

Two New Families of Lanthanide Mixed-Ligand Complexes, Oxalate–Carbonate and Oxalate–Formate: Synthesis and Structure of $[\text{Ce}(\text{H}_2\text{O})]_2(\text{C}_2\text{O}_4)_2(\text{CO}_3) \cdot 2.5 \text{H}_2\text{O}$ and $\text{Ce}(\text{C}_2\text{O}_4)(\text{HCO}_2)$

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Two new families of lanthanide complexes associating the ligands oxalate and carbonate or oxalate and formate have been prepared under autogenous pressure at 200°C using a pseudo-hydrothermal method. The two families have been extended to some lanthanides (*Ln*): oxalate–carbonate *Ln* = Ce, Pr, Nd, and Eu; oxalate–formate *Ln* = La, Ce, and Sm. The starting suspension contains either oxalate or a mixture of oxalate and oxalic acid. The structures have been solved for the element cerium. In both cases, the structure is built up from cerium atoms sharing all their oxygen atoms with oxalate and carbonate or oxalate and formate ligands, thus forming a three-dimensional network. The cerium polyhedra share either faces or edges or corners. The coordination scheme of the oxalate ligands is variable: bischelating, bischelating and monodentate, or bischelating and bimonodentate. The carbonate group acts as a bischelating and bimonodentate ligand while the formate group is chelating and monodentate. The characterization of these two original families by infrared spectra and thermal behavior is presented for some pure phases. A tentative explanation of the synthesis of these two phases will be emphasized. © 1996 Academic Press

INTRODUCTION

Mixed metal oxalates are often used as precursors for ceramics produced through their thermal decomposition. In our case, they are interesting as precursors for rare-earth sulfides. The γ phase of cerium sesquisulfide, the high-temperature (1100–1300°C) (1 and Refs. therein), may advantageously replace cadmium sulfoselenide as a red pigment in plastics (2–4). The cadmium compound is or will be forbidden in the near future due to its effects on the environment. The alkali metal elements may enhance the stability of the γ phase and allow its preparation at temperatures as low as 500°–600°C (2, 5–7) instead of 1100–1300°C. In a previous publication we have shown that mixed alkaline–lanthanide oxalate $[\text{MLn}(\text{H}_2\text{O})_n]$

$(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$ with *Ln* = La, ..., Gd, *M* = Li, *n* = 1, and *M* = Na, *n* = 2, may be prepared by pseudo-hydrothermal synthesis around 150°–200°C for 3 days (8).

We have continued the preceding study by varying the time of treatment or by adding oxalic acid in the suspension of cerium oxalate. Thus, we have isolated two new phases, lanthanide oxalate–carbonate and lanthanide oxalate–formate, which will be respectively referred to as **1** and **2**.

Complexes associating oxalate and carbonate may be of particular interest for oceanography and geochemistry. Light rare-earth elements are present in seawater as carbonate complexes (9). However, these latter phases evolve toward the formation of mixed complexes $\text{Ln}(\text{CO}_3)_x(\text{C}_2\text{O}_4)_y^{z-}$ through their leaching by natural waters which are rich in oxalate (10). Up to the present, there has been only one structural report on complexes of mixed oxalate–carbonate ligands, $\text{K}_4[\text{Zr}(\text{C}_2\text{O}_4)(\text{CO}_3)\text{F}_2] \cdot 4\text{H}_2\text{O}$ (11). The complexes $\text{K}_5[\text{Sm}(\text{CO}_3)_2(\text{C}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$ and $(\text{CN}_3\text{H}_6)_5[\text{Ln}(\text{CO}_3)_2(\text{C}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$ have been studied as powder compounds (10, 12). On the basis of spectroscopic data, some authors have ascertained the presence of mixed oxalate–carbonate in heating the corresponding oxalate complex. The heating of $\text{Sr}[\text{Zr}(\text{C}_2\text{O}_4)_3] \cdot 4\text{H}_2\text{O}$ would lead to $\text{Sr}[\text{Zr}_2\text{O}_2(\text{C}_2\text{O}_4)_3(\text{CO}_3)]$ (13). According to Sharov, oxalate–carbonates of the light lanthanides are prepared during the thermal decomposition of the corresponding oxalates (14); however, these results are largely controversial (15–34).

To our knowledge, lanthanide oxalate–formate is the first complex associating these two ligands.

The present paper describes the synthesis and structural determination of the cerium(III) complex as oxalate–carbonate or oxalate–formate. These families have been extended to some lanthanides. The infrared spectra and thermal behavior of the pure phases, europium oxalate–carbonate and cerium oxalate–formate, will be presented. As a conclusion, a tentative hypothesis of the formation of these two phases will be proposed.

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EXPERIMENTAL DATA

Synthesis and Analytical Data

The preparation of the title compounds was carried out in a Pyrex-lined steel bomb (autogenous pressure) at a temperature around 200°C over a period ranging from 3 days to 1 month. An aqueous suspension of cerium oxalate decahydrate was reacted either with alkali oxalate or with oxalic acid. After cooling, the resulting product was filtered, washed with distilled water, and dried at room temperature.

For **1** the optimal conditions were 0.5 mmole cerium oxalate decahydrate and 0.5 mmole potassium oxalate monohydrate in 10 ml water, heating time 7 days. Single crystals were obtained in this way. Nevertheless, this phase is not pure, although it constitutes the major phase (almost 70 wt%). This compound could also be prepared as an impure phase by using lithium oxalate or cerium carbonate instead of potassium oxalate. By heating less or more than 7 days, other phases were obtained, some known, some unknown. No single crystals developed for the unknown phases. We will present in this discussion the known phases, according to the heating time.

For **2** single crystals were obtained by heating an aqueous suspension of $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ and $\text{H}_2\text{C}_2\text{O}_4$ in the ratio free oxalic acid/oxalates(s) = 10 (s = solid) (0.5

mmole of cerium oxalate decahydrate and 15 mmole of acid oxalic dihydrate in 10 ml of water) for 1 week. The X-ray powder pattern of this phase did not show any impurities and could be wholly indexed on the basis of the cell constants and atomic positional data determined hereafter. The chemical analyses were in relatively good agreement with the formula determined by X-ray diffraction on a single crystal, $\text{Ce}(\text{C}_2\text{O}_4)(\text{HCO}_2)$; w%—observed: Ce = 48.5, C = 13.1, and H = 0.6; calcd: Ce = 51.3, C = 13.2, and H = 0.4.

