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Crystalline and Molecular Structures of Anhydrous Lanthanide Perchlorates $Ln(ClO_4)_3$ with Ln = La, Ce, Pr, Sm, Eu, Ho, Er, Tm, and Lu

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The anhydrous perchlorates $Ln(ClO_4)_3$, where ClO_4 is coordinated to Ln atoms (Ln = La, Ce, Pr, Sm, Eu, Ho, Er, Tm, and Lu) crystallize in two distinct groups of isostructural species. Rietveld refinements show that from lanthanum to thulium (low temperature form), the crystal system is hexagonal (space group $P6_3/m$, $Z = 2$) with 9.400(3) Å < a < 9.201(1) Å and 5.918(1) Å < c < 5.563(1) Å. The Rietveld refinement converged to R_F = 0.033, R_p = 0.029, and R_{wp} = 0.053 for $Eu(ClO_4)_3$. The channeled structure is built on the basis of slightly distorted tricaped trigonal Eu centered prisms of nine oxygen atoms belonging to nine tridentate $[ClO_4]$. Thullium (high temperature form) and lutetium crystallize in trigonal $R\bar{3}c$ unit cells ($Z = 6$) with, respectively, a = 8.13286(2) Å, c = 24.1586(1) Å, and a = 8.11559(4) Å, c = 24.0047(1) Å. For $Lu(ClO_4)_3$, R_F, R_p, and R_{wp} were 0.039, 0.046, and 0.061, respectively. Its molecular structure consists of infinite layers of Lu atoms in a tricaped trigonal antiprism surrounding of oxygens. Layers and linkages between layers are ensured by simultaneously bridging and chelating tridentate $[ClO_4]$. © 1998 Academic Press

INTRODUCTION

In the development of new preparative methods for metal oxides as dispersed powders, the thermolysis at *moderate* temperatures of a fully inorganic precursor with weak oxy-ligands should be an alternate method of synthesis which can promote attractive properties (1). For example, nitrates are compounds of choice for this method in the preparation of ceramics (2). The possibilities of varying the conditions of pressure, the heating rate, and the nature of the gaseous environment add further to the richness of the process. Perchlorates generally decompose below 250–300°C, giving fine powders of oxides in which the metal is in its highest oxidation state. However, starting from lanthanide perchlorates and with the exception of $Ce(ClO_4)_3$, the resulting powders are oxychlorides rather than oxides. In order to control the structure and morphology of the resulting material, it nevertheless remains of importance to know the structure of the precursor as well as those of the successive intermediate solids. In previous papers (3, 4) we described the synthesis of a series of anhydrous rare earth perchlorates, $M(ClO_4)_3$ with M = Y, La, Pr, Nd, Sm, Gd, and Er, and we proposed tentative structural assignments essentially based on infrared and Raman data, since perchlorates are obtained as microcrystalline powders rather than single crystals. Although X-ray powder diffraction techniques have significantly improved (5) over the past 10 years and are now used to solve the structures of ever more complex species (6), determination of the structure of anhydrous perchlorates by powder diffraction has never been reported. We have recently had the opportunity to be among the first users of the new beam line 16 at the European Synchrotron Radiation Facility (ESRF), which is devoted to X-ray powder diffraction. Recording data on this line has allowed us to determine the crystalline and molecular structures of a series of $Ln(ClO_4)_3$ compounds with Ln = La, Ce, Pr, Sm, Eu, Ho, Er, Tm, and Lu.

EXPERIMENTAL

Synthesis

Caution: Chlorine trioxide and perchlorates are highly reactive compounds particularly on contact with organic

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TABLE 1
Synthetic Data for Anhydrous Lanthanide Perchlorates

