



Synthesis, structure and photoluminescence properties of amine-templated open-framework bismuth sulfates



Subba R. Marri, J.N. Behera*

School of Chemical Sciences, National Institute of Science Education and Research (NISER), Bhubaneswar 751005, India

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ABSTRACT

Two organically-templated bismuth sulfates of the compositions, $[\text{C}_6\text{N}_2\text{H}_{14}] [\text{Bi}(\text{SO}_4)_2(\text{NO}_3)]$, (**1**) and $[\text{C}_4\text{N}_2\text{H}_{12}]_4[\text{Bi}_4(\text{SO}_4)_{10}(\text{H}_2\text{O})_4]$, (**2**), with open architecture have been synthesized and their structures determined by single crystal X-ray diffraction. **1** has a corrugated layered structure with 8-membered aperture wherein the SO_4 tetrahedra and the BiO_8 polyhedra join together to form (4, 4) net sheets of the metal centers while **2** has a three-dimensional structure possessing 8- and 12-membered channels. Both the compounds show good fluorescence properties exhibiting blue luminescence. Time-resolved fluorescence behavior of **1** and **2** shows mean fluorescence life time of 0.9 and 1.0 ns, respectively.

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1. Introduction

The synthesis of complex inorganic materials with open architecture is one of the major activities in contemporary solid state chemistry for their applications in the areas of catalysis, ion-exchange, sorption and separation process. During the last two decades or so large number of new materials with novel architectures have been synthesized and characterized. Accordingly, inorganic open-framework structures involving silicates [1], phosphates [2] and carboxylates [3,4] have been widely investigated in the past few years. It has been demonstrated recently that oxyanions such as selenite [5], selenate [6] and sulfate [7] can also be made use of to build up open architectures. Though many transitional metal sulfates have one- or-two dimensional structures, three-dimensional organically-templated sulfates of uranium [8], lanthanum [9], scandium [10], and nickel [11], however, have been reported. Organically-templated metal sulfates are mainly focused on transition (both d- and f-block) metals. However, main group (p-block) metal sulfates are very rarely reported [12] and no three-dimensional bismuth sulfate appears to be known.

Metal oxides accommodating lone pair cations such as Pb^{2+} and Bi^{3+} have been of great interest due to their rich structural chemistry [13]. Bi^{3+} with its ionic radius of 1.16 Å has one inert $6s^2$ electron pair and forms non-transition metal center complexes with higher coordination-number atoms. Therefore, bismuth is

expected to form higher dimensional frameworks. Bismuth containing compounds with their low-toxicity, low-cost, and good chemical stability [13d–13f] are promising for potential application in medicine treatment, catalyst and luminescence [14]. Also, bismuth can exist in a wide variety of coordination environment that can lead structures of different dimensionalities. We are interested in exploring the use of SO_4^{2-} tetrahedra to build open-framework materials of heavy main group metals. Open-framework materials are usually synthesized by employing hydro/solvothermal techniques that require the reaction mixture to be heated at a particular temperature in a sealed autoclave [15]. We have been able to prepare both layered and three-dimensional bismuth sulfates employing simple aqueous mediated reaction at room temperature. In this article, we report the synthesis, structure, and luminescence properties of $[\text{C}_6\text{N}_2\text{H}_{14}] [\text{Bi}(\text{SO}_4)_2(\text{NO}_3)]$, **1**, and $[\text{C}_4\text{N}_2\text{H}_{12}]_4[\text{Bi}_4(\text{SO}_4)_{10}(\text{H}_2\text{O})_4]$, **2**.

2. Experimental

2.1. Materials and methods

All materials were commercially available and used as received. Infrared spectra were recorded on a Perkin Elmer FTIR spectrometer equipped with an attenuated total reflectance accessory. UV-visible spectra were collected using a Perkin Elmer UV/Vis/NIR spectrophotometer (Lambda 750). Excited and emission spectra of ground mixture of polycrystalline powders of all three compounds were recorded using Perkin–Elmer LS 55 Fluorescence Spectrometer. In all

* Corresponding author. Tel.: +91 674 230 4094; fax: +91 674 230 4070.
E-mail address: jnbehera@niser.ac.in (J.N. Behera).

cases the maximum in the excitation spectrum was used to generate the emission spectrum. EDAX was performed by field emission scanning electron microscopy (FE-SEM, Zeiss, Oxford). Optical image of the sample was taken using a Zeiss LSM-780 confocal microscope. Time-resolved fluorescence measurement was carried out using a time-correlated single-photon counting (TCSPC) spectrometer (Edinburgh, OB920). Thermogravimetric analyses were carried out at a ramp rate of 10 °C/min under a flow of nitrogen using a NETZSCH TG 209F1. Powder X-ray diffraction data were collected on a Bruker D8 Advance X-ray powder diffractometer using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). Carbon, hydrogen and nitrogen analyses were obtained from the Sophisticated Analytical Instrument at Central Drug Research Institute, Lucknow, India.

