

Crystal Structure of Nonaquayttrium(III) Bromate at 100 K

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ABSTRACT: The structure of the nonaquayttrium (III) bromate, $[Y(H_2O)_9](BrO_3)_3$, at low temperature (100 K) has been studied by means of single-crystal X-ray diffraction. Crystallography shows a hexagonal unit cell, space group $P6_3/mmc$ (No. 194) with $Z = 2$, $a = b = 11.7104(11)$ Å, $c = 6.6259(5)$ Å and $V = 786.90(12)$ Å³ at 100 K. The hydrated trivalent yttrium(III) ion forms a tricapped trigonal prism, in which the yttrium(III) ion is surrounded by six equidistant water molecules in the prism and three more distant water molecules in capping positions with M-O bond distances of 2.370(2) and 2.446(3) Å, respectively. Relatively strong hydrogen bonds (2.818 and 2.851 Å) from water molecules to the bromate ions stabilize the trigonal prism around the yttrium(III) ions.

KEY WORDS: Crystal structure, Yttrium, Hydrate, Bromate, Single crystal X-ray diffraction.

INTRODUCTION

All metal ions are hydrated to some extent in aqueous solutions and in the solid state. The hydration number and water exchange reactions in solution are important in interpreting their kinetic and thermodynamic properties. However, to study the structure for solutions and dynamic behavior, data from three-dimensional atomic arrangements from crystal structures in the solid state can be of great help [1].

The structure of aqua ions in acidic aqueous solution can often be different from what is crystallized from saturated acidic solutions. This effect can be seen in non-coordinating trifluoromethanesulfonate anion. Hexahydrated isoelectronic mercury(II) and thallium(III) ions are found in perchlorate solution, but bisaquamercury(II)

trifluoromethanesulfonate, $[Hg(OH_2)_2(CF_3SO_3)_3]_{\infty}$, and aquathallium(III) trifluoromethane-sulfonate, $[Tl(OH_2)_3(CF_3SO_3)_3]$, compounds with low hydration numbers crystallize from trifluoromethane-sulfonate solutions [2,3]. From a solution of trifluoromethanesulfonate lanthanide(III) ions, a series of isostructural nonahydrated trifluoromethanesulfonate salts form, as also for the group 3 metal ions, scandium(III), yttrium(III) and lanthanum (III) [4-6]. The homeotypic series of non-aqualanthanide(III) ethylsulfates belong to the same space group [7-9]. The metal ions are in a crystallographic $\bar{6}$ site, surrounded by six equidistant water molecules in a trigonal prism and three additional water molecules in capping positions.

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The coordination chemistry of yttrium(III) is analogous with erbium(III) and holmium(III) due to the similarity of their ionic radii [10]. Hydration structure of yttrium(III) ion in solution can be obtained by comparing and analyzing X-ray absorption spectra solid hydrates and solutions, together with X-ray diffraction experiments [11].

We have recently published structure of the title compound with disordered bromate anions at room temperature, in which, each Br atom is surrounded by two fully occupied and two half-occupied oxygen atom sites in a nearly tetrahedral configuration. We aimed to study structure of the same crystal at low temperature (100 K) in order to investigate possible disordered bromate ions [12].

EXPERIMENTAL

Chemical

Compound nonaqua yttrium(III) bromate, $[Y(H_2O)_9](BrO_3)_3$, **1**, was synthesized according to the literature [12]. Crystals appropriate for crystallography were obtained after repeated recrystallization from water at room temperature.

Single crystal x-ray diffraction

Data collection were performed for $[Y(H_2O)_9](BrO_3)_3$ at 100 K using Mo-K α radiation on single crystals enclosed in thin-walled glass capillary. An Oxford Instruments Xcalibur diffractometer equipped with a CCD detector (crystal to detector distance 5.00 cm) was used. CrysAlis program package was used for indexing and integrating the crystal reflections. Absorption corrections were performed with the programs X-RED and X-Shape, using symmetry equivalent reflections to model crystal shape and size [13]. The structures were solved using SHELXS97 direct methods [14], and refined with SHELXL97 applying full-matrix least-squares on F^2 [15]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the water molecules were located from the residual density map and their positional parameters refined freely, with $U_{iso}(H) = 1.5 U_{eq}(O)$.

Crystallographic data have been deposited at the Inorganic Crystal Structure Database (ICSD), with CSD-number 416948. These data are available *via* <http://icsdweb.FIZ.Karsruhe.de>

Selected crystallographic and experimental details as well as Atomic coordinates together with equivalent isotropic displacement parameters are summarized in table 1 and 2.

