C7–C6	118.3(4)
H11–O11	0.99	O13–C7–C6	118.2(4)
			Gly
Hydrogen bonding			
D–H	H–A	D–A	D–H–A
O11–H11–O13 ^{vi}	0.99	1.70	2.661(5) 161.5
Ow1–H1b–O5	0.96	2.35	2.768(5) 105.4
Ow1–H1b–O10 ^{vii}	0.96	1.93	2.823(5) 153.4
Ow2–H2b–O4	0.94	2.50	2.677(5) 90.7
Ow2–H2a–O7 ^{viii}	0.94	1.82	2.745(5) 166.9
Ow2–H2b–O2 ^{ix}	0.94	2.48	3.231(5) 136.4
Ow2–H2b–O12 ⁱⁱⁱ	0.94	2.49	3.330(5) 149.5
Ow3–H3a–O1 ^v	0.95	1.83	2.698(4) 150.6
Ow3–H3b–O9 ^x	0.96	1.81	2.732(5) 159.0

Symmetry operators: (i) $-0.5 + x, 0.5 - y, 1 - z$; (ii) $1 - x, -y, 1 - z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $1.5 + x, y, 1.5 - z$; (v) $1 - x, 0.5 + y, 0.5 - z$; (vi) $1.5 - x, 0.5 + y, z$; (vii) $1 - x, -0.5 + y, 0.5 - z$; (viii) $0.5 - x, 0.5 + y, z$; (ix) $x, 1 + y, z$; (x) $0.5 - x, -0.5 + y, z$.

monocapped square antiprism, O5 being in the cap position [26]. A dihedral angle of $4.08(6)^\circ$ is observed between the “square” faces. The Ce2 atom is 10-fold coordinated (8 oxygen atoms plus two water molecules). The Ce2–O distances (average 2.608 Å) are rather dispersed: seven of them are ranging from 2.480(3) to 2.546(3) Å and the three remaining (O5^v, O6 and O6^v)

Table 4
Final least-squares atomic parameters with estimated standard deviations for Ce₂(C₂O₄)(H₃C₂O₃)₄ **2**

Atom	Wyckoff site	x	y	z	U _{eq} (Å ²)
Ce1	4c	1/4	1/4	1/4	0.0146(1)
Ce2	4b	3/4	1/4	1/2	0.0163(1)
O1	16k	0.2543(2)	0.3642(2)	0.4158(1)	0.0321(5)
O2	16k	0.6617(2)	0.0815(2)	0.4149(1)	0.0379(6)
O3	16k	0.5971(2)	0.2901(2)	0.3813(2)	0.0473(7)
O4	16k	0.4475(2)	0.2418(2)	0.2900(2)	0.0429(6)
C1	8h	1/4	0.3161(3)	1/2	0.0234(8)
C2	16k	0.5631(3)	0.0921(3)	0.3539(3)	0.0385(8)
C3	16k	0.5338(2)	0.2169(3)	0.3415(2)	0.0315(7)
H2	16k	0.6831	0.0145	0.4071	0.046
H2a	16k	0.5773	0.0777	0.2834	0.046
H2b	16k	0.4924	0.0725	0.3726	0.046

Table 5
Interatomic distances (Å) and angles (deg) for Ce₂(C₂O₄)(H₃C₂O₃)₄ **2**

Around the cerium atom			
Ce1–O4, O4 ^{i,iii,iii}	4 × 2.373(2)	Ce2–O3, O3 ^{iv,v,vi}	4 × 2.429(2)
Ce1–O1, O1 ^{i,iii,iii}	4 × 2.573(2)	Ce2–O2, O2 ^{iv,v,vi}	4 × 2.495(2)
Around the ligands			
O1, O1 ^{vii} –C1	2 × 1.251(2)	O1–C1–O1 ^{vii}	126.5(4)
C1–C1 ⁱ	1.547(8)	C1 ⁱ –C1–O1, O1 ^{vii}	2 × 116.8(2)
			Ox
O2–C2	1.415(4)	O2–C2–C3	109.3(2)
O2–H2	0.83	C2–O2–H2	104.9
O3–C3	1.249(4)	O3–C3–O4	123.3(3)
O4–C3	1.254(3)	O3–C3–C2	118.9(3)
C2–C3	1.509(4)	O4–C3–C2	117.8(3)
			Gly
Hydrogen bonding			
Atoms	D–H	A–H D...A	D–H–A
O2–H2...O1 ^{viii}	0.83	1.91 2.727(3)	168.3

