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The Crystal Structure of $La_7(OH)_{18}I_3$*

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The crystal structure of hexagonal $La_7(OH)_{18}I_3$ (space group $P6_3/m$, $a = 18{\cdot}315 \pm 0{\cdot}007$, $c = 3{\cdot}928 \pm 0{\cdot}001$ Å, $Z = 2$) has been refined from diffractometer-collected intensity data by full-matrix least-squares methods to a conventional R of 2·9%. The structure is derived from that of the UCl_3-type trihydroxide by iodide substitution on one-seventh of the anion sites. The unit cell is a complex arrangement of two regular and six slightly irregular trigonal prisms of $La(OH)_3$ plus six highly distorted trigonal prisms of $La(OH)_2I$ produced by accommodation of iodide ions in vacant channels of the parent structure. This type of accommodation mechanism maintains ninefold cation coordination and accounts for the occurrence of this structure type for several monovalent anions with substantially different sizes. The space groups of the substructure and superstructure have a single same-class subgroup relationship. The superstructure is the first example of the previously unknown $m = 7$ member of the {3,6} compound-tessellation series.

Introduction

Recent investigations (Haschke & Eyring, 1971; Haschke, 1974; Lance & Haschke, 1976) of ternary lanthanide monovalent anion systems have succeeded in elucidating the structural relationships and crystal chemistry of lanthanide hydroxide halides and hydroxide nitrates. Qualitative comparisons and subgroup–supergroup correlations (Neubüser & Wondratschek, 1966; Wondratschek, 1974) have been used (Haschke, 1976, 1977) to demonstrate the existence of close relationships between the structures. The $Y(OH)_2Cl$-type structure of the $Ln(OH)_2X$ phases (Ln = lanthanide, $X = NO_3^-$, Cl^-) and the high-temperature form of $La(OH)_2NO_3$ are closely related to the UCl_3-type structures of the lanthanide trihydroxides and trihalides, and the $PuBr_3$-type structure of the lanthanide trihalides respectively. However, an adequate understanding of the crystal chemistry of the hydroxide halide and hydroxide nitrate phases of the lighter lanthanides is incomplete without structural knowledge of the phase which forms between the trihydroxide and the $Ln(OH)_2X$ phase.

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The existence of pronounced substructure reflections in the powder diffraction data for the intermediate phase suggests that the structure is related to that of the UCl_3-type trihydroxide. An attempt to determine the structure of the nitrate-containing La phase permitted definition of the $La_7(OH)_{18}(NO_3)_3$ stoichiometry (Lance, Butler, Haschke, Alway & Peacor, 1976), but orientational disorder of the nitrate ion prevented determination of the positional coordinates of the nitrate oxygens. Such difficulties are prevented by substitution of monatomic, spherical anions, and the preparation of bromide- and iodide-containing phases has been pursued (Lance-Gómez & Haschke, 1977).

The present investigation was initiated after single crystals of $La_7(OH)_{18}I_3$ were obtained. Examination of the refined structure verified the presence of a pronounced superstructure, and an attempt has been made to identify symmetry correlations and compound-tessellation aspects of the substructure–superstructure relationships.

Crystal data

Cylinder: length 0·72 mm, radius 0·031 mm; hexagonal, space group $P6_3/m$, a = 18·315 (7), c = 3·928 (1) Å, ρ_c = 4·83 g cm^{-3}; $(\sin\theta/\lambda)_{\max}$ = 0·905 Å^{-1}; μ = 171·9 cm^{-1}.

Experimental

The crystal used for data collection was selected from those grown during a normal hydrothermal preparation (Lance-Gómez & Haschke, 1977) and mounted with the c axis along the spindle axis in the conventional manner. Weissenberg and precession data indicate hexagonal symmetry with space group $P6_3/m$ or $P6_3$.

A Syntex $P\bar{1}$ four-circle autodiffractometer using monochromatized (graphite crystal) Mo $K\alpha$ (λ = 0·71069 Å) radiation, a scintillation detector, and a θ–2θ scan technique were used to collect the intensity data. A variable scan rate, which was a function of the peak intensity, was used in order to obtain comparable counting statistics between the reflections. Background counts were measured at each end of a scan for a total time equal to a fixed fraction of the scan time. The intensities of three reflections (200, 020, 002) were monitored after every 50 reflections collected. No significant changes in their intensities were observed.