By varying the lanthanide elements some compounds isostructural with the corresponding cerium phase for **1** and **2** were obtained. The yield of the compounds of **1** was 60, 80, and 100 wt% for Pr, Nd, and Eu, respectively, while for **2**, all the compounds were pure. Their unit-cell constants, refined from the X-ray diffraction powder pattern using the least-squares technique (35), are listed in Table 1; they agree with the lanthanide contraction.

Infrared and Thermal Behavior

Infrared spectra were recorded with a Perkin-Elmer 1725X FT-IR spectrometer. The samples were in the form of powder dispersed in KBr pellets. Thermal gravimetric study was carried out on a Setaram apparatus, with a mixed O_2/He flow (1/1) and a heating rate of 5°C/min. A plateau was maintained at 900°C for 1 hr.

TABLE 1
Cell Parameters of $[\text{Ln}(\text{H}_2\text{O})]_2(\text{C}_2\text{O}_4)_2(\text{CO}_3) \cdot 2.5\text{H}_2\text{O}$ and $\text{Ln}(\text{C}_2\text{O}_4)(\text{HCO}_2)$

<i>Ln</i>	$[\text{Ln}(\text{H}_2\text{O})]_2(\text{C}_2\text{O}_4)_2(\text{CO}_3) \cdot 2.5\text{H}_2\text{O}$ (1)			$\text{Ln}(\text{C}_2\text{O}_4)(\text{HCO}_2)$ (2)	
La				$a = 7.397(2) \text{ \AA}$ $b = 10.881(3) \text{ \AA}$ $c = 6.784(2) \text{ \AA}$	$V = 546.1 \text{ \AA}^3$
Ce	$a = 6.329(2) \text{ \AA}$ $b = 8.743(2) \text{ \AA}$ $c = 13.004(4) \text{ \AA}$	$\alpha = 105.61(4)^\circ$ $\beta = 90.55(4)^\circ$ $\gamma = 105.10(4)^\circ$	$V = 670.9 \text{ \AA}^3$	$a = 7.322(1) \text{ \AA}$ $b = 10.825(2) \text{ \AA}$ $c = 6.738(1) \text{ \AA}$	$V = 534.1 \text{ \AA}^3$
Pr	$a = 6.298(5) \text{ \AA}$ $b = 8.673(7) \text{ \AA}$ $c = 12.970(8) \text{ \AA}$	$\alpha = 105.42(6)^\circ$ $\beta = 90.55(6)^\circ$ $\gamma = 105.01(6)^\circ$	$V = 657.4 \text{ \AA}^3$		
Nd	$a = 6.273(6) \text{ \AA}$ $b = 8.616(7) \text{ \AA}$ $c = 12.928(9) \text{ \AA}$	$\alpha = 105.50(6)^\circ$ $\beta = 90.52(7)^\circ$ $\gamma = 105.00(6)^\circ$	$V = 648.0 \text{ \AA}^3$		
Sm				$a = 7.129(1) \text{ \AA}$ $b = 10.680(2) \text{ \AA}$ $c = 6.653(1) \text{ \AA}$	$V = 506.3 \text{ \AA}^3$
Eu	$a = 6.179(1) \text{ \AA}$ $b = 8.464(1) \text{ \AA}$ $c = 12.856(2) \text{ \AA}$	$\alpha = 105.13(1)^\circ$ $\beta = 90.46(1)^\circ$ $\gamma = 104.86(1)^\circ$	$V = 625.3 \text{ \AA}^3$		

Structural Determination

Suitable single crystals of both types were mounted on a Enraf–Nonius diffractometer for data collection using MoK α radiation. Unit-cell parameters were refined with a least-squares technique based on 25 reflections in the ranges $\theta = 8.03^\circ$ – 18.69° and 9.38° – 16.41° for **1** and **2**, respectively. Corrections for Lorentz and polarization effects, as well as empirical absorption correction (36), were applied to the collected hkl data. The atomic scattering factors and anomalous terms were determined in Ref. (37). Complex **1** crystallizes in the triclinic system, space group $P\bar{1}$. For **2** the observed systematic extinction conditions, $0kl: k + l = 2n$, $hk0: h = 2n$, were compatible with the

orthorhombic $Pnma$ or $Pn2_1a$ space group. A solution was found in the $Pnma$ space group. The coordinates of the cerium atom were found by the Patterson synthesis (38). The other atoms, including hydrogen atoms, were localized using successive Fourier difference maps (39). The hydrogen atoms were introduced as fixed contributors. For the last cycles of refinement, a unit-weight scheme was used for the two structures and an extinction parameter was used for **2**. In the last Fourier difference map, residual peaks were less than $0.79 e/\text{\AA}^3$ and $0.84 e/\text{\AA}^3$ for **1** and **2**, respectively. Reliability factors converged to $R = 1.86\%$, $R_w = 2.13\%$ and $R = 1.91\%$, $R_w = 1.93\%$ for **1** and **2**, respectively. Table 2 lists the crystal data and the experimental details for the data collection.

TABLE 2
Crystal Data

	Experimental details	
Chemical formula	[Ce(H ₂ O)] ₂ (C ₂ O ₄) ₂ (CO ₃) · 2.5H ₂ O (1)	Ce(C ₂ O ₄)(HCO ₂) (2)
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$Pnma$
a (Å)	6.329(2)	7.322(1)
b (Å)	8.743(2)	10.825(2)
c (Å)	13.004(4)	6.738(1)
$\alpha(^{\circ})\beta(^{\circ})\gamma(^{\circ})$	105.59(2) 90.47(3) 105.13(3)	
Molecular weight (g)	1184.61	1092.61
Z	2	8
V (Å ³)	666.6(4)	534.1(2)
ρ_{cal} (g cm ⁻³)	2.95	3.40
μ (MoK α)(cm ⁻¹)	68.3	84.9
Transmission factors	min = 0.92, max = 1.09	min = 0.96, max = 1.07
Crystal shape	Parallelepiped	Triangular prism
Crystal size	0.30 × 0.20 × 0.15 mm	0.30 × 0.08 × 0.05 mm
	Data collection	
Temperature (°C)	20	20
Radiation	Mo(K α)	Mo(K α)
Monochromatization	Graphite	Graphite
Scan type	Ω scan	Ω scan
Scan width: $\Theta = \Theta_0 + B \tan \Theta_0$	$\Theta_0 = 0.90$, $B = 0.35$	$\Theta_0 = 0.90$, $B = 0.35$
Maximum Bragg angle	30°	30°
Scan speed	16.480°/min	8.24°/min
Time count	60s	70s
Intensity control		
Reflections used	$\bar{3}00/\bar{1}42/\bar{2}1\bar{3}$	$\bar{3}0\bar{2}/240/\bar{1}42$
Frequency	3600s	5400s
Orientation control		
Reflections used	$\bar{5}2\bar{5}/\bar{5}0\bar{1}/\bar{3}2\bar{8}$	004/ $\bar{5}32/\bar{1}42$
Periodicity	150	150
	Refinement	
Number of reflections		
Recorded	4203	946
Used ($I \geq 3\sigma(I)$)	3026	587
Number of refined parameters	202	53
Factors of reliability		
$R = \Sigma[(F_o) - (F_c)]/\Sigma(F_o)$	1.86	1.89
$R_w = \{\Sigma w[(F_o) - (F_c)]^2/\Sigma wF_o^3\}^{1/2}$	2.13	1.91
$w = A/[\sigma^2(F_o)]$	$A = 1$	$A = 0.8345$
s (goodness of fit)	1.290	1.049

