



Crystal structure, vibrational and optical properties of N-(3-ammoniumpropyl)-1,3 diammoniumpropane hexabromobismuthate monohydrate: $[\text{C}_6\text{H}_{20}\text{N}_3]\text{BiBr}_6 \cdot \text{H}_2\text{O}$



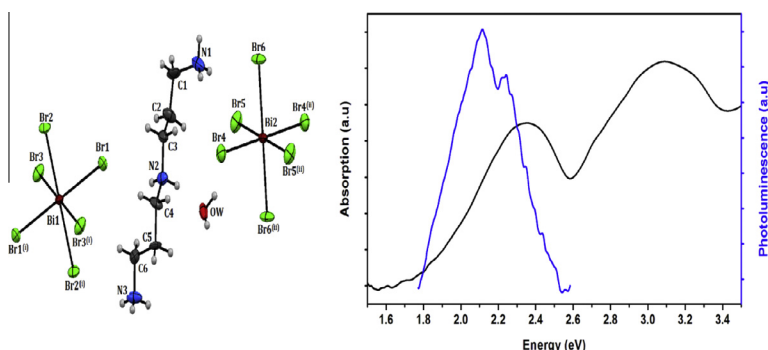
N. Elfaleh*, S. Kamoun

Laboratory of Materials Engineering and Environment (LR11ES46), BP 1173, ENIS, Sfax University, Tunisia

HIGHLIGHTS

- Crystal structure of a new zero dimensional alkyl tetra-ammonium bismuth bromide.
- Optical absorption and photoluminescence properties of $(\text{C}_6\text{H}_{20}\text{N}_3)\text{BiBr}_6 \cdot \text{H}_2\text{O}$.
- Investigation of the structure by IR and Raman vibrational spectroscopy.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 14 May 2014
Received in revised form 5 July 2014
Accepted 8 July 2014
Available online 15 July 2014

Keywords:

Organic–inorganic hybrids
Crystal structure
Vibrational assignment
Photoluminescence
Absorption

ABSTRACT

The chemical preparation, the main structural, vibrational and optical features are given for a new zero dimensional alkyl tri-ammonium bismuth halogenide. $(\text{C}_6\text{H}_{20}\text{N}_3)\text{BiBr}_6 \cdot \text{H}_2\text{O}$ crystallize in triclinic system, space group $P\bar{1}$. The crystal structure consists of discrete ionic pairs of N-(3-ammoniumpropyl)-1,3 diammoniumpropane cations, hexabromobismuthate anions and neutral water molecules linked via simple and bifurcated N–H...Br(OW) and O(W)–H...Br hydrogen bonds. Infrared and Raman spectra of $(\text{C}_6\text{H}_{20}\text{N}_3)\text{BiBr}_6 \cdot \text{H}_2\text{O}$ were recorded at 298 K and discussed. The assignment of the observed IR and Raman lines was performed by comparison with the homologous compounds. Optical properties are investigated by optical absorption UV–visible and photoluminescence (PL) techniques. The optical absorption spectra reveal the appearance of sharp optical gaps of 3.10 eV as well as two strong green–yellow photoluminescence emissions are observed at room temperature.

© 2014 Elsevier B.V. All rights reserved.

Introduction

This work is a part of our study on the crystal structure of alkyl-polyammoniumbismuthate(III) halogenides. This investigation was extended to aliphatic diamines of general formula $\text{NH}_2(\text{CH}_2)_n\text{NH}_2$ [1–6] and triamines of general formula $\text{NH}_2(\text{CH}_2)_n\text{NH}(\text{CH}_2)_n\text{NH}_2$

[7,8] in order to examine the effects of the flexible cation and the halogen atoms ($X = \text{Cl}, \text{Br}, \text{I}$) on the bismuth(III) coordination geometry. In these compounds the Bi atom shows a tendency toward distorted octahedral coordination with some rather long Bi–X bonds, which is attributed to the aspherical distribution of the lone pair electrons at Bi(III). These organic–inorganic hybrid alkylpolyammonium bismuthate(III) halogenides, typically characterized by covalent and ionic interactions, are new materials whose use is interesting for fundamental research and applied devices, due

* Corresponding author.

