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The Structure of Terbium Trihydroxide, Tb(OH)₃, by Neutron Diffraction*

*The Structure of Terbium Trihydroxide, Tb(OH)$_3$, by Neutron Diffraction**

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Crystals of Tb(OH)$_3$ are hexagonal, space group $P6_3/m$. The unit-cell constants are $a = 6.308$ (1), $c = 3.600$ (1)Å, and $Z = 2$. Three-dimensional intensity data were obtained on a full-four-circle goniometer at Brookhaven National Laboratory. The final reliability factors were $R = 0.0736$ and $R_w = 0.0771$ for 83 unique reflections. Earlier X-ray studies and this work are in agreement, in contrast to previous neutron work. Comparisons are made between X-ray and neutron refinements.

Introduction

Studies of the lanthanide trihydroxides by X-ray diffraction (Christensen, Hazell & Nilsson, 1967; Beall, Milligan, Dillin, Williams & McCoy, 1976; Beall, Milligan & Wolcott, 1977) have shown that the compounds are in space group $P6_3/m$ and have yielded accurate positions for the metal and O atoms. The position of the H atom was reported in a single-crystal neutron investigation (Lander & Brun, 1973). A comparison of the bond distances in the neutron study (Lander & Brun, 1973) and the isomorphous series of X-ray structures (Beall, Milligan & Wolcott, 1977) indicated that the neutron distances were inconsistent with the X-ray values. This inconsistency in bond distances prompted this study to determine if the O atom was indeed misplaced and what effect this would have on the H atom positions.

Experimental

Crystals of Tb(OH)$_3$ were grown in strong alkali at high temperature and pressure (Mroczkowski, Eckert, Meissner & Doran, 1970). The crystals were hexagonal cylinders and a suitable one, of approximate dimensions 2·6 mm in length × 1·1 mm in diameter, was mounted with the cylinder axis ([001] direction) parallel to the φ axis of the goniometer head. The diffractometer used was a computer-controlled four-circle model at the Brookhaven National Laboratory High-Flux Beam Reactor. A wavelength of 1·383 Å was obtained by means of a Ge(111) crystal monochromator. Three-dimensional intensity data were

collected at ambient room temperature with a $\theta:2\theta$ scan. The scans varied in width from 2·0 to 8·0° 2θ and data were collected to a maximum of 105° 2θ.

Two redundant sets of data were collected, comprising the wedge of the reciprocal sphere defined by the [001], [100], and [110] directions in the hexagonal system. Two standard reflections (111 and 010; with 030 replacing 010 at higher angles) were measured every 40 reflections throughout the course of the data collection and showed no systematic variation in intensity.

The data were corrected for Lorentz effects, and an analytical absorption correction was applied as a function of crystal shape [μ(neutrons) = 2·397 cm⁻¹]. The correction factor applied varied from 1·210 to 1·362. The redundant data were then averaged, with a residual error of 2·1%, which resulted in 83 unique reflections with $I > 3\sigma(I)$ for refinement.

Solution and refinement

The Tb was first placed in the special position $2(c):(\frac{1}{3},\frac{2}{3},\frac{1}{4})$ with the O in $6(h):(x,y,\frac{1}{4})$, where $x = 0.39$ and $y = 0.31$ in space group $P6_3/m$. After several cycles of full-matrix least-squares refinement an observed Fourier map revealed the position of the H atom.‡ The H atom was placed in the $6(h)$ position, with $x = 0.28$ and $y = 0.14$; the structure was refined anisotropically and a secondary extinction correction (Larson, 1967) was applied. Several cycles of least-squares refinement yielded an $R = 7.36\%$ and $R_w = 7.71\%$. The value of the extinction parameter was $g = 7$ (1) × 10⁻². The reliability factors R and R_w are: $R = $

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‡ The programs used in this refinement were obtained from Los Alamos Scientific Laboratories government reports LA Nos. 3198, 3259, 3309.