3637 independent reflection intensities were measured. The 3123 reflection intensities with $F^2_{\text{meas}} \geq 3\sigma$ were corrected for Lorentz–polarization effects (W. Schmonsees, *SYNCOR* data reduction program, Wayne State Univ.). No absorption correction was made owing to the relative equivalence of the absorption-correction factors for the cylindrical crystal (*International Tables for X-ray Crystallography*, 1959). As there is a significant imaginary component to the scattering factors, a comparison of the intensities of symmetry-equivalent positive and negative l value reflections was made to determine if the structure is noncentrosymmetric. The intensities were all equal within experimental error, and hence the test was inconclusive.

Structure refinement

An initial full-matrix least-squares refinement (Busing, Martin & Levy, 1962) of the scale factor using positional parameters obtained for La atoms in $La_7(OH)_{18}(NO_3)_3$ indicated that the metal atoms occupy approximately equivalent positions. Successive cycles of difference electron density synthesis (Zalkin, 1965) and structural refinement allowed the determination of the positions of all atoms except H. Refinement of all atomic positional parameters and anisotropic temperature factors was carried to convergence using scattering factors for all atoms in their standard oxidation states (Cromer & Waber, 1965) and an anomalous-dispersion correction for the La and I atoms (Cromer & Liberman, 1970). A final difference electron density synthesis showed no regions of significant electron density. Final refinement gave a value for the residual $[R = (\Sigma|\Delta F|/\Sigma|F_o|)]$ of 2·9% (including unobserved reflections) and a weighted residual $[R_w = (\Sigma w\Delta F^2/\Sigma wF_o^2)^{1/2}, w = 4F_o^2/\sigma^2(F_o^2)]$ of 4·5% (including unobserved reflections) with a maximum value for the (parameter shift)/error of 0·33. The final atomic positional parameters are listed in Table 1.* Selected values of bond lengths and angles in Table

Table 1. *Atomic positional parameters* ($\times 10^4$) *of* $La_7(OH)_{18}I_3$ ($z = \frac{1}{4}$ *for all atoms*)

Uncertainties in the last digits of positional parameters appear in parentheses.

	Site	x	y
La(1)	6(h)	1523·8 (2)	2314·9 (2)
La(2)	6(h)	4588·0 (2)	1398·5 (3)
La(3)	2(c)	$\frac{1}{3}$	$\frac{2}{3}$
I(1)	6(h)	4349·0 (3)	3904·1 (3)
O(1)	6(h)	5598 (3)	2921 (3)
O(2)	6(h)	3063 (3)	529 (3)
O(3)	6(h)	1267 (3)	29 (3)
O(4)	6(h)	2588 (3)	1809 (3)
O(5)	6(h)	3824 (3)	5555 (3)
O(6)	6(h)	2194 (3)	4007 (3)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33151 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances* (Å) *and angles* (°) *in* $La_7(OH)_{18}I_3$

Numbers in parentheses after the atomic symbol refer to atoms labeled in Fig. 1. Uncertainties in the last digits of distances and angles appear in parentheses.

(i) Interplanar distances [from La(1–3) at $z = \frac{1}{4}$ to anions at $z = \frac{3}{4}$]

La(1)–O(2)	2·573 (3)	La(2)–O(5)	2·507 (3)
La(1)–O(3)	2·609 (4)	La(2)–O(6)	2·524 (3)
La(1)–O(4)	2·579 (3)	La(2)–I(1)	3·549 (2)
La(3)–O(1)	2·604 (3)		

(ii) Interplanar distances [from La(1–3) to atoms in the same plane]

La(1)–O(3)	2·521 (6)	La(2)–O(1)	2·465 (5)
La(1)–O(4)	2·541 (5)	La(2)–O(2)	2·426 (5)
La(1)–O(6)	2·700 (5)	La(2)–I(1)	3·933 (2)
La(3)–O(5)	2·600 (5)		

(iii) Interatomic angles (among atoms in trigonal prisms)

O(2)–La(1)–O(3)	69·1 (1)	O(5)–La(2)–O(6)	70·7 (2)
O(3)–La(1)–O(4)	68·8 (2)	O(5)–La(2)–I(1)	70·6 (1)
O(2)–La(1)–O(4)	67·9 (1)	O(6)–La(2)–I(1)	81·6 (1)
O(1)–La(3)–O(1)	69·3 (1)		

2 were calculated (Busing, Martin & Levy, 1964) from the refined atom coordinates and lattice parameters using the full variance–covariance matrix of the atom coordinates and standard deviations of the lattice parameters.