TABLE 3
Final Least-Squares Atomic Parameters with Estimated Standard Deviations

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
3a: [Ce(H ₂ O)] ₂ (C ₂ O ₄) ₂ (CO ₃) · 2.5H ₂ O(1)				
Ce1	0.06026(3)	0.03013(2)	0.25725(2)	0.891(8)
Ce2	0.30963(3)	0.66699(2)	0.07528(2)	0.833(7)
O1	0.2649(5)	0.3183(4)	0.2837(2)	1.7(1)
O2	0.3358(5)	0.5412(4)	0.2240(3)	1.8(1)
O3	−0.0551(5)	0.1616(4)	0.1261(2)	1.6(1)
O4	0.0073(5)	0.3865(3)	0.0675(2)	1.5(1)
O5	0.4806(5)	0.2015(3)	0.0555(2)	1.6(1)
O6	0.3290(5)	−0.0283(3)	0.1030(2)	1.4(1)
O7	0.1857(6)	0.1479(5)	0.4542(2)	2.3(1)
O8	0.1418(7)	0.1282(5)	0.6209(3)	3.2(2)
O9	0.6619(4)	0.5693(3)	0.0761(2)	1.3(1)
O10	0.9870(4)	0.7310(3)	0.1601(2)	1.3(1)
O11	0.7031(5)	0.8307(3)	0.1602(2)	1.3(1)
Ow1	0.3607(5)	0.8971(4)	0.2936(3)	2.1(1)
Ow2	−0.2322(6)	0.1710(5)	0.3379(3)	2.7(1)
Ow3	0.7775(8)	0.4766(6)	0.3072(5)	5.7(3)
Ow4 ^a	−0.183(1)	0.2885(9)	0.5637(6)	2.7(1)
Ow5 ^a	−0.357(1)	0.258(1)	0.5433(6)	2.9(1)
Ow6 ^a	−0.464(1)	0.457(1)	0.5121(6)	3.0(1)
C1	0.2326(6)	0.3961(5)	0.2191(3)	1.2(1)
C2	0.0443(6)	0.3057(5)	0.1295(3)	1.1(1)
C3	0.4460(6)	0.0512(5)	0.0455(3)	1.1(1)
C4	0.0937(8)	0.0805(7)	0.5216(3)	2.1(2)
C5	0.7854(6)	0.7080(4)	0.1310(3)	1.0(1)
3b: Ce(C ₂ O ₄)(HCO ₂) ₂ (2)				
Ce	0.21001(4)	1/4	0.12921(5)	0.66(1)
O1	0.0454(6)	1/4	0.4652(7)	1.2(2)
O2	0.0527(7)	1/4	0.7925(6)	2.0(2)
O3	0.4207(4)	0.3781(3)	0.3551(5)	1.2(1)
O4	0.2699(4)	0.5397(3)	0.4766(5)	1.6(1)
C1	0.1237(8)	1/4	0.628(1)	1.3(2)
C2	0.4092(5)	0.4779(4)	0.4536(6)	1.1(1)

Note. $B_{\text{eq}} = 8\pi^2/3 \sum_i \sum_j U(i, j) a_i^* a_j^* a_i a_j$ (a^* : reciprocal parameter).

^a Atom refined isotropically.

The fractional coordinates and equivalent thermal displacements with their estimated standard deviations are given in Tables 3a and 3b. Selected bond lengths and angles are gathered in Tables 4a and 4b.

RESULTS

Description of the Structures

[Ce(H₂O)]₂[(C₂O₄)₂(CO₃)] · 2.5H₂O (**1**). There are two independent cerium atoms, three oxalate ligands Ox(1), Ox(2), and Ox(3), one carbonate group, and 4.5 water molecules per asymmetric unit cell. The crystal structure of **1** is tridimensional but it may be derived from the layered lanthanide oxalate structure (40–47). This latter consists of puckered 6-membered rings, [Ln(C₂O₄)]₆, shar-

ing all the [Ln(C₂O₄)] edges, each lanthanide polyhedron being isolated from the others. The layers are only held by hydrogen bonds via water molecules situated into the interlayer space.

The basic frame of these rings is preserved in **1**, but two oxalate ligands are missing. Nevertheless, the ring geometry is maintained through two face-sharing connections (O(6), O(10), and Ow(1)) between the polyhedra of Ce(1) and the Ce(2) (Fig. 1). These rings are fused by sharing of the (Ce(1)–Ox(3)–Ce(1)) edges along the [001] axis, resulting in a file parallel to the [010] axis. These files are connected through (O(4)–O(4)) edge-sharing between the Ce(2) polyhedra, forming a layer parallel to the (100) plane. The connections between the cerium polyhedra lead to a centrosymmetric tetranuclear entity (Ce(1)–Ce(2)–Ce(2)–Ce(1)) (Fig. 1). The Ox(2) groups which are situated outside the rings, below or above the Fig. 1 plane, bridge two tetranuclear entities, resulting in a tridimensional network (Fig. 2). This entity, through edge (O(9)–O(9)) or corner-sharing O(11) between the polyhedra of Ce(2)–Ce(2) or Ce(2)–Ce(1), leads to a chain parallel to the [100] axis (Fig. 3). Carbonate groups contribute to the cohesion of this chain via O(9) and O(11) oxygen atoms.

