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X-Ray Crysatllographic and Vibrational Spectroscopic Studies of Thorium Bromate Hydrate

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ABSTRACT

$Th(BrO_3)_3 \cdot H_2O$ single crystals were grown from its aqueous solution at room temperature. Single crystal XRD, Raman and FTIR techniques were used to investigate the crystal structure. The crystal structure was solved by Patterson method. The as grown crystals are in monoclinic system with space group P21/c. The unit cell parameters are a = 12.8555(18) Å, b = 7.8970(11) Å, c = 9.0716(10) Å, $\alpha = 90^\circ$, $\beta = 131.568^\circ$ and $\gamma = 90^\circ$ and unit cell volume is 689.1(2) $Å^3$. Z = 8, R factor is 5.9. The Raman and FTIR studies indicate the lowering of symmetry of bromate anion from C_{3V} to C_1. Hydrogen bonds with varying strengths are present in the crystal. The centrosymmetric space group P21/c of the crystal is confirmed by the non-coincidence of majority of Raman and IR bands.

Keywords: Thorium Bromate; X-Ray Diffraction; IR Spectroscopy; Raman; Crystal Structure; BrO_3^- Anion

1. Introduction

Hydrated bromates, coordinated to rare earth metals are an interesting group of compounds due its magnetic and optical properties [1,2]. Further, Bromates are attained considerable interest from chemists because its role in chemical oscillator systems and chemiluminescence systems and as an oxidizing agent for the fast oxidation of secondary alcohols [3-7]. Recently, Thionine-Bromate is identified as a new reaction system for kinetic spectrophotometric determination of hydrazine in cooling tower water samples [8]. However a limited attention is paid by researchers to understand structural and physical properties of bromate compounds. Single crystal XRD and vibrational spectroscopic techniques are being used by different authors for elucidating structure of hydrated metallic bromates [9-15]. Interestingly, most of these compounds having hydrogen bonded crystalline structure and oxyhalogen anions in these compounds posses distorted pyramidal structure. Thorium is one of the important actinide elements, actinide bromate compounds are rarely reported in the literature. In the present work we are reporting structural studies of hydrated rare earth thorium bromate by using X-ray diffraction, Raman and infrared spectroscopy for the first time.

2. Experimental

Crystals used in the present investigation were grown from aqueous solution of thorium bromate by slow evaporation at room temperature (32˚C) over a period of one month. Single crystal X-ray diffraction data were collected by using single crystal X-ray diffractometer sealed tube CAD4/MACH3, with Mo$K\alpha$ radiation (λ = 0.71073 Å). CAD4 Software. Version 5.0. Enraf-Nonius were used for data collection [16,17]. The cell data were obtained from the least-squares refinement**.** Structure was solved by using ShellX97 program. Raman spectrum of the sample was recorded using Bruker RFS 100/s Raman spectrometer equipped with Nd:YAG laser (Wavelength 1064 nm at a Laser power of 150 mW) in the stokes region from 50 - 4000 cm^{-1} with a spectral resolution better than 4 cm^{-1}. Standard Ge detector was used for detecting the Raman signals. FTIR spectrum of the sample in the range 400 - 4000 cm^{-1} was obtained from Shimadzu spectrometer by KBr pellet method and in the region 50 -

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400 cm^{-1} with polyethylene pellet method by using MAGNA 550 FTIR spectrometer.

3. Results and Discussion

3.1. X-Ray Crystal Structural Studies

The structure of the title compound is solved by Patterson method [16]. Thorium atoms are coordinated to oxygen atoms and some of these are coordinated to bromine and H_2O (**Figure 1**). The average bond length of water (oxygen) coordinated Th(1)-O1w is of the order of 2.6972(0.0232) Å which is comparable to Th-O (water) distance (2 - 46 Å) reported in thorium nitrate pentahydrate [18]. The thorium atom coordinated to the oxygen atoms of bromate group (Th(1)-O (of BrO_3) is of the order of 2.7766(0.0125) Å. Generally lanthanide hydrated bromates form disordered bromate anions at room temperature [15]. In the actinide bromate also disordered bromate anion is seen which is formed by the bonding of oxygen atoms with bromine and Thorium atoms is shown in the ORTEP diagram (**Figure 2**). The average Br(1)-O(1) distance is 1.6504(0.0133) Å, Br(1)-O(3) is 1.6573(0.0129) Å and Br(1)-O(2) 1.6712(0.0128) Å (**Table 1**). These distances are consistent with those of previously reported one in the literature [12-14].