Symmetry codes: (i) $-x + 1/2, -y + 1/2, z$; (ii) $-y + 1/2, -x + 1/2, -z + 1/2$; (iii) $y, x, -z + 1/2$; (iv) $-x + 3/2, -y + 1/2, z$; (v) $x, -y + 1/2, -z + 1$; (vi) $-x + 3/2, y, -z + 1$; (vii) $-x + 1/2, y, -z + 1$; (viii) $-x + 1, y - 1/2, z$; (ix) $x, -y + 1/2, -z$; (x) $x - 1, y, z$; (xi) $y + 1/2, x - 1/2, z - 1/2$.

are ranging from 2.745(3) to 2.883(3) Å (Table 3), which constitutes rather a long distance interaction. The coordination polyhedron of the Ce2 atom can be represented as a distorted bicapped square antiprism; the cap positions are occupied by O6 and O6^v oxygen atoms. The “square” faces make a dihedral angle of $12.58(5)^\circ$ and the angle O6–Ce2–O6^v is $158.51(1)^\circ$.

The dispersion in the Ce2–O distances is also reflected in the carbon-oxygen ones of the Ox2; e.g., C2–O3 = 1.278(5) Å versus C2–O4 = 1.228(5) Å (Table 3). The former is close to a single bond while the latter is near to a double bond. This difference is also slightly apparent in the corresponding angles. Such differences in bond lengths and angles can be attributed to the constraints imposed by the cerium atoms upon the oxygen atoms of Ox2. As far as we are aware, the coordination scheme of

3.1.2. $Ce_2(C_2O_4)(H_3C_2O_3)_4 \cdot 2$

It crystallizes in the tetragonal system, space group $P4_2/nbc$ ($N = 133$, choice 2). The asymmetric unit includes two independent cerium atoms, localized on $4c$ ($1/4, 1/4, 1/4$) and $4b$ ($3/4, 1/4, 1/2$) Wyckoff sites, one-fourth of an oxalate and one glycolate ligand (Table 4).

The Ce1 atom, bischelated by the oxalate group (via $4xO1$), build up infinite chain, $\{Ce1(C_2O_4)\}_n^{n+}$, running along the $[001]$ direction following the 4-fold screw axis 4_2 (Fig. 3). Completing the Ce1 coordination polyhedron four oxygen atoms O4, belonging to four carboxylate groups of the glycolate ligands, make a rather regular dodecahedron or bisdisphenoid $Ce1O_8$. Within these chains, each $Ce1O_8$ polyhedron is twisted by 90° every $c/2$ period with its close neighbors (Fig. 4).

The second unit of the structure is a block centered on Ce2, setting on a $\bar{4}$ inverse axis. The polyhedron around Ce2, i.e., $Ce2O_8$, is formed by four hydroxyl groups (O2) and four oxygen atoms (O3) of the glycolate ligand, in a chelating scheme. These blocks or entities $\{Ce2(H_3C_2O_3)_4\}_n^{-}$, are stacked along the $[001]$ direction, the sequence being tilted again by 90° with a period $c/2$ (Fig. 4). Such entities bridge two chains of $\{Ce1(C_2O_4)_4\}_n^{n+}$, the first at $(1/4, 1/4, n)$ and the second at $(1+1/4, 1/4, n)$ (Fig. 3). But, the absence of bonds, between the $\{Ce2(H_3C_2O_3)_4\}_n^{-}$ neighboring units stacked along the $[001]$ direction, would result to two networks, the origin of which being settled on Ce2 ($3/4, 1/4, 1/2$) for the former and on Ce2 ($3/4, 1/4, 0$) for the latter (Figs. 5 and 6). The structure becomes a remarkable example of a network exhibiting two identical interpenetrating sub-lattices