Reagents	Reaction products	Intermediate stage	Treatment	Final products
La_2O_3[a]	$HClO_4$, 72%[b]	$La(ClO_4)_3 \cdot nH_2O$	(i) Cl_2O_6[c] (ii) 65°C (1.33 Pa)	$La(ClO_4)_3$
$(NH_4)_2Ce(NO_3)_6$[d]	$K_2CO_3 \cdot H_2O$[j]	$Ce(CO_3)_3 \cdot nH_2O$	(i) Cl_2O_6 (ii) 50°C (1.33 Pa)	$Ce(ClO_4)_3$
Pr_6O_{11}[e]	$HClO_4$, 72%[b]	$Pr(ClO_4)_3 \cdot nH_2O$	200°C (1.33 Pa)	$Pr(ClO_4)_3$
Sm_2O_3[f]	$HClO_4$, 72%[b]	$Sm(ClO_4)_3 \cdot nH_2O$	(i) Cl_2O_6 (ii) 100°C (1.33 Pa)	$Sm(ClO_4)_3$
Eu_2O_3[d]	$HClO_4$, 72%[b]	$Eu(ClO_4)_3 \cdot nH_2O$	(i) Cl_2O_6 (ii) 100°C (1.33 Pa)	$Eu(ClO_4)_3$
Ho_2O_3[g]	$HClO_4$, 72%[b]	$Ho(ClO_4)_3 \cdot nH_2O$	(i) Cl_2O_6 (ii) 100°C (1.33 Pa)	$Ho(ClO_4)_3$
Er_2O_3[h]	$HClO_4$, 72%[b]	$Er(ClO_4)_3 \cdot nH_2O$	(i) Cl_2O_6 (ii) 70°C (1.33 Pa)	$Er(ClO_4)_3$
Tm_2O_3[e]	$HClO_4$, 72%[b]	$Tm(ClO_4)_3 \cdot nH_2O$	(i) Cl_2O_6 (ii) 100°C (1.33 Pa) or (ii) 245°C(1.33Pa)	$Tm(ClO_4)_3$ low. temp. $Tm(ClO_4)_3$ high. temp.
Lu_2O_3[e]	$HClO_4$, 72%[b]	$Lu(ClO_4)_3 \cdot nH_2O$	(i) Cl_2O_6 (ii) 100°C (1.33 Pa)	$Lu(ClO_4)_3$

[a] Labosi pur.
[b] Labosi analypur.
[c] See Ref. 3. Generally, Cl_2O_6 gives in a first step, $Ln(ClO_4)_3$, Cl_2O_6 and is removed under vacuum at T given in (ii).
[d] Fluka (> 99%).
[e] Aldrich (99.9%).
[f] Prolabo rectapur.
[g] Touzart and Matignon (99.9%).
[h] Apha Ventron (99.999%).
[j] Riedel-de Haën Ag (für Analyse).

substances and under shock. They must be handled with care and reactions must be continuously monitored.

The general methods of synthesis, purification, and handling of reagents have been previously described (3, 7, 19). Details of the synthesis as well as the origin and purity of the starting compounds are given in Table 1. For additional details see Ref. (3).

The hydrated perchlorates of La, Pr, Sm, Eu, Ho, Er, Tm, and Lu were prepared by slow dissolution of the corresponding oxides in boiling commercial perchloric acid. Slow dehydration at room temperature under vacuum (1.33 Pa) led to $Ln(ClO_4)_3 \cdot mH_2O$ with $m < 6$. When these hydrated complexes were treated with Cl_2O_6, only two chloryl salts, $(ClO_2)_{0.33}La(ClO_4)_{3.33}$ and $ClO_2Er(ClO_4)_4$, were isolated (3). Their thermal decomposition under vacuum (1.33 Pa) led to $Ln(ClO_4)_3$ complexes (Ln = La and Er) at 65 and 70°C, respectively. For other compounds, a mixture of $Ln(ClO_4)_3$ and Cl_2O_6 was generally obtained. To remove this intercalated or adsorbed Cl_2O_6, all of these complexes were heated at 100°C (1.33 Pa) before measurements. $Ce(CO_3)_3 \cdot nH_2O$ was prepared according to Imamoto (8) and subsequently treated with Cl_2O_6 to give $Ce(ClO_4)_3$.

X-Ray Powder Diffraction

In spite of their poor quality, a first observation of the X-ray powder patterns, obtained on a beryllium flat sample and using Cu$K\alpha$ radiation on an automated Philips PW1965/30 goniometer (9), shows that $Ln(ClO_4)_3$ complexes can be separated into two different groups of isostructural compounds. The first group includes La, Ce, Pr, Sm, Eu, Ho, Er, and Tm (low temperature form, LT) complexes, and the second group comprises Tm (high temperature form, HT) and Lu perchlorates.

