



Synthesis, crystal structure, and spectroscopic studies of organic–inorganic hybrid material: $[C_7H_{10}NO]_2BiBr_5$



Z. Aloui ^{a,*}, V. Ferretti ^b, S. Abid ^a, F. Lefebvre ^c, M. Rzaigui ^a, C. Ben Nasr ^a

^a Université de Carthage, Laboratoire de Chimie des Matériaux, Faculté des Sciences de Bizerte, 7021 Zarzouna, Tunisia

^b Department of Chemical and Pharmaceutical Sciences and Center for Structural Diffractometry, via Fossato di Mortara 17, I-44121 Ferrara, Italy

^c Laboratoire de Chimie Organométallique de Surface (LCOMS), Ecole Supérieure de Chimie Physique Electronique, 69622 Villeurbanne Cedex, France

ARTICLE INFO

Article history:

Received 8 February 2016

Received in revised form

9 April 2016

Accepted 11 April 2016

Available online 13 April 2016

Keywords:

Organic–inorganic hybrid material

Crystal structure

IR absorption

DFT calculations

ABSTRACT

A novel organic–inorganic hybrid compound, 2-methoxyanilinium pentabromobismuthate(III), $[C_7H_{10}NO]_2BiBr_5$, was synthesized and its structure determined by means of single crystal X-ray diffraction studies at room temperature. The molecule crystallizes in the orthorhombic $C222_1$ space group with cell parameters $a = 11.8870(4)$, $b = 23.4775(8)$, $c = 8.1232(3)$ Å, $V = 2267.0(1)$ Å³ and four molecules in the unit cell. The structure of the title compound is built up from one-dimensional $[BiBr_5]^{2n-}$ polyanionic zig-zag chains composed of deformed $BiBr_6$ octahedra share Br(2) apex and 2-methoxyanilinium cations. The assignment of the vibrational bands was based on comparison with vibrational mode frequencies of homologous compounds. Theoretical calculations were performed using density functional theory (DFT) for studying the vibrational spectrum of the investigated molecule in its ground state. The ¹³C CP-MAS NMR spectrum is in agreement with the X-ray structure.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Design and preparation of new nonlinear optical materials have been a subject of immense importance in recent years due to their potential applications in ultrafast signal processing, optical computing, telecommunications, optical limiting, optical data storage devices, optical communications and harmonic generation [1–5]. The essential characteristics of a compound to exhibit nonlinear optical (NLO) properties are the presence of high nonlinear susceptibility, delocalized electronic cloud with adequate thermal and mechanical stability. A fertile topic of research is represented by organic–inorganic hybrid materials, where the advantages of the organic components (straightforward synthetic approach, easily tailored molecular structure and functional properties) are merged with those of an inorganic network (chemical, thermal and mechanical stabilities); moreover, the combination between the two integrating parts, occurring at the molecular level, is often able to confer new properties, different from those of the single components, on the resulting hybrid materials. Many synthetic strategies have also been developed in the last years, e.g. intercalation process of organic compounds into layered structures,

development of organic–inorganic networks by solid-gel procedures and so on [6], aimed at obtaining hybrid materials with different properties. Aromatic derivatives, which are a group of organic compounds characterized by the delocalized of π electrons, can display a large NLO response which makes them attractive for applications in integrated optics [7–9]. As for the inorganic species suitable for the setting up of these materials, they are often metal halides or cyanides, polyoxometalates, metal chalcogenides containing transition metals such as Pb, Hg, Bi, Cd etc. [10]. In the case of bismuth-halide compounds, the organic-halogenobismuthates(III) were found to exhibit unique properties with potential applications such as nonlinear polar and nonlinear optical materials (NLO) [11–15].

