The coordination polyhedron of Hg is a tetrahedron with Hg–2I 2·772 (1) and Hg–2P 2·579 (3) Å. These distances are in good agreement with values reported earlier, *e.g.* Hg–4I 2·78 for tetrahedral HgI_2 (Huggins & Magill, 1927), Hg–I 2·759 (4), 2·858 (4), Hg–P 2·50 (1), 2·53 (1) Å for $HgI_2P_2SC_{28}H_{28}$ (Aurivillius & Fälth, 1973). The angles in the tetrahedron vary between 100·8 and 113·8° (Table 3). The coordination of P is also tetrahedral with P–Hg 2·579 (3), P–C(1) 1·83 (1), P–C(7) 1·80 (1) and P–C(13) 1·83 (1) Å. The P–C distances also agree well with analogous distances in $HgI_2P_2SC_{28}H_{28}$. The angles in the coordination polyhedron vary between 102·6 and 117·5°. The C–C distances in the ligand chain, 1·47 (2), 1·53 (2) Å, are normal compared with the value 1·531 (3) Å given in *International Tables for X-ray Crystallography* (1968).

The C–C distances in the phenyl rings average 1·382 (7) and 1·383 (12) Å respectively, in good agreement with values reported for similar compounds, *e.g.* $(AgIP_2SC_{28}H_{28})_2$ (Cassel, 1975). The largest deviations of a C atom from the least-squares planes through C(1)–C(6) and C(7)–C(12) of the two phenyl rings are 0·006 and 0·008 Å.

The different arrangements in $HgI_2P_2SC_{28}H_{28}$, built up of monomeric molecules, and $HgI_2P_2C_{29}H_{30}$, built up of endless chains, may have their origin in a faint interaction between Hg and S, the distance Hg···S being 3·71 (1) Å. In the present compound the corresponding distance Hg···C is 5·173 (2) Å.

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The Crystal Structure of $Pr(OH)_2NO_3$

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The structure of $Pr(OH)_2NO_3$ has been determined from single-crystal X-ray data and refined by least-squares methods. The crystals are monoclinic, space group $P2_1$ and the unit-cell dimensions are $a=6·449$, $b=3·881$, $c=7·747$ Å and $\beta=98·73°$. The cell contains two formula units. Each Pr atom is surrounded by a tricapped trigonal prism formed by nine O atoms. The polyhedra are linked together in the *ab* plane. Two of the three O atoms in the NO_3^- group are contained in the O polyhedron. The structure is closely related to the monoclinic form of $Y(OH)_2Cl$.

Introduction

In recent years an increasing awareness of manifold lanthanide hydroxy anion compounds has resulted primarily from low-temperature studies of crystals grown hydrothermally. Hydroxy compounds formed also contain the anions fluoride, chloride, nitrate and carbonate. Single-crystal X-ray structure examinations have been made of several trivalent metal hydroxide chloride phases including orthorhombic and monoclinic forms of $Y(OH)_2Cl$ (Klevtsova & Klevtsov, 1965, 1966; Dornberger-Schiff & Klevtsova, 1967) as well as monoclinic forms of $Ln(OH)_2Cl$, where Ln = La (Carter & Levinson, 1969), Pr, Sm and Gd (Klevtsova & Glinskaya, 1969). All these compounds have been treated crystallographically as though they had a centrosymmetric array of atoms in the unit cell, although Carter & Levinson (1969) noticed that $La(OH)_2Cl$ may have a noncentrosymmetric arrangement.

Haschke (1975) has recently reviewed the known structural information on the larger group of anion-substituted lanthanide and actinide MX_3 compounds and has proposed a systematization based largely upon

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structures having layers of $[MX_2]_n^{n+}$ and $[X]_n^{n-}$. Complete structural data are nonexistent at present and hence these hypotheses cannot be adequately tested.

The $Ln(OH)_2NO_3$ phases show great similarities to the chloride phases; hence they are important members of the related series to be correlated. A complete X-ray crystallographic investigation of $Pr(OH)_2NO_3$ was therefore undertaken.

Experimental

The compound $Pr(OH)_2NO_3$ was prepared by hydrothermal methods (Haschke, 1974). The crystals thus obtained consist of green, hexagonal plates.