High resolution X-ray diffraction patterns of europium, thullium (HT), and lutetium complexes were collected using the new diffractometer on beam line BM16 at the ESRF. A brief description of the line, the precision and resolution characteristics of the diffractometer, have been reported elsewhere (10). Owing to their high hygroscopicity, finely ground and sieved powders were sealed under extra dry argon into 0.5-mm thin-walled Lindeman glass capillaries. X-ray powder diffraction data were collected at room temperature with a monochromated incident beam of wavelenght 0.54994(1) Å. The wavelength and zero point were

TABLE 2
Details of Rietveld Refinement for $Eu(ClO_4)_3$ and $Lu(ClO_4)_3$

Formula	$Eu(ClO_4)_3$	$Lu(ClO_4)_3$
Space group	$P6_3/m$	$R3c$
Z	2	6
Wavelength (Å)	0.54994(1)	0.54994(1)
2θ range (°)	5.55–35.00	6.504–45.00
Step increment (2θ)	0.002	0.006
Number of reflections	259	445
Number of structure parameters	14	21
Number of profile parameters	9	10
Number of constrained distances	0	10
Number of atoms in asymmetric unit	5	6
R_F	0.0329	0.0387
R_B	0.0392	0.0410
R_p	0.0288	0.0460
R_{wp}	0.0525	0.0605

calibrated using the NIST Si standard 640*b* ($FWHM = 0.009°$ at 40° (2θ)). Data were scanned over $0° < 2\theta < 50°$ with a counting time of 0.38 s per point for 850 points per degree (2θ) in the scan range $0° < 2\theta < 30°$ and 0.28 s per point for 1242 points per degree (2θ) up to 30°. Data were normalized with various step lengths given in Table 2. The indexing of the powder patterns was carried out using the TREOR90 program (11). Rietveld refinements and profile matchings were performed using the FULLPROF program (12) on a PC computer.

STRUCTURE DETERMINATION

Indexing

The diffraction powder patterns were indexed on the basis of the first 30 observed lines giving the following results.

For $Eu(ClO_4)_3$, the best indexing solution with $M(30) = 42$ and $F_{30} = 80$ (.003967, 95) indicated an hexagonal unit cell with lattice parameters $a = 9.261(1)$ Å and $c = 5.730(1)$ Å. Systematic absences were consistent with the space group $P6_3/m$ indicating the existence of an isostructural relationship with $Yb(ReO_4)_3$ (13).

For $Tm(ClO_4)_3$ (HT) and $Lu(ClO_4)_3$, the patterns were indexed in hexagonal unit cells with figures of merit of $M(30) = 42$ and $F_{30} = 75$ (.002265, 142), and $M(30) = 28$ and $F_{30} = 55$ (.002582, 214), respectively. Nonrefined lattice parameters are $a = 8.132(1)$ Å and $c = 24.157(5)$ Å for thulium perchlorate (HT), and $a = 8.115(1)$ Å and $c = 24.008(1)$ Å for lutetium perchlorate. Both appear to be isostructural with $Sc(H_2PO_4)_3$, which crystallizes in the $R3c$ space group (14). Examination of systematic line absences in the patterns is in agreement with this assertion.

Structure Solutions and Refinements

Refinements were carried out using a pseudo-Voigt function for the peak shape profile with an angular variation of the mixing parameter η. Backgrounds were extracted by linear interpolation between several points in the overall angular range. A simplified two parameters form of the Berar and Baldinozzi asymmetry correction at low angles was adopted (15). Details of the Rietveld refinements for $Eu(ClO_4)_3$ and $Lu(ClO_4)_3$ are given in Table 2. Plots of the experimental and calculated X-ray diffraction patterns, and difference data after the final Rietveld refinements are depicted in Fig. 1. Using the same set of profile parameters, peak shape, and asymmetry, the profile matching option of FULLPROF allowed us to calculate the refined lattice parameters for other $Ln(ClO_4)_3$ compounds, with Ln = La, Ce, Pr, Sm, Ho, Er, and Tm (LT) (Table 3). Note that (i) the

