SHORT STRUCTURAL PAPERS

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Cerium Trihydroxide*

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Abstract. $Ce(OH)_3$, M_r = 191·14, hexagonal, $P6_3/m$, $Z = 2$, $a = 6{\cdot}4890$ (12), $c = 3{\cdot}8061$ (6) Å, $V = 138{\cdot}78$ Å^3, μ(Mo $K\alpha$) = 16·339 mm^{-1}, λ(Mo $K\alpha$) = 0·71073 Å. Least-squares full-matrix refinement (236 unique reflections, single-crystal X-ray diffractometer data) gave $R = 0{\cdot}041$ and $R_w = 0{\cdot}042$ for nine varied parameters. The Ce atom is nine-coordinated with two unique Ce—O bond distances and three independent O—O bond distances. The coordination polyhedron is a tricapped trigonal prism, with the Ce atom at its center.

Introduction. For the past three decades, researchers have tried (with little success) to prepare crystals of cerium trihydroxide suitable for single-crystal X-ray diffraction analysis. This inability can be attributed to the ease with which Ce^{III} oxidizes to Ce^{IV}. Most cited studies of cerous trihydroxide were achieved during the 1960's and only a very few of these employed X-ray diffraction methods.

Composition studies (Tananaev & Bokmel'der, 1960; Mironov & Chernyaev, 1961) of the basic salts of Ce were carried out by changing pH values and precipitation volumes where NaOH was the precipitating base. These investigators found that Ce^{III} hydroxide did not adsorb excess NaOH from solution. But later, after re-examining the composition of cerium hydroxide, Chernyaev & Mironov (1963) found the composition to be $Ce(OH)_3.0{\cdot}5H_2O$. The composition was determined by chemical analysis of the solid phase and thermal gravimetric analysis (TGA). The thermograms of Ce salts showed, in addition to decomposition, an exothermic effect resulting from oxidation of Ce^{3+} to Ce^{4+}. The available X-ray diffraction data related to the lattice constants of $Ce(OH)_3$ by powder methods are listed in *Landolt–Börnstein Auflage Zahlenwerte und Funktionen* (1975).

Single crystals of the trihydroxide of Ce were grown by hydrothermal aging at 613 K. A gel of cerium hydroxide, which was washed free of ion contamination, and a 30 *M* NaOH solution (1:3, respectively) were placed in a Teflon aging tube for three days. After harvesting, the $Ce(OH)_3$ crystals were thoroughly washed free of any possible residual base. Measurements from preliminary X-ray powder diffraction photographs obtained by using a Siemens Debye–Scherrer cylindrical camera and Cu radiation filtered with Ni foil (D = 114·8 mm, Cu $K\alpha_1$ = 1·54051 Å and Cu $K\alpha_2$ = 1·54433 Å) verified the crystal system and yielded accurate unit-cell dimensions.

A single hexagonal-prismatic crystal of the title compound (0·038 × 0·038 × 0·144 mm) was selected and mounted on an Enraf–Nonius CAD-4 diffractometer equipped with a dense graphite monochromator and a Si(Li) solid-state detector (Mullica, Beall, Milligan & Oliver, 1979). One of the applicable advantages of the energy dispersive detector is to allow routine fluorescence X-ray data to be collected on the same single crystal upon which X-ray diffraction data are collected (Mullica, Milligan, Beall & Reeves, 1978). The orientation matrix used for data collection (T = 290 K) was produced by using least-squares refinement on 25 centered reflections. Intensities were measured by the θ–2θ scan technique at a rate of 0·4–3·3° min^{-1}, determined by a fast prescan of 3·3° min^{-1}. 360 intensities were measured in the range of $3 < 2\theta < 70°$. No significant variation was observed in the intensities of the monitored standards (every 2 h of exposure time, <1·6% deviation). Intensities greater than 3σ were used in the refinement [$I_{net} > 3\sigma(I)$], according to $I_{net} = (I - 2\sum B)$ and $\sigma(I) = [I + 2\sum B + (0{\cdot}02I_{net})^2]^{1/2}$ where I_{net} is the total integrated peak intensity and B is the background count. After correcting for Lorentz and polarization effects, absorption corrections were made using a linear absorption coefficient for Mo $K\alpha$ of 16·339 mm^{-1}. The minimum and maximum corrections to the observed

