

On the Crystal Structures of HoOOH, ErOOH, and YbOOH

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Hydrothermal methods have been used in the preparation of HoOOH, ErOOH, and YbOOH.

Holmium oxide-hydroxide, HoOOH, is monoclinic; the space group is $P2_1/m$, with $a = 5.96 \text{ \AA}$, $b = 3.64 \text{ \AA}$, $c = 4.31 \text{ \AA}$, $\beta = 109.1^\circ$ and two formula units per unit cell. Each holmium atom is coordinated with seven oxygen atoms; one oxygen is coordinated with three holmium atoms, and the other with four holmium atoms. Six oxygens form a trigonal prism, and the seventh lies along a normal to a prism face. Atomic coordinates, temperature factors and other relevant crystallographic data are reported.

The structures of ErOOH and YbOOH have been shown to be similar to HoOOH. They are all isostructural with YOOH.

The preparation of yttrium oxide-hydroxide, samarium oxide-hydroxide and neodymium oxide-hydroxide by hydrothermal methods was reported by Shafer and Roy;¹ the compounds were characterized by unindexed X-ray powder patterns and were proposed to be isomorphous. Klevtsov, Klevtsova and Sheina² reported the hydrothermal preparation of yttrium oxide-hydroxide; the crystal structure of the compound was later reported by Klevtsova and Klevtsov.³ Hydrothermal preparation of ytterbium oxide-hydroxide was reported by Fricke and Dürrwächter⁴ and the compound was reported to be orthorhombic.

EXPERIMENTAL

Preparation of crystals. Crystals of the rare-earth oxide-hydroxides were formed by treating freshly precipitated rare-earth hydroxides with a sodium hydroxide solution in a pressure bomb of 20 ml volume, lined with pure silver. The temperature was measured by means of an Iron-Constantan thermocouple. The pressure was calculated from the percentage filling of the autoclave and the temperature, using tabulated values of the density of water.⁵ Table 1 gives the experimental conditions.

Analysis. The reaction products were analysed by EDTA titration.⁶ (Found: Ho 82.68. Calc. for HoOOH: Ho 83.33. Found: Er 83.45. Calc. for ErOOH: Er 83.52. Found: Yb 84.25. Calc. for YbOOH: Yb 83.84).

X-Ray technique. A needle-shaped HoOOH crystal of dimensions 0.04 mm \times 0.04 mm \times 0.2 mm was selected under the polarizing microscope. It was investigated

Table 1. Experimental conditions.

Temp. °C	Pressure atm	Time h	Conc. of NaOH solution	Result	Crystal size mm
440	460	24	12 m	HoOOH	0.2
435	450	24	15 m	ErOOH	0.2
440	460	24	12 m	YbOOH	0.2

by Weissenberg and precession methods. The needle axis proved to be [010]. The crystal was twinned along the [001] plane. Integrated precession photographs were taken using Zr-filtered MoK α -radiation of (*hk*0). Integrated Weissenberg photographs were taken of (*h*0*l*), using the multiple film technique, with Zr-filtered MoK α -radiation. Twinning was so pronounced that reflections for each twin could be measured separately for *h*0*l* reflections except for *h*00. From averages of intensity measurements the relative proportions of the two crystals were determined. 71 independent reflections were measured photometrically. No absorption correction was applied. The usual Lorentz-polarisation corrections were computed on a digital computer.

The X-ray powder patterns of HoOOH, ErOOH, and YbOOH were obtained with a Guinier camera using CuK α_1 radiation from a microfocus tube with a focal line of dimensions 0.1 mm \times 0.6 mm. In the powder patterns Ge (99.999 %) was used for reference. The patterns gave sharp lines permitting a reasonable accuracy in the determination of unit cell dimensions, and were indexed by a least squares method. Optical densities of the lines were measured by means of a recording double-beam microdensitometer. No effort was made to obtain accurate intensities from the powder patterns.

Physical measurements. Crystals of HoOOH, ErOOH, and YbOOH were tested for piezoelectricity. No piezoelectric effect was observed.

STRUCTURE DETERMINATION

HoOOH is monoclinic with two HoOOH units per unit cell. The only systematically absent reflections are of the type (0*k*0) with *k* odd, which indicates the space group $P2_1/m$ or $P2_1$. Since no piezoelectric effect was found the space group $P2_1/m$ was assumed.

