JOURNAL OF SOLID STATE CHEMISTRY **50**, 129–132 (1983)

BRIEF COMMUNICATION

Crystal Structure of $Yb(OH)_3$

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Received June 14, 1983

Introduction

Much work has been accomplished in the past decade regarding structural analyses and trends of the lanthanide trihydroxides (*1–5*). Researchers have tried (with little success) to prepare crystals of hexagonal ytterbium trihydroxide suitable for single-crystal X-ray diffraction analysis. This inability to isolate the product can be attributed to the ease with which $Yb(OH)_3$ transforms to YbOOH. A similar ease of transformation has been observed with cubic $Lu(OH)_3$ to monoclinic LuOOH (*6*). The most noted study dealing with the production of the title compound involved investigations on crystalline hydroxides of the rare earths by Fricke and Dürrwächter (*7*) using hydrothermal methods. The determined hexagonal lattice parameters obtained from powder X-ray examination were $a = 6.22$ and $c = 3.50$ Å. Since investigations of the morphological and structural properties of the lathanide hydrous oxides and hydroxides are part of our overall research program, it has been deemed necessary to complete the study of the hexagonal trihydroxides of the lanthanoid series. This completion is needed in order to make essential comparisons and so that parallels can be drawn to the corresponding actinoid series. Linkage between the actinide and lanthanide (Ln) trihydroxides has been established by demonstrating that $Am(OH)_3$ and $Cm(OH)_3$, as well as the radioactive lanthanide $Pm(OH)_3$, are isotypic to the $Ln(OH)_3$ compounds (*8–10*).

Experimental

Single crystals of the hexagonal trihydroxide of Yb were grown by hydrothermal aging at 421 K. Without further purification, ytterbium oxide obtained commercially (purity, 99.9%) and 5.5 *N* NaOH were placed into a Teflon aging tube. After 36 hr of hydrothermal treatment at the optimal temperature the thermostat of the heating oven was lowered to 353 K so as not to shock the system before cooling to room temperature. $Yb(OH)_3$ crystals, which were mixed with YbOOH crystalline material, were thoroughly washed free of any possible residual base (pH 7).

A single hexagonal-prismatic crystal of the title compound (0.078 × 0.078 × 0.180

0022-4596/83 $3.00

mm) was selected and mounted on an Enraf-Nonius CAD-4 automated diffractometer equipped with a dense graphite monochromator, which is assumed to be ideally imperfect, and a Si(Li) solid-state detector. A routine application of the energy dispersive detector is to allow routine fluorescence X-ray data to be collected on the same single crystal from which X-ray single-crystal data will be collected. Yb was quickly verified qualitatively from the appropriate identifying Lα, L$_{\beta_1}$, and L$_{\beta_2}$ lines. The orientation matrix used for the data collection (T = 290 K) and the lattice parameters were obtained from a least-squares fit of 25 centered reflections. Intensities were measured by the Ω–2θ scan technique at a rate of 0.38–3.35° min^{-1}, determined by a fast prescan of 3.35° min^{-1} in the range of $1.5 \leq \theta < 55°$. Selected standard reflections ($1\bar{2}2$ and $\bar{2}21$) were monitored every 2 hr of exposure time to check the reliability of the electronic hardware, X-ray intensity measurements, and crystal stability. No significant variation was observed and the deviation from the mean value of each standard was less than 1.2%. The data were corrected for Lorentz and polarization effects, and in order to minimize error due to absorption, corrections were applied as a function of crystal shape. After averaging redundant data, 457 reflections were found to be unique. The residual averaging error was 2.7%. All data with $I_{\text{rel}} > 3.0\ \sigma(I_{\text{rel}})$ were used in the solution and refinement of the structure. Crystal data, experimental conditions, and statistical summary are listed in Table I.

TABLE I

EXPERIMENTAL AND STATISTICAL DATA, Yb(OH)$_3$

a = 6.216(2) Å	Hexagonal
c = 3.474(3) Å	Systematic absences: 00l for l odd
V = 116.24 Å^3	Space group: $P6_3/m$
d_c = 6.400 Mg m^{-3}	Crystal size: 0.078 × 0.078 × 0.180 mm
M_r = 224.06 g mole^{-1}	μ(Mo$K\alpha$) = 399.4 cm^{-1}
λ(Mo$K\alpha$) = 0.71073 Å	trans. range: 0.06–0.16
$Z = 2$	$F(000) = 194e$
$R_1 = 0.031$; $R_2 = 0.041$	Average $\Delta\xi_i/\sigma(\xi_i) = 7.7 \times 10^{-4}$
Unique refl.: 457	$\Delta\omega$(°)($\omega - 2\theta$ scan): $1.25 + 0.35 \tan\theta$
$g = 8.3 \times 10^{-6}\ e^{-2}$	$\Delta\theta$(°): 1.5–55

Structural Refinement

Zachariasen (*11*) proposed the model for UCl$_3$ which is the prototype structure for the hexagonal lanthanide trihydroxides. Space groups $P6_3/m$ and $P6_3$ both satisfy the model, but successful refinement in $P6_3/m$ demonstrates that this space group is the better fit. The Yb atoms were placed in a special site, $\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$ (positional set 2c), and the oxygen atoms were deposited in positional set 6h (x, y, $\frac{1}{4}$) where x = 0.3968 and y = 0.3115. Tables II and III present the final positional and thermal parameters with their e.s.d.'s. Full-matrix least-squares refinement of the model employing anisotropic thermal parameters yielded $R_1 = \Sigma(\Delta F)/\Sigma|F_o| = 0.031$ and $R_2 = [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{1/2} = 0.041$ where $w = \sigma^{-2}(|F_o|)$ and $\Delta F = ||F_o| - |F_c||$.[1] The minimized quantity used in the least-squares refinement program was $\Sigma w(||F_o| - |F_c||)^2$. A correction for extinction, $g = 8.3 \times 10^{-6}\ e^{-2}$, was also made. In the final least-squares cycle of refinement the average value of abscission $[\Delta\xi_i/\sigma(\xi_i)]$, where ξ_i values are varied pa-

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[1] See NAPS document No. 04110 for 1 page of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material. Remit $1.50 for postage of any microfiche orders.

