

Communication

An Unusual Bismuth Ethanedisulfonate Network

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Abstract: The three dimensional bismuth ethanedisulfonate framework $\text{Bi}(\text{O}_3\text{SC}_2\text{H}_4\text{SO}_3)_{1.5}(\text{H}_2\text{O})_2$ was synthesized under hydrothermal conditions using the bidentate ligand 1,2-ethanedisulfonate and then characterized through X-ray diffraction and elemental analyses. The bismuth cation coordinates at three different ethanedisulfonate ligands and has a coordination number of eight, which is accompanied by a distorted square antiprismatic configuration. Here, we report on the crystal structure of this bismuth metal–organic framework and its coordination behavior, which has thus far not been reported in heavier main group elements.

Keywords: main group chemistry; bismuth complex; ethanedisulfonate; MOF

1. Introduction

Bismuth(III) complexes are used in a variety of fields including biology and medicine [1,2], materials chemistry [3,4], and catalysis [5]. For this reason, the synthesis of bismuth metal-organic frameworks (MOFs) has received considerable attention [6]. A handful of bismuth organic frameworks exist, which have a broad range of structures due to their different molecular topologies [7,8]. By varying the set of donor atoms in the organic ligand, it is possible to enlarge this growing class of organometallic compounds. The formation of such frameworks depends significantly on the dimension of the internal cavity, rigidity of the ligands, nature of the electronegative atoms, and complex forming properties of the anion that is involved in the coordination bonding [6]. Generally, Bi^{3+} with its ionic radius of 1.16 Å [9] has one inert $6s^2$ electron pair and forms non-transition metal center complexes with

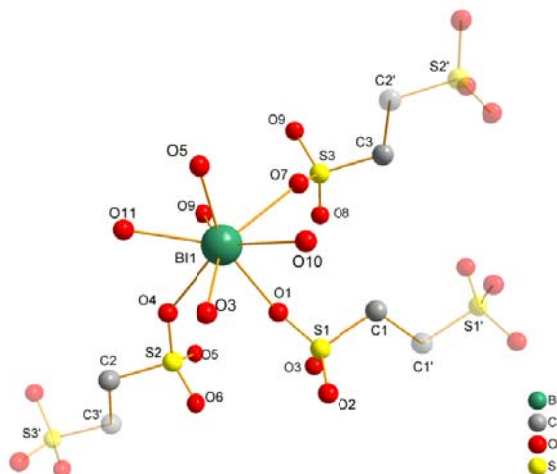
higher coordination-number atoms. Therefore, bismuth is predestined to form higher dimensionality cationic frameworks. The well-studied hydrolysis behavior of Bi^{3+} makes it an especially desirable system for conducting hydrothermal studies on $[\text{Bi}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_2][(\text{CH}_2)_2(\text{SO}_3)_2]_3$ and $[\text{Bi}_9\text{O}_8(\text{OH})_6][\text{CF}_3\text{SO}_3]_5$ [10]. Crystalline hybrid materials composed of main group elements are mostly based on metal carboxylates [11–14] and phosphonates [15,16], for further references please refer to Cambridge database [17]. The nature of sulfonate ligands has been less thoroughly investigated in terms of their ability to function as an organic linker in main group MOFs and coordination polymers. However, they may be used in potentially interesting applications such as gas separation, storage, as well as catalysis [18,19]. In particular, porous hybrid transition metal compounds based on carboxylates [20] and phosphonates [17,21,22] have attracted widespread interest in the past few years. However, there exist few MOFs that entail heavier main group elements with sulfonate linker ligands, for instance lead 4-sulfobenzoate complexes [23,24] and the wide range of tin disulfonic MOFs [25].

Research on bismuth based MOFs is rare [6–8]. Even so, some examples of compounds with diethanesulfonate ligands [10,26–31] can be found in the Cambridge Database [17]. For instance works about Ag and Cu ethandisulfonate complexes [27,28], bismuth clusters [10] or also mixed ligand cadmium complexes [32] to name only a few examples. Consequently, we would like to report on a three-dimensionally bismuth coordination polymer that encompasses a new structure type, which has not been observed, to the best of our knowledge, in any other MOF composed of heavier main group elements.

