Structural Refinement of Lutetium Hydroxide Oxide

By W. O. Milligan, D. F. Mullica and M. A. Hall

Departments of Chemistry and Physics, Baylor University, Waco, Texas 76703, USA

Abstract. LuOOH, monoclinic, $P2_1/m$, $a = 5.836$ (2), $b = 3.552$ (1), $c = 4.247$ (2) Å, $\beta = 109.33$ (2)°, $U = 8.308$ Å^3, $M_r = 207.98$, $Z = 2$, $D_c = 8.311$ Mg m^{-3}; Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å), μ(Mo $K\alpha$) = 58.71 mm^{-1}. R and R_w were both 0.035 for 128 reflections with $I > 3\sigma(I)$. The crystal size was 0.010 × 0.019 × 0.022 mm. The Lu atom is seven-coordinated with three hydroxyl groups and four O^{2-} ions. The coordination polyhedron is a distorted monocapped trigonal prism, with the Lu atom off-center. The mean bond lengths between the metal and O atoms in the O^{2-} ion and in the OH group are 2.24 and 2.40 Å respectively.

Introduction. Recently, aging studies on hydrous lutetium oxide under strict controls presented evidence of phase transitions from an amorphous gel to lutetium hydroxide oxide (Mullica, Milligan & Dillin, 1979). Three distinct phases of hydrous lutetium oxide were isolated, of which one was LuOOH and another was the newly discovered cubic (*Im3*) form of Lu(OH)$_3$ (Mullica & Milligan, 1980). Since only a few references to the hydrous lutetium oxides can be found in the literature and part of our research program is investigating hydrous lanthanide oxides, hydroxide oxides and trihydroxides, attention was deemed necessary on these hydrous compounds of lutetium.

In our laboratory, LuOOH crystals were grown too small for conventional single-crystal analysis. The Enraf–Nonius CAD-4 diffractometer used for data collection is equipped with a Li-doped Si X-ray energy-dispersive detector. The Si(Li) solid-state detector permitted the analysis of LuOOH, for the rotational photograph, which is normally used to produce a working orientation matrix, was completely featureless after one hour of exposure time. A study related to the applications of a solid-state detector on a modern automated diffractometer has recently been published (Mullica, Beall, Milligan & Oliver, 1979). Pronounced advantages over a conventional scintillation detector system are (*a*) better peak-to-background ratios are obtained, allowing more usable data to be collected, (*b*) the ability to obtain fluorescence X-ray data on the same single crystal from which X-ray single-crystal

diffraction data will be collected, and (*c*) the ability to analyze smaller crystals.

Details of crystal growth by hydrothermal aging are found elsewhere (Mullica, Milligan & Dillin, 1979) and, owing to twinning problems, much effort was applied to obtain a single crystal (0.010 × 0.019 × 0.022 mm). A thermal gravimetric analysis employing a Perkin–Elmer (TGS-1) thermobalance yielded 0.5 mol of water per formula unit. An infrared spectrum through the frequency range of 4000 to 200 cm^{-1} revealed no evidence of possible hydrogen bonding, only a stretching vibration of a free OH$^-$ ion was observed. Qualitative identification of the metal constituent in the oxide was quickly verified by X-ray fluorescence investigation. The cell parameters and orientation matrix were acquired by the least-squares fit of 25 automatically centered reflections representing all coequality groups, well distributed over reciprocal space. The observed Laue group was $2/m$ and, from the noted systematic absences ($0k0$, $k = 2n + 1$), the possible space groups were $P2_1$ or $P2_1/m$. The general distribution of the intensities of diffracted planes suggested that the space group was centrosymmetric ($P2_1/m$), and this conclusion was reinforced by applying Wilson's (1949) statistical test with $hk0$, $0kl$, $0k0$ and $h0l$ reflections, and a negative pyroelectricity test which by itself is only a weak check for centrosymmetry. The theoretical ratio of the square of the mean magnitude of the structure factors and the average intensity is 0.637 (0.629 experimentally in this work) for a centrosymmetric crystal as opposed to 0.785 for a noncentrosymmetric one (Wilson, 1949). Experimental conditions were: graphite-monochromatized Mo $K\alpha$ radiation (λ, mean = 0.71073 Å); ω–2θ scan, $\theta_{min} = 2°$, $\theta_{max} = 35°$; 2θ scan width, $(1.35 + 0.35 \tan \theta)°$; fixed aperture, 2 mm; maximum scan time, 300 s; scan-speed limits, 0.41–3.35° min^{-1}; $T = 290$ K. Electronic hardware reliability, X-ray intensity measurement and crystal stability were checked by monitoring two standard reflections every 2 h of exposure time. Only random variations from the mean intensity values were observed (<2.6% deviation). 626 observed reflections were recorded, of which 128 were independent having $I_{net} > 3\sigma(I)$, where $I_{net} = (I - 2\sum bg)$ and $\sigma(I) = [I + 2\sum bg + p^2 I_{net}^2]^{1/2}$; the

Table 1. *Fractional atomic coordinates and anisotropic temperature factors* ($\mathring{A}^2 \times 10^2$)