There are mainly two sets of distances Ce–Ce:

—across the connections between polyhedra (face-, edge-, or corner-sharing) ranging from 4.0999(7) Å to 5.114(1) Å,

—across the bischelating oxalate groups varying from 6.454(1) Å (Ox(1)) to 6.514(1) Å (Ox(2)). Inside the six-membered ring, two types of distances occur; the Ce–Ce angles range from 109.86(2) to 131.125(7). The ring deviates from planarity, presenting a chair-shaped configuration: the Ce(2) atoms deviate by ± 1.2219(7) Å from the Ce(1) atom least-squares plane. All the carbonate oxygen atoms, as well as O(4) and O(6), are μ_2 .

The Ce(1) atom is ninefold coordinated (seven oxygen atoms plus two water molecules) with distances ranging from 2.443(3) to 2.672(3) Å (Table 4a). The coordination geometry is close to that of a monocapped square antiprism, O(11) being the cap position. The Ce(2) atom is bound to nine oxygen atoms with distances varying from 2.449(3) to 2.664(3) Å but it presents a longer contact to a water molecule, Ow(1) (2.964(3) Å). Taking this long distance into account, the coordination polyhedron of the Ce(2) atom may be represented by a distorted dicapped square antiprism, O(9) and Ow(1) occupying the cap positions. The O(9)–Ce(2)–Ow(1) angle is 160.8(1). A dihedral angle of 8(1) or 14.43(8)° is observed between the “square” faces for the Ce(1) or Ce(2) atoms, respectively. The Ce–O distances fall into the range usually found for such compounds (8, 48–50).

The three oxalato ligands are bischelating. For Ox(1) and Ox(2) ligands, one oxygen atoms in the bite (O(4) for Ox(1), O(6) for Ox(2)) is bound unsymmetrically to

TABLE 4
Selected Bond Lengths (Å) and Angles (°)

4a: [Ce(H ₂ O)] ₂ (C ₂ O ₄) ₂ (CO ₃) · 2.5H ₂ O (1) (Ox = oxalate, Carb = carbonate)							
Ce1	O3	2.496(4)	Ce2	O10 ^d	2.449(3)		
Ce1	O8 ^b	2.520(4)	Ce2	O2	2.492(4)		
Ce1	O11 ^a	2.541(2)	Ce2	O6 ^f	2.560(3)		
Ce1	Ow1 ^c	2.574(4)	Ce2	O9	2.588(3)		
Ce1	O1	2.443(3)	Ce2	O4	2.664(3)		
Ce1	O10 ^a	2.496(3)	Ce2	O9 ^e	2.487(3)		
Ce1	O7	2.524(3)	Ce2	O5 ^e	2.503(3)		
Ce1	Ow2	2.563(4)	Ce2	O4 ^g	2.583(3)		
Ce1	O6	2.671(3)	Ce2	O11	2.591(3)		
			Ce2	Ow1	2.965(3)		
Ox(1)	C1	C2	1.547(5)	O2	C1	O1	125.1(3)
	C1	O1	1.260(6)	O2	C1	C2	118.0(4)
	C1	O2	1.250(5)	O3	C2	O4	126.8(3)
	C2	O3	1.242(5)	O4	C2	C1	116.5(3)
	C2	O4	1.263(6)	O1	C1	C2	116.8(3)
				O3	C2	C1	116.8(4)
Ox(2)	C3	C3 ^h	1.559(7)	O5	C3	O6	125.8(4)
	C3	O5	1.245(5)	O6	C3	C3 ^h	116.1(4)
	C3	O6	1.269(5)	O5	C3	C3 ^h	118.1(4)
Ox(3)	C4	C4 ^b	1.548(9)	O7	C4	C4 ^b	117.0(5)
	C4	O7	1.250(6)	O7	C4	O8	126.4(4)
	C4	O8	1.253(5)	O8	C4	C4 ^b	116.6(6)
Carb	C5	O9	1.274(4)	O9	C5	O10	123.4(4)
	C5	O10	1.276(5)	O10	C5	O11	118.0(3)
	C5	O11	1.282(5)	O9	C5	O11	118.6(3)
Ow1	H11	0.940(4)	H11	Ow1	H21	110.5(3)	
Ow1	H21	0.991(3)					
Ow2	H12	1.005(4)	H22	Ow2	H12	94.1(3)	
Ow2	H22	0.966(4)					
H11	Ow5 ⁱ	1.909(9)	Ow1	H11	Ow5 ⁱ	158.7(3)	
H11	Ow4 ^f	1.963(8)	Ow1	H11	Ow4 ^f	153.6(3)	
H21	Ow2 ^j	1.987(3)	Ow1	H21	Ow2 ^j	166.0(3)	
H12	Ow3 ^d	1.805(6)	Ow2	H12	Ow3 ^d	165.8(3)	
H22	Ow5	1.829(8)	Ow2	H22	Ow5	159.7(3)	
H22	Ow4	1.878(7)	Ow2	H22	Ow4	165.1(3)	
Symmetry operators							
a: x - 1,	b: -x, -y,	c: x, y - 1, z	d: x - 1, y, z				
y - 1, z	1 - z	g: -x, 1 - y,	h: 1 - x, -y,				
e: 1 - x,	f: x, 1 + y, z	-z	-z				
1 - y, -z	j: 1 + x, 1 + y,						
i: -x, 1 - y,	z						
1 - z							

another cerium atom (2.583(3) Å versus 2.664(3) Å for O(4)). Noncentrosymmetric Ox(1) is related to three metal atoms while the centrosymmetric Ox(2) is related to four ones. The ligand Ox(1) is planar to within 0.019(2) Å. Interatomic distances and angles within the oxalato ligands do not differ significantly and they agree well with the values observed in the literature (Table 4a) (40–47).