$\{Ce_2(C_2O_4)(H_3C_2O_3)_4\}_n$. Discarding the connections between the Ce1 atoms and the oxalate units (dotted lines, Fig. 6), the topology of the schematized net, shown in Fig. 6, is that of Cooperite (PtS), with Ce1 as tetrahedral representing S and Ce2 as square planar representing Pt [31–34]. This is new and unprecedented topology, never observed in inorganic or coordination polymers, also known as MOF (metal-organic framework). Moreover, this unprecedented 3D topology is 2-fold interpenetrated, related by a center of inversion [35,36]. The only link between these two independent networks is assumed by strong hydrogen bonds between the hydroxyl function (O2–H2) of the glycolate ligand and O1 of the oxalate group ($H2 \dots O1^{viii} = 1.90 \text{ \AA}$ and $O2-H2-O1 = 168.3^\circ$, Table 5) (Fig. 7). But, as this type of bond occurs four times for each $\{Ce_2(H_3C_2O_3)_4\}_n^{-}$ entity, the two interpenetrating sub-lattices are relatively well strengthened. Another example of two mutually interpenetrating 3D frameworks, also linked via hydrogen bonds, can be found in $\{[(CH_3)_3Sn]_3CrO_4(OH)\}$ [37].

Both cerium atoms, with their 8-fold coordination number, have no common oxygen atoms. The Ce1 atom has two sets of distance metal-oxygen ($\Delta = 0.200 \text{ \AA}$, average 2.473 \AA , Table 5). The shorter are observed with the oxygen atoms of the glycolates ($2.373(2) \text{ \AA}$) while the longer are observed with the oxygen of the oxalates ($2.573(2) \text{ \AA}$). The Ce(1) polyhedron can be represented as a dodecahedron of symmetry C_2 (Fig. 8a) [26]. Such a polyhedron may be described by two planar trapezoids $O4^{iii}$, $O1$, $O1^i$, $O4^{ii}$ and $O4$, $O1^{iii}$, $O1^{ii}$, $O4^i$ with a dihedral angle $87.51(7)^\circ$ (theoretically 90°). Note that in this polyhedron, the two trapezoids are the same, due to