An important class of low dimensional hybrid materials is the organic inorganic perovskite like family of the type $R_xM_yX_z$ (where R is protonated amine, M is a metal and X is a halide) which has received considerable interest in the past decades. The anionic structure can vary considerably ranging from isolated MX_6 octahedra to extended chains and up to 2- or 3D networks. In fact, the structural type depends on the experimental conditions, such as the solvent, ratio of reagents, and temperature. The organic cation size, charge, steric encumbrance, and the conformation can have a decisive influence. Concerning the observed difference in Bi–X bond lengths and X–Bi–X angles forming the mean values

* Corresponding author.

E-mail address: aloui_zouhaier@yahoo.fr (Z. Aloui).

characteristic of non-deformed polyhedral, they were revealed to be linked to the shift of the lone electron pair (LEP) of the Bi(III) atom toward the interaction. As for the difference in Bi–X bond lengths, they are correlated to the primary deformations emanating from the tendency of octahedrons $[\text{BiX}_6]^{3-}$ to share halogen atoms and secondary deformations generated from intermolecular interactions.

We report in this paper the synthesis, crystal structure and spectroscopic studies of a novel organic–inorganic halogenobismuthate(III) polymeric compound with 2-methoxyaniline, $[\text{C}_7\text{H}_{10}\text{NO}]_2\text{BiBr}_5$, which crystallizes in non-centrosymmetric space group showing enhanced NLO activity.

2. Experimental

2.1. Synthesis

All reagents were commercial products and were used without further purification. The $[\text{C}_7\text{H}_{10}\text{NO}]_2\text{BiBr}_5$ crystal was prepared at room temperature by dropwise addition of an aqueous solution of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.5 g, 1.03 mmol, 99%) to a solution of 2-methoxyaniline (0.25 g, 2.06 mmol, 98%) in ethanol (10 mL). To this mixture, was added, drop by drop a concentrated HBr solution (48 wt%) in stoichiometric conditions. After stirring and heating to 60 °C during 30 min, the solution was filtered and allowed to evaporate at room temperature till the formation of brown prismatic monocrystals (yield: 68%). Anal. Calc.: C, 19.60; H, 2.33; N, 3.26. Found: C, 19.78; H, 2.40; N, 3.34%.

2.2. X-ray structure determination

A single crystal was carefully selected under polarizing microscope in order to perform its structural analysis by X-ray diffraction. Diffraction data were collected on a Nonius Kappa diffractometer equipped with a CCD detector with graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71069$ Å). Intensities were corrected for Lorentz, polarization and absorption effects [16]. The structure was solved by direct methods with the SIR97 suite of programs [17] and refinements were performed on F^2 by full-matrix least-squares methods with all non-hydrogen atoms anisotropic. Hydrogens were included on calculated positions, riding on their carrier atoms. All calculations were performed using SHELXL-97 [18] implemented in the WINGX system of programs [19]. The crystal data are reported in Table 1. The drawings were made with Diamond [20] and ORTEP III [21].

2.3. NMR and IR measurements

The IR spectrum was recorded in the range 4000–400 cm^{-1} with a “Perkin–Elmer FTIR” spectrometer 1000 using a sample dispersed in spectroscopically pure KBr pressed into a pellet.

The ^{13}C NMR spectrum was recorded on a solid-state high-resolution Bruker DSX-300 spectrometer operating at 75.49 MHz with a classical 4 mm probehead allowing spinning rates up to 10 kHz. The NMR chemical shifts are given relative to tetramethylsilane (precision 0.5 ppm). The spectrum was recorded by use of cross-polarization (CP) from protons (contact time 2 ms) and MAS. Before recording the spectrum it was checked that there was a sufficient delay between the scans allowing a full relaxation of the protons (typically at least 10 s).

2.3.1. DFT calculations

The infrared spectrum and the ^{13}C NMR chemical shifts were calculated with the Gaussian 09 software [22]. All calculations were made with the B3LYP method. The 6-311++G** basis was chosen

for all atoms except for bismuth for which the LanL2DZ pseudo-potential was used. In all cases the positions of the atoms were those determined by the X-ray diffraction study except for the hydrogen atoms which were first optimized at the above level of theory. Indeed the positions determined by X-ray do not correspond to the location of the proton but to that of the barycenter of charges. The ^{13}C NMR chemical shifts were then calculated by use of the GIAO method.