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

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Lu	0·1879 (4)	$\frac{3}{4}$	0·3322 (6)	0·14 (7)	0·17 (8)	0·75 (10)	0	0·13 (6)	0
O·	0·095 (6)	$\frac{3}{4}$	0·777 (10)	0·9 (6)	1·6 (10)	5·6 (7)	0	0·5 (9)	0
O	0·567 (5)	$\frac{3}{4}$	0·776 (8)	0·3 (4)	0·1 (4)	1·5 (8)	0	0·3 (3)	0

ignorance factor $p = 0.02$ in this work. Corrections were applied for Lorentz and polarization effects and for absorption ($\mu = 58.71$ mm^{-1}; transmission-factor range, 0·319–0·465). The resultant residual averaging error was 0·012 ($R' = \sum |F_o - F_{av}| \sum |F_o|$).

The starting model from the work of Christensen (1965) was verified by employing Patterson mapping and a consequent difference Fourier projection. Lu atoms lie on a mirror plane at $x,\frac{3}{4},z$ [$P2_1/m$, No. 11, $2(e)$] and packing considerations place the O positions at 0·095, 0·75, 0·777, and 0·567, 0·75, 0·776. The prototype of this model is YOOH (Klevtsova & Klevtsov, 1964). Table 1 lists the final positional and thermal parameters with their e.s.d.'s for LuOOH.* The isotropic refinements produced an R value of 0·043 with no unusual relationships between variables evident in the correlation matrix. No secondary-extinction corrections were made and the final aniso-tropic full-matrix least-squares refinement program (Larson, 1967) yielded $R = \sum (||F_o| - |F_c||)/\sum |F_o| = 0.0350$ and $R_w = \sum w^{1/2}|(F_o - F_c)|/\sum w^{1/2}|F_o| = 0.0347$, where $w = \sigma^{-2}(F_o)$. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. The maximum absolute value of convergence [$\Delta E_i/\sigma(E_i)$, where E_i values are parameters varied] showed that none of the 19 variables shifted by more than 0·001% (maximum value 1.1×10^{-5}). A final difference electron density map was featureless revealing only a slight residual density of 1·6 (5) e $\mathring{A}^{-3}$, located near the metal atom, which is quite meaningless. Atomic scattering factors and the applied anomalous-dispersion corrections to the factors for all atoms were taken from Ibers & Hamilton (1974).

Discussion. The lutetium hydroxide oxide molecule is a seven-atom polyhedron, and is best described as a distorted capped trigonal prism (symmetry C_{2v}). Demitras, Russ, Salmon, Weber & Weiss (1972) described such a seven-atom system as one of three idealized symmetries for heptacoordinated structures, see Figs. 1 and 2. The Lu atom is located off-center and

* Lists of structure factors and interatomic distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35537 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
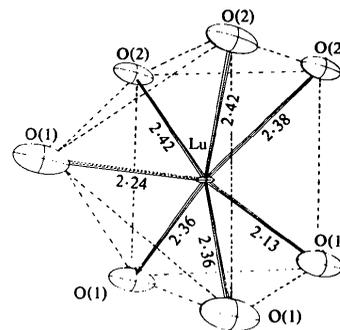
Fig. 1. The coordination polyhedron of Lu, showing the atom labeling and bond lengths ($\mathring{A}$).
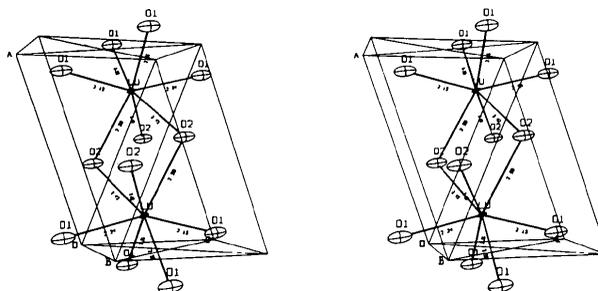
Fig. 2. A stereoscopic view of the molecular packing in the unit cell.

six of the heptacoordinated O atoms are located in apical positions of the trigonal prism [three hydroxyl groups, O(2), above and three oxygen ions, O(1), below the off-centered Lu^{3+} ion]. The remaining O^{2-} ion is equatorially located near the center of the rectangular face of the trigonal prism closest to the off-centered Lu^{3+} ion [there is C_2 symmetry about this Lu–O(1) bond]. The O^{2-} ion, O(1), and the hydroxyl group, O(2), coordinate, respectively, to four and three Lu atoms.

The experimental lattice constants are in good agreement with those determined by Klevtsov & Sheina (1965). The average Lu–O(1) distance is 2·24 Å, which is interpreted as the metal to oxygen ion (O^{2-}) bond length. The average value is consistent with the experimental values found in the *Bond Index of the Determination of Inorganic Crystal Structures* (1969–1977) and in the work of Templeton & Dauben (1954), 2·23 Å. The Lu–OH bond is defined to be the Lu–O(2) bond distance [av. Lu–O(2) distance 2·40 Å]. It is found that the sum of the Lu^{3+} radius

(0·861 Å; Shannon & Prewitt, 1970) and the average OH⁻ radius of 1·52 (3) Å determined in other seven-coordinated metal hydroxide oxide systems (Christensen, 1965) is in good agreement with the average Lu—O(2) bond length. Even though the O⋯O contact distances could be considered close enough for hydrogen bonding, an infrared study of LuOOH clarified any such misinterpretation. Table 2 presents pertinent interatomic distances and angles.