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Table 1. *Fractional atomic coordinates and anisotropic temperature factors* (Å^2 × 10^2)

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

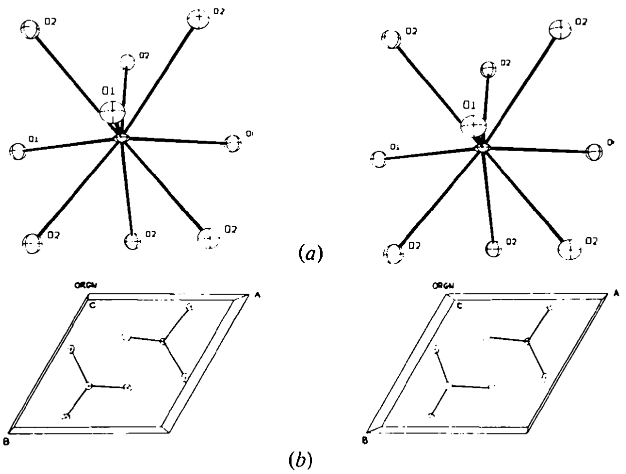
	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ce	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0·80 (2)	0·80 (2)	0·66 (3)	0·40	0	0
O	0·389 (1)	0·308 (1)	$\frac{1}{4}$	1·4 (2)	1·3 (2)	0·9 (2)	0·7 (2)	0	0

structure factors were 0·46 and 0·60 respectively. The symmetry-related reflections were averaged to give 236 independent and unique reflections. The residual averaging error of 0·023 was determined according to $R' = \sum ||F_o| - |F_{av}||/\sum |F_o|$. The standard deviations of the averaged data were calculated from $\sigma_{\langle F\rangle} = (1/N)\sum 1{\cdot}02\sigma_{F_i}$ (Peterson & Levy, 1957), where N is the number of redundant reflections and σ_{F_i} is the standard deviation for each individual reflection.*

The starting model was originally reported by Zachariasen (1948) [prototype UCl_3 (hexagonal, $P6_3/m$)], and was completely verified and used in a study of structural trends of the lanathanide trihydroxide series by Beall, Milligan & Wolcott (1977). The Ce and O atoms were placed in a special site $(\frac{1}{3},\frac{2}{3},\frac{1}{4})$ [positional set 2(c)], and at $x,y,\frac{1}{4}$ [positional set 6(h)], respectively. Table 1 lists the final positional and thermal parameters with their e.s.d.'s. An R of 0·063 was obtained from an isotropic full-matrix least-squares refinement program (Larson, 1967). After several cycles of anisotropic refinement with secondary-extinction corrections ($g = 1{\cdot}2 \times 10^{-6}$), final reliability factors of 0·041 and 0·042 were obtained. R and R_w are defined as $R = \sum(||F_o| - |F_c||)/\sum |F_o|$ and $R_w = \sum[|w^{1/2}(F_o - F_c)|]/\sum w^{1/2}|F_o|$, where $w = \sigma^{-2}(F_o)$. The minimized quantity used in the least-squares refinement program was $\sum w(|F_o| - |F_c|)^2$. The maximum and average abscission values $[\Delta\xi_i/\sigma(\xi_i)$, where ξ_i values are varied parameters] of the nine varied parameters were $6{\cdot}1 \times 10^{-5}$ and $1{\cdot}6 \times 10^{-5}$, respectively. A final difference electron density map revealed a maximum and minimum of 3·8 (4) and −2·3 (4) e Å^{-3}, respectively, in the vicinity of the Ce atom which is not unusual for the heavy lanthanides. Scattering factors were obtained from Cromer & Mann (1968) and the anomalous-dispersion corrections applied to the scattering factors were obtained from Cromer (1965).