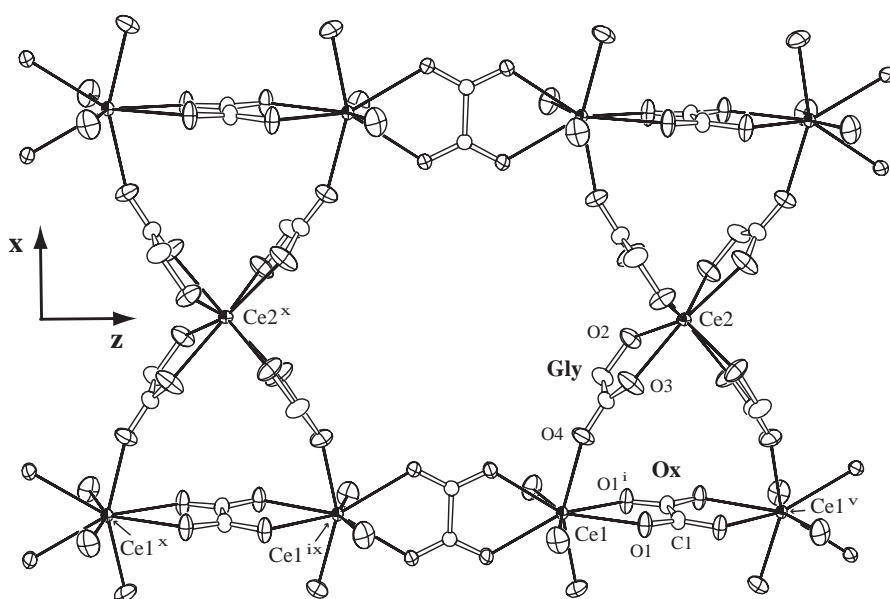


Fig. 3. View, along the $[010]$ direction, of adjacent chains, $\{Ce1(C_2O_4)\}_n^{n+}$, bridged by $\{Ce2(H_3C_2O_3)_4\}_n^{-}$ entities, for $Ce_2(C_2O_4)(H_3C_2O_3)_4 \cdot 2$. Thermal ellipsoids are represented at 50% probability. Symmetry codes are given in Table 5.

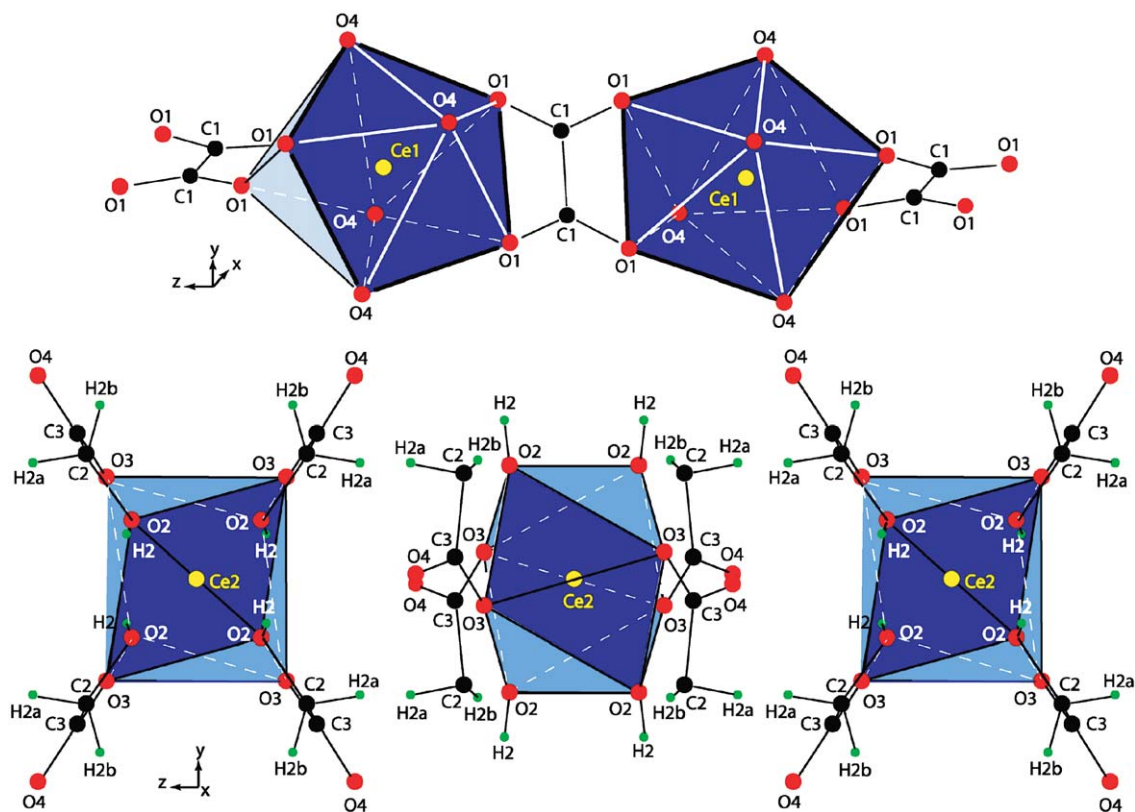


Fig. 4. View, along the [100] direction, of a $\{\text{Ce1}(\text{C}_2\text{O}_4)_n\}^n$ chain and of $\{\text{Ce2}(\text{H}_3\text{C}_2\text{O}_3)_4\}_n^{n-}$ entities stacked along the [001] axis for $\text{Ce}_2(\text{C}_2\text{O}_4)(\text{H}_3\text{C}_2\text{O}_3)_4 \cdot 2$.