The crystallographic analysis of an extremely small single crystal of LuOOH has expanded our base of structural refinements. The refinement has also provided more information related to the Lu—O bond length for which only a scant number of articles have been published. Further, it is believed that this study describes the first heptacoordinated Lu structure involving seven O atoms.

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

Lu—O(1)	2·36 (2)	O(1)—Lu—O(1)	78·9 (12)
	2·24 (4)		83·3 (11)
	2·13 (4)		97·4 (11)
Lu—O(2)	2·42 (2)		152·9 (16)
	2·38 (3)	O(1)—Lu—O(2)	75·0 (11)
O(1)—O(2)	3·08 (4)		75·6 (9)
	2·76 (4)	O(2)—Lu—O(1)	80·2 (8)
	2·86 (3)		132·1 (11)
O(1)—O(1)	3·06 (6)	O(2)—Lu—O(2)	94·5 (10)
	2·86 (6)		
O(2)—O(2)	2·84 (5)		
	2·89 (5)		

References

Bond Index of the Determination of Inorganic Crystal Structures (1969–1977). Institute for Materials Research, Hamilton, Canada.
CHRISTENSEN, A. N. (1965). *Acta Chem. Scand.* **19**, 1391–1396, 1504–1505.
DEMITRAS, G. C., RUSS, C. R., SALMON, G. F., WEBER, J. H. & WEISS, G. S. (1972). *Inorganic Chemistry*, pp. 162–163. New Jersey: Prentice-Hall.
IBERS, J. A. & HAMILTON, W. C. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 72–151. Birmingham: Kynoch Press.
KLEVTSOV, P. V. & SHEINA, L. P. (1965). *Izv. Akad. Nauk SSSR, Neorg. Mater.* **1**, 912–917.
KLEVTSOVA, R. F. & KLEVTSOV, P. V. (1964). *Zh. Strukt. Khim.* **5**, 860–865.
LARSON, A. C. (1967). US Government Reports 3198, 3259, 3309.
MULLICA, D. F., BEALL, G. W., MILLIGAN, W. O. & OLIVER, J. D. (1979). *J. Appl. Cryst.* **12**, 263–266.
MULLICA, D. F. & MILLIGAN, W. O. (1980). *J. Inorg. Nucl. Chem.* **42**, 223–227.
MULLICA, D. F., MILLIGAN, W. O. & DILLIN, D. R. (1979). *J. Cryst. Growth*, **47**, 635–638.
SHANNON, R. D. & PREWITT, C. T. (1970). *Acta Cryst.* B**26**, 1046–1047.
TEMPLETON, D. H. & DAUBEN, C. H. (1954). *J. Am. Chem. Soc.* **76**, 5237–5239.
WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318–321.

Structure de l'Hexachlorure de Dicadmium et de Nickel Dodécahydraté

PAR A. LECLAIRE ET M. M. BOREL

Laboratoire de Cristallographie et Chimie du Solide, LA 251, Laboratoires de Cristallographie–Minéralogie et de Chimie Minérale B, ISMRA, Université de Caen, 14032 Caen CEDEX, France

Abstract. $Cd_2NiCl_6 \cdot 12H_2O$, $Fdd2$, $a = 24\cdot4219$ (21), $b = 22\cdot3429$ (22), $c = 7\cdot5416$ (13) Å, $Z = 8$, $V = 4115$ Å³, $D_m = 2\cdot31$ Mg m⁻³, $\mu_{(MoK\bar{\alpha})} = 3\cdot76$ mm⁻¹. The structure was refined to an R of 0·031 ($R_w = 0\cdot030$) with 3034 reflexions $[I > 3\sigma(I)]$. The Cd atom is bonded to five Cl atoms and one H_2O molecule. The Ni atom is bonded to six H_2O molecules. The structure consists of infinite chains of $CdCl_5(H_2O)$ octahedra, $Ni(H_2O)_6$ octahedra and free water molecules held together by hydrogen bonds.

Introduction. Nous avons entrepris l'étude d'une série d'halogénures hydratés de formule Cd_xNi_y-$Cl_{2(x+y)} \cdot zH_2O$, afin de comparer le comportement structural de chacun des deux cations en présence de l'autre. Nous avons commencé par la détermination du composé de formule $Cd_2NiCl_6 \cdot 12H_2O$ qui a été mis en évidence par Bassett, Henshall, Sergeant & Shipley (1939) quand ils établirent le diagramme de solubilité $CdCl_2$–$NiCl_2$–H_2O.

Les cristaux se présentent sous la forme d'aiguilles transparentes vert pâle.

Les dosages du cadmium, du nickel et du chlore sont en accord avec la formule pondérale $Cd_2NiCl_6 \cdot 12H_2O$.

Les symétries et les extinctions systématiques observées sur les clichés réalisés à l'aide des chambres de