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

Ce–O(1)$_{equat}$	2·529 (6)	O(1)–Ce–O(2)	71·9 (2)
Ce–O(2)$_{apical}$	2·567 (4)	O(1)–Ce–O(2)	68·9 (2)
O(1)–O(2)	2·992 (5)	O(2)–Ce–O(2)	71·1 (2)
O(1)–O(2)	2·883 (10)		
O(2)–O(2)	2·984 (11)		



(*a*)

(*b*)

Fig. 1. Stereoscopic views of (*a*) the coordination polyhedron and (*b*) the molecular packing in the unit cell of hexagonal $Ce(OH)_3$.

Discussion. The Ce atom in $Ce(OH)_3$ is nine-coordinated with two unique metal–oxygen bond lengths. Helmholtz (1939) has previously described this type of coordination geometry. Table 2 reports these independent Ce–O bond distances and the three unique O–O contact lengths as well as other selected molecular dimensions. The coordination polyhedron, shown in Fig. 1(a), is a tri-capped trigonal prism. The Ce atom is located at its center and six of the nine coordinating oxygens [O(2)] are located in apical positions. The three remaining oxygens [O(1)] are equatorially positioned near the center of the rectangular faces of the near trigonal prism. A packing diagram ($Z = 2$) of the unit cell is presented in Fig. 1(b).

The recent study of structural trends in the lanthanide trihydroxide series (Beall, Milligan & Wol-

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* Lists of structure factors, anisotropic thermal parameters and interatomic distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34586 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

cott, 1977) presented very interesting graphic relationships between the two independent metal—oxygen bond distances and atomic numbers as well as crystal radii. Also plotted were O—O lengths *versus* atomic numbers and crystal radii. When the Ce—O(1,2) and the O—O distances are interpolated from the graphic structural trend presentations, it is found that all the bond distances experimentally determined in this study are within one standard deviation of the projected values. The apical Ce—O(2) bond distance of 2·567 (4) Å has significant meaning when the recent finding of Beall *et al.* (1977) is considered. These investigators found the radius of the hydroxyl group to be 1·487 (3) Å which compares well with the values found by Christensen (1965) and Hall & Britton (1972) of 1·51 (2) and 1·50 (2) Å, respectively. If one assumes the hydroxyl-ion radius to be 1·487 (3) Å, it is found that the crystal radius of Ce^{III} is 1·080 (7) Å. This value is within 1σ of the determined crystal radius proposed by Templeton & Dauben (1954) after correction to nine-coordination [1·073 (5) Å]. The results of the present study lend support to the work of Beall, Milligan & Wolcott (1977) and help to broaden and strengthen the possible parallel between the actinide and lanthanide series. One of the main objectives of this laboratory is to be able to predict readily the structural properties of the actinide trihydroxides. This will only be possible after all the related lanthanide structural studies have been completely and properly analyzed.

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Zinc(II) Chlorite Dihydrate

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Abstract. $Zn(ClO_2)_2.2H_2O$, monoclinic, $P2_1/n$, a = 6·425 (3), b = 6·892 (2), c = 6·454 (3) Å, β = 94·70 (4)° (at 295 K), V = 284·7 (2) Å^3, Z = 2, M_r = 236·30, D_c = 2·756 Mg m^{-3}, $F(000)$ = 232, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 5·316 mm^{-1}. R = 0·031 for 1158 diffractometer-measured reflections. The O atoms of ClO_2^- bridge octahedrally coordinated Zn^{2+}. Water molecules are also coordinated to Zn and are involved in hydrogen bonding with chlorite O atoms. Cl—O distances are 1·580 (3) and 1·590 (3) Å; the O—Cl—O angle is 111·4 (1)°; Zn—O distances range between 2·050 (2) and 2·133 (3) Å.

Introduction. The crystal chemistry of chlorites has not been studied very extensively. In an effort to correlate the structure and bonding of different metal chlorites, an X-ray analysis of zinc chlorite has been undertaken. The unit cell of the compound has been reported earlier (with no other structural information) (Levi & Scherillo, 1931). The compound was prepared by

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