2. Results and Discussion

The colorless crystals of $\text{Bi}(\text{O}_3\text{SC}_2\text{H}_4\text{SO}_3)_{1.5}(\text{H}_2\text{O})_2$ (**1**) crystallize in the space group $P2_1/c$. The asymmetric unit, shown in Figure 1, consists of an eight-coordinated bismuth cation, at which one and a half moieties of the 1,2-ethanedisulfonate ligand are coordinated, and two water molecules. The complete compound contains one crystallographic independent Bi^{3+} ion, which is surrounded by eight oxygen atoms. Six of these oxygen atoms are part of the R-SO_3^- groups (O1, O3, O4, O5, O7, O9), and two are coordinated with water molecules (O10 and O11).

Figure 1. Asymmetric unit of **1** and the prolongation of the ethanesulfonate ligands, which are drawn in transparency mode (hydrogen atoms are omitted for clarity).



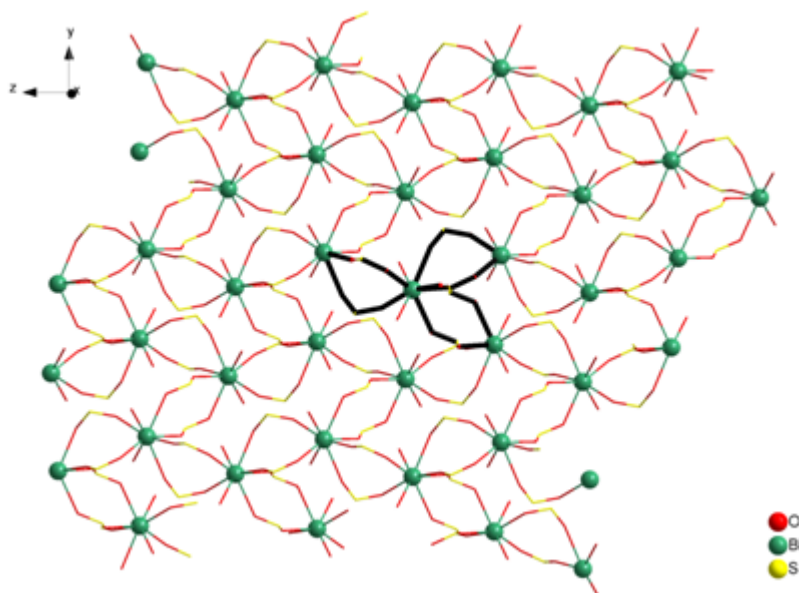
The bridging oxygen atoms (O1, O3, O4, O5, O7, O9) have slightly shorter bond lengths [10] with the bismuth atoms, ranging from 2.324(8) to 2.590(8) Å (Table 1). The bond lengths between water atoms (O10 and O11) and the bismuth lie in the range of other Bi–OH₂ bond lengths (Cambridge Database: 2.303–3.123 Å). A bond valence analysis reveals a value of 2.819 for the bismuth cation, which reflects the slightly insufficient coordination environment of the cation [33,34].

Table 1. Selected bond lengths (Å) for **1** with estimated standard deviations in parentheses.

Bond	Distance
Bi1—O1	2.427(9)
Bi1—O3	2.284(8)
Bi1—O4	2.590(9)
Bi1—O5	2.324(8)
Bi1—O7	2.591(8)
Bi1—O9	2.510(7)
Bi1—O10	2.420(8)
Bi1—O11	2.4249(5)

Consequently the ligands are spreading out in all three directions to the neighbor bismuth cations forming a metal organic framework with very small cavities. An ideal way to understand the structure is to investigate the bismuth-bridging SO₂ units and omit the ethylene groups (Figure 2). The resulting three-dimensional network built by the organosulfonate groups is cross-linked to the adjacent bismuth cation, and the MOF-like system can be seen clearly.

Figure 2. The Bi–SO₃ framework of **1**. The carbon and hydrogen atoms are omitted for clarity.



When the whole crystal structure is examined the alternating layers of bismuth cations and ligands becomes visible. Two different sheet systems can be distinguished. One has a large distance of around 6.5 Å as measured between the bismuth layers where the ligand lies stretched out in the *z*-direction (Figure 3). The second system has a shorter distance between the bismuth layers of around 3.8 Å due

to the ligands that lie in the x -direction. The structure does not contain solvent accessible voids, which could be calculated by PLATON Void-Analyser [35].

