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Synthesis, Spectroscopic Studies and Crystal Structure Analysis of 1:1 Lutetium/Indium Trihydroxide

D. F. MULLICA*, E. L. SAPPENFIELD and D. R. GABLE

Departments of Chemistry and Physics, Baylor University, Waco, Tex. 76798, U.S.A.

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Abstract

The crystal structure of 1:1 lutetium/indium trihydroxide has been determined by means of single-crystal X-ray diffraction techniques. The compound is isostructural with pure $Lu(OH)_3$ having a polyhedral framework consisting of two slightly distorted pentagonal dodecahedra and twelve heptahedra per cell in a body-centered cubic (bcc) system. The cubic form crystallizes in space group $Im\bar{3}(T_h^5$, No. 204) with a = 8.0440(8) Å obtained from a powder X-ray diffraction study, F_{20} = 71 (0.009, 30) and M_{20} = 132.3. A full-matrix least-squares refinement of the structure yielded R = 0.0173 and R_w = 0.0205. The Lu and In atoms share the same site, with a 50% occupancy for each ion. Six oxygen atoms are octahedrally coordinated about the metal (M) atoms. Thermal gravimetric and X-ray fluorescence analyses have been carried out. The important bond lengths are: M–O = 2.194 Å; O–O (intermolecular) = 2.725 and 2.837 Å.

Introduction

Investigative studies into the morphological and structural properties of hydrous rare-earth oxides and hydroxides have been a major part of the research program in this laboratory. Recent X-ray diffraction studies [1–5] of the lanthanide trihydroxides $Ln(OH)_3$ (where Ln = La–Yb) have shown that the series belongs to the hexagonal system ($P6_3/m$) except for lutetium trihydroxide. $Lu(OH)_3$ crystallizes in the cubic form (bcc), space group $Im\bar{3}$ [6, 7] and is isomorphous with $Sc(OH)_3$ and $In(OH)_3$.

$Lu(OH)_3$ has not been made in the hexagonal form nor have any of the lanthanides found in the hexagonal system been synthesized in the cubic form. However, interesting results encountered while proceeding toward the optimum conditions needed for the production of cubic single crystals of $Lu(OH)_3$ have prompted a continuation of research in the area [8]. All attempts to prepare single crystals of $Lu(OH)_3$ below 428 K have produced a crystalline complex phase which has proven to be a higher hydrate form ($Lu_2O_3 \cdot nH_2O$, where $n > 3$). TGA results have indicated 4.0 water molecules per formula unit. This complex phase, called 'phase-DR' (double-ring) for lack of a better name, has not been characterized as yet, but is believed to be the precursor to the $Lu(OH)_3$ cubic phase. This conclusion has been supported by a study employing X-ray powder diffractometry [8]. After studying the powder patterns of an aging series of hydrous lutetium oxide (preparation, concentration and temperature constant), it is found that the sequence of identifiable phases are: amorphous, phase-DR, cubic $Lu(OH)_3$ and LuOOH. Considerations regarding the 'phase-DR' of lutetium hydroxide have fostered similar preparatory studies with Yb, Tm and Er. Preliminary results have presented the 'phase-DR' for these hydrous lanthanide oxides which leads to the presumption that the cubic trihydroxide form of Yb, Tm and Er may exist. Unfortunately, efforts to produce single crystals have not been successful. A new approach is to use mixed systems and then increase the mole ratio of the desired constituent until the ideal conditions are established. At which time, a new cubic lanthanide trihydroxide series will hopefully be realized.

Further, a recent crystal structure of 1:1 gadolinium/ytterbium orthophosphate [9] has shown that a mixed system tends to maintain the same type of structural geometry as the pure system of either. A lanthanide series of compounds is always of interest both from the fundamental and practical point of view. Of basic concern, it is feasible to study the $4f^n$ transitions in a lanthanide series of interest. And, of practical interest, since perfect solid solutions (mixed crystals) for a lanthanide series may be formed over a wide range of mixed rare-earth compositions, it may be possible to control the local crystal-field strength at the lanthanide sites, hence controlling the optical, magnetic, and other properties of rare-earth dopant ions in mixed hosts such as $Ln_{1-x}M_x(OH)_3$ where M may be a lanthanide, transition or another metal element.