E-mail address: falehnizar@yahoo.fr (N. Elfaleh).

to their unique organic–inorganic combined attributes and the enhanced quantum confinement [9]. These materials offer the potential for electrical mobility, a wide range of band gaps, optical properties and dielectric properties. In the present work, we report the crystal structure, the vibrational (infrared and Raman) and the optical (photoluminescence and absorption) properties of a new zero-dimensional bismuth-bromide based compound: $(C_6H_{20}N_3)BiBr_6 \cdot H_2O$.

Experimental

Preparation

Crystals of the title compound were obtained by dissolving in concentrated solution of HBr (48%) a stoichiometric mixture of bismuth(III) oxide and N-(3-aminopropyl)-1,3 diaminopropane (molar ratio 1:2). The resulting aqueous solution was then kept at room temperature. After several weeks of slow evaporation at room temperature, yellow prismatic shaped monocrystals of $(C_6H_{20}N_3)BiBr_6 \cdot H_2O$ were obtained. They were washed with diethyl ether and dried for 4 h over anhydrous $CaCl_2$.

X-ray structure determination

A suitable yellow crystal, selected under a polarizing microscope and mounted on a glass fiber, was chosen for the structure determination. Experimental conditions used for the single-crystal diffraction data collection and structure refinement are reported in Table 1. The positional parameters for the bismuth and the bromine atoms were obtained from the three-dimensional Patterson map, whereas the remaining atoms were found from successive difference Fourier maps. After introducing anisotropic thermal factors for the non hydrogen atoms and isotropic thermal factors for H atoms, the hydrogen atoms were localized and optimized to fixed

Table 1
Crystal data and summary of intensity data collection and structure refinement of $(C_6H_{20}N_3)BiBr_6 \cdot H_2O$.

Empirical formula	$(C_6H_{20}N_3)BiBr_6 \cdot H_2O$
Molecular weight (g mol ⁻¹)	840.71
Temperature	296 K
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 8.0366 (17) \text{ \AA}$ $\alpha = 73.988 (11)^\circ$ $b = 11.262 (2) \text{ \AA}$ $\beta = 70.867 (8)^\circ$ $c = 12.252 (3) \text{ \AA}$ $\gamma = 70.833 (8)^\circ$
Volume	$971.9 (4) \text{ \AA}^3$
Z	2
Dm, Dx (g cm ⁻³)	2.870, 2.873
Diffraction	Bruker APEXII CCD
Radiation, graphite monochromator	Mo K α ($=0.71073 \text{ \AA}$)
Max. crystal dimension (mm)	$0.1 \times 0.1 \times 0.1$
Theta range for data collection	$3.9 < \theta < 24.1^\circ$
Absorption coefficient (mm ⁻¹)	21.40 mm^{-1}
Reflections measured	6130
Range of h, k, l	$-9 < h < 9, -12 < k < 12, -13 < l < 14$
Independent reflections	2879
Reflections with $I > 2\sigma(I)$	2456
Number of parameters	166
$F(000)$	760
Weights	$w = 1/[\sigma^2(F_o^2) + (0.0323P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Extinction coefficient	$0.0083(12)$
$R[F^2 > 2\sigma(F^2)]$	0.088
Rw	0.19
Computer programs	SHELXS97, SHELXL97 [10], WINGX [11] and MERCURY [12]

positions. Their contribution were isotropically introduced into calculation but were not refined. Corrections were applied for Lorentz and polarization effects and absorption. The final refinement cycles with 2456 reflections corresponding to $I > 2\sigma(I)$ yielded $R = 0.089$ and $Rw = 0.19$. All calculations were performed using SHELXS and SHELXL included in the WINGX package [10].