Figure 3. View of the Bi layers in the y -direction (the hydrogen atoms are omitted for clarity).

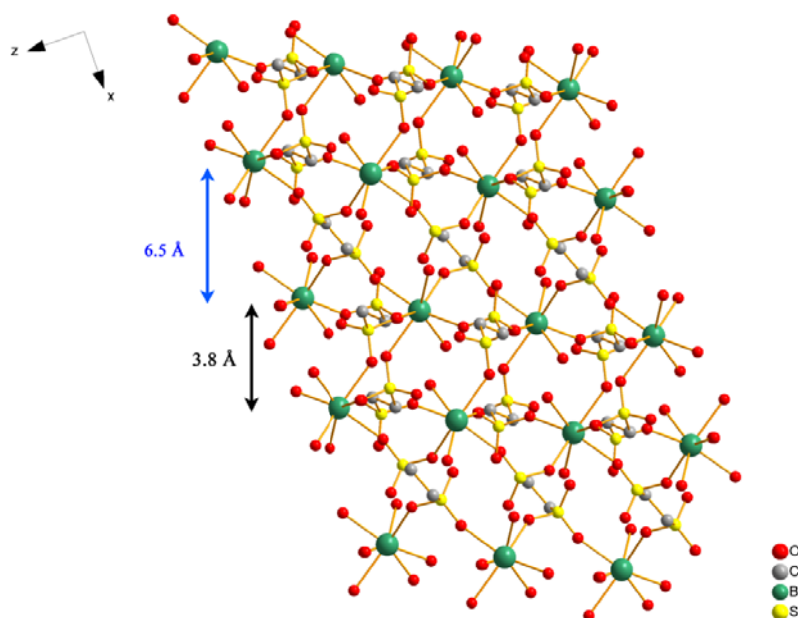


Table 2. Crystal structure data for **1**.

Crystal Data	1
Formula	$\text{C}_3\text{H}_{10}\text{BiO}_{11}\text{S}_3$
M_r	527.27
Cryst. size, mm^3	$0.18 \times 0.12 \times 0.07$
Crystal system	monoclinic
Space group	$P2_1/c$
a , Å	11.601(2)
b , Å	10.390(2)
c , Å	10.498(2)
β , deg	115.15(3)
V , Å ³	1145.3(4)
Z	4
D_{calcd} , g cm^{-3}	3.058
$\mu(\text{MoK}\alpha)$, cm^{-1}	15.994
$F(000)$, e	988
Refl. measd./unique	12498/10592
Param. refined	3144
$R(F)/wR(F^2)^a$ (all refl.)	0.0475/0.0283
GoF (F^2) ^a	1.124

The bulk material of compound **1** was confirmed through IR, powder X-ray-diffraction and elemental analyses. Even though compound **1** is the main product of the bulk material, a small amount of the compound $[\text{Bi}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_2][(\text{CH}_2)_2(\text{SO}_3)_2]_3$ [10] was always isolated after the first filtration and discarded.

For a better insight into the thermal stability a thermal analysis (TGA) under oxygen was performed: Single crystals of **1** were crushed thus only the pure phase could be investigated: up to the first decomposition peak starting at about 320 °C only the weight loss of the two coordinated water molecules can be observed (at about 139 °C and 222 °C, observed 6.7% calculated 6.8%). Higher temperatures led to the decomposition of the organic moiety in one step (320 °C–395 °C, observed 35.9%, calculated 35.8%), followed by weight gain of 2.5% till 870 °C, which could be possibly be explained by the adsorption of oxygen molecules. The crystal parameters used in the unit cell determination, and structure refinement parameters are summarized in Table 2.

3. Experimental Section

All reagents were obtained commercially and were used in the form that they were received in. The reactions were performed under hydrothermal conditions in air.

