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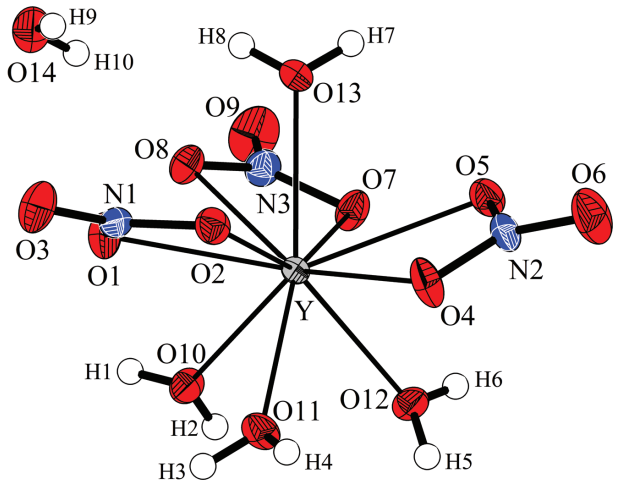
Redetermination of the crystal structure of yttrium(III) trinitrate(V) pentahydrate, $Y(NO_3)_3 \cdot 5\ H_2O$, $H_{10}N_3O_{14}Y$



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Abstract

$H_{10}N_3O_{14}Y$, triclinic, $P\bar{1}$ (no. 2), $a = 6.5965(12)$ Å, $b = 9.5374(17)$ Å, $c = 10.5249(19)$ Å, $\alpha = 63.809(13)°$, $\beta = 84.677(15)°$, $\gamma = 76.397(19)°$, $V = 577.46(18)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0330$, $wR_{ref}(F^2) = 0.0697$, $T = 223$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

$Y(NO_3)_3 \cdot 5\,H_2O$ was prepared by dissolving Y_2O_3 (Chempur, 99.9%) in hot aqueous nitric acid. From concentrated solutions single crystals were grown at room temperature within one day. The compound is highly hygroscopic, so out of the mother liquor crystals deliquesce within few minutes. Thus, for the X-ray data collection crystals have been immersed into perfluoroalkylether, which also acts as glue on a glass tip during the measurement.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.35 × 0.28 × 0.10 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	5.13 mm^{-1}
Diffractometer, scan mode:	STOE StadiVari, ω
θ_{max}, completeness:	26.0°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7245, 2228, 0.039
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1863
$N(param)_{refined}$:	203
Programs:	X-Area [1], SHELX [2, 3], Diamond [4]

Experimental details

The H atoms have been located from the difference Fourier map and refined with unrestrained atomic coordinates and isotropic displacement parameters.

Comment

Yttrium nitrate forms several crystalline hydrates. While $Y(NO_3)_3 \cdot 6H_2O$ is commercially available and its crystal structure was determined first [5], the existence of most of the other hydrates has been deduced from DSC experiments investigating the thermal decomposition of the hexahydrate. Pure phases have been found after recrystallisation from remains of the hexahydrate at enhanced temperature, $[Y(NO_3)_2(H_2O)_5][Y(NO_3)_4(H_2O)_2]$ at 361 K [6, 7], $Y(NO_3)_3 \cdot 3H_2O$ at 382 K [8], and $Y(NO_3)_3 \cdot H_2O$ at 443 K [9]. As an exception, the pentahydrate was not obtained after temperature dependent transformation from the hexahydrate, but was crystallized at room temperature directly from aqueous solution. [10] The crystal structure of $Y(NO_3)_3 \cdot 5H_2O$ was redetermined from single crystal data. Improving the results of the previous structure determination [10] lattice parameters, atomic coordinates and anisotropic displacement parameters of the non-H atoms have been obtained with a higher precision, and H atom positions have been located for the first time. During

