

Thermal Behavior and X-ray Powder Diffraction Structures of Two Polymorphic Phases of Anhydrous $\text{Yb}(\text{ClO}_4)_3$

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The chemical dehydration of $\text{Yb}(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ by chlorine trioxide leads to a low-temperature form (LT) of anhydrous perchlorato complexes of ytterbium(III). By controlled thermolysis of this compound, a high-temperature form (HT) of $\text{Yb}(\text{ClO}_4)_3$ was obtained. Its thermal decomposition leads to the corresponding oxide chloride, $\text{Yb}_3\text{O}_4\text{Cl}$, as a fine powder. The structures of the two polymorphic phases of $\text{Yb}(\text{ClO}_4)_3$ were determined by Rietveld analysis of high-resolution X-ray powder data (BL16, ESRF). The LT form crystallizes in a hexagonal $P6_3/m$ unit cell ($a = 9.219\ 70(7)\ \text{\AA}$, $b = 5.535\ 18(3)\ \text{\AA}$, and $Z = 2$). For the HT form, the space group is $R3c$ ($a = 8.124\ 06(3)\ \text{\AA}$, $b = 24.0818(1)\ \text{\AA}$, and $Z = 6$). The thermal decomposition pathway was also determined with the aid of TGA measurements and Raman spectroscopy.

Introduction

Although perchloric acid was discovered at the beginning of the 19th century,¹ the chemistry of unsolvated perchlorates is relatively young considering that it was only in 1961 that Hathaway and Underhill demonstrated, by infrared spectroscopy of anhydrous $\text{Cu}(\text{ClO}_4)_2$, the coordinating ability of the perchlorate group.² During the last four decades more than 100 unsolvated perchlorato complexes or salts of numerous elements over a wide range of the periodic table have been prepared by reliable synthetic methods.^{3–6} This emphasizes the coordinating properties of $[\text{ClO}_4]$, which can act, in the absence of a strong base, as a remarkable tetrahedral assembling ligand. Some of these compounds, particularly those with rare earths, have been successfully used in catalytic processes.^{7,8} However, the description of the crystalline and molecular edifice of these compounds, essential for the knowledge and understanding of their reactivity and physical properties, is limited to less than

15 single-crystal X-ray or EXAFS structures.^{9–14} Due to the strong oxidative properties and very weak basicity of ClO_4 , there is, at the present time, no suitable solvent for the preparation and crystallization of anhydrous perchlorates. They are generally obtained as microcrystalline powders rather than single crystals.

The significant improvement, over the past 10 years, of X-ray powder diffraction techniques allows the structure of ever more complex species to be solved.¹⁵ This adds attractive prospects to both the crystalline and molecular description of perchlorato

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complexes, especially in the new emerging field of their use as precursors for ceramics. Perchlorates decompose at moderate temperatures, below 250–300 °C, giving fine powders, generally of oxides. This alternative preparative method for ceramics has been largely developed using nitrates¹⁶ but could now be envisaged also with perchlorato complexes. To control the structure and morphology of the resulting materials, it remains of importance to know the structure of the precursor as well as those of the intermediate solids.

In a previous paper, we have fully characterized the channeled structure of Yb(ClO₄)₃·H₂O.¹⁴ We describe here its chemical dehydration by chlorine trioxide leading, in a first step, to an anhydrous low-temperature form (LT) of perchlorato complexes of ytterbium(III). The controlled thermolysis of this compound, as well as of the monohydrate, allows a high-temperature form (HT) of anhydrous Yb(ClO₄)₃ to be isolated. Its thermal decomposition leads to the corresponding oxide chloride, Yb₃O₄-Cl, as a fine powder. The structures of the two polymorphic phases of anhydrous Yb(ClO₄)₃ have been determined by Rietveld analysis of high-resolution X-ray powder diffraction data. The thermal decomposition pathway was also determined by TGA measurements and Raman spectroscopy.

Experimental Section

Caution! Chlorine trioxide and perchlorates are highly reactive compounds particularly on contact with organic substances and under shock. They must be handled with care, and reactions must be continuously monitored.

