Infrared and Raman Spectroscopic and Force Field Studies of $Y(H_2O)_9(BrO_3)_3$

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Abstract

Infrared and Raman spectra of the nonaaqua yttrium(III) bromate, $Y(H_2O)_9(BrO_3)_3$, compound have been recorded. Force field calculations have been performed for YO_9^{3+} moiety, with a tricapped trigonal prismatic oxygen atom arrangement in D_{3h} point group symmetry. The larger stretching force constant was found, 90.7 Nm^{-1}, for the Y-O prism in comparison with the corresponding value in the capped Y-O, 56.5 Nm^{-1}.

Introduction

All metal ions are hydrated to some extent in aqueous solutions and in the solid state. The hydration number is determined by the ionic size and by the electronic structure of the atom. In a certain compound, the hydration number sometimes appears different in aqueous solution and in the corresponding solid state, and the reason can be regarded to the packing effect in the solid state. The water molecules can either distribute in the holes between ions or directly coordinate to the central metal ion. Single crystal X-ray diffraction, extended X-ray absorption fine structure (EXAFS) and vibrational (IR and Raman) spectroscopies can be applied to study the structure and bonding in such compounds.

Earlier we have undertaken advanced study of structure and bonding in nonaaqua lanthanoid(III) trifluoromethanesulfonate compounds (Abbasi 2005). Also normal coordinate treatment was extended to some hydrated trivalent cations (Ti, V, Cr, Fe, Co, Rh, Ir) (Abbasi & Eriksson 2006). In this paper we continue the study of structure and bonding for the title compound and make comparison with the nonaaqua yttrium(III) trifluoromethanesulfonate. The structure from X-ray single crystal studies for the hydrated bromate and trifluoromethanesulfonate salts with the same hydration number shows different hydrogen atom positions for the capped water molecules, making hydrogen bonds to be different, which reflects also in spectroscopic features of the substances, i.e. Y–O

stretching frequencies and the corresponding force constants (Harrowfield *et al.* 1983, Mink & Mink 2004, Mink *et al.* 2003).

Experimental parts

Synthesis. The title compound was synthesized by adding aqueous $Y(ClO_4)_3$ to the stoichiometric amount of potassium bromate followed by cooling the solution to 15 °C. The precipitated potassium perchlorate was filtered off and the $Y(H_2O)_9(BrO_3)_3$ crystals were obtained by evaporating the excess of water.

Spectra measurements. Raman spectra of the solid compound were obtained using a Renishaw System 1000 spectrometer, equipped with a Leica DMLM microscope, a 20 mW diode laser (782 nm), and a Peltier-cooled CCD detector. The mid-infrared (400 – 4000 cm^{-1}, resolution 4 cm^{-1}, 128 scans) absorption spectrum of the solid compound was recorded in purged atmosphere using a Bio-Rad (Digilab) 6000 FT-IR spectrometer. Far-infrared (50 – 700 cm^{-1}) spectrum was obtained with a Bio-Rad (Digilab) FTS-45 dynamically aligned spectrometer equipped with wire-mesh beamsplitter, high-pressure mercury source and deuterotriglycine sulfate (DTGS) and polyethylene windows. Samples were diluted with nujol mulls (Mid-IR) and with polyethylene powder (Far-IR). All the spectra were measured at ambient temperature.

Force field analysis. Normal coordinate analysis of the spectra and force field calculations based on potential energy distribution (PED) were performed by means of Wilson's GF matrix method. A PC-

based program package developed by J. Mink and L. Mink was used to compute force constants and to fit vibrational frequencies using a symmetrized valence force field (Mink *et al.* 2005). The initial force constants were adopted the same as for corresponding trifluoromethanesulfonate, (Abbasi 2005) and refined to get satisfactory fit between calculated and experimental frequencies. The nonaaquacation was treated as MO_9 complex having perfect trigonal prismatic configuration (D_{3h} symmetry point group). Water molecules were treated as point masses (18 amu). Among a total of 16 fundamental skeletal normal modes, 11 Raman active vibrations belong to $3A_1' + 5E' + 3E''$ symmetry species, 8 infrared active absorption frequencies belong to $3A_2'' + 5E'$ species whereas $A_2' + A_1''$ are inactive modes.