The unit-cell dimensions determined from a Guinier X-ray powder pattern (Haschke, 1974) were: $a = 6{\cdot}449\ (5)$, $b = 3{\cdot}881\ (5)$, $c = 7{\cdot}747\ (8)$ Å and $\beta = 98{\cdot}73\ (6)°$.

A crystal $0{\cdot}24 \times 0{\cdot}19 \times 0{\cdot}07$ mm showing satisfactory diffraction by single-crystal techniques was selected for the collection of the X-ray diffraction data. The intensity data were collected with a Syntex $P\bar{1}$ autodiffractometer using Zr-filtered Mo $K\alpha$ radiation and a variable speed θ–2θ scan mode. For each reflection the scan speed, between 1 and 8° min^{-1}, was determined from the intensity found in a rapid sampling scan. The scans were taken over the range $2\theta(K\alpha_1) - 1{\cdot}0°$ to $2\theta(K\alpha_2) + 1{\cdot}0°$ with background counts for 0·25 of the scan time taken at each end. Of 2558 independent reflections investigated in the angular range $2\theta \le 80°$, a total of 1809 were retained that had $\sigma(F_o) \le 0{\cdot}20|F_o|$ where $\sigma(F_o)$ is defined by $\sigma(F_o) = 0{\cdot}02|F_o| + [C + k^2B/(2|F_o|Lp)]^{1/2}R$. C is the total count in a scan taken at the rate R and k is the ratio of the scanning time to the time for the total background count B. Three standard reflections were remeasured at intervals of 50 reflections. They showed a maximum random variation of 3% in intensity during the period of data collection.

Corrections were applied for Lorentz and polarization factors as well as for absorption, with a modified version of an absorption program by Tompa, DeMeulenaer and Alcock. The maximum absorption correction was $45 \pm 0{\cdot}5$% on F_o.

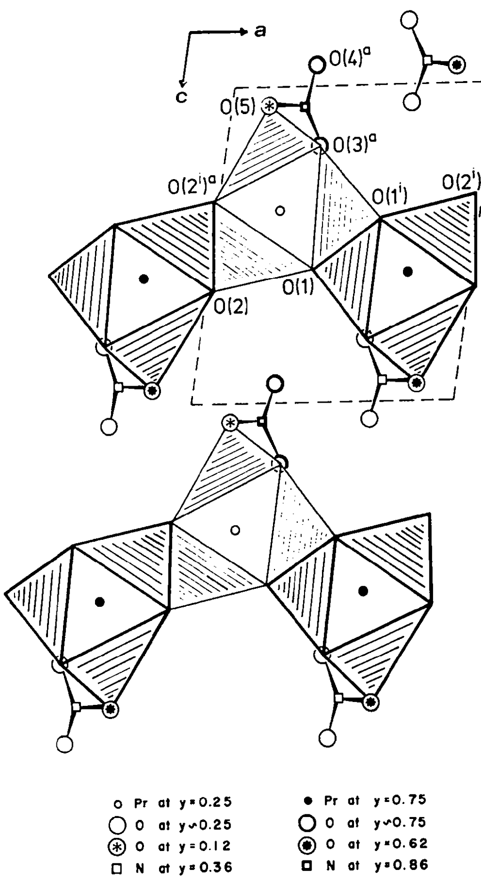

Fig. 1. The crystal structure of $Pr(OH)_2NO_3$ projected along [010].

Structure determination

The precession photographs showed monoclinic symmetry with systematic absences $0k0$ for $k = 2n+1$. This condition permitted the space group alternatives $P2_1$ (No. 4) and $P2_1/m$ (No. 11). The appearance of the precession photographs suggests that this compound has structural similarities to the monoclinic form of $Y(OH)_2Cl$ (Klevtsova & Klevtsov, 1966).

A Patterson function was calculated from which an approximate atomic position for praseodymium was determined. A three-dimensional difference Fourier synthesis based on this position revealed two double peaks representing the N and one O atom as well as four peaks showing anisotropy along the y direction. This may indicate a noncentrosymmetric structure with space group $P2_1$, or a disordered structure with centrosymmetric space group $P2_1/m$.

A few models with different arrangements of the light atoms, based on the noncentrosymmetric space group, were refined by full-matrix least-squares techniques (Busing & Levy, 1962). All the models converged to the same atomic arrangement, and this model was further refined.

A new three-dimensional difference Fourier synthesis including all the atoms showed no remaining peaks. An attempt was also made to refine the structure according to the assumption of a disordered arrangement of the light atoms. This time the difference Fourier maps contained residues of peaks; thus the space group $P2_1/m$ did not seem to be correct.