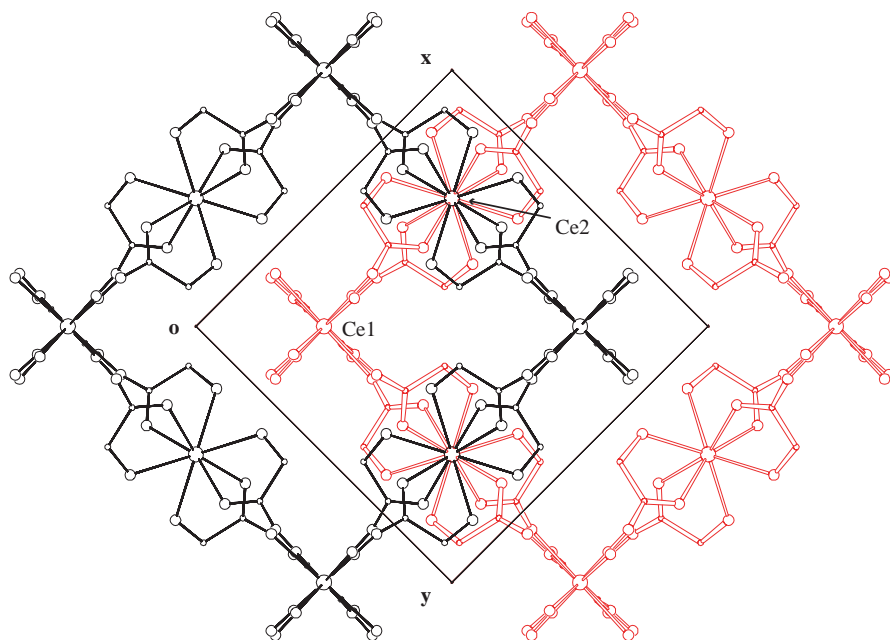


Fig. 5. Projection, along the [001] direction, of the two sub-lattices for $\text{Ce}_2(\text{C}_2\text{O}_4)(\text{H}_3\text{C}_2\text{O}_3)_4 \cdot 2$, with 2-fold interpenetration: the first sub-lattice, starting with Ce1 atom at $1/4, 1/4, 1/4$, is represented in red color and the second, starting with Ce1 atom at $3/4, 3/4, 1/4$, is in blue color. Thermal ellipsoids are arbitrary.

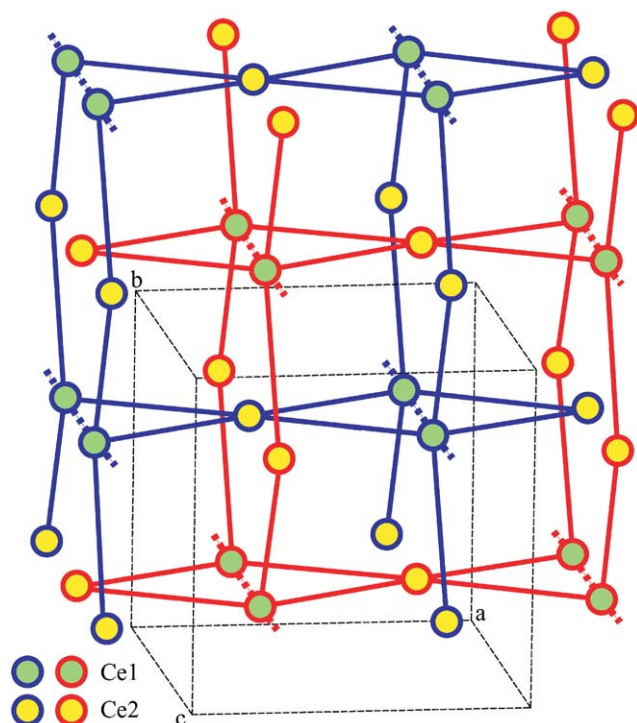


Fig. 6. Schematization, along the [001] direction slightly tilted, of the two interpenetrating sub-lattices the first in red and the second in blue, for $\text{Ce}_2(\text{C}_2\text{O}_4)(\text{H}_3\text{C}_2\text{O}_3)_4$ **2**. For the sake of clarity, only the cerium atoms directly linked between themselves via the glycolate groups, are represented. The connections between the Ce1 atoms and oxalate units are represented by dotted lines.