Materials. Yb₂O₃ (Aldrich, 99.9%) was used without further purification. Chlorine trioxide, Cl₂O₆, and perchlorates were prepared in a vacuum line according to previously given methods.⁶ Because of their hygroscopicity, reactants as well as products were handled in a glovebox filled with extra dry nitrogen or argon. Hydrated ytterbium perchlorate was prepared by dissolution of the corresponding oxide in boiling commercial perchloric acid (Labosi, Analphur, 72%). Slow dehydration at room temperature under vacuum (1.33 Pa) led to Yb(ClO₄)₃·mH₂O with $m < 6$. This white Yb(ClO₄)₃·mH₂O, stored in one of the two arms of a reactor sealed under vacuum (1.33 Pa), was heated to 170 °C while the other arm was cooled with liquid nitrogen. After a few days colorless needles of Yb(ClO₄)₃·H₂O were isolated in the warmed arm.

Synthesis of Yb(ClO₄)₃, Low-Temperature Form (LT). Yb(ClO₄)₃ (LT) was synthesized by treating Yb(ClO₄)₃·mH₂O or Yb(ClO₄)₃·H₂O with Cl₂O₆. At this stage in the synthesis of anhydrous perchlorates, a chloryl salt is usually obtained. However, as has been observed for other lanthanides,⁶ no ytterbium chloryl salt was isolated. To remove absorbed or intercalated traces of chlorine trioxide, the resulting product, Yb(ClO₄)₃·cCl₂O₆, was heated at 70 °C (1.33 Pa).

Synthesis of Yb(ClO₄)₃, High-Temperature Form (HT). Under dynamic vacuum (1.33 Pa) at 175 °C, the complete loss of the coordinated water from Yb(ClO₄)₃·H₂O leads to the high-temperature form of Yb(ClO₄)₃. This HT form can also be obtained by thermal treatment of the low-temperature form of Yb(ClO₄)₃. After a few hours at 200 °C (1.33 Pa), the high-temperature form of Yb(ClO₄)₃ is quantitatively obtained. This phase transformation from the LT to the HT form is irreversible.

Physical Measurements. Raman spectra were collected at room temperature with a DILOR spectrometer using a Spectra Physics argon laser (5145 or 4880 Å). Samples were contained in sealed Pyrex tubes (outside diameter 4 or 8 mm).

X-ray Powder Analysis of Yb(ClO₄)₃, Low- and High-Temperature Forms. High-resolution X-ray diffraction patterns of these two complexes were collected using the new diffractometer on beam line BM16 at the European Synchrotron Radiation Facility (ESRF). A brief

Table 1. Details of Rietveld Refinements for Yb(ClO₄)₃ LT and HT Forms

compd	Yb(ClO ₄) ₃ (LT)	Yb(ClO ₄) ₃ (HT)
space group	<i>P</i> 6 ₃ / <i>m</i>	<i>R</i> 3 <i>c</i>
lattice	<i>a</i> = 9.219 70(7)	<i>a</i> = 8.124 06(3)
params (Å)	<i>c</i> = 5.535 18(3)	<i>c</i> = 24.081 8(1)
<i>Z</i>	2	6
X-ray wavelength (Å)	0.549 94(1)	0.549 94(1)
2θ range (deg)	6.50–35.00	6.50–45.00
step incr (2θ)	0.0025	0.005
<i>N</i> _{reflens}	251	446
<i>N</i> _{struct params}	14	21
<i>N</i> _{profile params}	9	10
<i>N</i> _{restraints}	0	10
<i>N</i> _{atoms}	5	6
<i>R</i> _F	0.0366	0.0414
<i>R</i> _B	0.0397	0.0472
<i>R</i> _p	0.0508	0.0437
<i>R</i> _{wp}	0.0728	0.0584

description of the line, the precision, and resolution characteristics of the diffractometer have been reported elsewhere.¹⁷ Owing to their high hygroscopicity, finely ground and sieved white 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 wavelength 0.549 94(1) Å. The wavelength and zero point were calibrated using the NIST Si standard 640b (fwhm = 0.009° at 40° (2θ)). Data were scanned over 0° < 2θ < 50° with a counting time of 0.38 s per point for 850 points per degree (2θ) in the scan range 0° < 2θ < 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 1. The indexing of the powder patterns was carried out using the TREOR90 program.¹⁸ Rietveld refinements were performed using the FULLPROF program on a PC computer.¹⁹

The diffraction powder patterns were indexed on the basis of the first 25 observed lines with the following results:

For Yb(ClO₄)₃(LT), the best indexing solution with *M*(25) = 122 and *F*₂₅ = 213 (0.001951, 58) indicated an hexagonal unit cell with lattice parameters *a* = 9.2163(4) Å and *c* = 5.5346(3) Å. Systematic absences were consistent with the space group *P*6₃/*m* indicating the existence of an isostructural relationship with the related anhydrous perhenate compound, Yb(ReO₄)₃.²⁰