A comparison of the observed and calculated weak reflections showed better agreement for the noncentrosymmetric version, and the space group $P2_1$ was used for further refinement of the structure. The enantiomorphous forms of the structure were tried and one fitted the data better than the other.

Atomic scattering factors for ionized atoms (Cromer & Mann, 1968) were used with the application of the real and imaginary part of the dispersion correction.

Corrections were made for secondary extinction by means of Zachariasen's (1968) formula. The maximum extinction correction was 31 % of $|F_o|$, for the 001 reflection.

The structure factors were weighted according to the formula $w=[A_0+A_1|F_o|^2+A_2|F_o|^3]^{-1}$ with $A_0=0{\cdot}5$, $A_1=5\times10^{-4}$ and $A_2=1\times10^{-6}$.

Isotropic temperature factors were applied during the first stage of the refinement, yielding an R value of 9·5 %. Finally, anisotropic temperature factors for the Pr atoms were refined, and an R value of 5·7 % was obtained. When the temperature factors of the light atoms were made anisotropic there was no further improvement in the R value. A three-dimensional difference Fourier synthesis based on subtraction of all atoms except H showed no significant indication of anisotropic temperature factors for O and N, and did not reveal any hydrogen peaks. Attempts were made to refine the H atoms in the most probable positions, but without success. The final refinement was made without the H atoms. The atomic parameters and their standard deviations are presented in Table 1.*

Table 1. *Final positional and thermal parameters*

Standard deviations are given in parentheses.

	x	y	z	B
Pr	0·23242 (6)	0·25000	0·40342 (6)	*
O(1) (OH)	0·3787 (9)	0·7575 (66)	0·5724 (8)	0·70 (7)
O(2) (OH)	0·0247 (10)	0·2400 (67)	0·6452 (9)	0·88 (8)
O(3)	0·3661 (11)	0·7443 (86)	0·2093 (9)	1·09 (9)
O(4)	0·3103 (17)	0·7285 (75)	0·9262 (14)	2·16 (18)
O(5)	0·1591 (19)	0·1203 (33)	0·0630 (16)	1·71 (15)
N	0·2775 (17)	0·8648 (32)	0·0618 (15)	1·17 (13)

* Anisotropic temperature factors in the form $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\times10^{-4}]$

β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
35 (1)	52 (3)	41 (1)	21 (4)	17 (1)	−7 (4)

Results and discussion

The crystal structure of $Pr(OH)_2NO_3$ may be described as a layer structure (Fig. 1) where each layer contains identical polyhedra, each consisting of a Pr surrounded by nine O atoms to create a tricapped trigonal prism. The polyhedra are stacked on top of each other and have their triangular faces parallel to the *ac* plane in common. The columns thus created are mutually joined by zigzag strings of shared edges to form corrugated infinite layers, extending parallel to the *ab* plane. The corners of the coordination polyhedron are occupied by six O atoms from the OH^- groups and three from two NO_3^- groups. The N and the third O in the NO_3^- groups project into the space between the layers.

The distortion of the tricapped trigonal prism is shown in Fig. 2. The interatomic distances are given in Table 2. There are six shorter Pr–O distances within the polyhedra ranging from 2·425 to 2·574 Å and three longer distances varying between 2·656 and 2·693 Å. The latter occur between the metal and the O atoms belonging to the NO_3^- groups.

The O polyhedron is irregular, with all O–O distances in the range of 2·801–3·621 Å, except one considerably shorter, of 2·176 Å, which is the distance between two O atoms belonging to a NO_3^- ion.

Table 2. *Interatomic distances in* $Pr(OH)_2NO_3$ *and angles in the* NO_3^- *group*

Standard deviations are given in parentheses.