As to the bromate ion, according to the literature, its geometry in nonaaqua yttrium(III) bromates deviates significantly from the prefect C_{3v} observed in potassium bromate.[3] Therefore, the treatment of this ion was undertaken in C_s symmetry group.

The experimental frequencies (IR and Raman) together with their assignment are given in Tab. 1 and the refined force constants in Tab. 2. Description of symmetry coordinates for tricapped trigonal prismatic $Y(OH_2)_9{}^{3+}$ ions are explained in Tab. 3. Figs. 1-2 show the Raman spectra of solid $KBrO_3$ and $Y(H_2O)_9(BrO_3)_3$ compounds, respectively, and the Far-IR spectrum of $Y(H_2O)_9(BrO_3)_3$ comes in fig. 3.

Table 1. Experimental and calculated frequencies for $Y(H_2O)_9(BrO_3)_3$ and $KBrO_3$, cm⁻¹ in 200 – 900 cm⁻¹ region and their assignment

$Y(H_2O)_9(BrO_3)_3$			$KBrO_3$			Symm. species	Assign.
IR	R	Calc.	IR	R	Calc.		
			810	810	810	A_1	$\nu_s(BrO)$
			790	790	790	E	$\nu_{as}(BrO)$
822	822	822				A'	$\nu(BrO_{short})$
791	790	789				A''	$\nu_{as}(BrO_{long})$
778	780	781				A'	$\nu_s(BrO_{long})$
			428	428	428	A_1	$\delta_s(BrO_3)$
			361	361	361	E	$\delta_{as}(BrO_3)$
463	463	463				A'	$\delta(BrO_2)$
	368	367				A''	$\delta_{as}(BrO_3)$
358		356				A'	$\delta_s(BrO_3)$
	312	312				A_1'	$\nu_s(YO_{prism})$
326		326				A_2''	$\nu(YO_{prism})$
319	319	319				E'	$\nu(YO_{prism})$
	320	320				E''	$\nu(YO_{prism})$
	247	247				A_1'	$\nu_s(YO_{cap})$
235		235				E'	$\nu(YO_{cap})$

Results and discussion

In the vibrational spectra several sets of frequencies were observed. Those above 3300 cm⁻¹ were attributed to O–H stretching bands and those in the 1500 cm⁻¹ region belong to the OH_2 bending. Stretching vibrations of bromate anion were observed near 800 cm⁻¹: the highest one at 822 cm⁻¹ was attributed to the "short" Br – O bond while the intense doublet at 790 – 779 cm⁻¹ – to asymmetric (higher, 790 cm⁻¹) and symmetric (lower band, 779 cm⁻¹) vibrations of BrO_2 group participating in formation of hydrogen bond with water molecules

coordinated to the metal ion (these bands originates from doubly degenerated E vibration in $KBrO_3$).