Description of the structure

A three-dimensional *ORTEP* (Johnson, 1965) diagram of the unit cell of the $La_7(OH)_{18}I_3$ structure type is shown in Fig. 1. Fig. 2 is a two-dimensional projection diagram showing the packing of the coordination polyhedra.

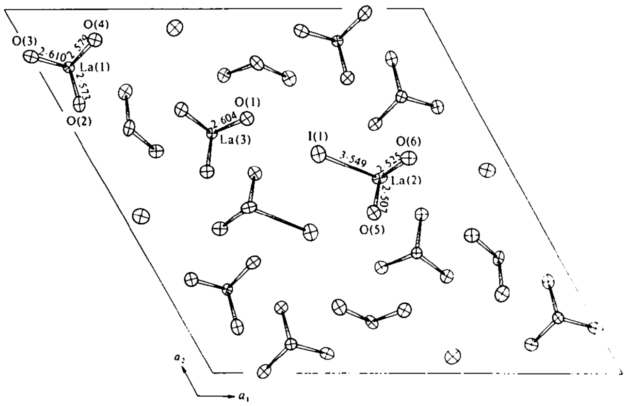

Fig. 1. *ORTEP* diagram of hexagonal $La_7(OH)_{18}I_3$ projected on (0001). The thermal ellipsoids are at the 95% probability level. Lightly drawn atoms are at $z = \frac{1}{4}$; heavily drawn atoms are at $z = \frac{3}{4}$. Unique bond lengths are written above the bond and the unique atoms are labeled.

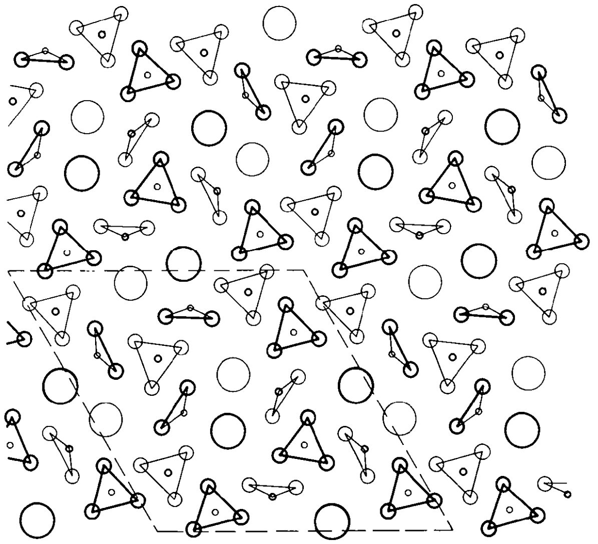

Fig. 2. Two-dimensional representation of the structure of $La_7(OH)_{18}I_3$ projected on (0001). Metal, hydroxide, and iodide positions are indicated by small, intermediate, and large circles respectively. Lightly drawn atoms are at $z = \frac{3}{4}$. The direction of stacking of the trigonal prisms is indicated by the triangles with a La in the center. The $La(OH)_2^+$ units are indicated by a triangle connecting two OH^- ions and a La^{3+} ion not in the same plane. The I atoms are unconnected.

