

From a geometrical point of view the Tl^+ ions can be described as forming a deformed hexagonal close packing (Fig. 2). On account of the disorder of the $S_2O_3^{2-}$ tetrahedra the position O(2) outside the mirror planes at $y = \pm \frac{1}{4}$ contains both S and O.

In a $S_2O_3^{2-}$ group the S-S distance is 1.979 (3) Å and the S-O distances 1.484 (3), 1.472 (3) and 1.475 (3) Å (Manojlović-Muir, 1975). With respect to the occupancy factors for the S(2) and O(2) positions in the present thiosulphate tetrahedron a calculated distance S(1)-S(2) of 1.73 Å and S(1)-O(2) of 1.61 Å can be obtained from the reported distances of Manojlović-Muir (1975). These results are in good agreement with the observed distances S(1)-S(2) and S(1)-O(2) of 1.75 (2) and 1.66 (2) Å, respectively. The distance S(1) to O(1) between the atoms which are not disordered is 1.49 Å. The disorder explains the high temperature factors of S(2) and O(2) (*cf.* Manojlović-Muir, 1975). S(1) and O(1) also have high temperature factors, probably due to the fact that the axis S(1)-O(1) of the tetrahedron may have a minor oscillatory movement caused by the imperfection.

The fact that the structure is partly disordered makes it difficult to discuss the environments of Tl(1) and Tl(2) (Fig. 1). Tl(1) is coordinated to two O(1), not statistically distributed, at identical distances of 3.15 Å (Table 2). Tl(1) is also surrounded by five S or O atoms ranging from 3.07 to 3.22 Å. Further, three O or S atoms are situated at approximately 3.46 Å.

Tl(2) has two O(1) at 2.91 and 3.06 Å and seven S or O atoms ranging from 3.11 to 3.29 Å. These distances are in agreement with reported values for other Tl^I compounds (Table 3). A comparison with the isostructural Rb_2SO_4 (Nord, 1974) reveals no apparent differences in the environments of the corresponding cations (Table 2). This indicates that the Tl ions in $Tl_2S_2O_3$ may be stereochemically inactive, as in $TlZnSO_4Cl$ (Bosson, 1976a), $Tl_3[Hg(SO_4)_2][HgSO_4Cl]$ (Bosson, 1976b) and $Tl_2[Cu(SO_3)_2]$ (Hjertén & Nyberg, 1973).

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Table 3. Tl-O distances in some compounds

	Nearest Tl-O distances (Å)	Next distance (Å)	Reference
$TlZnSO_4Cl$	2.89-3.24	3.48	Bosson (1976a)
$Tl_3[Hg(SO_4)_2][HgSO_4Cl]$	2.80-3.25 2.60-3.21 2.68-3.20	3.45 3.40 3.44	Bosson (1976b)
$Tl_2[Cu(SO_3)_2]$	2.82-3.04	3.28	Hjertén & Nyberg (1973)
$Tl_2S_2O_3$	3.07-3.22 2.91-3.29	3.46	This work

References

- BOSSON, B. (1976a). *Acta Cryst.* To be published.
 BOSSON, B. (1976b). *Acta Chem. Scand.* To be published.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891-1898.
 DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390-397.
 HJERTÉN, I. & NYBERG, B. (1973). *Acta Chem. Scand.* **27**, 345-356.
 MCGINNETY, J. A. (1972). *Acta Cryst.* **B28**, 2845-2852.
 MANOJLOVIĆ-MUIR, L. (1975). *Acta Cryst.* **B31**, 135-139.
 NORD, A. G. (1974). *Acta Cryst.* **B30**, 1640-1641.

Acta Cryst. (1976). **B32**, 2227

Refinement of Neodymium Trihydroxide*

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Abstract. $Nd(OH)_3$, hexagonal, $P6_3/m$, $Z=2$, $a=6.418$ (2), $c=3.743$ (1) Å (single-crystal data), $a=$

6.422 (2), $c=3.742$ (2) Å (high-angle powder data). The structure was refined independently from both powder and single-crystal X-ray intensity data. The powder sample was prepared by dissolving Nd_2O_3 in dilute HCl and precipitating with NH_4OH ; the resulting amorphous gel was washed and aged in deionized water at 100°C for six days. Single crystals were grown by aging in strong alkali at high temperature and pressure. The single-crystal data refinement ($R=$

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0.0296, observed reflections only) yielded nine hydroxide groups in the coordination sphere of the Nd atom in approximately D_{3h} symmetry and distances, Nd–O, 2.492 (3) and 2.522 (3) Å, O–O 2.819 (5), 2.929 (6) and 2.964 (5) Å. The powder refinement ($R=0.059$) yielded nearly identical results.

