

Structure of $Y_4O(OH)_9NO_3$ from X-Ray and Neutron Powder Diffraction Data

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The crystal structure of $Y_4O(OH)_9NO_3$ was investigated using synchrotron X-ray and neutron powder diffraction data, and the structure was refined by profile analysis of the neutron powder diffraction data. The structure is monoclinic, space group $P2_1$ (No. 4) with the lattice parameters from the synchrotron X-ray diffraction data $a = 9.3852(4)$, $b = 16.3935(5)$, $c = 3.6266(1)$ Å, $\beta = 101.067(5)^\circ$, $Z = 2$, and has three YO_7 coordination polyhedra and one YO_9 coordination polyhedron. The Y–O distances are in the range 2.17–2.59 Å, and the O–H distances are in the range 0.99–1.03 Å. Four synchrotron X-ray powder patterns were measured of the compound on three different diffractometers, and comparisons between the powder patterns and the diffractometers are presented.

Aqueous solutions of yttrium nitrate and rare-earth nitrates readily form gels of yttrium hydroxide and rare-earth hydroxides when mixed with aqueous solutions of ammonia. These amorphous gels can be aged hydrothermally to form the crystalline hydroxides $Y(OH)_3$ and $RE(OH)_3$, (RE: La to Lu). The structures and hydrogen atom positions in these isomorphous hydroxides are well established.^{1–3}

In a special preparative procedure similar to that outlined above, it is possible to obtain a crystalline product other than $Y(OH)_3$ ^{2,4,5} which was first assumed to be a new crystalline modification of $Y(OH)_3$.^{4,5} The compound in Ref. 2 was initially reported as Phase III with an unknown composition, and then later quoted (in error) as a modification of $Y(OH)_3$.⁶ The composition $Y_2(OH)_{6-x}(NO_3)_x$ with $x = 0.6 \pm 0.1$ was later suggested for the yttrium compound,⁷ and $Er_4O_2(OH)_8 \cdot HNO_3$ for the corresponding erbium compound.⁸ The latter was derived from a diffractometer single-crystal X-ray structure analysis, where the final R -value was reported as 3.01%. The structure of $Er_4O_2(OH)_8 \cdot HNO_3$ can thus be assumed to be correct with respect to the packing of the erbium and oxygen atoms. An isomorphous series of compounds $RE_4O_2(OH)_8 \cdot HNO_3$ was reported for RE from dysprosium to lutetium.⁸

The structure analysis of $Er_4O_2(OH)_8 \cdot HNO_3$ did not draw any conclusions with respect to the hydrogen atom positions, but suggested that a molecule of nitric acid, HNO_3 , was located within the structure. Owing to the aqueous solution in the hydrothermal preparation having a pH of approximately 8, this is rather unlikely. For this

reason, it is suggested that the formula of the compound reported in Ref. 8 is $Er_4O(OH)_9NO_3$, and that of the yttrium compound,⁷ and Phase III of Ref. 2, is $Y_4O(OH)_9NO_3$. To investigate this hypothesis a combination of X-ray and neutron powder diffraction profile analysis⁹ has been used. The compound $Y_4O(OH)_9NO_3$ has a great number of reflections in the X-ray powder pattern, and therefore to obtain well resolved X-ray patterns synchrotron sources were utilised along with more traditional X-ray technology.

Experimental

Sample preparation. The compound was made from $Y(NO_3)_3 \cdot 5H_2O$ (Alfa Inorganics) which was dissolved in water, and a gel of yttrium hydroxides was precipitated with 4 M ammonia. The gel was treated hydrothermally at 190 °C for 48 h, and the product of $Y_4O(OH)_9NO_3$ was washed with water and dried at room temperature. The composition $Y_4O(OH)_9NO_3$ agrees with the previously reported² chemical analysis: Found: Y 61.8. Calc.: Y: 60.6.