The $La_7(OH)_{18}I_3$-type structure is derived from the UCl_3-type structure by an ordered substitution of iodide for hydroxide. The substituent iodides are accommodated by distortion of the regular trigonal-prismatic cation coordination polyhedra in the UCl_3-type structure and actually occupy vacant channels in the parent structure (Haschke, 1976). The unusual composition, $Ln_7(OH)_{18}X_3$ ($X = NO_3^-, Cl^-, Br^-, I^-$), of the asymmetric unit and the supercell–subcell relationship are consequences of this ordered substitution. The ordering of the substituent anions creates a supercell which is a sevenfold volume multiple of the subcell. The lattice parameters of the supercell can be derived from those of the subcell by use of the matrix

$$\begin{bmatrix} 2 & \bar{1} & 0 \\ 1 & 3 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

As seen in Figs. 1 and 2, there are three positionally different La atoms in the asymmetric unit and each is coordinated to six anions, which form a trigonal prism. As indicated by the bonds in Fig. 1 and the triangles in Fig. 2, three anions are located in a plane $c/2$ above and below the planes of each La. The cations are further coordinated to three coplanar anions. As in the UCl_3-type structure, these anions occupy positions above the three rectangular faces of the trigonal prism and complete the tricapped trigonal-prismatic coordination polyhedra. As seen in Table 2, the distance of the La atoms to the coplanar hydroxides is less than the distance to the hydroxides forming the trigonal prisms. Regular, tricapped, trigonal prisms like those of the trihydroxide are observed for the La atoms labeled La(3) in Fig. 1. As in $La(OH)_3$, the metals with this regular coordination geometry are located along the trigonal axes of the cell. This regular prism is surrounded by three distorted $La(OH)_2I$ prisms [*cf.* bond lengths to La(2) in Fig. 1] which are displaced by $\pm c/2$ relative to the central prism. Three slightly distorted $La(OH)_3$ trigonal prisms [*cf.* bond lengths to La(1) in Fig. 1] lie on the same level as the undistorted $La(OH)_3$ unit. One anion of the distorted $La(OH)_3$ units occupies a face of the adjacent $La(OH)_2I$ unit. This assemblage of undistorted $La(OH)_3$ units comprises the $La_7(OH)_{18}I_3$ moiety. As shown in Fig. 2, six slightly distorted $La(OH)_3$ prisms meet at each cell origin and form three-subcell trihydroxide domains which surround vacant channels similar to those of the parent UCl_3-type structure.

Discussion

The $La_7(OH)_{18}I_3$-type structure is characterized by a three-dimensional framework that dictates its crystal-growth habit. As in $La(OH)_3$ and other UCl_3- or $Y(OH)_3$-type structures, the repeat distance along [0001] is short because of its coincidence with the stacking direction of the trigonal-prismatic coordination polyhedra. Normal to [0001] the ordering is long-range. Coherent crystal growth in this dimension requires the addition of at least one $Ln_7(OH)_{18}X_3$ asymmetric repeat unit. In the light of the structural data, it is not surprising that crystals of the $La_7(OH)_{18}I_3$-type phases grow as very thin needles (Lance-Gómez & Haschke, 1977).

One of the interesting features of this structure is its ability to accommodate widely varying sizes of anions, *i.e.* Cl^-, Br^-, I^-, NO_3^-. As seen in Fig. 2, accommodation of larger substituent anions occurs so that they occupy six-sevenths of the vacant channels around the 6_3 axes in the UCl_3-type substructure and destroy the 6_3 symmetry elements in these channels. The $NaNdF_4$- and β-K_2UF_6-type structures of several mixed-metal halides are derived from the UCl_3-type structure by cation occupancy of these channels (Haschke, 1977), but previous examples of anion occupancy are unknown. In some ways the anion accommodation process resembles the behavior of a clathrate; however, in this case the clathrate-like structure is formed by a three-dimensional $La_7(OH)_{18}^{3+}$ framework defined by the $La(OH)_2$ triangles and the $La(OH)_3$ prisms in Fig. 2. The vacant anionic sites of this cationic structure may be filled by a variety of monovalent anions, including OH^-, the distortion-free trivial case, as well as I^- and NO_3^-, for which the distortion is substantial.

The inability to prepare any hydroxide iodide substitution phases of Nd (Lance-Gómez & Haschke, 1977) is evidence that the $La_7(OH)_{18}I_3$-type structure cannot accommodate any size of anion or cation. The cationic lanthanide hydroxide framework of the structure contracts with decreasing cation radius, and at Nd a large ion such as I^- apparently cannot be accommodated.