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*Author to whom correspondence should be addressed.

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The present work investigates the structural properties of the mixed solid solution $Lu_{0.5}In_{0.5}(OH)_3$.

Experimental

All compounds used in the crystal growth of lutetium/indium trihydroxide were obtained commercially (reagent grade, purity 99.99%) and were used without further purification. Small amounts of a mixture of Lu_2O_3 and In_2O_3 (1:1 mole ratio) were placed directly into Teflon bombs half-filled with 30 N NaOH, which were being maintained in a hot water bath in order to prevent solidification of NaOH. The Teflon bombs were quickly sealed and placed into safety capsules. Hydrothermal aging at 503 K for 5 days yielded crystals large enough for single crystal analysis.

TABLE I. Experimental and Statistical Summary of 1:1 Lu/In(OH)$_3$

Formula: $Lu_{0.5}In_{0.5}(OH)_3$
a = 8.0440(8) Å, powder
a = 8.040(2) Å, single crystal
V = 520.49 Å^3
Cubic, $Im\bar{3}$
M_r = 195.93
D_c = 5.00(1) Mg m^{-3}
Z = 8
F(000) = 696 e
Crystal size: 0.223 × 0.205 × 0.177 mm
$R_{int.}$ = 0.023
$\Delta\theta$: 1.5–35.0°
Unique reflections ($I > 3\sigma(I)$): 84
R = 0.0173; R_w = 0.0205
Maximum shift/error: 1.6×10^{-4} (average 6.7×10^{-5})
$\zeta = 1.40 \times 10^{-6}$ e^{-2}
GNFT(Σ_2) = 1.18

A Debye–Scherrer cylindrical camera (114.6 mm, 293 K, under vacuum) using Ni-filtered Cu Kα radiation (λ_{mean} = 1.54184 Å) was used to obtain the X-ray powder diffraction data. Lutetium/indium trihydroxide crystals were finely ground and placed into a 0.2 mm capillary. The unit cell parameter was refined by placing measured S-values into a least-squares X-ray powder diffraction data program [10] which employs the Nelson–Riley extrapolation function. The refined lattice constant is 8.0440(8) Å (see Table I) with figures of merit values of F_{20} = 71(0.009, 30) and M_{20} = 132.3 [11, 12]. Observed d-spacing values (Å) and the visually estimated relative intensities, based on 100 as the strongest observed reflection, are presented in Table II.

A Perkin-Elmer TGS-1 thermobalance run at 2.5 °C min^{-1} while being purged with nitrogen (20 cm^3 min^{-1}) was used to determine thermal dehydration, 2.96(3) water molecules-formula unit^{-1}.

TABLE II. X-ray Powder Diffraction Data for 1:1 Lu/In(OH)$_3$

$h\,k\,l$	$2\theta_o$	$2\theta_c$	I/I_o	d_o	F_N[a]
2 0 0	22.100	22.101	100	4.022	450(0.001, 2)
2 2 0	31.450	31.456	90	2.844	147(0.003, 4)
3 1 0	35.276	35.284	10	2.544	117(0.005, 5)
2 2 2	38.774	38.780	40	2.322	129(0.005, 6)
3 2 1	42.024	42.029	5	2.150	145(0.005, 7)
4 0 0	45.076	45.083	40	2.011	142(0.005, 8)
4 2 0	50.751	50.757	80	1.7989	130(0.005, 10)
4 2 2	56.000	56.004	60	1.6421	128(0.005, 12)
4 3 1	58.502	58.506	3	1.5777	137(0.005, 13)
4 4 0	65.674	65.659	15	1.4217	109(0.006, 15)
5 3 0	67.951	67.951	5	1.3795	124(0.006, 16)
6 0 0	70.201	70.201	30	1.3407	138(0.005, 17)
5 3 2	72.426	72.426	3	1.3049	153(0.005, 18)
6 2 0	74.653	74.618	30	1.2714	108(0.007, 19)
6 2 2	78.952	78.945	30	1.2126	104(0.007, 21)
6 3 1	81.102	81.086	3	1.1858	97(0.007, 22)
4 4 4	83.248	83.213	10	1.1606	81(0.009, 23)
6 4 0	87.454	87.434	15	1.1153	74(0.010, 25)
6 4 2	91.648	91.648	20	1.0749	77(0.009, 27)
8 0 0	100.131	100.117	20	1.0054	71(0.009, 30)