Another group of bands is observed at 312 – 368 cm⁻¹. The highest doublet of bands at 358 and 368 cm⁻¹ belongs to BrO_3 asymmetric bend (belonging in $KBrO_3$ to E symmetry). Corresponding symmetric vibration is observed at higher frequency, at 463 cm⁻¹. Other bands above 300 cm⁻¹ belong to prismatic MO stretchings and at 235 – 247 cm⁻¹ – to equatorial (capped) ones.
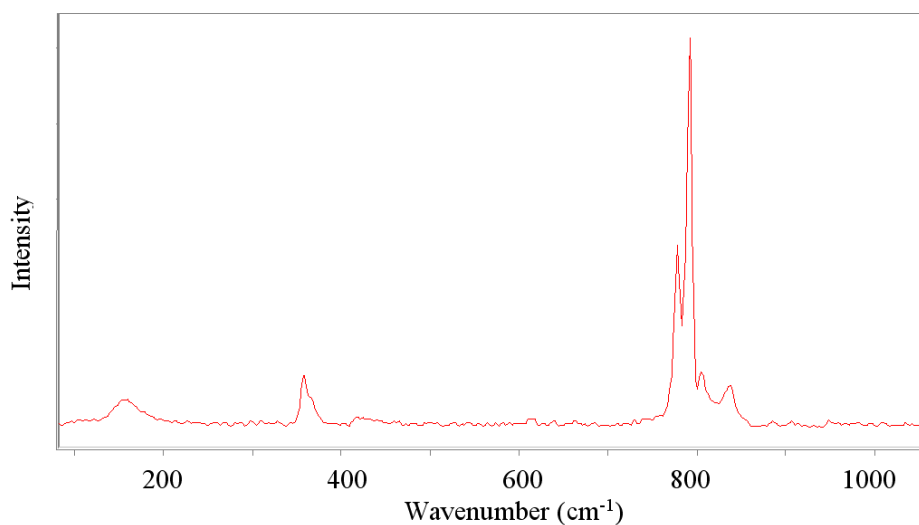
Fig. 1. Raman spectrum of solid KBrO$_3$
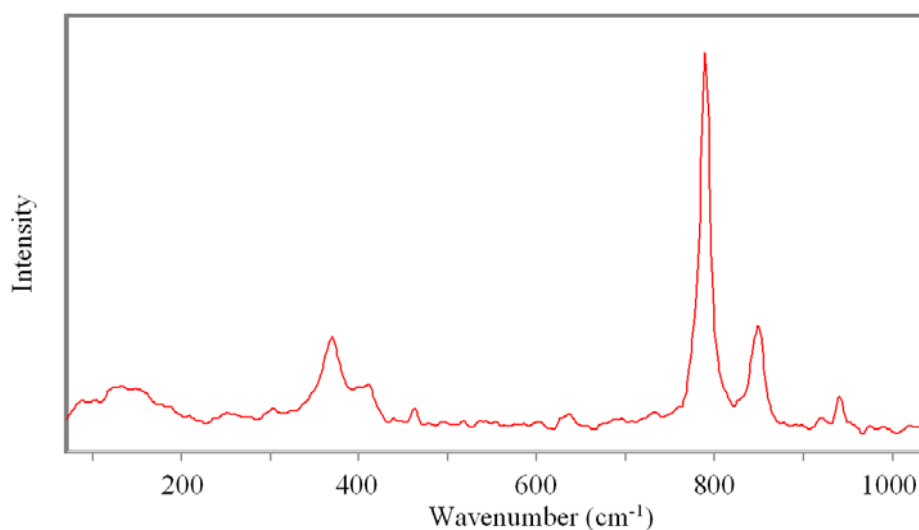
Fig. 2. Raman spectrum of Y(H$_2$O)$_9$(BrO$_3$)$_3$

Tab. 2. Refined force constants. Force constant units: [a] Nm^{-1}; [b] 10^{-18} Nmrad^{-2}; [c] 10^{-8} Nrad^{-1})

Coordinate	Y(H$_2$O)$_9$(BrO$_3$)$_3$	Y(H$_2$O)$_9$(CF$_3$SO$_3$)$_3$[d]	KBrO$_3$	Units
Stretch				
K(YO$_{prism}$)	90.7	93.5		a
K(YO$_{eq}$)	56.5	56.3		a
K(BrO)	514.2; 469.0		494.4	a
Stretch-stretch				
F(YO, YO), PP	0.001	0.003		b
F(YO, YO), PP'	-0.028	−0.032		b
F(YO, YO), PP"	0.062	0.065		b
F(YO, YO), CC	-0.042	−0.035		b
F(BrO, BrO)	-0.071		-0.195	b
Bend				
H(BrO$_2$)	0.683; 0.654		0.645	c
h(BrO$_2$, BrO$_2$)	0.007		-0.026	c

[d] Skripkin *et al*. unpublished results.