TABLE 4—Continued

4b: Ce(C ₂ O ₄)(HCO ₂) (2) (For = formate, Ox = oxalate)							
Ce	O4 ^b	2.502(3)					
Ce	O4 ^a	2.502(3)					
Ce	O3 ^d	2.534(3)					
Ce	O3 ^c	2.534(3)					
Ce	O1 ^e	2.537(4)					
Ce	O2 ^f	2.545(5)					
Ce	O1	2.565(4)					
Ce	O3	2.573(3)					
Ce	O3 ^g	2.573(3)					
For	C1	O1	1.237(8)	O2	C1	O1	127.3(6)
	C1	O2	1.225(8)	O2	C1	H	116.2(6)
	C1	H	1.035(6)	O1	C1	H	116.5(6)
Ox	C2	C2 ^h	1.546(8)	O4	C2	O3	125.7(4)
	C2	O3	1.271(5)	O3	C2	C2 ^h	114.6(4)
	C2	O4	1.229(5)	O4	C2	C2 ^h	119.6(5)
	H	O2 ⁱ	2.179(5)	C1	H	O2 ⁱ	164.1(4)
Symmetry operators							
a: 0.5 - x, 1 - y,	b: 0.5 - x, y - 0.5,	c: x - 0.5, 0.5 - y,					
z - 0.5	z - 0.5	0.5 - z					
d: x - 0.5, y, 0.5 - z	e: 0.5 + x, 0.5 - y,	f: x, y, z - 1					
g: x, 0.5 - y, z	0.5 - z	i: 0.5 + x, 0.5 - y,					
	h: 1 - x, 1 - y,	1.5 - z					
	1 - z						

The carbonate group is planar. It is bischelating, but again two oxygen atoms, namely O(9) and O(10), are linked to another cerium atom (Fig. 3). This coordination scheme may be compared with that of a carbonate group found in lanthanite (La, Ce)₂(CO₃)₃ · 5H₂O (51). The bond distances and angles within the carbonate are quite comparable to those observed in lanthanite (Table 4a).

The water molecules are mainly localized into the six-membered ring space (Fig. 1). The first bridges two cerium atoms, the second is bound only to a cerium atom, Ce(2), and the others are free; some of them, Ow(4), Ow(5), and Ow(6), are disordered. Although the hydrogen atoms were not located for some water molecules (Ow(3)–Ow(6)), the existence of hydrogen bonds seems probable (Table 4a). This feature is quite comparable to the “decahydrate” lanthanide oxalate where this number ranges from 9.5 to 10.5 due to disordered water molecules (41, 43, 44).

Ce(C₂O₄)(HCO₂) (2). The structure of **2** is tridimensional and it may be described in the following way. The cerium coordination polyhedra linked by faces build infinite zigzagging chains parallel to the [100] axis (Fig. 4). The Ce–Ce–Ce angles of these chains are equal to 132.06(2)°. The Ce–Ce distance between neighboring atoms is equal to 4.0066(5) Å. The formate ligands bridge these chains to give infinite layers parallel to the (010) plane at

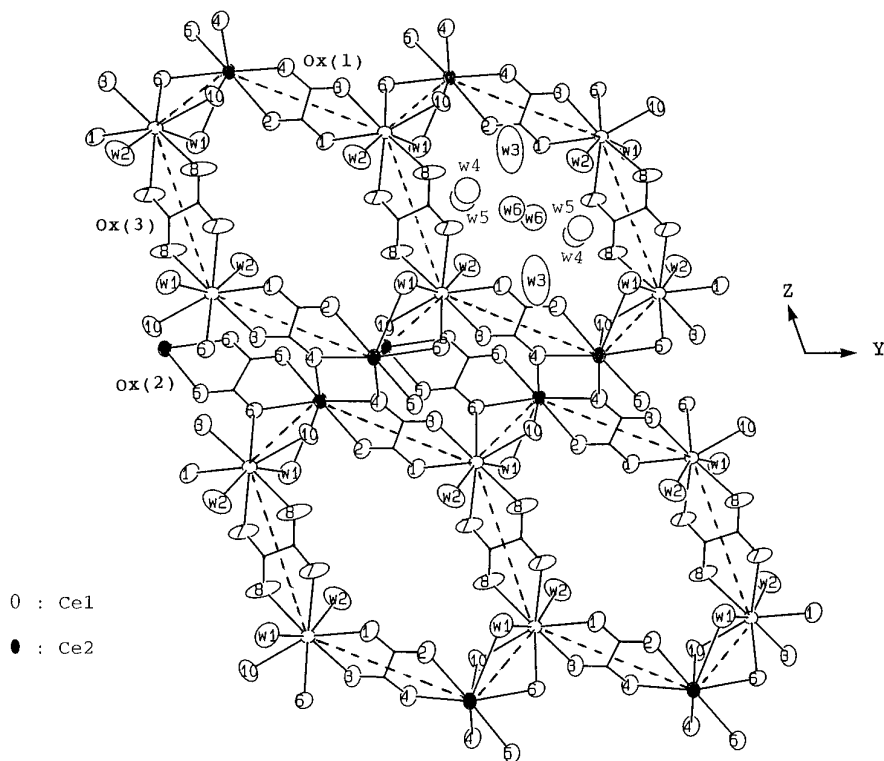


FIG. 1. Representation of the six-membered rings parallel to the (100) plane for **1**. In order to show the 6-membered rings, dotted lines are drawn between the cerium atoms. For the sake of clarity, not all the oxygen atoms bound to cerium are represented. The same remarks and labels are also true for Figs. 2 and 3.

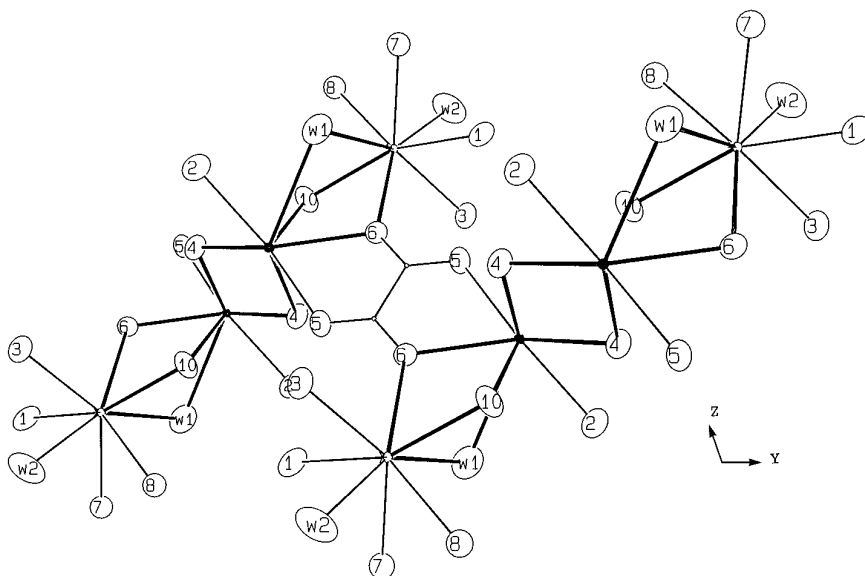


FIG. 2. View of the Ox(2) ligand connecting the two centrosymmetric tetranuclear entities for **1**.