Average percent deviation = 0.0127

[a] $F_N = (1/|\overline{\Delta 2\theta}|)(N_0/N_p)$ where N_p is the number of independent diffraction lines possible up to the n-th observed line. $|\overline{\Delta 2\theta}|$ is the averaged absolute discrepancy value. 2θ is in (°) and d-values are in Å.

The metal elements in the titled compound were confirmed by X-ray fluorescence analysis, employing a Novascan 30 scanning electron microscope (SEM) equipped with PGT microprobe.

A clear single crystal of $Lu_{0.5}In_{0.5}(OH)_3$, 0.223 × 0.205 × 0.177 mm, was chosen on the basis of optical quality and was mounted on an automated diffractometer (Enraf–Nonius CAD-4F), equipped with a dense graphite monochromator which is assumed to be ideally imperfect (take-off angle 5.8°). The orientation matrix used for data collection (experimental temperature, 293 K) resulted from a least-squares refinement of twenty-five accurately centered reflections which also established the cell dimension, a = 8.040(2) Å, which is in good agreement with the X-ray powder work, 8.0440(8) Å. Measured intensities were collected by the ω–2θ scan technique (Mo Kα radiation, λ_{mean} = 0.71073 Å) at a scan rate of 0.4–3.35° min^{-1}, determined by a fast prescan of 3.35° min^{-1}. During the prescan, all reflections having less than 75 counts above the background were deemed unobserved. Data were collected in the range of $3 < 2\theta < 70°$. No significant variations were observed in the intensities of the monitored standards ($\bar{2}4\bar{2}$, $\bar{2}02$; every 2 h of exposure time, <0.5% deviation). Thus, the reliability of the electronic hardware and crystal stability were verified.

Intensities greater than 3σ were used in the structural refinement. Lorentz and polarization corrections were applied to the data. Some 212 reflections were observed and after averaging redundant data, 84 reflections were unique (R_{int} = 0.023). Table I lists the experimental and statistical summary for $Lu/In(OH)_3$.

Systematic absences ($h + k + l = 2n + 1$) and unequal intensities of related pairs of reflections ($hk0 \neq kh0$ ↻ and $hk0 \neq kh0$ ↻) suggested space group $Im\bar{3}$ (No. 204). Since the titled compound is isostructurally related to cubic $Lu(OH)_3$, this starting model was used to initiate the full-matrix least-squares refinement [13]. A secondary extinction correction (ζ) was applied and, after varying the anisotropic thermal parameter of the oxygen atom, final reliability factors were obtained: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0173$; and $R_w = \Sigma\sqrt{w}||F_o| - |F_c||/\Sigma\sqrt{w}|F_o| = 0.0205$. Final difference Fourier mapping revealed some density in the vicinity of the heavy metal atoms (max 2.1(2), min −1.8(2) e $Å^{-3}$) which is quite common for the heavy metals. Elsewhere, the electron density map was virtually featureless, revealing only a random fluctuating background ($\ll$0.5 e $Å^{-3}$). Hence, it was not possible to locate hydrogen positions. Atomic scattering factors and anomalous dispersion correction factors were taken from the International Tables [14]. Final atomic coordinates and thermal parameters are presented in Tables III and IV. Relevant derived bond lengths, contact distances and bond angles are reported in Table V. Tables of observed and calculated structure factors are available from the authors.