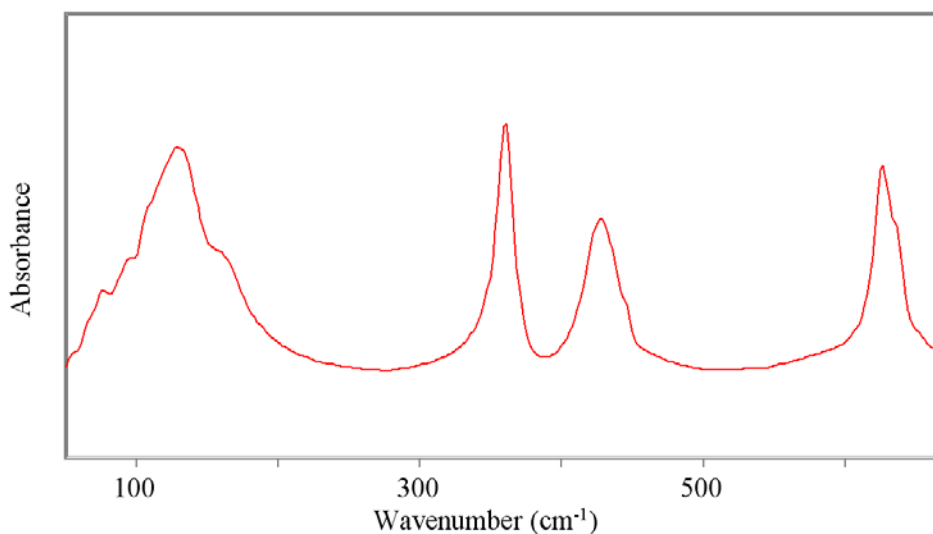Abbreviations: P – prismatic, C – capped bonds

Fig. 3. Far-IR spectrum of $Y(H_2O)_9(BrO_3)_3$

The hydrogen bonds formation leads to rather distinct change of BrO stretching force constants compare to "neat" bromate ion, as in potassium bromate. The force constant for the oxygen atoms involved in hydrogen bonds formation decreases by ca. 5% compare to $KBrO_3$ and also the average value of BrO stretching force constant decreases by 2.5-3.0%.