3.2. Raman and FTIR Spectral Studies

$Th(BrO_3)_3 \cdot H_2O$ crystallizes in the monoclinic crystal system (space group P21/c, Z = 8) and all the atoms are occupying in the C_1 sites. The factor group analysis was carried out by the correlation method developed by Fateley *et al*. [19]. The total irreducible representation, excluding the acoustic modes, are distributed as

$$\Gamma 189 = 48A_g + 48B_g + 47A_u + 46B_u .$$

The BrO_3^- anion with C_{3V} symmetry has four fundamental modes of vibrations, symmetric stretching ν_1—805 (A_1), asymmetric stretching ν_3—805 (E), symmetric bending ν_2—418 (A_1) and asymmetric bending ν_4—358 (E) cm^{-1} [13,14,16-20]. For XY_3 pyramidal (C_{3v}) molecules $\Gamma = 2A_1+2E$, and all the modes are active both in the Raman and IR spectra [20]. In Raman spectrum, a strong band is observed at 820 cm^{-1} followed by a shoulder at 796 cm^{-1} and another strong band is appeared at 784 cm^{-1} (**Figure 3**). The strongest band observed in the IR spectrum is at 789 followed by a strong shoulder at 821 cm^{-1}. These bands correspond to ν_1-ν_3 modes of BrO^{3-} anion. These spectral band positions are in the same region as reported previously in the literature which is having comparable Br-O distance [21-25]. The symme-tric stretching frequency of BrO_3^- anion observed in this crystal is almost similar (784 cm^{-1}) to that of reported in crystals like $Cd(BrO_3)_2 \cdot 2H_2O$, $Nd(BrO_3)_3 \cdot 9H_2O$, $Gd(BrO_3)_3 \cdot 9H_2O$ and $La(BrO_3)_3 \cdot 9H_2O$ [23-26]. This

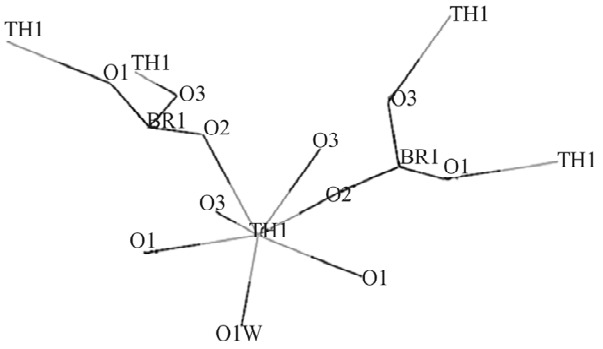

Figure 1. ORTEP diagram of hydrated thorium bromate.

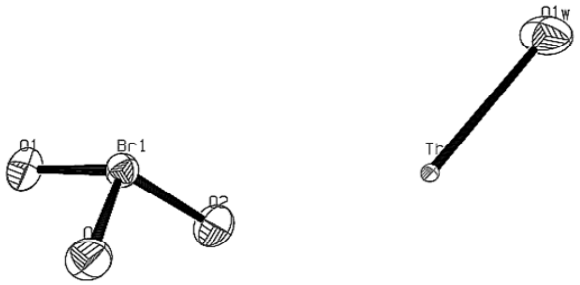

Figure 2. BrO_3^- anion and thorium water coordination in hydrated thorium bromate.

Table 1. Selected bond distances of thorium bromate hydrate .

Br(1)-O(1)	1.6504(0.0133) Å
Br(1)-O(2)	1.6712(0.0128) Å
Br(1)-O(3)	1.6573(0.0129) Å
Th(1)-O(1)w	2.6972(0.0232) Å
Th(1)-O (of BrO_3)	2.7766(0.0125) Å

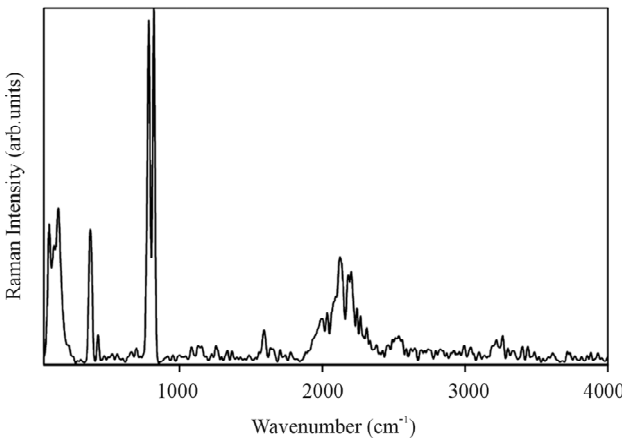

Figure 3. FT Raman spectrum of hydrated thorium bromate in the region 50 - 4000 cm^{-1}.

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downward shift is attributed to the presence of hydrogen bonding, which is attached to water molecules.

Symmetric bending mode ν_2 is observed at 429 cm^{-1} as a weak band in the Raman spectrum similar to that in the case of [Cu $(H_2O)_6$] $(BrO_3)_2$ (**Table 2**) [25]. The degeneracy of the ν_4 mode of BrO_3^- anion is lifted in the Raman spectrum and two bands are observed at 371 and at 383 cm^{-1} (**Figure 3**). Lifting of degeneracy is also observed in the IR spectrum and two bands are observed at 363 and 389 cm^{-1}. The lifting of degeneracy of ν_4 mode both in the Raman and IR spectra indicate the lowering of symmetry of BrO_3^- anion from C_{3v} pyramidal to lower one at C_1. A moderately intense broad band is observed at 152 cm^{-1} in Raman spectra is assigned to the BrO_3^- rotational mode [27].

Table 2. Raman and IR Spectral data of thorium bromate hydrate (cm^{-1}).