In-house X-ray powder diffraction. A Guinier diffraction photograph of $Y_4O(OH)_9NO_3$ along with an internal standard of silicon ($a_{Si} = 5.43050$ Å) was acquired with a Nonius–Guinier camera using $Cu K\alpha_1$ radiation ($\lambda = 1.540598$ Å). The positions and intensities of the diffraction lines were measured using a photometer. Two X-ray powder diffraction patterns were also obtained using a Stoe diffractometer with position-sensitive detectors and $Cu K\alpha_1$ radiation. The Stoe diffractometer has a Guinier geometry

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for transmission diffraction and has a curved Ge monochromator that selects the $Cu K\alpha_1$ component of the radiation. The sample was in a 0.3 mm diameter capillary that was rotated with a frequency of 1 Hz to reduce the effects of preferred orientation. Initially the Stoe diffractometer was calibrated with a standard of $Ag_6Ge_{10}P_{12}$ ($a = 10.312 \text{ \AA}$). The pattern Stoe I was measured with a position-sensitive curved detector that covers 40° in 2θ and has a resolution of 0.17° in 2θ . With two positions of the detector a 2θ -range of approximately 80° is measured. The data reduction of the measurements yielded a pattern with a 2θ -range of 4.27 – 84.97° with $\Delta 2\theta = 0.03^\circ$. The pattern Stoe II was measured with a position-sensitive detector with a range 6° in 2θ and a resolution of 0.08° in 2θ . The detector was moved in steps of 0.5° to produce a pattern with a 2θ -range of 7.20 – 92.88° with $\Delta 2\theta = 0.02^\circ$.

Synchrotron X-ray powder diffraction. Four powder diffraction patterns were obtained from three different instruments.

(i) *Daresbury.* The diffraction pattern was obtained using the diffractometer¹⁰ at Station 8.3 at Daresbury using $\lambda = 1.2323 \text{ \AA}$. The sample was mounted in a flat-plate geometry and was rotated to reduce the effect of preferred orientation. The pattern was measured in the 2θ -range 5.00 – 100.00° with $\Delta 2\theta = 0.01^\circ$.

(ii) *HASYLAB wiggler.* A general purpose diffractometer¹¹ on the wiggler W1 beam line at HASYLAB was modified for use as a powder diffractometer.^{12,13} The sample was mounted in a 0.3 mm diameter glass capillary which was rotated with a frequency of 1 Hz. The diffraction pattern was obtained with a position-sensitive detector in a step scan mode using $\lambda = 1.2998 \text{ \AA}$. The detector had a 2θ -range of 2.7° . The data reduction yielded a pattern with a 2θ -range of 4.358 – 62.000° with $\Delta 2\theta = 0.00926^\circ$.

(iii) *HASYLAB.* A dedicated powder diffractometer¹⁴ on the B2 beam line was used to obtain a powder diffraction pattern at 300 K and a pattern at 70 K using $\lambda = 1.5407 \text{ \AA}$. The sample was a flat plate supported on a single crystal of silicon cut along the (711) plane so that no scattering contribution from the silicon was observed. The sample was glued to the support by a thin film of vacuum grease (Baysilon Paste from Bayer) and rotated to reduce effects of preferred orientation. The patterns were measured in steps of 0.01° in 2θ below $2\theta = 50^\circ$ and in steps of 0.02°

above $2\theta = 50^\circ$. The 300 K pattern was measured in the 2θ -range 9.00 – 91.00° and the 70 K pattern in the range 10.00 – 100.00° . The powder patterns measured at the two temperatures were practically identical with respect to the intensities of the reflections, thus suggesting that no phase transition occurs when cooling from 300 to 70 K.

Neutron powder diffraction. A powder neutron diffraction pattern was measured at room temperature on the D1B diffractometer at the Laue–Langevin Institute with 1.278 \AA neutrons. The diffractometer has a 400 cell multidetector covering 80° in 2θ . The pattern was measured in the 2θ -range 9.0 – 89.0° with $\Delta 2\theta = 0.2^\circ$. The sample was in a 12 mm diameter vanadium container.

Indexing of X-ray powder patterns

Two of the measured X-ray powder patterns, the Guinier film and the synchrotron powder pattern from Daresbury, were used to determine the unit cell with the indexing program FZON,¹⁵ and the results are listed in Table 1. The patterns were indexed with an orthorhombic cell with a volume twice that of the monoclinic cell reported in Ref. 8. However, one of the patterns, the Guinier film, was also indexed with a monoclinic cell with dimensions very similar to the unit cell dimensions for $Er_4O_2(OH)_8 \cdot HNO_3$.⁸ It was thus assumed that the structure of $Y_4O(OH)_9NO_3$ resembles the structure reported in Ref. 8.

The intensities of the X-ray powder pattern of $Y_4O(OH)_9NO_3$ were calculated using only the scattering contributions from the yttrium atoms and the program LAZY-PULVERIX.¹⁶ Two models were used: a model similar to that of Ref. 8 and a model derived from the model of Ref. 8 but using the orthorhombic space group $Cmc2_1$ and the unit cell $a = 3.626$, $b = 18.416$, $c = 16.393 \text{ \AA}$. The two powder patterns proved to be very similar to each other. As a monoclinic cell and space group were found in Ref. 8, the space group $P2_1$ is used in the following model calculations.