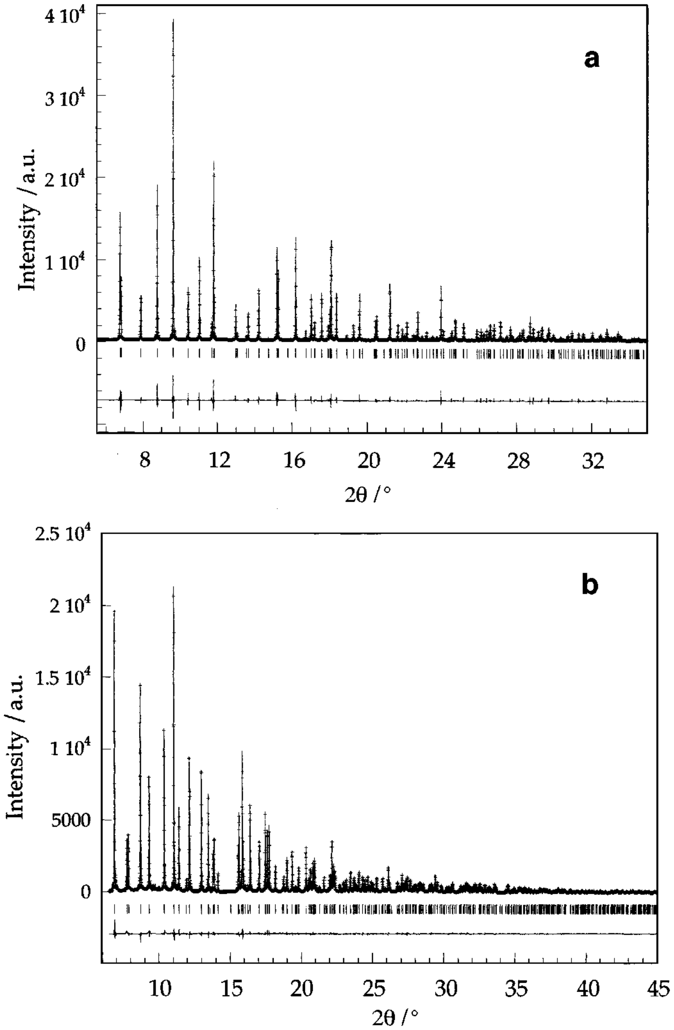

FIG. 1. Observed (line), calculated (crosses), and difference plots for (a) $Eu(ClO_4)_3$ and for (b) $Lu(ClO_4)_3$.

TABLE 3
Crystalline Data for Anhydrous Lanthanide Perchlorates

Compound	$La(ClO_4)_3$[a]	$Ce(ClO_4)_3$[a]	$Pr(ClO_4)_3$[a]	$Sm(ClO_4)_3$[a]	$Eu(ClO_4)_3$[b]	$Ho(ClO_4)_3$[a]	$Er(ClO_4)_3$[a]	$Tm(ClO_4)_3$ low temp.[a]	$Tm(ClO_4)_3$ high temp.[b]	$Lu (ClO_4)_3$[b]
Space group	$P6_3/m$	$P6_3/m$	$P6_3/m$	$P6_3/m$	$P6_3/m$	$P6_3/m$	$P6_3/m$	$P6_3/m$	$R3c$	$R3c$
Lattice Parameters/Å	$a = 9.400(3)$ $c = 5.918(1)$	$a = 9.378(1)$ $c = 5.875(1)$	$a = 9.365(4)$ $c = 5.844(3)$	$a = 9.259(3)$ $c = 5.746(2)$	$a = 9.25952(2)$ $c = 5.73029(1)$	$a = 9.218(1)$ $c = 5.618(1)$	$a = 9.201(1)$ $c = 5.590(1)$	$a = 9.211(3)$ $c = 5.563(1)$	$a = 8.13286(2)$ $c = 24.1586(1)$	$a = 8.11559(4)$ $c = 24.0047(1)$
Volume/$Å^3$	452.84(1)	447.42(1)	443.53(2)	426.68(2)	425.472(1)	413.42(1)	409.82(1)	408.72(2)	1383.849(1)	1369.196(1)
Z	2	2	2	2	2	2	2	2	6	6

[a] From data recorded on a Philips PW1965/35 laboratory goniometer.
[b] From data recorded on an ESRF BM16 diffractometer.

poorer quality of the data recorded with our nonmonochromated laboratory diffractometer results in lower accuracy of the lattice parameters, and (ii) the expected decrease of the volume of the lattice along the lanthanide series.