TABLE II

POSITIONAL PARAMETERS FOR $Yb(OH)_3$ ($\times 10^4$)

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$U_{eq}{}^a(10^3)(\sigma)$
Yb	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	6.11(5)
O	3968(6)	3115(6)	$\frac{1}{4}$	10.7(7)

[a] $U_{eq} = (U_{11} \times U_{22} \times U_{33})^{1/3}$.

TABLE III

ANISOTROPIC THERMAL PARAMETERS FOR $Yb(OH)_3$ ($Å^2 \times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Yb	5.67(4)	U_{11}	7.08(8)	$U_{11}/2$	0	0
O	10.7(7)	8.8(6)	13(1)	5.5(5)	0	0

Note. The anisotropic temperature factors are of the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^*\cos\gamma^* + 2U_{13}hla^*c^*\cos\beta^* + 2U_{23}klb^*c^*\cos\alpha^*)]$ where U_{ij} values are the thermal parameters denoted in terms of mean-square amplitudes of vibration.

rameters, was 7.7×10^{-4}. A final difference Fourier map revealed some density in the vicinity of the Yb atoms which is not unusual for the heavy lanthanides. Elsewhere, the map was virtually featureless, revealing only a random fluctuating background. Atomic scattering factors and anomalous dispersion correction factors for all atoms were taken from the *International Tables* (*12*).

Discussion

The nine-coordinated Yb atom with two unique metal–oxygen bond lengths have been discussed elsewhere (*1*). Table IV reports these independent Yb–O bond distances and the three O–O contact lengths, as well as other selective molecular dimensions. Also included in Table IV are comparable bond distances and angles determined from idealized cell constants obtained from least-squares linear equations of a_0 and c_0 versus ionic radii (*4*). The involved study was an investigation of rare earth trihydroxide parameters which not only produced empirical equations but also presented crystal radii for the lanthanides. Using the same approach, it is found that the experimental crystal radius of ytterbium is equal to Yb–O(2): 1.487 Å, 0.884(2) Å. The agreement between this and the literature value, 0.891(5) Å, is within the summation of the standard deviations. The literature value of the six-coordinate ionic

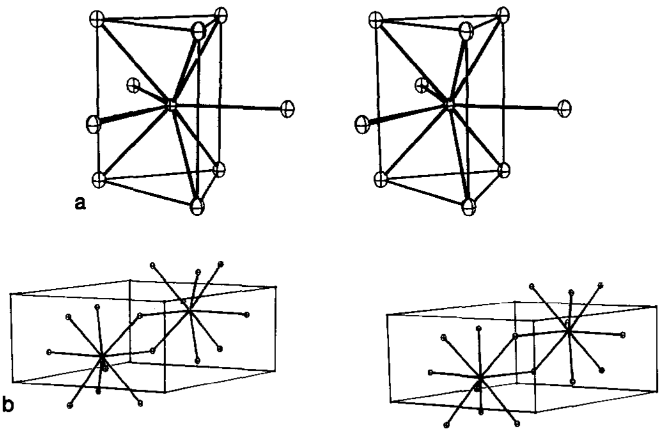

FIG. 1. Stereoview of (a) the coordination polyhedron, and (b) the molecular packing of the unit cell of hexagonal $Yb(OH)_3$.

TABLE IV

BOND AND CONTACT DISTANCES (Å) AND BOND ANGLES (°)

		Idealized cell constants ($a = 6.205(3)$; $c = 3.484(5)$ Å)
Yb–O(2)[a] apical	2.371(2)	2.373(2)
Yb–O(1) equat.	2.430(2)	2.425(2)
O(1)–O(2)	2.842(2)	2.841(2)
O(1)–O(2)	2.674(4)	2.674(4)
O(2)–O(2)	2.795(4)	2.790(4)
O(1)–Yb–O(2)	72.58(9)	72.62(9)
O(1)–Yb–O(2)	67.67(7)	67.73(7)
O(1)–Yb–O(2)	72.24(7)	72.03(7)

[a] Estimated standard deviations are given in parentheses.

radius for Yb (0.858 Å) experimentally determined by Templeton and Dauben (*13*) is corrected to a nine-coordinate system according to Pauling's treatment (*14*), and the assumption of a value of 12 for the Born exponent (ligancy 9, $n = 12$, correction factor, 1.038). The coordination polyhedron is best described as a tri-capped trigonal prism, with the Yb atom at its center, see Fig. 1a. Six of the nine coordinating oxygen atoms O(2) are located in apical positions. The three remaining oxygens O(1) are equatorially positioned near the center of the rectangular faces of the near trigonal prism. Fig. 1b is a packing diagram of the unit cell ($Z = 2$).

Acknowledgment

The authors express their gratitude for financial support of this work by The Robert A. Welch Foundation (Grant AA-668) and Baylor University.

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