3. Results and discussion

3.1. Structure description

The $[\text{C}_7\text{H}_{10}\text{NO}]_2\text{BiBr}_5$ belongs to orthorhombic system, crystallizing in acentric space group $C222_1$. Configurations of the different organic and inorganic species of $[\text{C}_7\text{H}_{10}\text{NO}]_2\text{BiBr}_5$ are shown in Fig. 1. Selected bonds and angles are listed in Table 2. Bismuth and one bromine atom (Br2) are located in special position, while the Br1 and Br3 atoms are situated in a general position. The bismuth(III) ion is surrounded by six bromine atoms as shown in the packing diagram (Fig. 2). The Bi–Br bond lengths vary from 2.711(2) Å to 2.997(1) Å, the longest distance involving the bridging bromine atom. This is in line with what is generally found in polymeric bromobismuthate structures (85 hits in CSD): the mean Bi–Br distances are 2.720(3) and 3.025(6) Å for non-bridging and bridging Br atoms, respectively. The Br–Bi–Br bond angles fall in the range 83.45(11)–97.39(12)°, differing from 90° by more than 7° which suggests a slight distortion of the $[\text{BiBr}_6]^{3-}$ octahedron. This might be due to the presence of the lone electron pair (LEP) of Bi(III). As already observed, the LEP is responsible for the deformation of the octahedron coordination sphere of Bi(III) [23]. The Bi–Br2–Bi angle (159.3°) along the chain reflects that the BiBr_6 octahedra are also somewhat rotated relative to each other in the [001] direction. All the aromatic rings of the 2-methoxyanilinium cations are essentially planar, with no carbon and nitrogen atoms deviating from the least-squares planes by more than 0.011(3) Å. Their bond distances and angles (Table 2) are similar to those observed in other compounds containing the same cation [24]. The C–C–C and C–C–N are similar to those expected for sp^2 hybridization.

As for the crystal packing, the N–H ... Br hydrogen bonds, whose geometrical parameters are reported in Table 3, play an important role in establishing the structure. These intermolecular interactions additionally distort the $[\text{BiBr}_6]^{3-}$ octahedra shifting the halogen atoms in the direction of the positive charge located on the cations.

It is possible to recognize an anionic sublattice of $[\text{C}_7\text{H}_{10}\text{NO}]_2\text{BiBr}_5$ consisting of one-dimensional $[\text{BiBr}_5]^{2n-}_n$ polyanionic zig-zag chains, composed of distorted $[\text{BiBr}_6]^{3-}$ octahedra connected via Br(2) apex spreading in the [001] direction at $y = 0$ and $y = 1/2$ (Fig. 2). In this structural variety, the two anionic chains are doubly tilted and further linked together via intermolecular hydrogen-bonding N–H ... Br and weak C–H ... Br and van der Waals interactions to form a 3D supramolecular framework (Fig. 3). The spaces between the inorganic entities are filled by organic cations assuring their connection by means of N–H ... Br interactions (Table 3).

3.2. FT-IR spectral analysis

The FT-IR spectrum of $[\text{C}_7\text{H}_{10}\text{NO}]_2\text{BiBr}_5$ is shown in Fig. 4. The spectrum was recorded in the 4000–400 cm^{-1} spectral range in order to confirm the presence of functional groups in the molecule. The characteristic vibrational modes of this compound can be compared to those of similar materials [25–27]. The IR spectrum shows, at high wavenumbers (3100–2900 cm^{-1} region) very large

Download English Version:

<https://daneshyari.com/en/article/1408822>

Download Persian Version:

<https://daneshyari.com/article/1408822>

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