In the space group $P2_1/m$ the Ho atoms must lie on a mirror plane or a centre of symmetry. The Patterson projection $P(u,0,w)$ gave the position of the Ho atom (0.188, 0.75, 0.333).

The Ho contributions determine the signs of nearly all structure factors and difference Fourier projections were calculated with *h*0*l* and *hk*0 reflections. This gave possible oxygen positions at *xz* = (0.55, 0.79) and (0.06, 0.73), and *xy* = (0.54, 0.75) and (0.06, 0.75). Packing considerations gave the oxygen positions (0.55, 0.75, 0.79) and (0.06, 0.75, 0.73).

The refinement was carried out by the method of Bhuiya and Stanley.⁷ The structure factors were calculated, using the atomic scattering factor for oxygen from Vol. III of *International Tables for X-ray Crystallography*, and the atomic scattering factor for holmium reported by Cromer,⁸ and by using the interpolation formula of Bassi.⁹ *h*0*l* and *hk*0 reflections were used simultaneously. The refinement yielded an *R*-value of 5.5 %. The programme used was written by Danielsen.¹⁰

CRYSTAL DATA

The crystallographic data obtained are reported below: Crystal system: monoclinic, $a = 5.96 \pm 0.01$ Å, $b = 3.64 \pm 0.01$ Å, $c = 4.31 \pm 0.01$ Å, $\beta = 109.1^\circ \pm 0.1^\circ$. Space group: $P2_1/m$, (No. 11). Density calc. (for two formula units in the unit cell): 7.43 g/cm³. Density determined pycnometrically: 7.15 g/cm³. MoK α -radiation, absorption coefficient $\mu = 460$ cm⁻¹.

Table 2. Atomic coordinates and temperature factors.

Atom	x	σx	y	z	σz	$B(\text{Å}^2)$	$\sigma B(\text{Å}^2)$
Ho	0.1899	0.0005	0.75	0.3337	0.0008	0.23	0.04
O ₁	0.057	0.009	0.75	0.765	0.012	1.54	0.96
O ₂	0.563	0.010	0.75	0.765	0.014	2.47	1.23

Table 3. Interatomic distances l and O—Ho—O angles v in coordination polyhedra HoO₇ (cf. Fig. 1).

	l	σl		v	σv
Ho—O ₁	2.25	0.06 Å	O ₁ —Ho—O ₂	81.1°	2.0°
Ho—O ₂	2.39	0.05 Å	O ₁ —Ho—O ₅	141.7°	1.7°
Ho—O ₃	2.47	0.05 Å	O ₂ —Ho—O ₅	137.3°	2.1°
Ho—O ₅	2.32	0.05 Å	O ₁ —Ho—O ₇	77.0°	1.6°
Ho—O ₇	2.29	0.03 Å	O ₁ —Ho—O ₃	71.2°	1.5°
			O ₇ —Ho—O ₅	80.0°	1.5°
O ₁ —O ₂	3.01	0.08 Å	O ₃ —Ho—O ₅	80.4°	1.6°
O ₁ —O ₇	2.83	0.05 Å	O ₇ —Ho—O ₆	105.3°	1.4°
O ₂ —O ₃	2.83	0.06 Å	O ₃ —Ho—O ₄	95.1°	1.6°
O ₃ —O ₇	2.95	0.08 Å			
O ₅ —O ₃	3.09	0.05 Å			
O ₅ —O ₇	2.96	0.07 Å			
O ₃ —O ₄	3.64	0.01 Å			

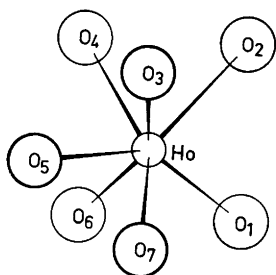
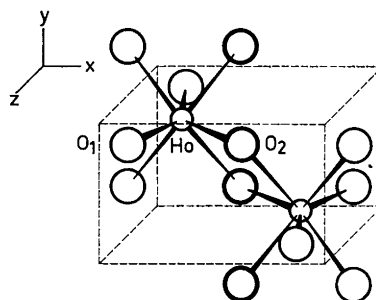
Fig. 1. Coordination polyhedra HoO₇.Fig. 2. Axonometric drawing of the unit cell showing coordination of the holmium atoms. O²⁻ and OH⁻ ions are differentiated by light and heavy circles, respectively.