As to the Y-O stretching force constants, the comparison of the corresponding values for the capping positions in bromate and trifluoromethane-sulfonate reveals rather similar values (56.5 and 56.3 Nm^{-1}). This result seems to be rather unusual because of the corresponding Y-O bond length is far shorter in bromate (2.434 Å) compare to trifluoromethanesulfonate (2.525 Å). Probably, this shortening of Y-O bond is compensating by stronger hydrogen bonds, which is far shorter for bromate (2.87 Å versus 3.00 Å). The difference in the position of water molecule (in plane of capping O atoms-bromate-or perpendicular to this plane-trifluoromethane-sulfonate) also contribute into relatively small force constants for the capping Y-O bonds in nonaaqua yttrium(III) bromate (Figs. 4-5).
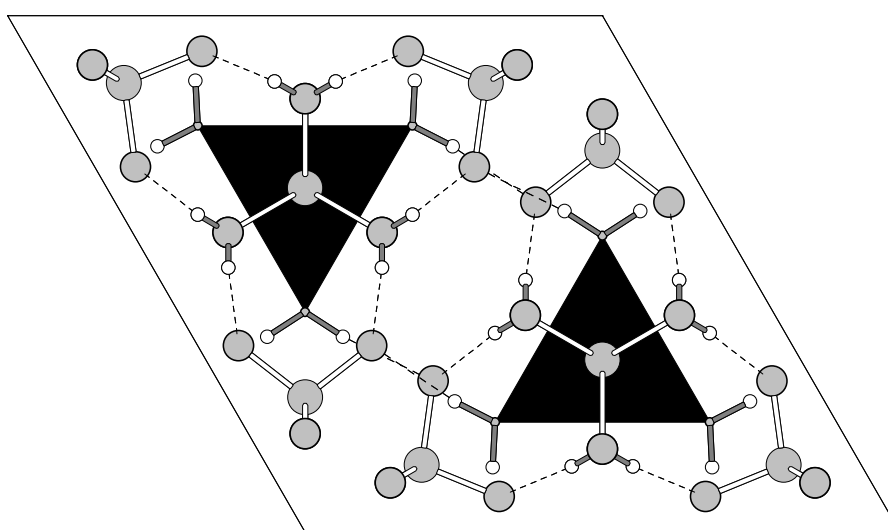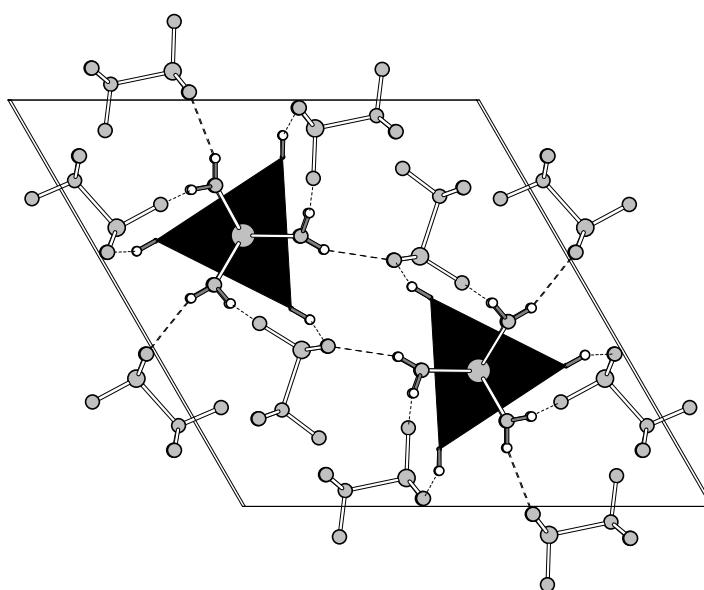

Fig. 4. Hydrogen bonding in a packing view along c-axis for the $Y(H_2O)_9(BrO_3)_3$ (ref. 3)

Tab. 3. Description of symmetry coordinates for tricapped trigonal prismatic Y(OH$_2$)$_9$$^{3+}$ions.