RESULTS AND DISCUSSION

Compound **1** was satisfactorily described in hexagonal space group $P6_3/mmc$ (194) at 100 K. The crystal structure comprises discrete nonaqua yttrium(III) complex (Fig. 1) and bromate ions. The trivalent metal ions are located in the (2c) site of $\bar{6}$ symmetry. Six surrounding water oxygen atoms (O2) are located at the vertices of a trigonal prism, Y-O2 2.370(2) Å, and three capping water oxygen atoms (O1), Y-O1 2.446(3) Å (table 3).

The bromate ions in the current structure are disordered, in two partly occupied sites, in which each Br atom is surrounded by two fully (O3) and two (O4) half-occupied oxygen atom sites in nearly tetrahedral configuration.

The O4 atom has a relatively high displacement parameter and is located in two positions in close contact with corresponding oxygen atoms from other bromate ions (O4), 2.017(5) Å. This short contact distance is an effect of the disordered bromate anions. The hydrogen bond distance for water oxygen in capping (O1) and prism (O2) positions to the oxygen bromate (O3) is found to be 2.851 and 2.818 Å, respectively (table 4 and Figs. 2 and 3).

The hydrogen atoms of the capping water molecules are placed in the capping plane (see molecular view, Fig. 3), while in the nonhydrated yttrium(III) ethyl sulfate and trifluoromethanesulfonate they are perpendicular to the capping plane, and that makes different hydrogen bonds [4,9].

The refined thermal parameters of all the atoms in the crystal structure of $[Y(H_2O)_9](BrO_3)_3$ compound indicates a smaller value at low temperature in comparison to ambient temperature [12].

This change is significantly higher for the disordered bromate anion, which shows much lower thermal parameter values at lower temperature. This indicates less atomic movements at lower temperature. All the bond lengths in **1** and **2** appear to be similar within their estimated standard deviations.

Table 1: Crystallographic data for $[Y(H_2O)_9](BrO_3)_3$ at low temperature (150 K), 1, and at room temperature, 2 (Ref. [12]).

	1	2
Formula	$Br_3H_{18}O_{18}Y$	
M	634.78	
Crystal system	Hexagonal	
Space group	$P6_3/mmc$	
a/Å	11.7104(11)	11.7237(16)
c/Å	6.6259(5)	6.6855(9)
V/Å ³	786.90(12)	795.78(19)
T/K	291(2)	100(2)
Z	2	
D _{calcd} /g.cm ⁻³	2.679	2.649
$\mu(Mo-K\alpha)$ mm ⁻¹	11.411	11.28
Crystal size/mm	0.3×0.1×0.08	0.3×0.1×0.08
Measured reflections	6655	12059
Unique reflections	470	336
Observed reflections I>2 σ (I)	400	311
Θ /°	4.0-32.3	5.1-25.8
$h_{min, max}$	-16, 16	-14, 14
$k_{min, max}$	-16, 16	-14, 14
$l_{min, max}$	-6, 9	-8, 8
R _{int}	0.0636	0.0849
Final R ₁ , wR ₂ [I > 2 σ (I)] ^a	0.0214 0.0424	0.0285 0.0726
(all data)	0.0284 0.0433	0.0335 0.0886

a) R values are defined as: $R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$ wR₂ = $[\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}]^{1/2}$

CONCLUSIONS

The structure of the nonaqua-yttrium(III) bromate, $[Y(H_2O)_9](BrO_3)_3$, at low temperature (100 K), was revealed and compared with the data previously reported at ambient temperature. The structure of the title compound was described in hexagonal unit cell, in which the yttrium(III) ion is surrounded by nine water molecules in tricapped trigonal prism (TTP) configuration. The bromate ions hydrogen bonded to

Table 2: atomic coordinates and U_{iso} for compound 1.

Atoms	X	Y	Z	U _{iso}
Y1	0.6667	0.3333	0.7500	0.01091(15)
Br	0.129811(19)	0.25962(4)	0.7500	0.02494(14)
O1	0.78724(13)	0.5745(3)	0.7500	0.0247(6)
O2	0.8398(2)	0.41991(10)	0.5097(3)	0.0182(4)
O3	0.06825(17)	0.36102(18)	0.7500	0.0175(4)
O4	0.0950(3)	0.1899(5)	0.5450(10)	0.0519(16)

Table 3: Selected bond lengths and angles (Å, °).