the high symmetry of the Ce1 atom. Such trapezoid discards from the planarity by $0.079(2)$ Å. Again, two sets of distances, Ce2–O, are also observed, but with a distribution much narrower than for Ce1, from $2.429(2)$ to $2.495(2)$ Å (average 2.462 Å). The longer distance comes from the hydroxyl function (O2). The Ce2 coordination polyhedron is the same than that of Ce1, i.e., a dodecahedron (Fig. 8b). One trapezoid discards from the planarity by $0.116(2)$ Å and they make between themselves a dihedral angle of $86.25(3)^\circ$.

The C–O, C–C and O–C–O distances and angles of oxalate and glycolate groups are in the expected range for this type of bonding (Table 5).

At last, it is worthwhile to note that compound **2** is anhydrous. One knows that hydrothermal syntheses can reduce greatly the number of water moles, bound to the lanthanide [13,14 compared to 11–13]. But scarce are the examples of anhydrous lanthanide carboxylate, prepared by using such technique [15,19,30].

3.2. Characterization of the family 2

The family **2** spreads from cerium to lutetium elements, as pure phase. The cell parameters of the various compounds were determined after indexing and refinement of their X-ray powder pattern; they are reported in Table 6. They agree well with the so-called lanthanide contraction, versus the lanthanide radius

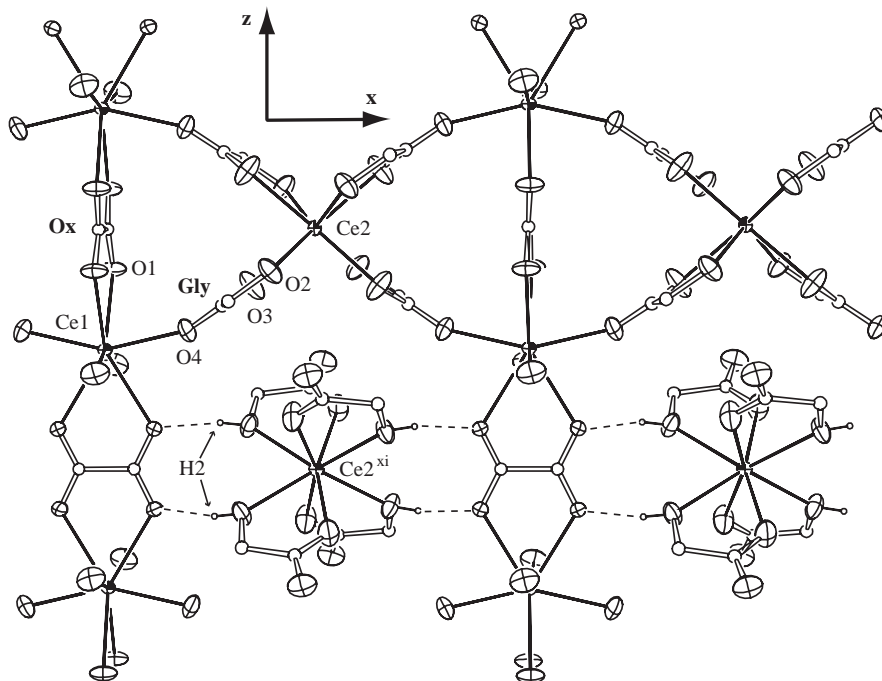


Fig. 7. View, along the [010] direction, of the hydrogen bonding between the two interpenetrating sub-lattices for $\text{Ce}_2(\text{C}_2\text{O}_4)(\text{H}_3\text{C}_2\text{O}_3)_4$ **2**. Except hydrogen atoms, which are further reduced; thermal ellipsoids are represented at 50% probability. Symmetry codes are given in Table 5. Dotted lines represent hydrogen-bond interactions.