A_1': $S_1 = r_1 + r_2 + r_3 + r_4 + r_5 + r_6$ $S_2 = r_7 + r_8 + r_9$ $S_3 = \alpha_{12} + \alpha_{13} + \alpha_{23} + \alpha_{45} + \alpha_{46} + \alpha_{56} - 1/\sqrt{2}\,(\alpha_{18} + \alpha_{19} + \alpha_{27} + \alpha_{29} + \alpha_{37} + \alpha_{38} + \alpha_{48} + \alpha_{49} + \alpha_{57} + \alpha_{59} + \alpha_{67} + \alpha_{68})$
A_1'': $S_4 = \alpha_{18} + \alpha_{29} + \alpha_{37} + \alpha_{49} + \alpha_{57} + \alpha_{68} - \alpha_{19} - \alpha_{27} - \alpha_{38} - \alpha_{48} - \alpha_{59} - \alpha_{67}$
A_2': $S_5 = \alpha_{18} + \alpha_{29} + \alpha_{37} - \alpha_{49} - \alpha_{57} - \alpha_{68} - \alpha_{19} - \alpha_{27} - \alpha_{38} + \alpha_{48} + \alpha_{59} + \alpha_{67}$
A_2'': $S_6 = r_1 + r_2 + r_3 - r_4 - r_5 - r_6$ $S_7 = \alpha_{12} + \alpha_{13} + \alpha_{23} - \alpha_{45} - \alpha_{46} - \alpha_{56}$ $S_8 = \alpha_{18} + \alpha_{19} + \alpha_{27} + \alpha_{29} + \alpha_{37} + \alpha_{38} - \alpha_{48} - \alpha_{49} - \alpha_{57} - \alpha_{59} - \alpha_{67} - \alpha_{68}$
E': $S_{9a} = 2r_1 - r_2 - r_3 + 2r_4 - r_5 - r_6$ $S_{9b} = r_2 - r_3 - r_5 + r_6$ $S_{10a} = 2r_7 - r_8 - r_9$ $S_{10b} = r_8 - r_9$ $S_{11a} = 2\alpha_{12} - \alpha_{13} - \alpha_{23} + 2\alpha_{45} - \alpha_{46} - \alpha_{56}$ $S_{11b} = \alpha_{13} - \alpha_{23} + \alpha_{46} - \alpha_{56}$ $S_{12a} = 2\alpha_{78} - \alpha_{79} - \alpha_{89}$ $S_{12b} = \alpha_{79} - \alpha_{89}$ $S_{13a} = 2\alpha_{18} - \alpha_{29} - \alpha_{37} + 2\alpha_{48} - \alpha_{59} - \alpha_{67} + 2\alpha_{49} - \alpha_{57} - \alpha_{68} + 2\alpha_{19} - \alpha_{27} - \alpha_{38}$ $S_{13b} = 2\alpha_{18} - \alpha_{29} - \alpha_{37} + 2\alpha_{48} - \alpha_{59} - \alpha_{67} - 2\alpha_{49} + \alpha_{57} + \alpha_{68} - 2\alpha_{19} + \alpha_{27} + \alpha_{38}$
E'': $S_{14a} = 2r_1 - r_2 - r_3 - 2r_4 + r_5 + r_6$ $S_{14b} = r_2 - r_3 - r_5 + r_6$ $S_{15a} = 2\alpha_{12} - \alpha_{13} - \alpha_{23} - 2\alpha_{45} + \alpha_{46} + \alpha_{56}$ $S_{15b} = \alpha_{13} - \alpha_{23} - \alpha_{46} + \alpha_{56}$ $S_{16a} = 2\alpha_{18} - \alpha_{29} - \alpha_{37} - 2\alpha_{48} + \alpha_{59} + \alpha_{67} + 2\alpha_{49} - \alpha_{57} - \alpha_{68} - 2\alpha_{19} + \alpha_{27} + \alpha_{38}$ $S_{16b} = 2\alpha_{18} - \alpha_{29} - \alpha_{37} - 2\alpha_{48} + \alpha_{59} + \alpha_{67} - 2\alpha_{49} + \alpha_{57} + \alpha_{68} + 2\alpha_{19} - \alpha_{27} - \alpha_{38}$

Fig. 5. Hydrogen bonding in a packing view along c-axis for the Y(H$_2$O)$_9$(CF$_3$SO$_3$)$_3$ (ref. 4)

The Y-O bonds in prism positions are stronger in trifluoromethanesulfonate salt. That is confirmed by both bond distances (2.344 Å versus 2.434 Å in bromate) and by force constants (93.5 and 90.7 Nm^{-1} respectively). The difference in both sets of values (bond distances and force constants) is nearly equal: 3-4%. Force constants in the prismatic Y-O stretching in both bromate and trifluoromethane-sulfonate compounds are not influenced significantly by the corresponding hydrogen bonds due to the similarity in the geometry of water molecules. However, little stronger hydrogen bonds for trifluoromethane-sulfonate result only in a little less difference in force constant (3.1%) compare to bond distances (3.8%).

Conclusions

Raman and Infrared studies have enabled assignment of Y-O stretching modes of nonaaqua yttrium(III) bromate compound in solid state. A force field study of the tricapped trigonal prismatic coordination of the title compound has been performed and compared with the isotypic nonaaqua yttrium(III) trifluoromethanesulfonate. Values of stretching force constants for prismatic and capping positions correlate rather well with corresponding bond distances, however, small difference in force constants of capping bonds for bromate and trifluoromethanesulfonate is explained by their significant difference in hydrogen bonding.

References

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