$\Sigma \|F_o\| - |F_c\|/\Sigma |F_o|$, $R_w = \Sigma w\|F_o| - |F_c\|/\Sigma w|F_o|$, where $w_i = 1/(F_o + 0.02 F_o^2)^{1/2}$.

The scattering amplitudes used were: $b(Tb) = 0.76$, $b(O) = 0.575$, and $b(H) = -0.372$ cm (all × 10^{-12}). An absorption correction was applied with crystal shape employed. The refinement employed lattice constants obtained from accurate high-angle powder X-ray diffraction.*

Discussion

The structure of $Tb(OH)_3$ consists of a nine-coordinate Tb enclosed in a tricapped trigonal prism with an O at each corner of the prism and one in the middle of each rectangular face. There are two independent metal to O distances. The first is from the metal to the O atoms at each corner of the prism (apical), and the second is from the metal to the O atoms in the middle of each face (equatorial). The structure contains no hydrogen bonds. All the hydrogens are pointing toward holes in the structure located at $(0,0,z)$.

Table 1 contains a comparison of positional and thermal parameters for the neutron and X-ray refinements. There is agreement between both neutron and X-ray refinements in the x and y positional parameters for both the O and H atom. The thermal parameters for this work and the X-ray study (Beall, Milligan & Wolcott, 1977) are in good agreement. There is also qualitative agreement between the thermal parameters of this work and the neutron study of Lander & Brun (1973).

Table 2 contains a comparison of the bond distances found in the neutron and X-ray structures. The bond distances and angles in this work are in complete agreement with those found in the X-ray studies (Beall,

* A list of structure factors for the neutron refinement has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32646 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Milligan & Wolcott, 1977). In comparison the values for the M—O apical bond and two of the O—O bonds reported by Lander & Brun (1973) are in disagreement with this work and the X-ray studies (Beall, Milligan & Wolcott, 1977). The H—O distances for the two neutron studies are in good agreement. The reason for the discrepancy in the M—O and O—O distances could not be in the fractional coordinates of the atoms, since the y position of the O is the only parameter which deviates by more than 3σ (it differs by 3.5σ) but must be in the lattice constants employed in the three studies. The values used in the X-ray study (Beall, Milligan & Wolcott, 1977), $a_0 = 6.315$ (4) and $c_0 = 3.603$ (2) Å, and in this work, $a_0 = 6.308$ (1) and $c_0 = 3.600$ (1) Å, are in good agreement. The values employed by Lander & Brun (1973) of $a_0 = 6.270$ (5) and $c_0 = 3.560$ (5) are in very poor agreement with the other two studies. Lander & Brun (1973) stated that all the lanthanide trihydroxides had approximately the same lattice constants. If one corrects the bond distances of Lander

Table 2. *Comparison of distances* (Å) *and angles* (°) *for* $Tb(OH)_3$ *from neutron and X-ray measurements*

	Neutron	X-ray*	Neutron†	Neutron corrected‡
M—O				
Apical	2.443 (3)	2.444 (3)	2.416 (4)	2.439 (3)
Equatorial	2.455 (4)	2.458 (3)	2.456 (4)	2.471 (4)
O—O	2.900 (4)	2.905 (3)	2.875 (5)	2.898 (4)
	2.861 (7)	2.859 (7)	2.828 (8)	2.845 (7)
	2.737 (5)	2.737 (6)	2.731 (7)	2.754 (5)
O—H	0.950 (9)	–	0.929 (10)	0.935 (9)
O_{EQ}—M—O_{AP}	72.6 (1)	72.7 (1)	72.4 (2)	72.4 (1)
	68.0 (1)	67.9 (1)	68.2 (2)	68.3 (1)
O_{AP}—M—O_{AP}	71.7 (1)	71.6 (1)	71.7 (2)	71.4 (1)

* X-ray results of Beall, Milligan & Wolcott (1977).
† Neutron results of Lander & Brun (1973).
‡ Neutron results of Lander & Brun (1973) corrected with our lattice constants.