Substitutional accommodation of a large anion generally results in a reduction of the cation coordination number, as is the case for the $Y(OH)_2Cl$-type structure (Haschke, 1975). But in the $La_7(OH)_{18}I_3$-type structure, all of the metal atoms retain a ninefold coordination polyhedron with a minimum of distortion. The greatest distortion of a coordination polyhedron occurs in the $La(OH)_2I$ unit, which forms the most irregular trigonal prism. The larger anion is not aligned with the perpendicular bisector of a line drawn between the two hydroxides (*cf.* Fig. 2) and the La atom is displaced back, almost into the face of the prism. This distortion causes a distinct shortening of the La—OH distances in the $La(OH)_2I$ unit. This shortening occurs for both the coplanar and extraplanar hydroxides (*cf.* Table 2). Retention of the ninefold coordination polyhedra seems to be an important factor in the stability of the structure.

As noted above, the $La_7(OH)_{18}I_3$-type structure is a clear example of a substructure–superstructure relationship. Prior nomenclature (Buerger, 1947) would define the $La_7(OH)_{18}I_3$-type structure as a substitutional derivative of the UCl_3-type structure. The space group of the $La_7(OH)_{18}I_3$-type structure ($P6_3/m$) is the same as the space group of the UCl_3-type structure of $La(OH)_3$. As expected for same-class subgroup relationships (Wondratschek, 1974), certain translational operators are suppressed in two ways. First, insertion of a large dissimilar anion into six-sevenths of the vacant channels destroys the translational symmetry around the trigonal axes and distorts the parent UCl_3-type structure. This distortion causes the hydroxides of the $La(OH)_3$ trigonal prisms not on the trigonal axes of the $La_7(OH)_{18}I_4$-type structure to become positionally independent. Second, this positional independence removes the translational operator linking the $La(OH)_3$ units not on the trigonal axes. This destruction of translational symmetry with retention of overall symmetry results in the unique subcell–supercell relationship.

The $La_7(OH)_{18}I_3$-type structure is also a hitherto unknown example of the $m = 7$ member of the {3,6} compound-tessellation series (Takeda & Donnay, 1965). The compound tessellation is a consequence of the equivalent space-group relationship between the superstructure and the $La(OH)_3$ substructure, the $m = 1$ member of the {3,6} series. Those space groups that have equivalent space groups as a subgroup have recently been defined (Billiet, 1973). As with $P6_3/m$, it is necessary that a single same-class relationship exist between a space group and its equivalent subgroup.

Because of their unusual structural features, $La_7(OH)_{18}I_3$-type materials might be useful as host lattices for studies of crystal-field effects on the behavior of lanthanides and other doped ions. The wide range of halide accommodation results in a correspondingly wide range of distortion at certain cationic sites. Although the miscibility levels of the isostructural hydroxide chlorides, hydroxide bromides, and hydroxide iodides have not been investigated, they are expected to be substantial and ranges of continuous structural distortion might be easily achieved.

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Dichlorodioxobis(triphenylphosphine oxide)tungsten(VI), $WO_2Cl_2[OP(C_6H_5)_3]_2$

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$C_{36}H_{30}O_4P_2Cl_2W$, $M_r = 843\cdot1$; monoclinic, $P2_1/c$, $a = 18\cdot89\ (1)$, $b = 9\cdot99\ (1)$, $c = 19\cdot23$ Å, $\beta = 112\cdot20\ (5)°$; $Z = 4$, $D_c = 1\cdot666$, $D_m = 1\cdot670$ g cm^{-3}; $U = 3359\cdot9$ Å^3; μ(Mo $K\alpha$) = $35\cdot5$ cm^{-1}. The molecule adopts a distorted octahedral coordination around the W atom, the two triphenylphosphine ligands, as well as the two double-bonded O atoms, being oriented *cis* to each other. The final R for 3007 observed reflexions was 0·046.

Introduction

Colourless single crystals of the title compound were prepared as described by Brisdon (1967), and recrystallized from nitromethane. Intensity data were collected on a crystal which was ground and solvent-etched to spherical shape with dimensions sufficiently small (radius 0·072 ± 0·07 mm) to render absorption errors negligible. Accurate cell dimensions were obtained by least-squares refinement from angular data on 25 high-order reflexions measured on a Philips PW 1100

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