Since europium perchlorate appears to be isostructural with $Yb(ReO_4)_3$, the atomic coordinates of Yb, in the $2\bar{6}$ special position, and Re, in the $6m$ position, were used as starting positions for Eu and Cl atoms, respectively. Due to the large differences between reported distances for Re–O bonds and the expected Cl–O distances, the initial positions of the oxygen atoms were calculated from a relationship established elsewhere (16) [$d(M\text{–}O) = f(R)$, where M–O = the metal–oxygen distance and R = the Brown and Shanon effective ionic radii of the metallic center (17)] and the Cl–O distances and angles were set at values consistent with tridentate perchlorates (3). With one terminal oxygen atom per Cl, the multiplicity of the crystallographic position of this terminal oxygen should be 6. Since Cl–O distances are inconsistent with a $6\bar{1}$ position, O_2 atom should lie in a $6m$ position. These Eu, Cl, and O_2 positions constrain O_1 atoms to lie in the same (x, y) plane as Eu, Cl, and O_2 atoms, i.e. in a special $6m$ position. The two other oxygens should occupy a single general position ($12l$). In the final stage of the refinement, 24 parameters were refined, including the scale factor, 9 profile parameters and 14 structural parameters giving final intensity R-factors $R_F = 3.3\%$ and $R_B = 3.9\%$, and profile R-factors $R_p = 2.9\%$ and $R_{wp} = 5.3\%$. Final atomic positions and isotropic temperature parameters are given in Table 4.

For $Lu(ClO_4)_3$, $Sc(H_2PO_4)_3$ was used as a model. In the Rietveld refinement, scandium and phosphorus atomic positions were used as starting coordinates for the heaviest atoms, Lu and Cl, respectively, but at this stage it was not possible to correctly fit the oxygen positions. In $Sc(H_2PO_4)_3$, bidentate phosphates build a distorted octahedral environment around Sc atoms, while for lanthanide perchlorates a higher coordination might be expected. For the $P6_3/m$ form of other lanthanide elements a coordination number of nine is observed. On the basis of ninefold coordinated Lu atoms, the initial positions of oxygen atoms were then extracted from the $d(M\text{–}O) = f(R)$ relation (see above) and the $[ClO_4]$ geometry was kept consistent with a tridentate perchlorate. Thirty-one parameters were refined including 10 profile parameters and 21 structural parameters (atomic coordinates and isotropic thermal factors). The refinement converged to final R factors, $R_F = 3.9\%$, $R_B = 4.1\%$, $R_p = 4.6\%$ and $R_{wp} = 6.0\%$. Atomic coordinates and isotropic thermal parameters are given in Table 5.

DESCRIPTION OF THE STRUCTURES AND DISCUSSION

In both the structural types of the studied $Ln(ClO_4)_3$ complexes, tridentate perchlorates form channeled three-

TABLE 4
Refined Atomic Coordinates and Thermal Parameters for $Eu(ClO_4)_3$

Atom	x	y	z	B_{iso} ($Å^2$)
Eu	0.33333	0.66667	0.25	0.88(2)
Cl	0.3845(3)	0.2929(2)	0.25	1.14(5)
O_1	0.4401(5)	0.4696(5)	0.25	0.96(12)
O_2	0.2138(6)	0.1923(6)	0.25	1.37(13)
O_3	0.5432(3)	0.7443(4)	− 0.0456(4)	1.89(9)