Table 4. X-Ray diffraction data for HoOOH.

$a = 5.96 \pm 0.01 \text{ \AA}, b = 3.64 \pm 0.01 \text{ \AA}$ $c = 4.31 \pm 0.01 \text{ \AA}, \beta = 109.1^\circ \pm 0.1^\circ$					
<i>d</i> obs	<i>d</i> calc	<i>h</i>	<i>k</i>	<i>l</i>	<i>j</i>
5.661	5.632	1	0	0	64
4.074	4.073	0	0	1	48
3.980	3.975	-1	0	1	73
3.064	3.057	1	1	0	100
2.883	2.883	1	0	1	45
2.821	2.816	2	0	0	13
2.781	2.781	-2	0	1	21
2.715	2.714	0	1	1	30
2.685	2.685	-1	1	1	65
2.230	2.227	-2	1	0	45
2.211	2.210	-2	1	1	10
2.150	2.154	-1	0	2	18
2.033	2.036	0	0	2	13
	2.027	2	0	1	
1.987	1.988	-2	0	2	2
1.879	1.877	-3	0	0	16
1.852	1.853	-1	1	2	2
1.822	1.820	0	2	0	34
1.775	1.777	0	1	2	18
1.771	1.771	2	1	1	31
1.741	1.741	1	0	2	26
1.731	1.732	1	2	0	17
	1.731	-3	1	1	
1.678	1.681	-3	0	2	4
1.669	1.669	3	1	0	4
1.663	1.662	0	2	1	4
1.655	1.655	-1	2	1	6
1.571	1.571	1	1	2	5
1.540	1.539	1	2	1	12
1.530	1.529	2	2	0	5
1.526	1.526	-3	1	2	6
	1.526	3	0	1	
1.524	1.523	-2	2	1	13
1.491	1.490	-4	0	1	12
1.438	1.441	2	0	2	2
1.408	1.408	4	0	0	5
	1.407	3	1	1	
1.390	1.390	-4	0	2	9
	1.390	-1	2	2	
1.380	1.379	-4	1	1	2
1.356	1.358	0	0	3	4
	1.357	0	2	2	
1.330	1.332	-1	1	3	9
1.322	1.325	-3	0	3	5
	1.321	-2	1	3	
1.314	1.313	4	1	0	5
1.308	1.307	-3	2	0	12
1.259	1.258	1	2	2	5
1.244	1.245	-3	1	3	
1.235	1.235	-3	2	2	
1.214	1.214	4	0	1	
1.188	1.190	-5	0	1	
1.171	1.169	3	2	1	
1.164	1.163	0	3	1	
1.155	1.153	-4	2	1	
1.131	1.130	2	2	2	

Table 2 gives atomic coordinates and temperature factors with their standard deviations. Table 3 gives interatomic distances. Fig. 1 is a drawing of the coordination polyhedra. Fig. 2 is an axonometric drawing of the structure of HoOOH. A list of calculated and observed structure factors has been sent to the editor but is not printed to save space. The author will gladly supply copies of this table on request. Table 4 shows the indexing of the powder pattern of HoOOH.

DISCUSSION

When refinement was completed it was realized, that the structure was analogous to that of YOOH reported by Klevtsova and Klevtsov.³ If the axes chosen here are transformed according to the following scheme: $a' = c$, $b' = b$, $c' = -a - c$ the unit cell parameters $a' = 4.31 \text{ \AA}$, $b' = 3.64 \text{ \AA}$, $c' = 6.10 \text{ \AA}$, $\beta = 112.7^\circ$ are obtained for HoOOH. This unit cell is close to that of YOOH³: $a = 4.28 \text{ \AA}$, $b = 3.63 \text{ \AA}$, $c = 6.05 \text{ \AA}$, $\beta = 112.5^\circ$. Transformation of atomic coordinates of YOOH³ to the setting used in this investigation shows, that the two compounds are isostructural.

The author has reinvestigated the structure of YOOH using counter diffractometer data and hopes in a forthcoming paper to discuss the YOOH structure further.