Comparison of X-ray powder patterns

To compare the powder patterns of a compound measured on different diffractometers, the two in-house patterns Stoe

Table 1. Results of indexing of two of the X-ray powder patterns with the program FZON.¹⁵

Source	No. of reflections used	No. of indexed reflections of the first 20	Figure of merit, M_{20}	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\alpha/^\circ$	$\beta/^\circ$	$\gamma/^\circ$	Bravais lattice
Guinier film	36	20	63.1	3.624	18.393	16.394	90.0	90.0	90.0	C
Guinier film	36	20	28.9	9.373	16.394	3.624	90.0	101.15	90.0	P
Daresbury	36	20	31.1	3.626	18.416	16.393	90.0	90.0	90.0	C
Unit cell ⁸				9.338	16.369	3.608	90.0	101.16	90.0	P

Table 2. Refined parameters and B -values from the least-squares profile program EDINP for two in-house X-ray powder patterns and for four synchrotron X-ray powder patterns.

	Er atoms ⁹	Stoe I	Stoe II	Daresbury	HASYLAB wiggler	HASYLAB 300 K	HASYLAB 70 K
Y1							
x/a	0.2692(1)	0.266(1)	0.2707(8)	0.2694(4)	0.2638(11)	0.2692(10)	0.2684(8)
y/b	0.0	0.0	0.0	0.0	0.0	0.0	0.0
z/c	0.6347(3)	0.681(7)	0.6383(44)	0.6550(22)	0.6841(35)	0.6293(56)	0.6331(27)
$B/\text{Å}^2$	0.62(2)	0.1(2)	1.5(1)	1.5(1)	1.7(3)	2.0(2)	1.8(2)
Y2							
x/a	0.7271(1)	0.722(1)	0.7293(8)	0.7298(5)	0.7364(13)	0.7303(9)	0.7265(7)
y/b	0.2896(1)	0.286(1)	0.2889(4)	0.2897(2)	0.2893(6)	0.2898(5)	0.2901(4)
x/c	0.8637(3)	0.844(3)	0.8681(46)	0.8611(31)	0.8698(36)	0.8859(59)	0.8829(28)
$B/\text{Å}^2$	0.60(2)	1.4(2)	1.2(1)	1.0(1)	6.6(4)	1.7(2)	1.5(1)
Y3							
x/a	0.0540(1)	0.059(2)	0.0564(6)	0.0548(4)	0.0488(10)	0.0513(9)	0.0525(7)
y/b	0.1872(1)	0.182(1)	0.1852(4)	0.1876(3)	0.1856(7)	0.1875(6)	0.1882(6)
z/c	0.5270(3)	0.517(9)	0.5339(36)	0.5269(31)	0.5492(48)	0.5029(56)	0.5262(28)
$B/\text{Å}^2$	0.59(2)	4.0(4)	1.4(1)	1.1(1)	3.7(4)	1.8(1)	0.9(2)
Y4							
x/a	0.4002(1)	0.402(1)	0.4013(6)	0.4012(4)	0.3954(9)	0.4022(8)	0.4019(6)
y/b	0.1824(1)	0.179(1)	0.1831(4)	0.1840(2)	0.1834(6)	0.1846(5)	0.1836(4)
z/c	0.2003(3)	0.199(9)	0.2044(37)	0.2023(31)	0.1639(46)	0.1917(54)	0.1635(15)
$B/\text{Å}^2$	0.57(2)	2.1(3)	1.4(1)	1.1(1)	2.3(3)	1.6(2)	3.2(1)
O/N							
$B/\text{Å}^2$		1.0(1)	0.8(1)	0.8(1)	3.1(1)	0.8(1)	1.8(1)
U		0.52(1)	0.2923(1)	0.0251(6)	0.0726(16)	0.0618(9)	0.0542(11)
V		-0.322(6)	-0.2665(1)	0.0046(2)	-0.0005(3)	-0.0203(3)	0.0013(3)
W		0.116(2)	0.0755(1)	-0.0006(1)	-0.0004(1)	0.0027(1)	-0.0003(1)
T		0.127(3)	0.0625(10)	0.0495(3)	0.0330(5)	0.0379(5)	0.0426(5)
R_E		11.0 %	5.1 %	3.4 %	5.6 %	17.6 %	16.0 %
R_P		15.5 %	7.6 %	11.6 %	8.9 %	21.6 %	20.3 %
R_{WP}		21.2 %	11.2 %	15.8 %	13.9 %	26.0 %	24.6 %
R_F		9.5 %	6.8 %	6.3 %	17.8 %	16.5 %	18.0 %
R_I		17.3 %	11.9 %	9.9 %	24.3 %	25.6 %	17.8 %
$\lambda/\text{Å}$	0.7107	1.5405	1.5405	1.2323	1.2998	1.5407	1.5407
$\sin \theta/\lambda_{\max}$	0.65	0.44	0.47	0.57	0.40	0.46	0.50
Recording time of pattern/h							
		0.5	18	12	2	12	12
Sample capillary diameter/mm							
		0.3	0.3		0.3		
Sample flat plate							
				Yes		Yes	Yes