TABLE 5
Refined Atomic Coordinates and Thermal Parameters for $Lu(ClO_4)_3$

Atom	x	y	z	B_{iso} ($Å^2$)
Lu	0.0	0.0	0.5598(1)	1.32(1)
Cl	0.3456(6)	0.3118(5)	0.0	2.67(7)
O_1	0.4407(9)	0.5052(7)	0.0074(3)	3.10(23)
O_2	0.3442(9)	0.2121(9)	0.0497(2)	4.11(23)
O_3	0.1450(8)	0.2315(9)	− 0.0132(3)	3.44(20)
O_4	0.4305(8)	0.2562(9)	− 0.0430(2)	2.31(21)

TABLE 6
Distances (Å) and Angles (°)

Eu(ClO$_4$)$_3$				Lu(ClO$_4$)$_3$			
Eu–O$_1$ (3×)	2.471(4)			Lu–O$_2^{I}$ (3×)	2.452(6)	^{V}O$_2$–Lu–O$_2^{VI}$	119.0(1)
Eu–O$_3$ (6×)	2.404(3)			Lu–O$_3^{I}$ (3×)	2.403(7)	^{I}O$_3$–Lu–O$_3^{VI}$	72.7(3)
				Lu–O$_4^{II}$ (3×)	2.284(6)	^{VII}O$_4$–Lu–O$_4^{II}$	79.9(2)
		O$_1$–Cl–O$_2$	113.8(3)	Cl–O$_1$	1.371(6)	O$_1$–Cl–O$_2$	112.2(4)
Cl–O$_1$	1.453(4)	O$_1$–Cl–O$_3$	108.5(2)	Cl–O$_2$	1.434(7)	O$_1$–Cl–O$_3$	113.9(5)
Cl–O$_2$	1.389(5)	O$_2$–Cl–O$_3$	110.2(2)	Cl–O$_3$	1.438(6)	O$_1$–Cl–O$_4$	111.7(4)
Cl–O$_3$ (2×)	1.470(3)	O$_3$–Cl–O$_3$	105.3(2)	Cl–O$_4$	1.454(7)	O$_2$–Cl–O$_3$	103.7(4)
						O$_2$–Cl–O$_4$	106.9(4)
						O$_3$–Cl–O$_4$	107.9(4)
O$_1$...O$_3^{I}$	2.742(4)	O$_1$–Eu–O$_3$	70.0(1)	O$_2$...O$_3$	2.274(9)		
O$_1$...O$_3^{II}$	2.797(4)	O$_1$–Eu–O$_3^{V}$	68.5(1)	O$_2$...O$_4$	2.307(8)		
Eu...Eu^{III}	5.73029(1)	O$_3$–Eu–O$_3$	75.7(1)	O$_3$...O$_3^{III}$	2.85(1)	Lu...Lu^{VIII}	6.161(0)
Eu...Cl	3.721(2)	O$_1$–Eu–O$_1$	120.0(0)	O$_4$...O$_4^{IV}$	2.93(1)	Lu...Cl	3.038(4)
Eu...Cl^{IV}	3.768(1)						

Note. Symmetry operations for Eu(ClO$_4$)$_3$: I, $y-x$, $1-x$, $3/2-z$; II, x, y, $3/2-z$; III, x, y, $1+z$; IV, $1+x$, $1+y$, $-1/2+z$; V, $x-y$, $1-x$, z.
Symmetry operations for Lu(ClO$_4$): I, $-y$, $-x$, $1/2+z$; II, $x-2/3$, $y-1/3$, $z+2/3$; III, $-y$, $x-y$, z; IV, $1+y-x$, $1-x$, z; V, x, $x-y$, $z+1/2$; VI, $y-x$, y, $1/2+z$; VII, $y-x+1/3$, $2/3-x$, $z+2/3$; VIII, $1/3+x$, $2/3+y$, $2/3+z$.

dimensional networks in which lanthanide atoms are ninefold coordinated. However, the resulting polyhedra as well as the coordination mode of the perchlorates differ significantly between the structures. The corresponding main interatomic distances and angles are collected in Table 6.