$\text{Bi}(\text{O}_3\text{SC}_2\text{H}_4\text{SO}_3)_{1.5}(\text{H}_2\text{O})_2$ (**1**)

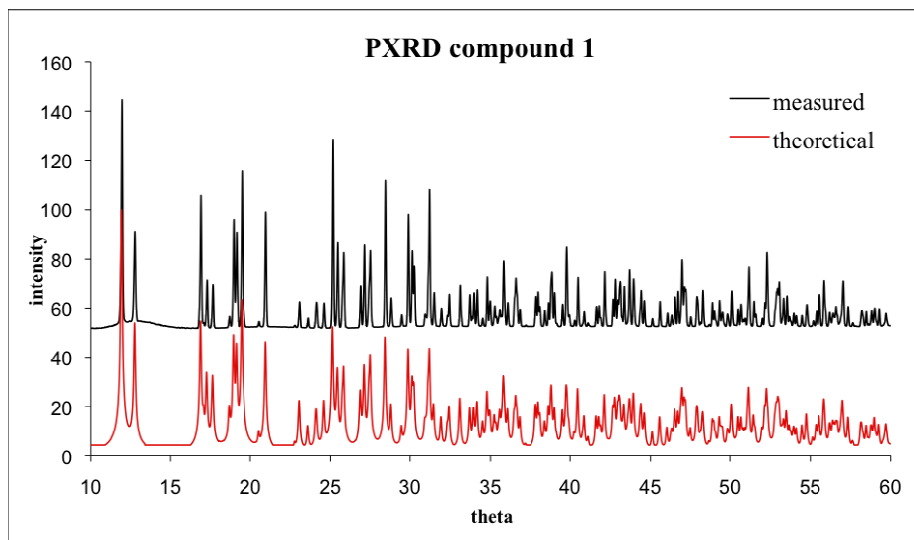
A mixture of Bi_2O_3 (1.16 g, 2.4 mmol), 1,2-ethanedisulfonic acid (2.5 g, 1.3 mmol), and H_2O (20 mL) was placed into a 25 mL teflon-lined stainless steel autoclave and kept for 3 days at 170 °C. After slowly cooling the autoclave to room temperature, a colorless solution with a little $[\text{Bi}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_2][(\text{CH}_2)_2(\text{SO}_3)_2]_3$ precipitate [10] had formed. The solution was filtered, and the mother liquor was allowed to evaporate in an open beaker. After two weeks, white crystals had formed. The crystals were filtered, washed with water, and then dried in air. Yield of the pure crystals: 20%.

Single-crystal measurements were carried out on a Stoe IPDS-II diffractometer with a MoK_α sealed tube at room temperature ($\lambda = 0.71073 \text{ \AA}$). The structure was solved using direct methods and refined in anisotropic approximation using the SHELX program suite [36].

A crystal was selected for single-crystal X-ray diffraction. The composition of the bulk material was confirmed through IR, powder X-ray-diffraction and elemental analyses. $-\text{C}_3\text{S}_3\text{BiO}_{11}\text{H}_{10} \cdot 2\text{H}_2\text{O}$ (632.66): calcd. C 6.19 Bi 38.5; found C 5.74, Bi 38.43, TGA: decomposition at 395 °C. FTIR (cm^{-1}): 3467 (O–H), 2967 and 2920 (C–C), 1632 (O–H), 1457 (C–H), 1159 (C–C) 1024 (S=O), 895 (C–H), 613 (C–S).

Powder X-ray diffraction (PXRD) data were recorded using a Bruker ASX D8 Advance powder diffractometer with CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$). Lattice parameters of the bulk material of **1** according to the PAWLEY fit could be found as; $a = 11.596$, $b = 110.385$, $c = 10.4926$, $\beta = 115.197$. The reflections of the powder pattern can be assigned to compound **1** (Figure 4, Table S1).

Figure 4. Experimental powder pattern of the sample in comparison to the theoretical powder pattern of **1** as based on the single-crystal structure determination.



4. Conclusions

We have demonstrated that a simple and direct reaction between bismuth oxide and 1,2-ethanedisulfonic acid under hydrothermal conditions yields a new bismuth network structure with an organosulfonic ligand. The bismuth atom has an eight-coordinated environment and is the first three-dimensionally coordinated bismuth ethanedisulfonate framework to be documented.

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Conflict of Interest

The authors declare no conflict of interest.

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