2.2. Synthesis and characterization

Compounds **1** and **2** were synthesized by slow evaporation at room temperature. In a typical synthesis of **1**, 0.485 g of Bi(NO₃)₃·4H₂O was dissolved in 10 mL of distilled water in a 20 mL scintillation vial under constant stirring. To this mixture, 0.5 mL of H₂SO₄ followed by 0.162 g of piperazine (PIP) were added and the mixture was stirred for 30 min to obtain the clear solution. The final mixture with the molar composition of Bi(NO₃)₃·4H₂O/H₂SO₄/PIP/H₂O (1:9:2:55) was kept at room temperature in open air. After one month needle-shaped white crystals were collected after filtration, washed with water and dried in air (yield 80% with respect to Bi). Compound **2** was synthesized in a similar way to that of **1** by using 1,4-diazabicyclo[2,2,2]octane (DABCO) as the structure directing amine. 0.485 g of Bi(NO₃)₃·4H₂O was dissolved in 10 mL of distilled water in a 20 mL scintillation vial under constant stirring. To this mixture, 0.5 mL of H₂SO₄ followed by 0.228 g of DABCO were added and the mixture was stirred for 30 min to obtain the clear solution. The scintillation vial containing the reaction mixture with the molar composition of Bi(NO₃)₃·4H₂O/H₂SO₄/DABCO/H₂O (1:9:2:55) was kept at room temperature in open air. After one month needle-shaped crystals were collected with 73% yield.

Initial characterization of **1** and **2** was carried out by powder X-ray diffraction (PXRD), energy dispersive analysis of X-rays (EDAX), chemical analysis, thermogravimetric analysis (TGA) and IR spectroscopy. The PXRD pattern exclusively exhibited reflections of a hitherto unknown material; and was consistent with the structure determined by single crystal XRD, which gave the compositions of **1** and **2** as [C₆N₂H₁₄][Bi(SO₄)₂(NO₃)], and [C₄N₂H₁₂]₄[Bi₄(SO₄)₁₀(H₂O)₄], respectively. All the compounds gave satisfactory elemental analysis. The experimental and calculated (in wt%) values of C, H, N were as follows. **1**: C, 12.5; N, 7.3; H, 2.5 (calc.: C, 12.6; N, 7.4; H, 2.3). **2**: C, 8.5; N, 5.2; H, 2.2 (calc.: C, 8.7; N, 5.1; H, 2.6). EDAX, indicated the ratios of Bi and S to be 1:2, and 1:2.5 in **1** and **2**, respectively, in agreement with the molecular formulae.

The IR spectra for the compounds were recorded as KBr pellets (Perkin–Elmer FT-IR SPECTROMETER–RX1). The IR spectroscopic studies exhibit typical peaks corresponding to the hydroxyl group, the amino groups, etc. (Supporting Information, Fig. S1). The main IR bands are (KBr): $\nu(\text{H}_2\text{O}) = 3230\text{--}3450 \text{ cm}^{-1}$, $\nu(\text{N–H}) = 3070\text{--}3110 \text{ cm}^{-1}$, $\nu(\text{C–H}) = 2670\text{--}2780 \text{ cm}^{-1}$, $\nu(\text{C–H}) = 1300\text{--}1500 \text{ cm}^{-1}$, $\nu_1(\text{SO}_4) = 950\text{--}1000 \text{ cm}^{-1}$, $\nu_3(\text{SO}_4) = 1100\text{--}1150 \text{ cm}^{-1}$, $\delta(\text{SO}_4) = 500\text{--}700 \text{ cm}^{-1}$. In general, the free sulfate ions exhibit two bands at 1105 and 615 cm⁻¹, which are assigned to the $\nu_3(\text{F}_2)$ stretching [$\nu_d(\text{SO})$] and $\nu_4(\text{F}_2)$ stretching [$\delta_d(\text{OSO})$] modes, respectively. The coordination of the free sulfate group to the metal centers would lower the overall symmetry of the sulfate group and lead to the splitting of the ν_3 and ν_4 modes. The spectra show multiple strong bands in the 900–1040 cm⁻¹ region due to ν_1 and in the 1050–1250 cm⁻¹ region due to ν_3 vibration modes of the sulfate group [16]. The bending modes of SO₄²⁻ are found in the 500–550 and 600–795 cm⁻¹ regions.