The molecular structures of Eu(ClO$_4$)$_3$ and *Ln*(ClO$_4$)$_3$ with *Ln* = La, Ce, Pr, Sm, Ho, Er, and Tm (low temperature form) comprise tridentate perchlorates which form catenated rings including six metal atoms (Eu...Eu distance at 5.73 Å). As depicted in Fig. 3, these rings are linked to one another to form channels along the *c* axis. Eu atoms are surrounded by nine oxygen atoms belonging to nine tridentate ClO$_4$ groups, building a slightly distorted tricaped trigonal prism, with six Eu–O$_3$ at a mean distance of 2.404 Å forming the regular trigonal prism and three O$_1$ atoms capping the rectangular faces at a longer distance from Eu (2.471 Å). These O$_1$ atoms do not strictly correspond to the center of the rectangular faces but are displaced by a slight rotation around the threefold axis in the (Eu, O$_1$, O$_1$, O$_1$) plane giving two different O$_1$...O$_3$ distances at 2.797 and 2.742 Å. These Eu–O$_3$ and Eu–O$_1$ distances are close to those expected from the effective ionic radii of Shanon and Prewitt (17), and are in good agreement with EXAFS results on praseodymium Pr(ClO$_4$)$_3$ complexes (Pr–O = 2.51 Å) (4)

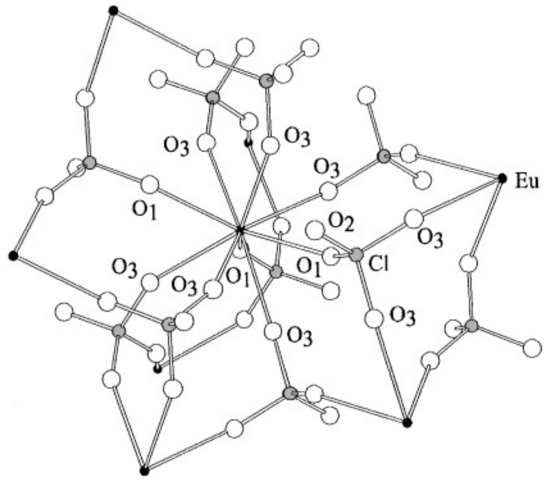

FIG. 2. Molecular structure of Eu(ClO$_4$)$_3$ showing the coordination shell around Eu atoms.

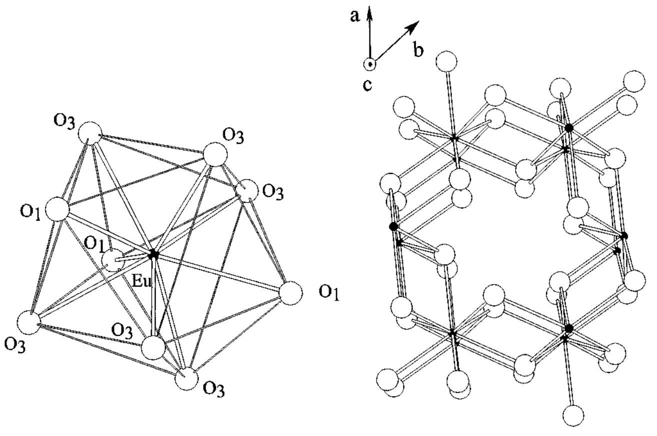

FIG. 3. Coordination polyhedra around Eu atom and a schematic packing in the structure of Eu(ClO$_4$)$_3$. Black circles represent Eu atoms and large open circles represent perchlorate groups.

and on $Gd(ClO_4)_3$ (Gd–O = 2.40 Å) (18). Note that these EXAFS results have also predicted nine chloride atoms at mean distances of 3.90 Å for $Pr(ClO_4)_3$ and 3.76 Å for $Gd(ClO_4)_3$, which agree with Eu...Cl at 3.72 and 3.76 Å. The distances and angles of the coordinated perchlorates are characteristic of tridentate ClO_4 and the distortions are of the same order of magnitude as those found for nickel and cobalt perchlorate (19) or in $Yb(ClO_4)_3 \cdot H_2O$ (20).