I and Stoe II, the pattern from Daresbury, the HASYLAB wiggler pattern and the two HASYLAB patterns from B2 measured at 300 and 70 K were used in profile refinement of the structure of $Y_4O(OH)_9NO_3$, assuming the model of Ref. 8, and the results are listed in Table 2. Profile analyses were made using the least-squares program EDINP¹⁷ and

X-ray form factors for neutral atoms.¹⁸ The average scattering contribution of all the yttrium atoms in $Y_4O(OH)_9NO_3$ is 87.2 %. For this reason, only the positional parameters of the yttrium atoms of the model were refined, and the positional parameters of the remaining atoms were kept constant. The following parameters were refined: a zero

point for the diffractometer, four profile parameters, four unit cell parameters, eleven positional parameters, and four isotropic temperature factor parameters for the four yttrium atoms, and one overall isotropic temperature factor parameter for the remaining atoms in the model. In Table 2 are listed values for some of the refined parameters and the R -values of the refinements. Of the two X-ray diffractometer powder patterns measured in the laboratory (Stoe I and II), the Stoe II pattern gives the highest precision of the refined parameters and the lowest R -value. For the four synchrotron X-ray powder patterns (Daresbury, HASYLAB wiggler, HASYLAB 300 and 70 K), the Daresbury pattern yields the highest precision of the parameters and the lowest R -values. The Daresbury pattern was also measured out to the highest values of $\sin \theta/\lambda$. The HASYLAB wiggler pattern was only measured to $\sin \theta/\lambda = 0.40$. The recording time of this pattern was 2 h and the instrument used was not a dedicated powder diffractometer. The recording time used for the measurements on the two dedicated powder diffractometers (the Daresbury pattern and the patterns HASYLAB 300 and 70 K) was much longer, up to 12 h. The precisions of the yttrium coordinates from the three HASYLAB patterns are comparable. The concept of using a step scan mode with a position-sensitive detector (the HASYLAB wiggler pattern) is thus rather promising, because a high-resolution powder pattern can be measured in a short time.

The full widths at half maximum, FWHM, of the diffraction peaks for five of the powder patterns are calculated with the parameters of Table 2 from eqn. (1) and are

$$\text{FWHM} = (U \tan^2 \theta + V \tan \theta + W)^{1/2} + T/\cos \theta \quad (1)$$

displayed in Fig. 1. For the three synchrotron X-ray powder patterns measured at the three different instruments the FWHM values are comparable, and the two in-house patterns have larger values for FWHM, the larger values as expected for the pattern measured with the large position-sensitive detector (Stoe I).

Fig. 2 is a display of four of the recorded X-ray powder patterns showing the results of the profile refinements (see above).

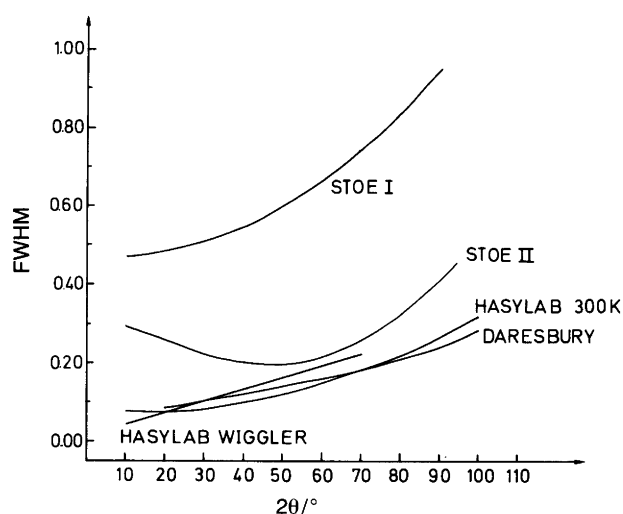


Fig. 1. Calculated full width at half maximum in degrees of the diffraction peaks for five powder patterns from eqn. (1). The patterns are: two in-house X-ray powder patterns, Stoe I and Stoe II, and three synchrotron X-ray powder patterns, Daresbury, HASYLAB wiggler and HASYLAB 300 K.