Y-O1	2.446(3)	Br-O3	1.669(2)
Y-O2	2.370(2)	Br-O4	1.531(5)
O2-Y1-O2	136.52(4)	O1-Y1-O1	120.0 (3)
O2-Y1-O2	84.39(10)	O4-Br-O4	125.0(5)
O2-Y1-O2	79.82(8)	O4-Br-O3	106.52(14)
O2-Y1-O1	68.258(19)	O3-Br-O3	103.93(13)
O2-Y1-O1	137.81(5)		

Table 4: Hydrogen-bond geometry (Å, °).

D-H...A	D-H	H...A	D...A	D-H...A
O ₂ -H ₂ ...O ₃	0.72(2)	2.11(2)	2.818(2)	168(3)
O ₁ -H ₂ ...O ₃	0.86(4)	2.00(4)	2.851(2)	171(3)

the water molecules in capping positions stabilize the crystal structure. One oxygen from bromate ion appears in two positions with 50% occupancy factor and makes the disordered bromate to assume a nearly octahedral configuration. Thermal parameters, which is an indicative of atomic movements for all the atoms, show lower value at low temperature compared to ambient temperature.

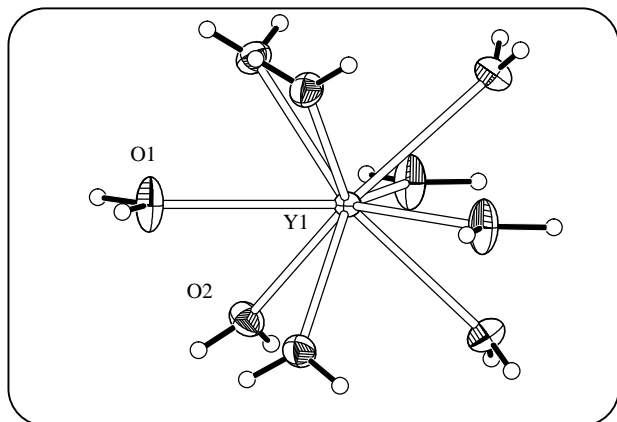


Fig. 1: Trigonal prism (O2) and capping (O1) water oxygen atoms around yttrium(III) ion, with 50% probability displacement ellipsoids.

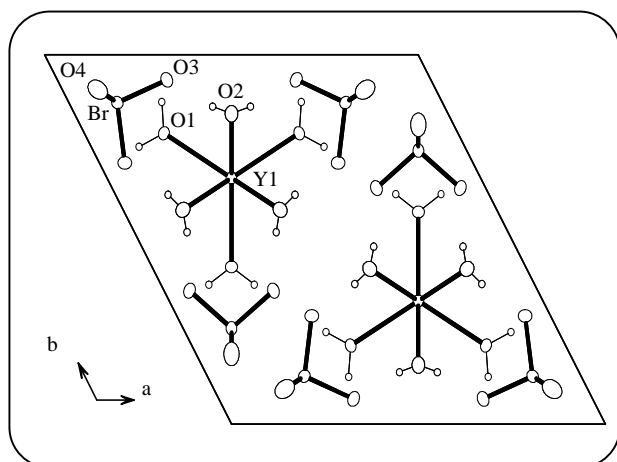


Fig. 2: A packing diagram for 1, in a view along c axis.

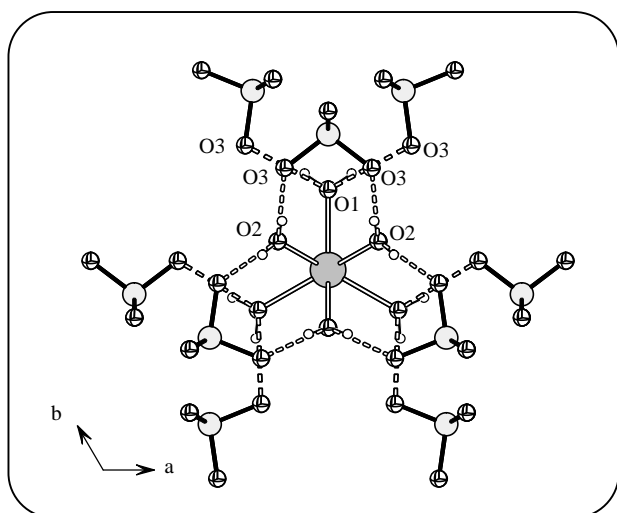


Fig. 3: A molecular view for 1 along c axis showing hydrogen bonding.

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