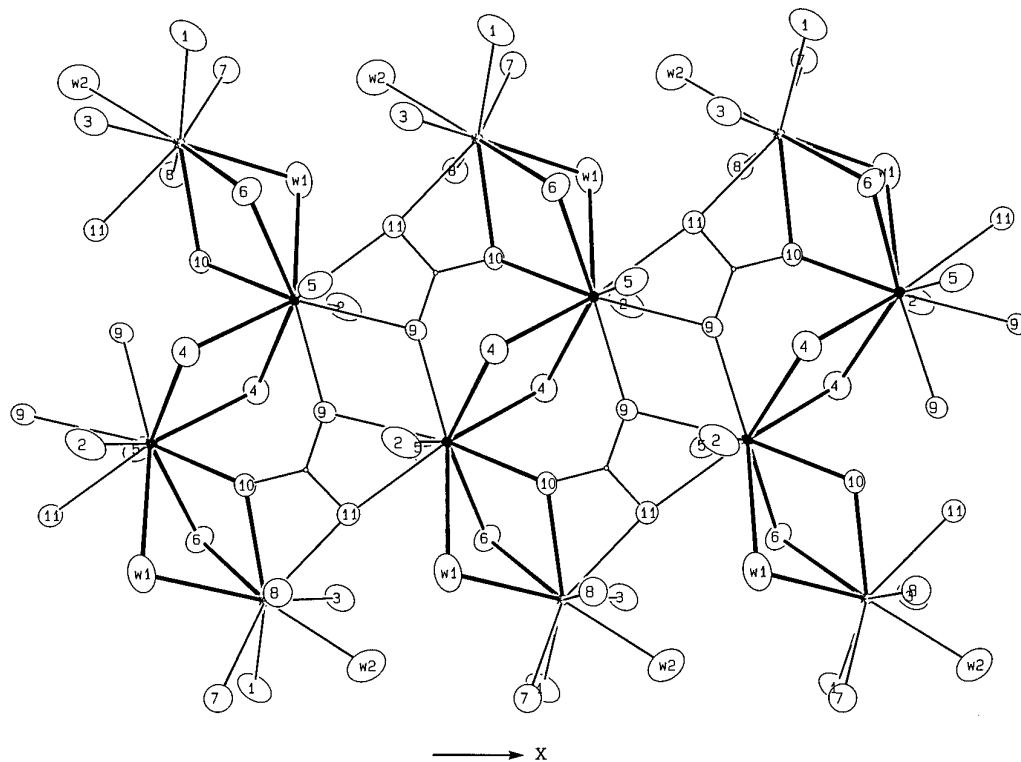


FIG. 3. View of the chain parallel to the [100] axis for 1.

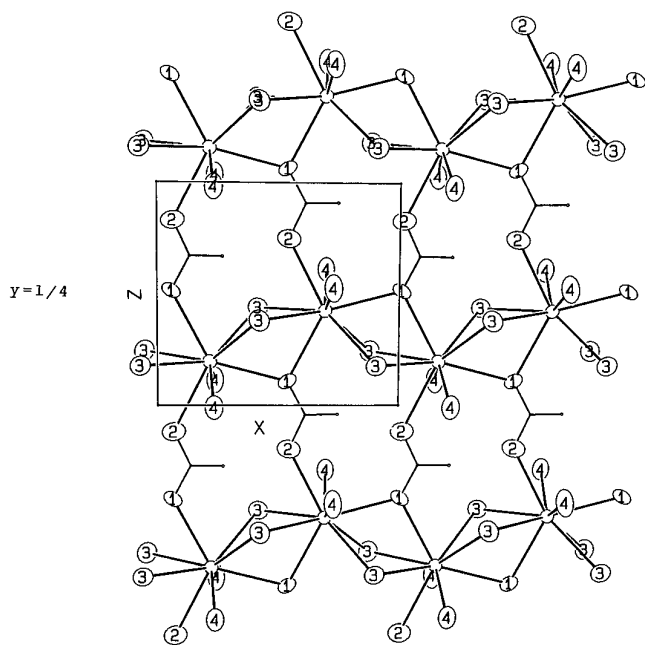


FIG. 4. View of a layer built by the zigzagging chains (cerium polyhedra) connected by the formate groups for 2.

the level $y = 1/4$ or $y = 3/4$. Adjacent layers are bound by oxalate groups (Fig. 5). The Ce–Ce distance across the bischelating oxalate is equal to 6.4641(9) Å. The oxygen atoms O(1) and O(3), respectively, from formate and oxalate ligands, and μ_2 .

The cerium atom is coordinated to all the oxygen atoms (CN = 9) with a narrow range of distances (2.502(3) to 2.574(3) Å) (Table 4b). The coordination polyhedron may be represented by a distorted monocapped square antiprism, O(4) occupying the cap position. A dihedral angle of 3(2)° occurs between the “square” faces.

The centrosymmetric oxalate is bischelating, but again one oxygen of the bite O(3) is linked to another cerium atom, and it may be compared to Ox(2) in the previous structure. However, some discrepancy may be noted between the C–O distances (C(2)–O(4) = 1.230(5) Å versus C(2)–O(3) = 1.271(5) Å). The former is close to a double bond while the latter is near to a single bond. This difference is also apparent from the angles around the oxalate (Table 4b). The difference in bond lengths and angles may be attributed to the constraint imposed by the cerium atom upon the oxygen atoms. The cerium atom is fourfold bound to O(3) atoms in different symmetry operations with a narrow range of distances (2.534(3) Å versus 2.574(3) Å) (Table 4b). This may result in a longer C(2)–O(3) bond, thus giving a shorter C(2)–O(4) bond.