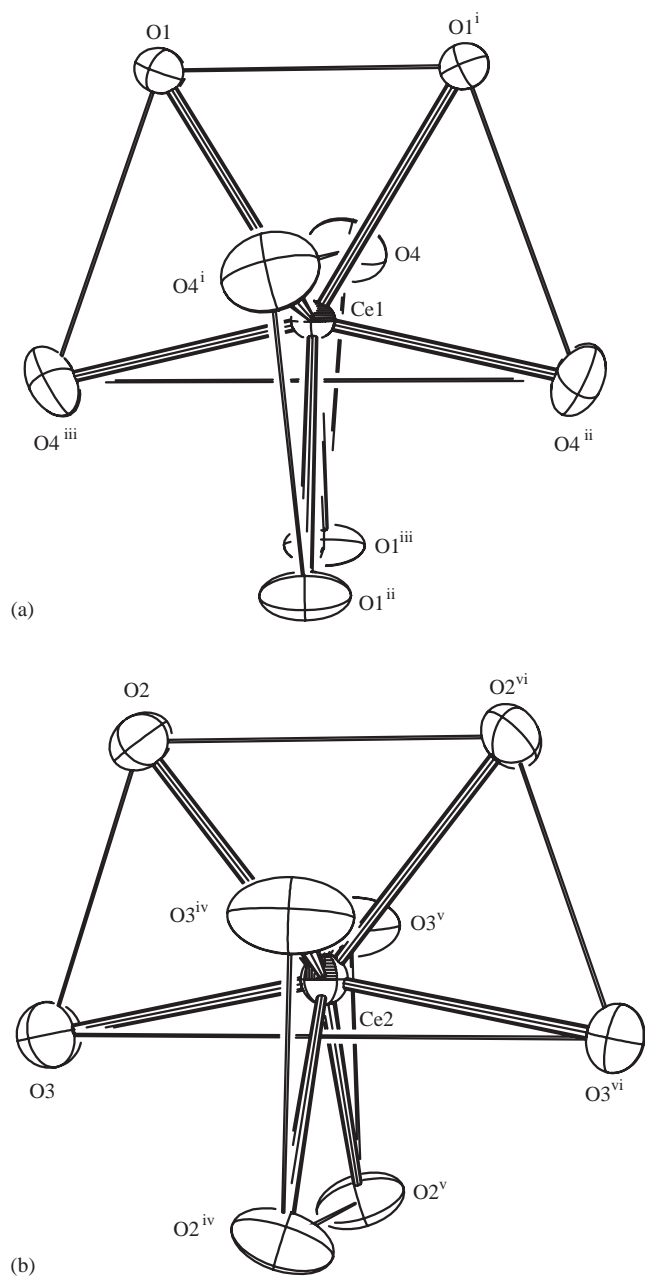


Fig. 8. Coordination polyhedron of the cerium atoms, (a) for Ce1 and (b) for Ce2, for $Ce_2(C_2O_4)(H_3C_2O_3)_4$ **2**. Thermal ellipsoids are represented at 50% probability. Symmetry codes are given in Table 5.

[38] and furthermore they respect almost exactly the Vegard rule.

A relevant feature of the infrared spectrum of this family is the presence of one large band, centered about 3150 cm^{-1} characteristic of the O–H stretching vibration [39].