Each holmium atom has seven oxygen neighbours. O_1 is coordinated with 4 holmium atoms, and O_2 is coordinated with 3 holmium atoms. Six oxygens form a trigonal prism and the seventh lies along a normal to a prism face. The coordination about holmium is similar to that found in the anions NbF_7^{2-} and TaF_7^{2-} reported by Hoard¹¹ and in monoclinic Sm_2O_3 reported by Cromer.¹²

The coordination polyhedra contain holmium at (0.1899, 0.75, 0.3337), and at (0.8101, 0.25, 0.6663). These polyhedra share edges, and are stacked along the (010) direction.

Table 3 shows the Ho-O distances in the coordination polyhedra. There are two sets of Ho-O distances, one set with an average Ho-O distance of $2.29 \pm 0.05 \text{ \AA}$ and one set with an average Ho-O distance of $2.43 \pm 0.05 \text{ \AA}$. The two average distances are possibly significantly different.

A Ho-O distance of 2.25 \AA has been reported in HoOCl by Templeton and Dauben,¹³ and the Ho-O distances in cubic Ho_2O_3 vary from 2.20 \AA to 2.33 \AA according to Fert.¹⁴ If the Ho-O distance of 2.29 \AA is interpreted as a distance between a holmium atom and an oxygen atom, the use of Pauling's radius for O^{2-} gives an ionic radius for Ho^{3+} of 0.89 \AA ; using a value of 1.53 \AA for the radius of OH^- (Wells¹⁵), gives a Ho-OH distance of 2.42 \AA . Apparently the Ho-O distance of 2.43 \AA can be interpreted as a distance between a holmium atom and a hydroxyl group. The oxygen atoms which are bonded to the holmium atoms with the long bonds are coordinated with 3 holmium atoms. This is acceptable with the interpretation of these oxygen atoms as belonging to OH-groups. The oxygen atoms which are bonded to the holmium atoms with the shorter bonds are coordinated with 4 holmium atoms.

Table 5 gives the unit cell parameters of ErOOH and YbOOH, based on a monoclinic unit cell. The powder patterns are very similar and the compounds are probably isomorphous with HoOOH.

Table 5. Unit cell parameters for ErOOH and YbOOH

	a (Å)	b (Å)	c (Å)	β
ErOOH	5.94 ± 0.01	3.62 ± 0.01	4.30 ± 0.01	$109.3^\circ \pm 0.1^\circ$
YbOOH	5.87 ± 0.01	3.58 ± 0.01	4.27 ± 0.01	$109.3^\circ \pm 0.1^\circ$

A linear relationship between the cubic root of the unit cell volumes and the atomic number of the cations was observed. The powder pattern of YbOOH prepared in this investigation could not be indexed on the basis of the orthorhombic unit cell previously reported by Fricke and Dürrwächter,⁴ and the data given does not permit a comparison of the powder pattern from the present investigation.

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REFERENCES

1. Shafer, M. W. and Roy, R. *J. Am. Ceram. Soc.* **42** (1959) 563.
2. Klevtsov, P. V., Klevtsova, R. F. and Sheina, L. P. *Zh. Strukt. Khim.* **5** (1964) 583.
3. Klevtsova, R. F. and Klevtsov, P. V. *Zh. Strukt. Khim.* **5** (1964) 860.
4. Fricke, R. and Dürrwächter, W. *Z. anorg. allgem. Chem.* **259** (1949) 305.
5. Kennedy, G. C. *Am. J. Sci.* **248** (1950) 540.
6. Schwarzenbach, G. *Die komplexometrische Titration*, Stuttgart 1960, p. 69.
7. Bhuiya, A. K. and Stanley, E. *Acta Cryst.* **16** (1963) 981.
8. Cromer, D. T. *et al. Acta Cryst.* **17** (1964) 1044.
9. Bassi, M. G. *Acta Cryst.* **15** (1962) 617.
10. Danielsen, J. *Algol programme D45*, printed in this laboratory.
11. Hoard, J. L. *J. Am. Chem. Soc.* **61** (1939) 1252.
12. Cromer, D. T. *J. Phys. Chem.* **61** (1957) 753.
13. Templeton, D. H. and Dauben, C. H. *J. Am. Chem. Soc.* **75** (1953) 6069.
14. Fert, A. *Bull. Soc. Franc. Mineral. Crist.* **85** (1962) 267.
15. Wells, A. F. *Structural Inorganic Chemistry*, Oxford 1962, p. 548.

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