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Y	0.24426(5)	0.34906(4)	0.29472(4)	0.01196(11)
N1	0.4689(5)	0.2818(3)	0.5548(3)	0.0169(6)
O1	0.2952(4)	0.3817(3)	0.5087(3)	0.0220(6)
O2	0.5519(4)	0.2135(3)	0.4782(3)	0.0204(6)
O3	0.5483(5)	0.2561(3)	0.6655(3)	0.0296(7)
N2	0.5201(5)	0.2133(4)	0.1251(3)	0.0210(7)
O4	0.5028(4)	0.1400(3)	0.2579(3)	0.0261(6)
O5	0.4065(4)	0.3559(3)	0.0667(3)	0.0219(6)
O6	0.6383(5)	0.1555(4)	0.0566(3)	0.0383(8)
N3	0.0243(5)	0.6860(4)	0.1459(3)	0.0205(7)
O7	0.0616(4)	0.5816(3)	0.0955(3)	0.0215(6)
O8	0.1053(4)	0.6380(3)	0.2660(3)	0.0210(6)
O9	−0.0809(5)	0.8197(3)	0.0813(3)	0.0365(8)
O10	−0.0906(4)	0.3855(3)	0.3938(3)	0.0210(6)
H1	−0.153(7)	0.457(6)	0.421(5)	0.028(12)*
H2	−0.177(9)	0.372(6)	0.363(6)	0.046(17)*
O11	0.1966(5)	0.1000(3)	0.4680(3)	0.0212(6)
H3	0.140(7)	0.080(5)	0.547(5)	0.016(11)*
H4	0.261(7)	0.017(5)	0.483(5)	0.017(12)*
O12	0.0258(5)	0.2634(3)	0.1944(3)	0.0212(6)
H5	0.034(7)	0.164(6)	0.228(5)	0.023(11)*
H6	0.006(8)	0.306(6)	0.116(6)	0.036(15)*
O13	0.5142(4)	0.5024(3)	0.2219(3)	0.0188(6)
H7	0.544(7)	0.536(6)	0.139(6)	0.031(14)*
H8	0.493(7)	0.571(6)	0.250(5)	0.030(13)*
O14	0.0031(6)	0.9537(4)	0.2799(3)	0.0291(7)
H9	0.112(11)	0.882(8)	0.296(7)	0.07(2)*
H10	−0.062(10)	0.957(7)	0.223(7)	0.055(19)*

the final refinement cycles the H atoms were refined with unrestrained atomic coordinates and isotropic displacement parameters. The crystal structure of $Y(NO_3)_3 \cdot 5H_2O$ is formed by a $[Y(NO_3)_3(H_2O)_4]$ complex and an additional free water molecule. The three crystallographically independent nitrate anions are almost perfectly planar and act as bidentate ligands of the Y atom, exhibiting N—O bond lengths between 1.260(4) Å to 1.289(4) Å as well as 1.216(4) Å to 1.221(4) Å when including the coordinating and non-coordinating O atoms, respectively. The water molecules show O—H bond lengths from 0.74(6) Å to 0.86(5) Å and angles between 99(3)° and 114(5)°. The Y atoms are in a tenfold coordination of O atoms, provided by three bidentately coordinating nitrate anions and by four water molecules. The nitrate ligands are arranged in an equatorial plane separating one water ligand from the other three, as seen in the figure. The NO_3 molecule planes are slightly tilted with respect to the main complex axis as defined by the Y-O13 bond forming a propeller-like shape. The shortest Y-O bonds between 2.336(3) Å to 2.370(3) Å are formed by the three H_2O ligands at one side of the $Y(NO_3)_3$ plane while the remaining Y-O(H_2) bond is in the same range as the shortest Y-O(NO_2) bonds. The nitrate ligands are slightly unsymmetrically coordinating with one shorter and one longer Y-O distance for each independent NO_3 anion. These molecular building units, i. e. metal complex and free water molecules, are connected by almost linear hydrogen bonds; more specifically, eight of the ten independent H atoms form hydrogen bonds shorter than 2.30 Å with O—H···O angles above 164°, while atoms H2 and H10 from bifurcated and slightly longer hydrogen bonds.

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