The immediate structural environment of lutetium (or thulium) and a schematic representation of the packing of $Lu(ClO_4)_3$ (or $Tm(ClO_4)_3$ (high temperature form)) are depicted in Figs. 4 and 5, respectively. The molecular structure of the $Lu(ClO_4)_3$ complex consists of infinite layers of lanthanide atoms built through simultaneously bridging and chelating tridentate perchlorates. Through every Lu atom, these layers are linked by the same kind of tridentate ClO_4 forming channels of two-membered $Lu_2Cl_3O_{12}$ rings (Lu...Lu = 6.161 Å). The nine closest oxygen atoms around lutetium, belonging to six different ClO_4 groups, build a polyhedron resembling more closely a tricaped trigonal antiprism than the above described prism for Eu compound. Trigonal faces, formed by three O_3 atoms, with $Lu–O_3$ = 2.403 Å, and three O_4, with $Lu–O_4$ = 2.284 Å, are twisted by about 20° around the threefold axis. The Lu environment is completed by three O_2 atoms at 2.452 Å from Lu, capping the “rectangular” faces of the “prism.” Moreover, Lu is out of the plane formed by O_2 atoms and the angle between $Lu–O_2$ bonds and the C_3 axis is about 92°, moving these oxygens closer from O_3 atoms. These distortions are consistent with the fact that O_2 and O_3 atoms belong to the same perchlorate group, giving it its chelating character. O_4 is the bridging oxygen through shorter $Lu–O_4$ and longer $Cl–O_4$ contacts. This original double character of the perchlorate ligand, simultaneously bridging and chelating, leads to distances and angles ranging from 1.371 to 1.454 Å, and from 103.7 to 113.9°, respectively, comparable to those of perchlorate in $Eu(ClO_4)_3$ described above.

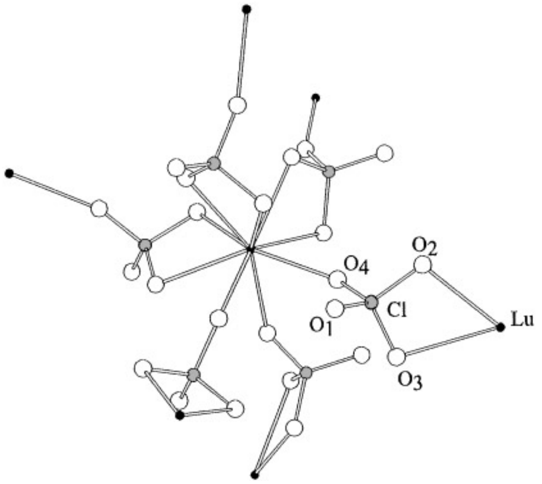

FIG. 4. Molecular structure of $Lu(ClO_4)_3$ showing the coordination shell around Lu atoms.

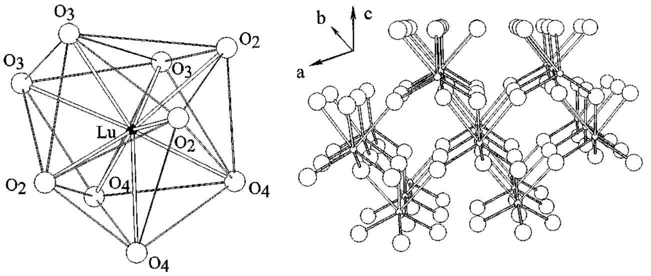

FIG. 5. Coordination polyhedra around Lu atom and a schematic packing in the structure of $Lu(ClO_4)_3$. Small open circles represent Lu atoms and large open circles represent perchlorate groups. Gray bonds indicate the chelating character of ClO_4.

CONCLUSION

Lanthanide complexes are known to show some heterogeneities in their structures along the series as in chloride (21), hydroxi-nitrate (22), oxide (23), or oxychloride (24) compounds. This is also confirmed by the present work. The studied perchlorates of lanthanides crystallize in two distinct groups of isostructural species. Erbium and thulium exist in either form depending on the final temperature of synthesis. From Er to Lu, the temperature of the irreversible transition from low to high temperature form decreases with the atomic number. However, the temperature of the phase transition of $Er(ClO_4)_3$ is close to that of oxychloride formation, and only traces of the corresponding high temperature form were detected during the thermolysis. On the other hand, for the lutetium complex, the thermal Cl_2O_6 desorption, at around 100°, did not allow us to synthesize the low temperature form.

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