Spectroscopic measurements

Raman spectra of the sample was recorded at room temperature using 448 nm line laser as excitation wave length in the region $100\text{--}2000 \text{ cm}^{-1}$ on a DILOR XY set up. The incident power was kept less than 5 mW to avoid the degradation of the sample by heating. Infrared absorption spectrum was recorded at room temperature in the $400\text{--}4000 \text{ cm}^{-1}$ frequency range on a Perkin-Elmer spectrometer equipped with a Universal ATR Accessory (UATR).

Results and discussion

Structure description

The asymmetric unit of the title compound consists of two distinct bismuth sites which sit on an inversion center, the fully protonated template N-(3-aminopropyl)-1,3 diaminopropane and a water molecule. A perspective view of the arrangement of these constituent entities is shown in Fig. 1 together with the atom numbering scheme. The both of $[BiBr_6]^{3-}$ anions located on an inversion center exhibit a distorted octahedral coordination environment with Bi–Br bond lengths ranging from 2.829 (2) Å to 2.8643 (19) Å. These values are much shorter than the sum of Vander Waal's radii of Bi and Br (4.7 Å) according to Pauling [13]. The bond-valence sum (BVS) calculation of the Bi(1) and Bi(2) cations, using the parameters given by Brown [14], gave respectively values of 2.94 and 3.03 valence units. These results confirm primary the presumed oxidation state of Bi(III) and secondary the stereochemical activity of Bi lone electron pair. The $[BiBr_6]^{3-}$ anions are connected through $O(W)\cdots H\cdots Br$ hydrogen bonds, so that infinite one-dimensional chains parallel to the [1 1 1] direction with an anionic period $[BiBr_6(H_2O)]^{3-}$ is formed in the structure (Fig. 2(a)). The total negative charge (–3) on the framework is balanced by the presence of one independent fully protonated $[NH_2((CH_2)_3NH_3)_2]^{3+}$ molecule. These entities have a trans configuration with a non crystallographic inversion center. Table 2 reports the principal geometrical features of this organic group. The C–N and C–C bond lengths vary from 1.43(3) Å to 1.53(4) Å and 1.47(4) Å to 1.57(3) Å, respectively. They are similar to those reported in other N-(3-ammoniumpropyl)-1,3 diammoniumpropane salts such as $(C_6H_{20}N_3)BiCl_6 \cdot H_2O$ [8] and $(C_6H_{20}N_3)_2[V_4O_4F_{14}] \cdot 2H_2O$ [15]. The intermolecular hydrogen bonding contacts $N\cdots H\cdots Br$, $N\cdots H\cdots O(W)$ and $O(W)\cdots H\cdots Br$ provide linkage between the $[NH_3(CH_2)_3NH_2(CH_2)_3NH_3]^{3+}$ cations, the water molecules and the $[BiBr_6(H_2O)]^{3-}$

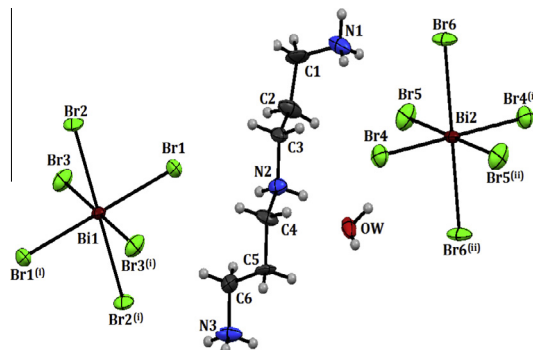


Fig. 1. A view of the asymmetric unit of the title compound. Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x, -y, -z$.

Download English Version:

<https://daneshyari.com/en/article/1402315>

Download Persian Version:

<https://daneshyari.com/article/1402315>

[Daneshyari.com](https://daneshyari.com)