Introduction. *Single-crystal refinement:* A single crystal having the shape of a hexagonal prism with dimensions of $0.063 \times 0.120 \times 0.190$ mm was mounted on a Syntex $P\bar{1}$, computer-controlled, four-circle diffractometer equipped with a graphite-crystal incident-beam monochromator. Least-squares refinement of 15 centered reflections produced the orientation matrix for data collection and gave cell constants $a=6.418$ (2) and $c=3.743$ (1) Å.

Data were collected in the range $0^\circ < 2\theta < 102^\circ$ with Mo $K\alpha$ ($\lambda=0.71069$ Å) radiation. The θ - 2θ scan technique with a variable scan rate from 2.0 to $24.0^\circ \text{ min}^{-1}$ and a scan range from 2θ Mo $K\alpha$ -0.8° to 2θ $K\alpha$ $+0.8^\circ$ was used. Additional details about the method of data collection and assignment of standard deviations, $\sigma(I)$, have been described previously (Cotton, Frenz, Deganello & Shaver, 1973). Periodic measurement of three standard reflection intensities showed no significant changes. A total of 720 reflections were recorded of which 574 were $> 3\sigma(I)$ and the usual data-reduction procedures were applied.* An absorption correction which treated the crystal as a non-re-entrant polyhedron was applied ($\mu=192.8 \text{ cm}^{-1}$), resulting in transmission factors varying from 9 to 22%. A comparison of observed and calculated structure factors indicated a secondary extinction correction was necessary (Larson, 1967). The extinction coefficient was found to be 1.09 (6) $\times 10^{-5}$.

The UCl_3 prototype structure by Zachariasen (1948) was used as the starting model. The Nd atoms were

* The following computer programs were used: *DATARED* by Frenz for data reduction; *SYABS*, a modification of *ORABS*, by R. E. Davis for absorption correction; *XFLS* by Steinfink and *NUCLS4* by Ibers & Doedens, based on Busing & Levy's *ORFLS*, for least-squares refinement; and *DISTA* by Okaya for distances and angles. Final least-squares refinement was performed using *GENLES* by A. C. Larson.

placed in the special position $2(c)$ ($\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$) and the oxygens were placed in $6(h)$ ($x, y, \frac{1}{4}$) with $x=0.39$ and $y=0.32$. The model was refined using a full-matrix least-squares program and converged after several cycles to $R=0.0296$, $R_w=0.0293$, where R and R_w are defined as: $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ and $R_w = \frac{\sum w_i (|F_o|_i - |F_c|_i)}{\sum w_i |F_o|_i}$; where $w_i = 1/\sigma^2$. The function minimized was: $\sum w (|F_o| - |F_c|)^2$. Attempts to locate hydrogens were unsuccessful.

The scattering factors used were obtained from Cromer & Mann (1968). Real and imaginary anomalous dispersion corrections were made for Nd (Cromer, 1965). A final difference Fourier had only one significant peak. The peak was at $0.0, 0.0, 0.25$ and was $2.4 \text{ e} \text{ \AA}^{-3}$ in height. The possibility of a small amount of occluded water cannot be excluded. The largest $\Delta \xi_i / \sigma(\xi_i)$ after the final cycle of refinement was 0.11 .*

Powder refinement: The powder sample was ground and passed through a 325 mesh screen, encased in Epon 812 binder and finely polished. Powder intensity data were collected with a G.E. XRD-6 diffractometer by continuous θ - 2θ scans to a maximum 2θ of 150° . Copper $K\alpha$ radiation ($\lambda=1.5418$ Å) was monochromatized with a diffracted-beam LiF curved-crystal monochromator ($\theta_m=22.5486^\circ$). Sections of the X-ray diffraction profiles were scanned as many as 12 times, and the separate runs were then normalized and averaged. A linear background was fitted to each diffraction profile. A total of 28 separate intensities containing 81 Bragg reflections was measured.

The same model used in the single-crystal study was refined with the powder data by isotropic full-matrix least-squares techniques. Because of the overlapping reflections, the function minimized in this case was $\sum_m w (k \sum_i I_c - I_o)^2$, where I_o = observed intensity of a single peak, $\sum_i I_c$ = sum of the i calculated intensities for all reflections contained in each observation, k is a scale factor, w is a weighting factor (Hughes, 1941), and m is the number of observations. Each I_c =

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31699 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Positional and thermal parameters* ($\beta^2 \times 10^4$) of $\text{Nd}(\text{OH})_3$

Anisotropic thermal parameters are in the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$. Parameters for $\text{Y}(\text{OH})_3$ and $\text{Tb}(\text{OH})_3$ are listed for comparison.