For Yb(ClO₄)₃(HT) the patterns were indexed in hexagonal unit cells with figures of merit of *M*(25) = 60 and *F*₂₅ = 135 (0.001363, 142). Nonrefined lattice parameters were *a* = 8.124(4) Å and *c* = 24.08(2) Å. This compound appears to be isostructural with Sc(H₂PO₄)₃, which crystallizes in the *R*3*c* space group.²¹ Examination of systematic line absences in the patterns is in agreement with this assignment.

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-parameter form of the Berar and Baldinozzi asymmetry correction at low angles was adopted.²² Details of the Rietveld refinements for Yb(ClO₄)₃, LT and HT forms, are given in Table 1. Plots of the experimental and calculated X-ray diffraction patterns and difference data after the final Rietveld refinements are depicted in Figure 2.

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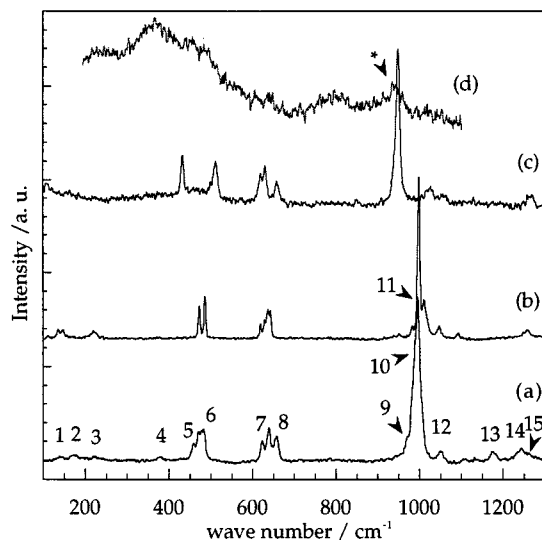


Figure 1. Raman spectra of $\text{Yb}(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ (a), $\text{Yb}(\text{ClO}_4)_3$ LT (b), $\text{Yb}(\text{ClO}_4)_3$ HT (c), and $\text{Yb}_3\text{O}_4\text{Cl}$ (d). Assignments done for the monohydrated compound can be transposed for anhydrous complexes: 1 lattice modes (trid); 2, lattice modes (bid); 3, lattice modes (trid); 4, H_2O libration; 5, δ_s (bid); 6, δ_s (trid); 7, δ_{as} (bid, trid); 8, δ_{as} (bid); 9, $\nu_{as}(\text{ClO}_b)$ (bid); 10, $\nu_s(\text{ClO}_b)$ (bid); 11, $\nu_s(\text{ClO}_b)$ (trid); 12, $\nu_{as}(\text{ClO}_b)$ (trid); 13, $\nu_s(\text{ClO}_t)$ (bid); 14, $\nu_{as}(\text{ClO}_t)$ (bid); 15, $\nu(\text{ClO})$ (trid). Bid and trid are abbreviations for respectively bidentate and tridentate perchlorato groups, and b and t subscripts, for respectively bridging and terminal oxygen atoms, *, perchlorate traces (?).

Results and Discussion

Raman Spectroscopy. To establish structural models before the recording of X-ray data, the chemical and thermal dehydration of $\text{Yb}(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ leading to the two different forms, low (LT) and high temperature (HT), of anhydrous $\text{Yb}(\text{ClO}_4)_3$ were followed by Raman spectroscopy.

The spectra of the monohydrate and LT complexes, depicted in Figure 1, look similar, suggesting the same coordination mode of the $[\text{ClO}_4]$ groups in both complexes. The large splitting of the stretching mode frequencies between 900 and 1300 cm^{-1} and the complexity of the spectra in the deformation range unambiguously show that the perchlorato groups are strongly coordinated to the ytterbium. The line frequencies and their shape agree with those of $\text{Ce}(\text{ClO}_4)_3$ ²⁵ or $\text{M}(\text{ClO}_4)_2$ ($\text{M} = \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}$ or Cd),^{5,12,13,26} in which the $[\text{ClO}_4]$ groups are bridging tridentate. This coordination mode is also consistent with the molecular structure of $\text{Yb}(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$, which includes simultaneously tridentate and bidentate perchlorato groups.¹⁴ Note that this double bonding mode also explains the greater width of the $\nu(\text{ClO}_b)$ (O_b : bridging oxygen) line at 998 cm^{-1} in the hydrated form than in the anhydrous. Moreover, the moderate shift in frequency of this stretching line $\nu(\text{ClO}_b)$ from 998 cm^{-1} for the LT compound to 992 cm^{-1} for $\text{Yb}(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ confirms a stronger coordination of the perchlorate in the anhydrous compound. Given the stoichiometry of the LT complex and the bonding mode, a 9-fold coordination for the metal is deduced.