TABLE III. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 1:1 $Lu/In(OH)_3$

Atom	x	y	z	U_{eq}[a]
Lu[b]	0.28	0.25	0.25	0.5(2)[c]
In[b]	0.25	0.25	0.25	0.01(2)[c]
O	0.00	0.324(1)	0.169(1)	0.008(2)

[a] Isotropic equivalent thermal parameter (U_{eq}) defined as one-third the trace of the orthogonalized U_{ij} tensor. [b] Fifty-percent occupancy. [c] Refined isotropically.

Results and Discussion

The completion of the single crystal analysis of $Lu_{0.5}In_{0.5}(OH)_3$ denotes that the non-hydrogen

TABLE V. Selected Bond and Contact Distances (Å) and Bond Angles (°) with e.s.d. values for 1:1 $Lu/In(OH)_3$

M–O	2.194(3)	O(1)–M–O(2)	86.8(4)
O(1)–O(2), intra	3.014(10)	O(1)–M–O(5)	93.2(4)
O(1)–O(5), intra	3.190(11)	M–O(1)–M	132.8(4)
O(1)–O(7), inter	2.725(19)	M–O(1)–O(2, 3)	46.6(2)
O(1)–O(13), inter	2.837(18)	M–O(1)–O(5, 6)	43.4(2)

TABLE IV. Anisotropic Thermal Parameters for 1:1 $Lu/In(OH)_3$[a]

Atom	$U(1, 1)$	$U(2, 2)$	$U(3, 3)$	$U(1, 2)$	$U(1, 3)$	$U(2, 3)$
Lu[b]	0.475[c]					
In[b]	0.015[c]					
O	0.006(3)	0.006(4)	0.010(4)	0	0	0.003(4)

[a] The form of the anisotropic thermal parameter is: $\exp\{-2\pi^2[U(1,1)h^2a^{*2} + U(2,2)k^2b^{*2} + U(3,3)l^2c^{*2} + 2U(1,2)hka^*b^* + 2U(1,3)hla^*c^* + 2U(2,3)klb^*c^*]\}$. [b] Fifty-percent occupancy. [c] Refined isotropically.

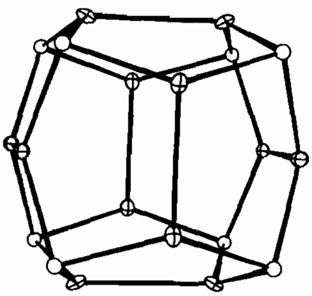

Fig. 1. $Lu/In(OH)_3$. The metal atoms are designated by circles and the oxygen atoms are ellipsoidal. The polyhedral framework is obvious, a pyritohedron.

crystallographic data best fit space group $Im\bar{3}$. Six oxygen atoms are octahedrally coordinated about the metal atoms and each oxygen atom is bonded to two metal atoms forming a polyhedral framework consisting of two slightly distorted pentagonal dodecahedra and twelve heptahedra per unit cell. The 20 vertices of the dodecahedron are occupied by 8 metal atoms and 12 oxygen atoms. Twenty-four of the edges are defined by M–O bonds and the remaining six of the 30 defining edges of the pyritohedron are O···O contact distances, see Fig. 1. The dodecahedra exhibit obvious distortions in metric which is evidenced by the inequality of the O···O and M–O bond edges, 2.725 and 2.194 Å, respectively. This type of arrangement has been completely discussed by Jefferey and McMullan [15] and has been found in a neutron diffraction study of indium trihydroxide [16]. The centers of the two dodecahedra are at 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and share a common vertex at the octahedral metal atoms which are positioned on the three-fold axis. The twelve heptahedra complete the space-filling arrangement. Each has six pentagonal faces and one square face. Figure 2 is a stereodrawing of the contents of the unit cell (50% equiprobability ellipsoids). The metal–oxygen bond length of 2.194(3) Å is quite reasonable when compared to the sum of the radii given by Shannon [17]: $[r(Lu^{3+}) + r(In^{3+})]/2 + r(OH) = 2.18$ Å. The M–O–M angle of the infinite Lu–O–In chains is 132.8(4)°. The intermoiety oxygen–oxygen contact distances of 2.725 and 2.837 Å are significantly different, which is attributed to different strengths of hydrogen bonding, *i.e.* strong and weak. The strength of hydrogen bonds has been shown by Brown [18] to be dependent upon the O···O interatomic distances. Assuming no geometric contraints, strong hydrogen bonds have O···O contact distances of approximately 2.73 Å and hydrogen bonding becomes progressively weaker as the contact distances increase. These types of relationships were observed and discussed in the neutron structural investigation of indium trihydroxide [16]. Future work has been initiated regarding mixed systems so as to establish ideal conditions in the hope of discovering a new cubic lanthanide trihydroxide series.