2.3. Single-crystal structure determination

A suitable single crystal of each compound was carefully selected under a polarizing microscope and mounted at the tip of the thin glass fiber using cyanoacrylate (super glue) adhesive. Single crystal X-ray data were collected on a Bruker Smart Apex II diffractometer equipped with an Oxford Cryostream low-temperature device and a fine-focus sealed-tube X-ray source (MoK α radiation, $\lambda = 0.71073 \text{ \AA}$, graphite monochromated) operating at 50 kV and 30 mA. Raw data collection and refinement were done using SMART. Data reduction was performed using SAINT [17] and corrected for Lorentz and polarization effects. An empirical absorption correction based on symmetry equivalent reflections was applied using SADABS [18]. The structure was solved by direct methods using SHELXS-97 [19], which readily revealed all the heavy atom positions (Bi, S) and enabled us to locate the other non-hydrogen (N, O and C) positions from the difference Fourier maps. For the final refinement, hydrogen atom of both the framework as well the ammonium ion in **1** and **2** were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions, anisotropic thermal parameters for all the non-hydrogen atoms, isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares structure refinement against |F_o| was carried out using the SHELXL-PLUS [20] package of programs. Details of the structure determination and final refinements for **1** and **2** are listed in Table 1. X-ray diffraction patterns of **1** and **2** were in good agreement with the simulated patterns based on single-crystal data, indicative of their phase purity (Fig. S2 in the Supporting information).

3. Results and discussion

3.1. Layered [C₆N₂H₁₄][Bi(SO₄)₂(NO₃)], **1**

The asymmetric unit of **1** contains 23 non-hydrogen atoms out of which 15 belong to the inorganic framework and 8 belong to the extra framework amine molecule (Fig. 1a). It has one crystallographically independent Bi³⁺ cation, two sulfate anions, one nitrate anion and one diprotonated DABCO cation. The Bi³⁺ cation in **1** is eight-coordinated to two sulfate and one nitrate ions in the bidentate fashion and two sulfate ions in the monodentate fashion. The Bi–O bond distances are in the range of 2.344(18)–2.740(2) Å [(Bi–O)_{av} = 2.490 Å]. The O–Bi–O bond angles are in the

Table 1
Crystal data and structure refinement parameters for **1** and **2**.

Parameters	1	2
Empirical formula	C ₆ H ₁₄ BiN ₃ O ₁₁ S ₂	C ₁₆ H ₄₈ Bi ₄ N ₈ O ₄₄ S ₁₀
<i>a</i> (Å)	9.70(4)	19.84(9)
<i>b</i> (Å)	13.36(6)	19.35(9)
<i>c</i> (Å)	20.74(8)	13.21(6)
α (°)	90	90
β (°)	90	91.93(10)
γ (°)	90	90
<i>V</i> (Å ³)	2691(19)	5071.3(4)
<i>Z</i>	8	4
Formula weight	577.30	2213.14
Space group	<i>Pbca</i> (61)	<i>P2₁/c</i> (14)
<i>T</i> (°C)	23	23
λ (MoK α) Å	0.71073	0.71073
ρ_{calc} (g cm ⁻³)	2.850	2.899
μ (mm ⁻¹)	13.484	14.381
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0215 <i>wR</i> 2 = 0.0531	<i>R</i> 1 = 0.0385 <i>wR</i> 2 = 0.0761
<i>R</i> (all data)	<i>R</i> 1 = 0.0273, <i>wR</i> 2 = 0.0555	<i>R</i> 1 = 0.0628, <i>wR</i> 2 = 0.0837

$$^a R_1 = \sum |F_o| - |F_c|; \quad ^b wR_2 = \{ [w(F_o^2 - F_c^2)^2] / [w(F_o^2)^2] \}^{1/2}, \quad w = 1 / (\sigma^2(F_o)^2 + (aP)^2 + bP) \\ P = [F_o^2 + 2F_c^2] / 3; \quad \text{where } a = 0.0300; b = 0.30 \text{ for } \mathbf{1}, a = 0.0350; b = 2.50 \text{ for } \mathbf{2}.$$

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