Table 1. *Atomic coordinates and anisotropic thermal parameters* (×10^4) *for* $Tb(OH)_3$ *from neutron and X-ray studies*

The temperature factor is of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	$2\beta_{12}$
Tb	1/3	2/3	1/4	40 (15)	–	50 (43)	–
O	0.3946 (6)	0.3117 (6)	1/4	73 (21)	56 (23)	82 (46)	46 (32)
H	0.2754 (10)	0.1426 (16)	1/4	117 (29)	127 (34)	30 (74)	−15 (25)
Tb*	1/3	2/3	1/4	44 (1)	–	69 (2)	–
O*	0.3953 (7)	0.3120 (6)	1/4	88 (7)	53 (6)	146 (16)	47 (6)
H*	0.28	0.14	1/4	(approximate positions)			
Tb†	1/3	2/3	1/4	50	–	120	–
O†	0.3952 (4)	0.3096 (4)	1/4	60 (10)	60 (10)	170 (30)	40 (10)
H†	0.278 (1)	0.143 (1)	1/4	160 (20)	140 (20)	720 (70)	60 (10)

* X-ray results of Beall, Milligan & Wolcott (1977).
† Neutron results of Lander & Brun (1973).

& Brun (1973) by employing the lattice constants used in this study, the bond distances listed in Table 2 are obtained. It can be seen that the bond distances that were in disagreement earlier have all been corrected, but now the equatorial $M-O$ and the third $O-O$ distances deviate by 4σ and 3.4σ respectively. This is somewhat better agreement, but obviously a shift of approximately 2σ in the y parameter of the O atom would bring these distances into line. These studies graphically illustrate the need to pay closer attention to determination of accurate lattice constants if accurate bond distances are to result.

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The Structures of Some Cadmium 'Apatites' Cd$_5$(MO$_4$)$_3$X.
I. Determination of the Structures of Cd$_5$(VO$_4$)$_3$I, Cd$_5$(PO$_4$)$_3$Br, Cd$_5$(AsO$_4$)$_3$Br and Cd$_5$(VO$_4$)$_3$Br

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The compounds are approximately isostructural with fluorapatite, Ca$_5$(PO$_4$)$_3$F, ($P6_3/m$, $Z = 2$) and the positional parameters of the nonhalogen atoms are very similar for all. The halogen atoms, however, do not occupy the ideal positions $\pm(0,0,\frac{1}{4})$ or any unique positions $\pm(0,0,z)$ on the hexad axis. Relative to the O atoms they are present in less than stoichiometric amounts, the deficiency decreasing from about 27% for the iodide to ~8% for the arsenate bromide. This deficiency appears to result from steric hindrance, the usual ionic diameters of the halogens exceeding $\frac{1}{2}c$ by 10–20%. Refinements of the crystal structures of the title compounds and of Cd$_5$(PO$_4$)$_3$Cl (final R's about 0.05) indicate that the formulae should be written Cd$_{5-x}$(MO$_4$)$_3$X$_{1-2x}$, where x can be as large as 0.13 in one (the iodide) case.

Introduction

Cadmium has been linked to hardening of the arteries and high blood pressure (Carroll, 1966; Schroeder, 1965). As a pollutant in the Jintsu river in Japan, cadmium caused many cases of *itai itai* (Tsuchiya, 1969), a very painful bone disease with some osteoporotic-like effects. In several areas of the USA, cadmium and arsenic levels in the water supply have been found to be in excess of those permitted by US Public Health Service standards–50 parts per billion (10^9) for As, and 10 ppb for Cd (Carper, 1971). Both of these metals are readily incorporated in the apatite structure, the model system for the inorganic portion of bones and teeth. Hence, crystal structure studies of apatites in which Cd has replaced Ca and those in which As has replaced P take on relevance in dental research.