Raman	IR	Assignments
	66 vvw	
85 ms	86 vvw	libr. BrO_3^-
	113 w	
125 w	126 ms	rot. BrO_3^-
	146 ms	
152 ms	156 m	
	163 m	
	199 m	
	218 m	
200 vw	236 m	
	251 m	
	260 m	
	295 m	
371 ms	363 vvs	ν_4 BrO_3^-
383 sh	389 s	
429 vw	522 w	ν_2 BrO_3^-
760 sh		
784 vs	789 vs	ν_1 BrO_3^-
796 sh		
820 vs	821 sh	ν_3 BrO_3^-
	1026 sh	
	1597 s	ν_2 H_2O
2050 m		
2122 ms	2075 w	Res.Raman
2204 m		
	2857 vvw	
	2992 vvw	
	3155 sh	ν_1-ν_3 H_2O
	3458 vvs br	
	3521 sbr	

vvw, very very weak; vw, very weak; w, weak; wsh, weak shoulder; sh, shoulder; br, broad; vs, very strong; s, strong; vvs, very very strong; ms, moderately strong; m, moderately; sbr, strong and broad; rot., rotational; libr., librational.

In the stretching mode region of H_2O a broad band extending from 3000 - 3708 cm^{-1} is obtained in the IR spectrum (**Figure 4**) with shoulder at 3155 and followed by in tense peaks 3458 and 3521 cm^{-1}. In the bending mode region, a moderately intense band is observed at 1597 cm^{-1} in the IR spectrum. The appearance of OH stretching modes at lower wavenumber than those of free state values of H_2O indicate the presence of hydrogen bonds in the crystal [24]. Due to hydrogen bonds, OH bending modes are usually expected to shift upwards. But the coordination of Thorium atoms to the water Oxygen atoms causes a downward shift. Therefore, this almost equally energetic upward and downward pulling of O atoms causes the intense OH bending modes to appear without any shift in wavenumber values with respect to its free state value (1595-ν_2 H_2O). The appearance of additional bands in the OH stretching regions and broad spectral profile of both bending and stretching regions confirms the existence of hydrogen bonds of different strengths in the crystal [24,25]. The bands observed below 250 cm^{-1} are mostly of lattice modes and are assigned in **Table 2**. Interestingly, majority of the Raman and IR bands are not coinciding each other which indicate that the hydrated thorium bromate is crystallized in centrosymmetric space group which is in agreement with X-ray crystallographic information.

The strong Raman bands observed at 2130 and 2206 cm^{-1} probably attributed to resonance Raman scattering process since there is no vibrational bands are expected in this region for the title compound. Thorium is having closely lying "f" electronic energy levels, the electronic transitions between these levels initiate the formation of bands in the region 1925 - 2280 cm^{-1} similar to that reported previously in several U(IV) and Zr(IV) bis (ketimide) complexes, and in a few Th(IV) compounds [28,29].

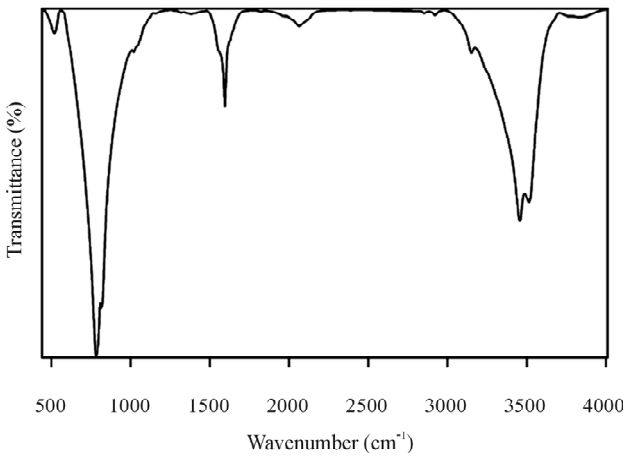

Figure 4. FTIR spectrum of the hydrated thorium bromate in the region 500 - 4000 cm^{-1}.

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4. Conclusion

The crystal structure of hydrated thorium bromate shows the Br(1)-O(1) distance is 1.6504(0.0133) Å, Br(1)-O(2) 1.6712(0.0128) Å and Br(1)-O(3) is 1.6573(0.0129) Å. Additional bands obtained in the vibrational spectra in the region of v_1 modes in the thorium bromate hydrate are due to the lifting of degeneracy of BrO_3^- ion, which occupies a site of lower symmetry than its free state at C_{3v}. The lifting of degeneracy of v_4 mode both in the Raman and IR spectra indicate the lowering of symmetry of BrO_3^- anion from C_{3v} pyramidal to lower one. The shifting of stretching modes of water towards low wavenumber region as compared to that of its free state value and the broadening of the stretching bands of H_2O indicate the presence of hydrogen bonds of varying strengths in the crystal. Non-coincidence of majority of Raman and IR bands confirms the centrosymmetric space group P21/c of the crystal. Resonance Raman scattering process is seen in addition to vibrational bands attributed to closely lying "f" electronic energy levels. The present compound may be useful to study as a chemical oscillator and chemiluminescence systems in future.

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