The distances and angles within the formate ligand are

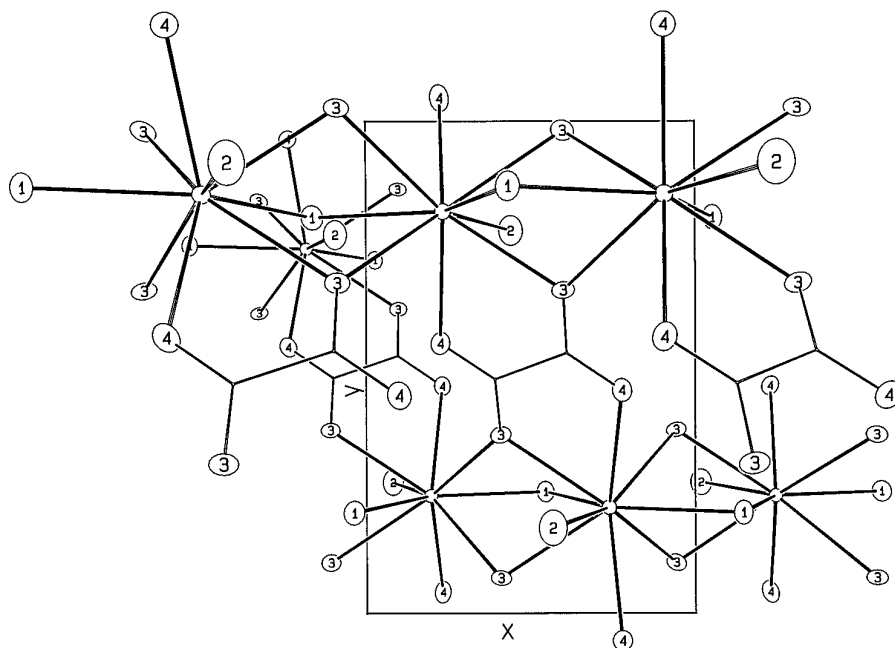


FIG. 5. Representation of two layers connected by the oxalate ligands for **2**.

normal (52). Two formate groups are connected by a weak hydrogen bond (Table 4b). The absence of water molecules is worth noting; because of it, this compound is better compared to the light lanthanide formate instead of the oxalate (15).

Infrared and Thermal Behavior of the Two Phases

This study was done on pure phases, Eu for **1** and Ce for **2**. The infrared spectra of the phases **1** and **2** and those of single-ligand lanthanide complexes (oxalate, formate, and carbonate) are represented in Fig. 6 (53). For compounds **1** and **2** the respective spectra may be considered the sums of the single-ligand complexes, but some peaks are shifted.

The presence of the CO_3^{2-} group in compound **1** is ascertained mainly by the bands at 1099 and 844 cm^{-1} (Figs. 6d and 6e). In comparison to cerium oxalate decahydrate (Fig. 6c) there is a broadening of the bands assigned to oxalate groups for **1** (Fig. 6d). A shoulder is observed at 1684 cm^{-1} and some peaks are degenerate (1311, 1322 cm^{-1}). A possible explanation of this effect is not the result of any variation of the C-C and C-O distances (Table 4a) but rather is due to the change in symmetry and coordination mode of the oxalate groups for the two compounds. In cerium oxalate decahydrate three centrosymmetric oxalate ligands which were only bischelating were found, while in compound **1** the Ox(1) is noncentrosymmetric and more-

over the close environments of oxalate groups range from two to four metal atoms.

The band at 1428 cm^{-1} , assigned to the C-H bending mode, is proof of the existence of formate within compound **2** (54). The 1720 cm^{-1} band, which is not present in the spectra of the single ligand (Figs. 6a and 6b), may be attributed to the shortening of one C-O bond length, which is close to a double bond (Table 4b).

The total decomposition of phase **1** involves four mass losses. The dehydration is a two-stage process. Three and one-half water molecules are lost between 50 and 140°C, while the last one evolves between 210 and 280°C. It is tempting to attribute this last water molecule to that bridging the two metals, Ow(1). The anhydrous compound may be obtained through a narrow range of temperature (280–320°C). On further heating, decomposition of the ligands takes place in two overlapping steps: formation of a dioxo-monocarbonate intermediate in the temperature range from 430 to 530°C and then decarbonation of this last product to yield the sesquioxide from 530 to 720°C (15–18). The total mass losses observed and calculated are 43.6 and 43.32%, respectively.

For **2**, ceria (CeO_2) is obtained through a single process which ranges from 340 to 410°C. The calculated and observed mass losses are close (36.98% versus 37.0%). The thermal behavior of **2** is similar to that of cerium complexes for which no intermediates such as oxocarbonate are observed (15, 18, 20, 26, 34).

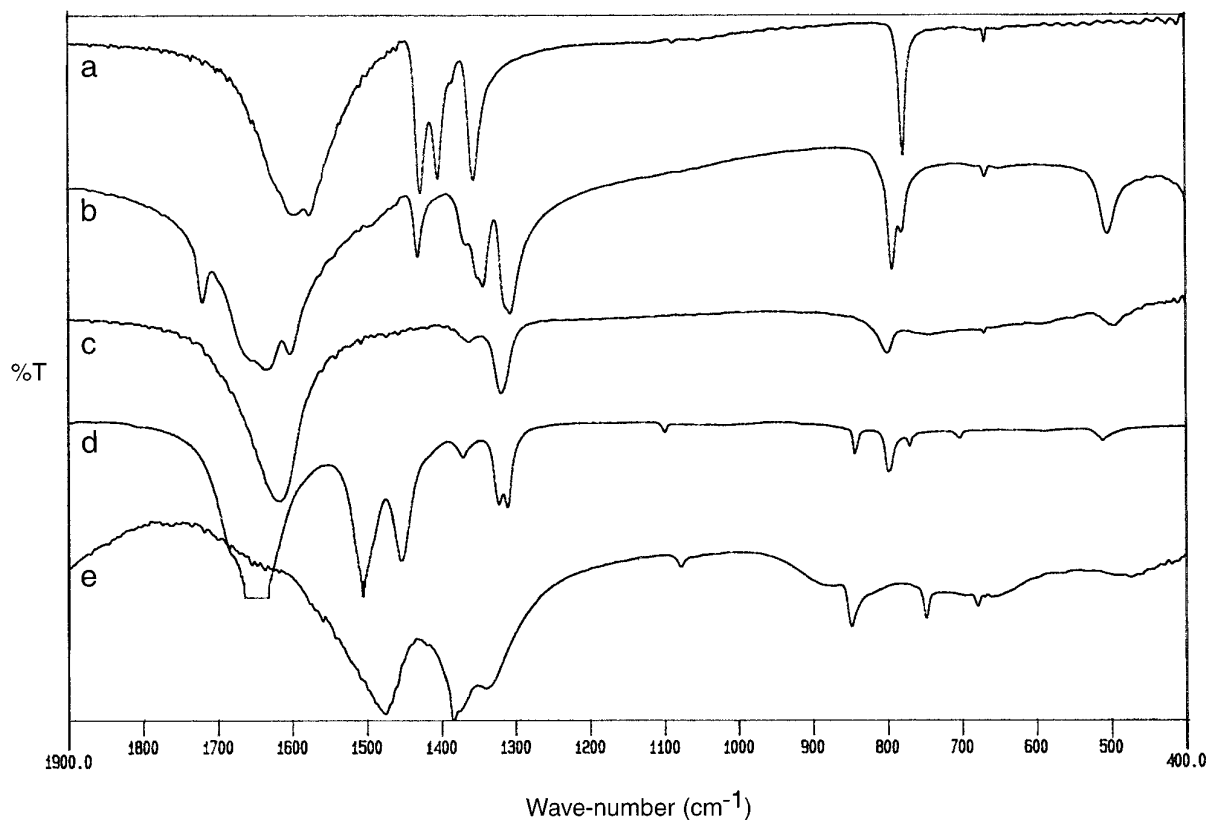
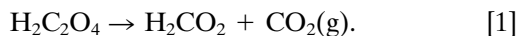