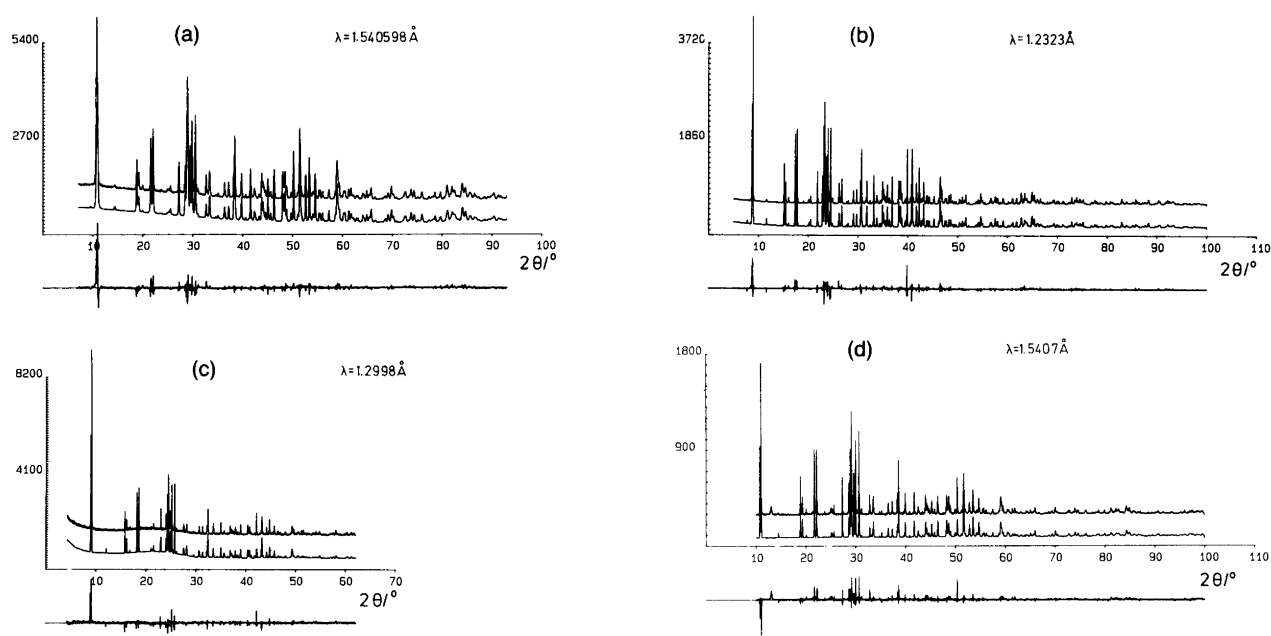


Fig. 2. Observed and calculated X-ray powder patterns (upper and lower curves, respectively) and difference plot below the 2θ axis. (a) Stoe II, (b) Daresbury, (c) HASYLAB wiggler, (d) HASYLAB 70 K.

Model for hydrogen atom positions from packing considerations

Assuming that $Y_4O(OH)_9NO_3$ has a structure similar to that reported in Ref. 8, a sketch can be made of the packing of the four Y–O coordination polyhedra. Fig. 3 shows this sketch in a projection along c^* . The yttrium atoms Y1, Y3 and Y4 form YO_7 coordination polyhedra of the type found in $YOOH$,¹⁹ and Y2 forms a YO_9 coordination polyhedron of the type found in $Y(OH)_3$.² The oxygen atom O1 is coordinated to two yttrium atoms, and O2 is coordinated to four oxygen atoms. The remaining oxygen atoms O3 to O10 are coordinated to three yttrium atoms. Electroneutrality considerations suggest that the oxygen atom O1 belongs to an OH^- ion, and that the atoms O3 to O10 are oxygen atoms in OH^- ions. Assuming a square-planar coordination of O1, tetrahedral coordination of O3 to O10 and O–H distances of 1 Å yields the approximate hydrogen atom coordinates listed in Table 3.