The spectrum of the HT form is different. Although the line shape and frequency, around 1250 cm^{-1} , remain analogous to

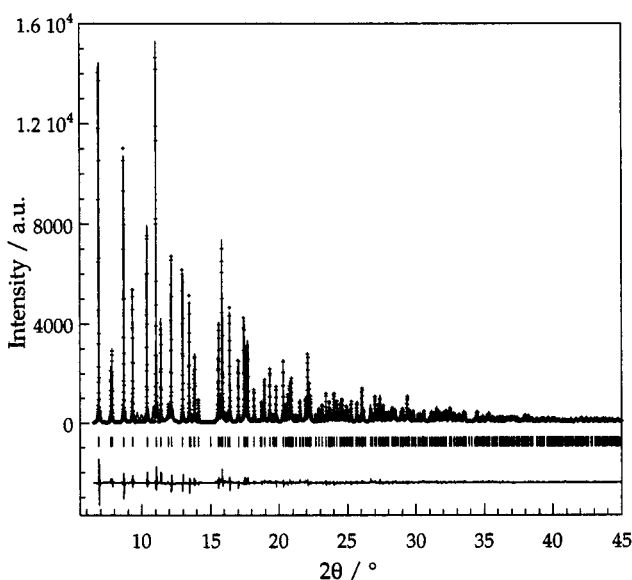
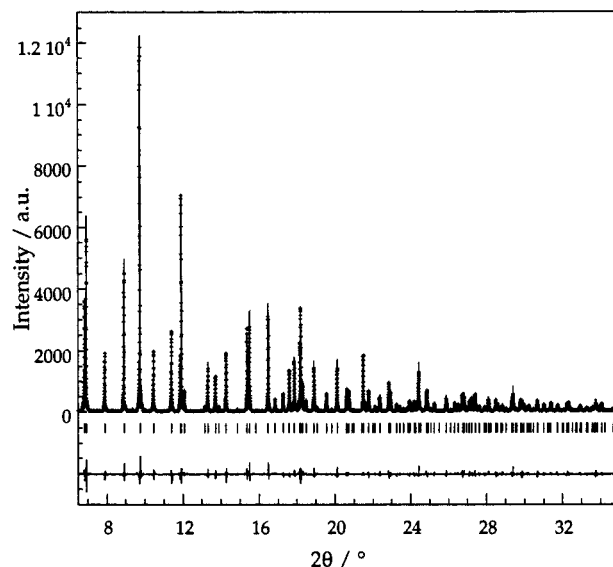


Figure 2. Observed (line), calculated (crosses), and difference plots and peak markers for $\text{Yb}(\text{ClO}_4)_3(\text{LT})$ (top) and $-(\text{HT})$ (bottom) after the final Rietveld refinement.

those observed in the monohydrated and LT forms, the $\nu(\text{ClO}_b)$ symmetric and antisymmetric modes are shifted to lower frequencies by about 50 cm^{-1} . In the same way, the deformation modes at 620 cm^{-1} (δ_{antisym}) and between 400 and 500 cm^{-1} (δ_{sym}) are strongly split in energy. Nevertheless, on the basis of this first vibrational analysis, a tridentate mode of the perchlorate coordination could also be expected for this HT complex. However, this splitting of the valency as well as the deformation modes, which can be compared with those of the chelating bidentate $[\text{ClO}_4]$ in $\text{Ti}(\text{ClO}_4)_4$,¹⁰ is characteristic of a high level of constraint in the perchlorate. Instead of an usual bridging mode, a chelating character of the supposed tridentate $[\text{ClO}_4]$ could be envisaged.

At $295 \text{ }^\circ\text{C}$ under reduced pressure (1.33 Pa), $\text{Yb}(\text{ClO}_4)_3$ HT form loses 45% of its weight corresponding to decomposition to $\text{Yb}_3\text{O}_4\text{Cl}$. The Raman spectrum of this ytterbium oxide chloride shows two large bands centered at 400 cm^{-1} corresponding to $\nu(\text{YbO})$ modes.