Pr----Pr^{i}	4·043 (1) Å	O(3)—O(1^{i})	2·879 (29) Å
Pr——O(1)	2·472 (20)	O(1^{i})^{a}	2·948 (30)
O(1)^{a}	2·425 (20)	O(2^{i})^{a}	2·913 (10)
O(1^{i})	2·486 (6)	O(4)^{a}	2·169 (13)
O(2)	2·463 (7)	O(5)	2·911 (30)
O(2)^{a}	2·573 (20)	O(5)^{a}	2·176 (26)
O(2^{i})	2·513 (20)	O(4)—O(1)	2·844 (13)
O(3)	2·660 (24)	O(2)	3·242 (25)
O(3)^{a}	2·693 (24)	O(3^{i})	3·107 (29)
O(5)	2·656 (12)	O(3^{i})^{a}	3·183 (30)
O(1)–2O(1^{i})	2·828 (9)	2O(4^{i})^{a}	3·195 (17)
O(2)	3·156 (24)	O(5^{i})^{a}	3·070 (17)
O(2^{i})	2·878 (9)	O(5)^{a}	2·168 (25)
O(2)^{a}	3·071 (24)	O(5)—O(2^{i})^{a}	3·621 (21)
O(3)	2·801 (9)	O(2)^{a}	3·255 (14)
O(2)–2O(2^{i})^{a}	2·951 (10)	N----O(3)	1·286 (18)
O(5^{i})^{a}	3·084 (19)	O(4)^{a}	1·223 (20)
		O(5)^{a}	1·252 (17)

O(3) –N–O(4)^{a}	119·64 (1·72)°
O(4)^{a}–N–O(5)^{a}	122·29 (1·45)
O(3) –N–O(5)^{a}	118·07 (1·51)

(*a*) Atom in the next unit cell. (i) Symmetry-related atom.

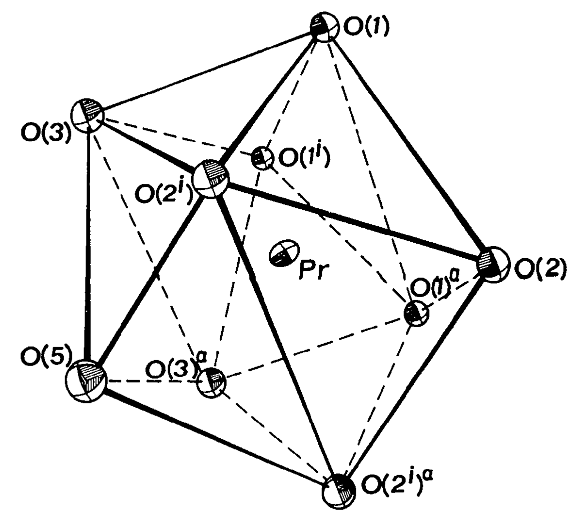

Fig. 2. The tricapped trigonal prism of O atoms surrounding the Pr atom. O(1), O(2^{i}), O(3), O(1)^{a}, O(2^{i})^{a} and O(3)^{a} form the trigonal prism and the rectangular faces are capped by O(1^{i}), O(2) and O(5).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31867 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The N–O distances within the NO_3^- group vary between 1·223 and 1·286 Å.

The $Pr(OH)_2NO_3$ structure is very closely related to the monoclinic form of $Y(OH)_2Cl$, even though Klevtsova & Klevtsov (1966) have indicated that this compound crystallizes in the centrosymmetric space group $P2_1/m$. On the other hand, Carter & Levinson (1969) found evidence that $La(OH)_2Cl$ crystallized in a noncentrosymmetric structure with the space group $P2_1$, the same space group as that found for $Pr(OH)_2NO_3$.

Some lanthanide dihydroxide chlorides, for example $Pr(OH)_2Cl$ (Klevtsova & Glinskaya, 1969) are isostructural with $Y(OH)_2Cl$. The Pr atom in this case is surrounded by six O and two Cl to form a somewhat distorted dicapped trigonal prism. The polyhedra are, however, linked to each other in the same way as in $Pr(OH)_2NO_3$.

The M–Cl distances are noticeably longer (3·00 Å) than the M–O distances (2·43–2·49 Å). Therefore the $Pr(OH)_2Cl$ structure may be considered as built of alternating layers of $[Pr(OH)_2]_n^{n+}$ and $[Cl^-]_n^{n-}$ (Haschke, 1975). In the $Pr(OH)_2NO_3$ structure the corresponding distances are only slightly longer than the other M–O distances; therefore it seems more natural to include the nine closest O atoms in the same polyhedral layer as the metal atoms. The layers are presumably linked to each other by hydrogen bonds.

The tricapped trigonal prism has been observed earlier in the structures of $Y(OH)_3$ (Schubert & Seitz, 1947) and UCl_3 (Zachariasen, 1948) where the polyhedra are fused by edge- and face-sharing to create a three-dimensional network.

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