Refinement of the model with neutron powder diffraction data

The neutron powder diffraction data were used in a profile refinement of the model of the structure, using the atomic coordinates reported in Ref. 8 for the metal, oxygen and nitrogen atoms and the atomic coordinates of the hydrogen atoms arrived at from packing considerations. The oxygen atom O14 of Ref. 8 was omitted. The least-squares profile refinement program EDINP¹⁷ was used with nuclear scattering contributions from Ref. 20. The following parameters were refined: a zero point for the diffractometer, three profile parameters, four unit cell parameters, eighty positional parameters, four isotropic temperature factor

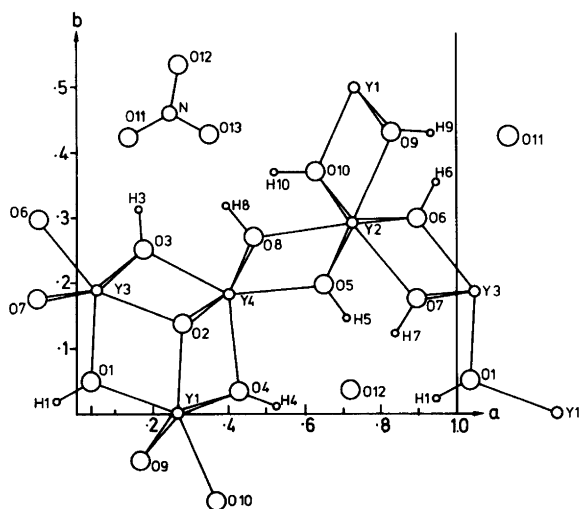


Fig. 3. Model of the structure of $Y_4O(OH)_9NO_3$ with the positions of the metal, oxygen and nitrogen atoms from Ref. 8 and the hydrogen atom positions from packing considerations, assuming O–H bonds of 1 Å.

Table 3. Coordinates and values of refined parameter for the structure of $Y_4O(OH)_9NO_3$; least-squares profile refinement program EDINP was applied.^a

Atom	x/a	y/b	z/c	$B/\text{Å}^2$
Y1	0.278(4) [0.2694(4)]	0.0	0.637(19) 0.6550(22)]	1.60(5)
Y2	0.726(4) [0.7298(5)]	0.290(2) 0.2897(2)	0.855(14) 0.8611(31)]	1.65(5)
Y3	0.060(4) [0.0548(4)]	0.190(2) 0.1876(3)	0.571(21) 0.5269(31)]	2.03(5)
Y4	0.404(4) [0.4012(4)]	0.188(2) 0.1840(2)	0.193(18) 0.2023(31)]	3.12(5)
O1	0.041(3)	0.046(2)	0.515(22)	0.72(5)
O2	0.283(5)	0.140(3)	0.653(23)	0.72(5)
O3	0.169(4)	0.254(2)	0.085(17)	0.72(5)
O4	0.429(3)	0.039(2)	0.210(17)	0.72(5)
O5	0.648(3)	0.199(2)	0.304(16)	0.72(5)
O6	0.908(4)	0.302(2)	0.430(18)	0.72(5)
O7	0.900(4)	0.181(2)	0.973(19)	0.72(5)
O8	0.476(4)	0.277(2)	0.742(17)	0.72(5)
O9	0.835(3)	0.426(2)	0.953(14)	0.72(5)
O10	0.625(3)	0.365(2)	0.291(16)	0.72(5)
O11	0.147(4)	0.414(3)	0.035(14)	0.72(5)
O12	0.273(5)	0.534(2)	0.061(13)	0.72(5)
O13	0.348(6)	0.437(4)	−0.082(14)	0.72(5)
N	0.262(3)	0.458(2)	0.149(12)	0.72(5)
H1	−0.056(4) (−0.05)	0.035(4) 0.03	0.567(18) 0.50)	1.05(5)
H3	0.177(8) (0.15)	0.310(2) 0.31	0.200(16) 0.09)	1.05(5)
H4	0.517(5) (0.52)	0.007(3) 0.01	0.188(15) 0.22)	1.05(5)
H5	0.713(6) (0.70)	0.150(2) 0.15	0.311(22) 0.30)	1.05(5)
H6	0.950(6) (0.92)	0.358(2) 0.36	0.479(24) 0.45)	1.05(5)
H7	0.872(5) (0.84)	0.122(2) 0.12	0.955(28) 0.95)	1.05(5)
H8	0.392(5) (0.40)	0.314(3) 0.31	0.764(24) 0.75)	1.05(5)
H9	0.938(4) (0.92)	0.434(3) 0.43	0.904(29) 0.95)	1.05(5)
H10	0.544(4) (0.52)	0.351(5) 0.37	0.419(17) 0.30)	1.05(5)