Structural Solutions. Since $\text{Yb}(\text{ReO}_4)_3$ appears to be isostructural with LT ytterbium perchlorate, the atomic coordinates of the Yb, Re, and O atoms were used as starting

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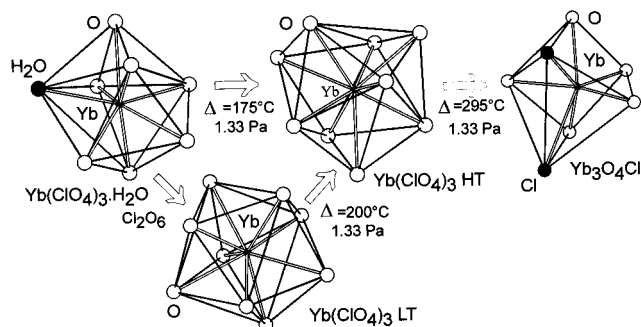


Figure 3. Ytterbium coordination polyhedra at various stages of thermolysis.

positions for Yb, Cl, and O atoms, respectively. 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 $R_F = 3.7\%$ and $R_B = 4.0\%$ and profile R -factors $R_p = 5.1\%$ and $R_{wp} = 7.3\%$.

$\text{Sc}(\text{H}_2\text{PO}_4)_3$ was used as model for the HT form. In the Rietveld refinement, scandium and phosphorus atomic positions were used as starting coordinates for the heaviest atoms, Yb and Cl, respectively, but at this stage, it was not possible to correctly fit the oxygen positions. In $\text{Sc}(\text{H}_2\text{PO}_4)_3$, bidentate phosphato groups build a distorted octahedral environment around Sc atoms, while for lanthanide perchlorato complexes a higher coordination, up to eight, might be expected. In view of the Raman spectroscopy results, the $[\text{ClO}_4]$ groups are tridentate. According to the stoichiometry of this compound, a 9-fold coordination of the ytterbium atoms should be considered. The initial positions of oxygen atoms were then calculated from a relationship established elsewhere²³ [$d(\text{M}-\text{O}) = f(R)$ where $d(\text{M}-\text{O}) = \text{metal}-\text{oxygen}$ distance and $R = \text{Brown and Shanon effective ionic radii of the metallic center}^{24}$], while Cl–O distances and angles were constrained at values consistent with coordinated tridentate perchlorato groups. A total of 31 parameters were refined including 10 profile parameters and 21 structural parameters (atomic coordinates and isotropic thermal factors), while 10 distances were constrained. The refinement converged to final R factors, $R_F = 4.1\%$, $R_B = 4.7\%$, $R_p = 4.4\%$, and $R_{wp} = 5.9\%$.

Structural Relations. In both structural types of the studied perchlorato complexes of ytterbium, tridentate perchlorato groups and also bidentate groups for the monohydrated compound, lead to channeled three-dimensional networks. However, as shown in Figure 3, the coordination polyhedra around Yb atoms as well as the coordination modes of the perchlorates differ significantly between the structures.

In $\text{Yb}(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$, four bidentate and three tridentate perchlorato groups, and one H_2O molecule, build a distorted square antiprism of eight oxygen atoms around ytterbium. The structure comprises catenated rings including six Yb atoms ($\text{Yb}-\text{Yb}$ distances range from 5.77 to 5.92 Å) forming large channels that contain water molecules. When these H_2O molecules are removed, the three-dimensional channeled structure remains, even though bidentate groups become tridentate in the LT anhydrous form. These Yb atoms are thus coordinated by nine oxygen atoms belonging to nine bridging tridentate ClO_4 groups, building a slightly distorted tricapped trigonal prism. The three capping O atoms do not strictly correspond to the center

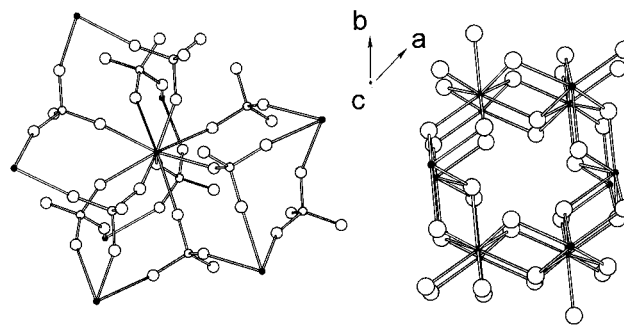


Figure 4. Left: Molecular structure of $\text{Yb}(\text{ClO}_4)_3(\text{LT})$ form showing the coordination shell around Yb atoms. Black circles represent Yb, large open circles are for O, and medium open circles are for Cl atoms. Right: Schematic packing. Black circles are for Yb, and large open circles represent perchlorato groups.