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References

1 G. W. Beall, W. O. Milligan and H. A. Wolcott, *J. Inorg. Nucl. Chem., 39,* 65 (1977).
2 D. F. Mullica, W. O. Milligan and G. W. Beall, *J. Inorg. Nucl. Chem., 41,* 525 (1979).
3 D. F. Mullica, J. D. Oliver and W. O. Milligan, *Acta Crystallogr., Sect. B, 35,* 2668 (1979).
4 R. G. Haire, D. R. Dillin, W. O. Milligan and M. L. Beasley, *J. Inorg. Nucl. Chem., 50,* 53 (1977).
5 W. O. Milligan, D. F. Mullica, D. A. Grossie and C. K. C. Lok, *J. Solid State Chem., 50,* 129 (1983).
6 D. F. Mullica and W. O. Milligan, *J. Inorg. Nucl. Chem., 42,* 223 (1980).
7 D. F. Mullica and E. L. Sappenfield, *Powder Diffraction, 2(1),* 39 (1987).
8 D. F. Mullica, W. O. Milligan and D. R. Dillin, *J. Cryst. Growth, 47,* 635 (1979).
9 D. F. Mullica, D. A. Grossie and L. A. Boatner, *Inorg. Chim. Acta, 118,* 173 (1986).
10 R. B. Roof, Jr., *LASL. Report,* Los Alamos-Scientific Laboratory, 1968.
11 G. S. Smith and R. L. Synder, *J. Appl. Crystallogr., 12,* 60 (1979).
12 P. M. DeWolff, *J. Appl. Crystallogr., 1,* 108 (1968).
13 ENRAF-NONIUS, 'Enraf-Nonius VAX Structure Determination Package', Delft, 1982.

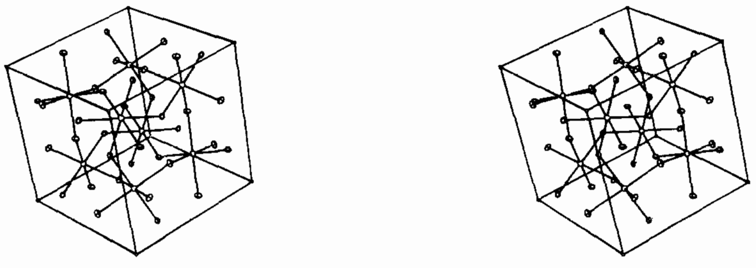

Fig. 2. $Lu/In(OH)_3$. A representative stereoview of the molecular packing within the unit cell.

14 J. A. Ibers and W. C. Hamilton, 'International Tables X-Ray Crystallography', Vol. IV, Kynoch Press, Birmingham, 1974, p. 72.
15 G. A. Jefferey and R. K. McMullan, *Prog. Inorg. Chem.*, *8*, 43 (1967).
16 D. F. Mullica, G. W. Beall, W. O. Milligan, J. D. Korp and I. Bernal, *J. Inorg. Nucl. Chem.*, *41*, 277 (1979).
17 R. D. Shannon, *Acta Crystallogr.*, *Sect. A*, *32*, 751 (1976).
18 I. D. Brown, *Acta Crystallogr.*, *Sect. A*, *32*, 24 (1976).