^aCoordinates of hydrogen atoms in parentheses from packing considerations. Coordinates of yttrium atoms from refinement of synchrotron X-ray powder data, Daresbury pattern, using EDINP, in square brackets. Refined parameters: zero = $-0.104(13)^\circ$, $U = 0.36(26)$, $V = -0.20(12)$, $W = 0.20(3)$; $a = 9.376(2)$, $b = 16.376(3)$, $c = 3.623(1)$ Å, $\beta = 101.17(18)^\circ$; $R_p = 1.2\%$, $R_{wp} = 1.6\%$, $R_F = 6.9\%$, $R_I = 11.2\%$, $R_E = 0.6\%$; $FWHM = (U \tan^2 \theta + V \tan \theta + W)^{1/2}$.

parameters for the yttrium atoms and one overall temperature factor parameter for the remaining atoms. Patterns measured on the diffractometer D1B do not have a high resolution and contain only 400 data points, and for this reason no attempts were made to refine individual isotropic temperature factor parameters for all the atoms of the model. A final Fourier map was calculated to check for additional atoms of the model, especially for mass density of the position of O14 of Ref. 8. No additional atoms were

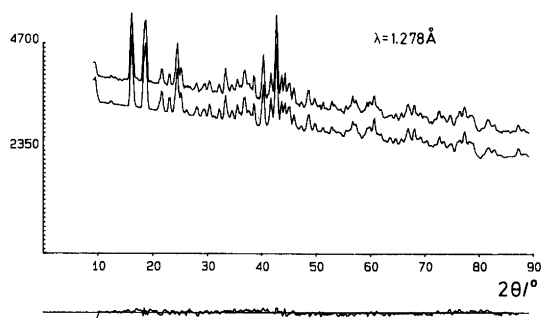


Fig. 4. Neutron diffraction powder patterns of $Y_4O(OH)_9NO_3$. Upper curve, observed profile; lower curve, calculated profile, with difference in the lower part of the figure.

found. A list of the atomic positions of the model and of the values of some of the refined parameters is given in Table 3. Fig. 4 shows the observed and calculated powder patterns and a difference plot. Fig. 5 is a stereoscopic drawing of the model in the [001] direction. Selected interatomic distances are listed in Table 4.

Discussion

The refinement of the structure with the powder neutron diffraction data shows that the composition of the compound is $Y_4O(OH)_9NO_3$. The structure has yttrium–oxygen coordination polyhedra known from the structure of $Y(OH)_3$,² and $YOOH$,¹⁹ and the Y–O distances in the structure are comparable with interatomic distances in these two compounds. Fourier maps did not show any indication of mass density at the position of O14,⁸ and did not indicate the presence of a HNO_3 molecule in the structure. The nitrogen atom and the oxygen atoms O11, O12 and O13 form a nitrate ion in which the average nitrogen–oxygen

Table 4. Interatomic distances (in Å) in $Y_4O(OH)_9NO_3$, calculated from the neutron diffraction data; standard deviations 0.1–0.3 Å.^a

Y1–O2	2.29	Y3–O2	2.26
Y1–O1	2.29	Y3–O7	2.26
Y1–O9	2.33	Y3–O3	2.28
Y1–O4	2.35	Y3–O6	2.29
Y1–O10	2.35	Y3–O1	2.36
Y1–O4	2.41	Y3–O7	2.37
Y1–O9	2.42	Y3–O3	2.38
Y2–O6	2.29	Y4–O2	2.17
Y2–O8	2.32	Y4–O5	2.27
Y2–O7	2.36	Y4–O2	2.35
Y2–O10	2.38	Y4–O4	2.41
Y2–O5	2.41	Y4–O3	2.42
Y2–O10	2.43	Y4–O8	2.45
Y2–O9	2.44	Y4–O8	2.46
Y2–O5	2.51		
Y2–O6	2.59		

Y–O distances in $Y(OH)_3$, Ref. 2. Y–O 2.403(3) to 2.437(3).
Y–O distances in $YOOH$, Ref. 19. Y–O 2.24(3) to 2.44(2).