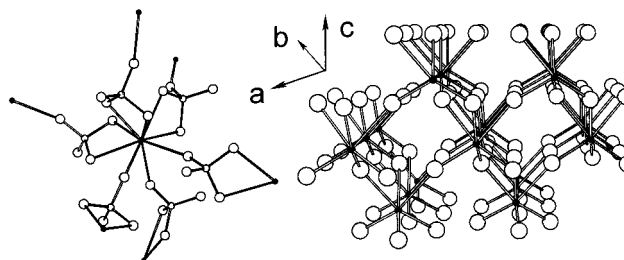


Figure 5. Left: Molecular structure of $\text{Yb}(\text{ClO}_4)_3(\text{HT})$ form showing the coordination shell around Yb atoms. Black circles represent Yb, gray circles are for Cl, and open circles are for O atoms. Right: Schematic packing. Black circles are for Yb, and large open circles represent perchlorato groups.

of the rectangular faces but are displaced by a slight rotation around the 3-fold axis. The $\text{Yb}-\text{O}$ distances, ranging from 2.42 to 2.46 Å, are close to those expected from the effective ionic radii of Shanon and Prewitt²⁴ and are in good agreement with previous EXAFS results on praseodymium $\text{Pr}(\text{ClO}_4)_3$ complexes ($\text{Pr}-\text{O} = 2.51$ Å)²⁷ and on $\text{Gd}(\text{ClO}_4)_3$ ($\text{Gd}-\text{O} = 2.40$ Å).²⁸ Note that these EXAFS results have also predicted nine chloride atoms at mean distances of 3.90 Å for $\text{Pr}(\text{ClO}_4)_3$ and 3.76 Å for $\text{Gd}(\text{ClO}_4)_3$, which agree with $\text{Yb} \cdots \text{Cl}$ at 3.66 and 3.72 Å in the LT form. As for $\text{Yb}(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$, the structure of this LT compound could also be described on the basis of six-membered rings (see Figure 4). The $\text{Yb}-\text{Yb}$ distance decreases to 5.54 Å because of the loss of water molecules and a slightly different packing.

A schematic representation of the packing of the HT form is depicted in Figure 5. The molecular structure consists of infinite layers of lanthanide atoms built through simultaneously bridging and chelating tridentate perchlorato groups. Note that this double character is (i) described accurately for the first time in perchlorato complexes and (ii) in perfect agreement with the characteristics of the Raman spectra (see Figure 1). The nine closest oxygen atoms around ytterbium, belonging to six different ClO_4 groups, build a polyhedron resembling more closely a tricapped trigonal antiprism than the above-described prism for LT compound. Trigonal faces are twisted by about 20° around the 3-fold axis. The ytterbium environment is completed by three oxygen atoms at longer distances, capping the “rectangular” faces of the “prism”. These distortions are consistent with the simultaneously bridging and chelating character of the perchlorato group. Three bridging oxygens

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complete the coordination of Yb through shorter contacts. This original double character of the perchlorate groups leads to distances and angles ranging from 1.37 to 1.47 Å, and from 102.8 to 113.3°, respectively, comparable to those of perchlorate in the LT form described above.

At 295 °C, due to the reduction from Cl(VII) to Cl(-I) during the thermolysis of the Yb(ClO₄)₃ HT form, the structure of the resulting ytterbium oxide chloride, Yb₃O₄Cl, is completely rebuilt on the basis of a square-based pyramid of oxygen atoms around Yb (Yb–O distances range from 2.14 to 2.27 Å). Two faces of this polyhedron are capped by chlorine atoms through long Yb–Cl contacts (3.11 Å).²⁹ Note that this material is

obtained as a fine dispersed powder. The size of the spherical particles was estimated by electron microscopy at 0.2–0.5 μm.

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Supporting Information Available: Final fractional coordinates (Tables S2 and S3) and bond distances and angles (Table S4) (2 pages). Ordering information is given on any current masthead page.

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