	x	y	z	B	β_{11}	β_{22}	β_{33}	β_{12}	
Nd	0.3333	0.6667	0.25	0.340 (6)	34 (1)	34 (1)	79 (2)	17 (1)	} Single-crystal data
O	0.3923 (7)	0.3108 (6)	0.25	0.77 (4)	79 (6)	62 (5)	164 (12)	44 (5)	
Nd	0.3333	0.6667	0.25	1.3 (1)					} Powder data
O	0.399 (5)	0.322 (4)	0.25	3.5 (5)					
Y	0.3333	0.6667	0.25	0.64 (1)					} Christensen <i>et al.</i> (1967)
O	0.3957 (8)	0.3115 (7)	0.25	0.75 (6)	72 (12)	63 (12)	167 (29)	79 (22)	
Tb	0.3333	0.6667	0.25	0.6 (1)					} Landers & Brun (1973)
O	0.3952 (4)	0.3096 (4)	0.25	0.65	60 (10)	6 (10)	140 (30)	40 (3)	

$M \cdot L_p \cdot |F_{hkl}|^2$, where M is the multiplicity and $L_p = (1 + \cos^2 2\theta) \cos^2 2\theta_m / (\sin \theta \sin 2\theta)$ (Levy, 1971). Several cycles of refinement converged to $R = 0.059$, where $R = \sum_m |I_c - I_o| / \sum I_o$. The atomic scattering factor table for Nd was obtained from Cromer & Waber (1965) that for oxygen was obtained from Ibers (1962). Both real and imaginary components of anomalous dispersion were applied to Nd (Cromer, 1965).

Discussion. Until recently there has been little structural information on the lanthanide trihydroxides due mainly to difficulties in growing suitable single crystals. References to the earlier work in this area may be found in Landers & Brun (1973) and Atoji & Williams (1959). Part of our interest in refining structures of lanthanide compounds is that some of the corresponding actinides are isostructural. For example, Milligan, Beasley, Lloyd & Haire (1968) have presented strong electron-diffraction evidence that Am(OH)₃ is isostructural with Nd(OH)₃. As a continuation of our efforts to structurally characterize the hydrous oxides and hydroxides of the lanthanides so that parallels may be drawn to corresponding compounds of the actinides, we have refined the structure of Nd(OH)₃ employing both powder and single-crystal data. The powder data were refined independently of the single-crystal data to ascertain the relative applicability of this method for determining accurate structural information for these compounds. We anticipate that due to the extreme scarcity of many of the actinides, much of the structural work on these compounds will have to be done using the powder method.

Nd(OH)₃ contains nine hydroxide ions surrounding each Nd ion in approximate D_{3h} symmetry in the crystalline state. A similar coordination geometry has been shown to exist in [Nd(H₂O)₉][BrO₃]₃ (Helmholtz, 1939) and in LaFe(CN)₆·5H₂O (Bailey, Williams & Milligan, 1973). There are two independent Nd–O distances of 2.492 (3) Å (both atoms at z) and 2.522 (3) Å (Nd at z , O at $z \pm \frac{1}{2}$), and three independent O–O distances of 2.929 (6) Å (O's at same z), 2.964 (5) and 2.819 (5) Å (O's at z and $z + \frac{1}{2}$). Significant angles are O–Nd–O, 120° (all atoms at z) and O(1)–Nd–O(2), 68.33 (12) and 72.32 (12)° [O(1) and Nd at z , and O(2) at $z \pm \frac{1}{2}$, respectively].

The final positional and thermal parameters are listed in Table 1 for both powder and single-crystal refinements. It can be seen that there is very good agreement between the two refinements. The most striking difference is in thermal parameters. One might expect this difference when considering the small number of independent observations in the powder data set and also the lack of high-angle data. A comparison of the positional and thermal parameters of Y(OH)₃ (Christensen, Hazell & Nilsson, 1967) and Tb(OH)₃ (Landers & Brun, 1973) is also given in Table 1.

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References

- ATOJI, A. & WILLIAMS, D. E. (1959). *J. Chem. Phys.* **31**, 329–331.
- BAILEY, W. E., WILLIAMS, R. J. & MILLIGAN, W. O. (1973). *Acta Cryst.* **B29**, 1365–1368.
- CHRISTENSEN, A. N., HAZELL, R. G. & NILSSON, A. (1967). *Acta Chem. Scand.* **21**, 481.
- COTTON, F. A., FRENZ, B. A., DEGANELLO, G. & SHAVER, A. (1973). *J. Organomet. Chem.* **50**, 227–240.
- CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- HELMHOLTZ, L. (1939). *J. Amer. Chem. Soc.* **61**, 1544–1550.
- HUGHES, E. (1941). *J. Amer. Chem. Soc.* **63**, 1737–1752.
- IBERS, J. A. (1962). *International Tables for X-ray Crystallography*, Vol. III, p. 201. Birmingham: Kynoch Press.
- LANDERS, G. H. & BRUN, T. O. (1973). *Acta Cryst.* **A29**, 684–691.
- LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
- LEVY, H. (1971). Private communication.
- MILLIGAN, W. O., BEASLEY, M. L., LLOYD, M. H. & HAIRE, R. G. (1968). *Acta Cryst.* **B24**, 979–980.
- ZACHARIASEN, W. H. (1948). *Acta Cryst.* **1**, 265–267.