N–O11	1.32	O5–H5	1.00
N–O12	1.34	O6–H6	1.00
N–O13	1.28	O7–H7	1.03
O1–H1	0.99	O6–H8	1.02
O3–H3	0.99	O9–H9	1.02
O4–H4	1.01	O10–H10	1.00

^aThe standard deviations are high, 0.1–0.2 Å for the Y–O distances and for the N–O distances and 0.1–0.3 Å for the O–H distances. This is due to the limited number of data (400 data points), with maximum $\sin \theta/\lambda = 0.55$, and the low resolution of the powder pattern. Standard deviations for the Y–O distances calculated with data from the Daresbury diffraction pattern (9500 data points) are 0.02–0.07 Å.

distance is well within the expected value for a NO_3^- ion. This ion is situated in a channel in the structure formed by

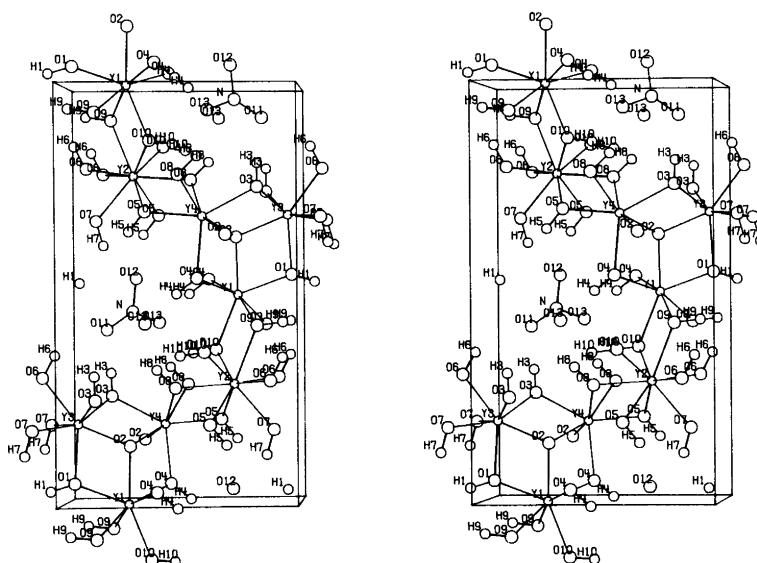


Fig. 5. Projection of the structure of $Y_4O(OH)_9NO_3$ along [001]. The a -axis is along the page.

the oxygen atoms O1 and O3 to O10. All these oxygen atoms belong to OH groups where the hydrogen atoms are situated on the inside of the channel. The NO_3^- ion is held in the channel by hydrogen bonds to the OH^- ions. The coordination polyhedra and the channel character of the structure can be seen in Fig. 5. The structure also has a layer character. Layer character has been observed for a number of yttrium and rare-earth compounds with a short crystallographic axis of 3.6–4.0 Å. Examples are the structures of $\text{La}_7(\text{OH})_{18}\text{I}_3$,^{21,22} $\text{La}_7(\text{OH})_{18}(\text{NO}_3)_3$,²¹ $\text{Pr}(\text{OH})_2\text{NO}_3$,²³ $\text{Nd}(\text{OH})_2\text{NO}_3$,²⁴ $\text{Gd}(\text{OH})_2\text{NO}_3$,²⁴ $\text{Nd}(\text{OH})_2\text{NO}_3\cdot\text{H}_2\text{O}$,²⁵ $\text{La}(\text{OH})_2\text{NO}_3$,²⁶ and $\text{La}(\text{OH})_2\text{NO}_3\cdot\text{H}_2\text{O}$.²⁶ Structural correlations of yttrium and rare earth compounds of earlier studies have been made by Haschke.^{27,28} The difference between the present structure and the structures of the nitrates listed above is that the NO_3^- ions in the present structure are hydrogen-bonded to the oxygen atoms of the yttrium–oxygen coordination polyhedra, and in the other structures some of the oxygen atoms of the NO_3^- ions are also oxygen atoms of the rare-earth–oxygen coordination polyhedra.

The synchrotron X-ray powder patterns of $\text{Y}_4\text{O}(\text{OH})_9\text{NO}_3$ have sharp Bragg peaks that are well resolved. However, the FWHM values indicate some line-broadening. The patterns measured at Daresbury have FWHM values at least twice those for a Si sample SRM640b.¹⁰

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