The thermal behavior of some samples of this family is schematized in Table 7. First, it confirms the anhydrous character of this family and second the total mass loss is in agreement with the formula of **2**, resulting in the formation of the corresponding lanthanide oxide,

Table 6

Cell constants of $Ln_2(C_2O_4)(H_3C_2O_3)_4$ **2**, determined on powder pattern X-ray diffraction

<i>Ln</i>	R_{Ln}^{3+} (Å) ^a	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å) ³
Ce	1.143	11.701(2)	13.257(3)	1815.7(6)
Pr	1.126	11.6515(9)	13.161(2)	1786.7(3)
Nd	1.109	11.633(1)	13.094(2)	1772.0(3)
Sm	1.079	11.563(1)	12.948(2)	1731.2(3)
Eu	1.066	11.544(2)	12.911(3)	1720.6(6)
Gd	1.053	11.500(2)	12.851(3)	1699.5(6)
Tb	1.040	11.4850(8)	12.805(2)	1689.1(3)
Dy	1.027	11.439(2)	12.736(2)	1666.5(5)
Y	1.019	11.4272(8)	12.697(1)	1658.0(4)
Ho	1.015	11.426(1)	12.698(2)	1657.8(3)
Er	1.004	11.411(1)	12.659(2)	1648.4(3)
Tm	0.994	11.382(1)	12.607(2)	1633.2(3)
Yb	0.985	11.3489(8)	12.566(1)	1618.5(2)
Lu	0.977	11.327(3)	12.523(3)	1606.7(7)

^aIonic radii of the trivalent lanthanide with eight coordination number [38].

through the existence of some amorphous or bad-crystallized intermediate compounds (dilanthanide dioxymonocarbonate). As for simple lanthanide oxalate compounds, the onset of the first loss depends on the lanthanide element but in this case, the first loss are always more steeply than lanthanide oxalates [40,41]. The presence of dilanthanide dioxymonocarbonate, stoichiometric or non-stoichiometric, agrees also with the thermal behavior of lanthanide oxalate.

4. Conclusion

Two new families of lanthanide mixed-ligands, oxalate and glycolate, have been hydrothermally prepared: $[Ln_2(H_2O)_3](C_2O_4)_{2.5}(H_3C_2O_3)$ with $Ln = La, Ce$ and $Ln_2(C_2O_4)(H_3C_2O_3)_4$ with $Ln = Ce \dots Lu$. The second family presents a very nice case of 2-fold interpenetrated 3D identical sub-lattices that are only connected by hydrogen bonds. This family, that exists from cerium to lutetium elements, presents a relatively very strong lattice.

The supplementary material has been sent to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK and it can be obtained by contacting the CCCD: No. CDCC 254612 for $[Ce_2(H_2O)_3](C_2O_4)_{2.5}(H_3C_2O_3)$ and No. CDCC 254613 for $Ln_2(C_2O_4)(H_3C_2O_3)_4$.

Acknowledgments

Thanks are due to Rhodia for the free furniture of some salts of lanthanide.

Table 7

Observed (Ob.) and theoretical (Th.) mass loss (%), versus the temperature (°C), of some samples of the **2** family, $Ln_2(C_2O_4)(H_3C_2O_3)_4 \cdot 2$

Ce		→ 280–370 °C Ob. 48.9 (Th. 48.48)		CeO ₂
Nd	→ 370–450 °C Ob. 44.0 (Th. 43.75)	Nd ₂ O ₂ CO ₃	→ 600–670 °C Ob. 6.4 (Th. 6.50)	Nd ₂ O ₃
Gd	→ 420–470 °C	(Gd ₂ O ₂ CO ₃) ^a	→ 470–600 °C	Gd ₂ O ₃
Ho	→ 400–460 °C	Ob. 48.6 (Th. 48.39) ^a (Ho ₂ O ₂ CO ₃) ^a	→ 460–570 °C	Ho ₂ O ₃
Yb	→ 390–450 °C	Ob. 48.6 (Th. 48.39) ^a (Yb ₂ O ₂ CO ₃) ^a Ob. 46.2 (Th. 46.32) ^a	→ 450–540 °C	Yb ₂ O ₃

^aFor these elements the dilanthanide dioxymonocarbonate is non-stoichiometric. When going from Gd to Yb, the $Ln_2O_2CO_3$ phase is less stable and only the total loss is given.

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