FIG. 6. Infrared spectra of phases 1 and 2 and of the single-ligand lanthanide complexes. (a) $\text{Ce}(\text{HCO}_2)_3$; (b) $\text{Ce}(\text{C}_2\text{O}_4)(\text{HCO}_2)$; (c) $[\text{Ce}(\text{H}_2\text{O})_3]_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$; (d) $[\text{Eu}(\text{H}_2\text{O})]_2(\text{C}_2\text{O}_4)_2(\text{CO}_3) \cdot 2.5\text{H}_2\text{O}$; (e) $\text{Ce}_2(\text{CO}_3)_3 \cdot 5\text{H}_2\text{O}$.

DISCUSSION

The decomposition of metal oxalates has been the subject of extensive publications (15–34). However, they dealt mainly with thermal decomposition of solids in terms of thermogravimetry, differential scanning calorimetry, or evolved gas analysis. Data concerning the decomposition of oxalate in solution are scarce. However, Fein *et al.* have recently studied “the effect of aqueous complexation on the decarboxylation rate of oxalate” (55). In this study, the rate was measured in solution with or without aqueous aluminum, a strongly complexing cation of the oxalate ligand, at 160, 170 and 180°C. Whatever the conditions, the decarboxylation of oxalate takes place; aqueous complexation (aluminum cations) can significantly enhance the thermal stability of oxalate. The “thermal stability of aqueous oxalate species” has been also studied by Crossey (56), who demonstrates that oxalic acid decomposes to formic acid in aqueous solution over the temperature range 180–230°C, following an apparent first-order reaction kinetics; the decarboxylation rates of oxalic acid vary inversely with increasing pH. The reaction proposed by Crossey is



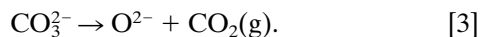
In addition, Leitner has demonstrated that formic acid may be formed by a reaction of H_2O and $\text{CO}(\text{g})$ (57) (see the following reactions).

This scheme of decarboxylation of oxalic acid in solution allows one to interpret the formation of phase 2 but it does not explain the formation of phase 1. In that regard, the decomposition of solid oxalates may be helpful.

For many metal oxalates, such as those of alkalis or rare earths, the onset of the decomposition process is represented by the following equation:



This stage starts at temperatures higher than 500°C for alkali oxalates. For cerium oxalate it begins around 275°C (15, 19, 20, 26, 34). Due to the transformation of cerium(III) to cerium(IV), ceric oxide is reached by a steep weight loss at around 300°C. The total decomposition of the cerium oxalate may be represented by reactions [2] plus [3] and the concomitant oxidation of Ce(III) to Ce(IV) in air, these two reactions occurring nearly at the same temperature:

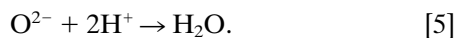


We have checked that this decomposition is shifted toward lower temperatures as a function of either decreasing heating rate or increasing heating time; badly crystallized yellow CeO_2 is obtained by heating cerium oxalate at 200°C for 2 days.

In the phases isolated from solutions, colorless oxalate-carbonate and oxalate-formate, the presence of cerium(IV) may be excluded. Complexes or salts of Ce(IV) are generally yellow; also, Ce(IV) ions act as an oxidant in the presence of the oxalate ligand (58). When the hydrothermal vessel was opened at room temperature, there was a strong pressure, due probably to the gases evolved from reactions [1], [2], and perhaps [3]. We were unable to isolate these gases in order to determine their exact nature. In solution, reaction [3] goes on through



or in acidic medium through



The starting suspension is made of cerium plus alkali oxalates. The first phase obtained after a few days (1 to 3) corresponds to the mixed Ce-Li(Na) oxalate previously described (8). This latter phase disappears as the treatment time becomes longer and longer, particularly at temperatures around 200°C. Reaction [2] goes on; as soon as the carbonate concentration is important enough, a cerium oxalate-carbonate precipitates. Further evolutions involving reactions [3] and [4] (one month at 200°C) allow to obtain a mixture of phases, the ancyllite CeOHCO_3 , already known and structurally described (59–61), and the ceria. The cell constants of ancyllite found in this study are as follows: orthorhombic, $a = 7.332(1) \text{ \AA}$, $b = 5.020(1) \text{ \AA}$, $c = 8.561(1) \text{ \AA}$; hexagonal, $a = 7.283(3) \text{ \AA}$, $c = 9.973(4) \text{ \AA}$. The orthorhombic ancyllite is obtained in the presence of alkali oxalate while the hexagonal one is formed in the presence of cerium carbonate. According to Caro, the orthorhombic ancyllite is more difficult to prepare under hydrothermal conditions than the hexagonal modification, type bastnaesite, LnFCO_3 (62). The two modifications, found in this study, are synthesized under the same conditions of temperature and pressure. The factors having an effect on the formation of such modifications must be elsewhere: the presence of alkali element?

Though the alkali element does not enter the oxalate-carbonate phase, it is worth noting that this phase is obtained only in the presence of potassium or lithium oxalate. Either in the absence of alkali oxalate or in the presence of sodium oxalate, a new phase or a mixture of phases, but no single crystals suitable for X-ray diffraction, are obtained. The singular behavior of sodium with respect to lithium and potassium may be due to its ionic radius: in-

deed, the sodium and cerium ionic radii are close (1.16 versus 1.14 Å (63)) and thus sodium may enter the cerium phases more easily. The role of alkali oxalate is not clearly understood and further experiments are needed; it may buffer the solution pH.

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