

Two novel 3-D bismuth oxalates with organic amines protruding in channels

Xiaohong Yu, Hanhui Zhang*, Yanning Cao, Zhongjian Hu, Yiping Chen, Zhen Wang

Department of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, PR China

Received 27 March 2006; received in revised form 2 June 2006; accepted 4 June 2006

Available online 14 June 2006

Abstract

Two novel 3-D oxalate-containing bismuth compounds of formula $(C_3N_2H_5)_2 [Bi_2(C_2O_4)_4(H_2O)_2] \cdot 2H_2O$ **1** and $[NH(C_2H_5)_3][Bi_3(C_2O_4)_5]$ **2** were obtained by hydrothermal synthesis and characterized by single-crystal X-ray diffraction. Compound **1** crystallizes in the monoclinic $P2_1/n$ space group with $a = 9.7541(13) \text{ \AA}$, $b = 17.7404(15) \text{ \AA}$, $c = 14.6321(6) \text{ \AA}$, $\beta = 97.280(3)^\circ$, $Z = 4$, $R_1 = 0.0340$ and $wR_2 = 0.0766$ for unique 4734 reflections $I > 2\sigma(I)$. Compound **2** belongs to the orthorhombic $Pbcn$ space group with $a = 14.803(4) \text{ \AA}$, $b = 19.783(7) \text{ \AA}$, $c = 8.202(2) \text{ \AA}$, $Z = 4$, $R_1 = 0.0222$ and $wR_2 = 0.0568$ for unique 2472 reflections $I > 2\sigma(I)$. The Bi^{III} centers have nine-fold coordination for **1** and eight-fold for **2** with the Bi atoms in distorted monocapped square antiprism and distorted dodecahedron, respectively. And oxalate ligands adopt different coordination modes: bidentate for **1**, bidentate and tricoordinate for **2**. Compounds **1** and **2** are both 3-D open-framework structures containing channels with guest molecules. These two compounds exhibit intense blue luminescence with the emission peaks at 419 nm for **1** and 442 nm for **2**, respectively, in the solid state at room temperature. These compounds with novel structural frameworks could be useful in the field of photoactive materials.

© 2006 Elsevier Inc. All rights reserved.

Keywords: Bismuth; Oxalate; Crystal structure; Channel

1. Introduction

Currently, metal-organic porous materials have been widely used in many applications such as ion exchange, gas separation and storage, catalysis, magnetism, sensor, etc. [1–7]. Therefore, the design and construction of such materials with specific structure and the investigation of their properties have become important and a popular subject. One common method to construct such structure is to select appropriate bridging ligands containing N or O donors to bind metal centers to acquire novel architectures. Carboxylates are often employed as bridging ligand to construct porous coordination polymers due to their versatile coordination modes. For instance, the rigid oxalate ligand can act as a linker between metal centers to yield a 3-D connectivity with channels or cavities [8–12]. Organic amines often play a crucial role in the formation of inorganic sieve structures, where they act as template

molecules or structure-directing agents to yield new carboxylates [13]. So far, more and more transition-metal, rare-earth-metal oxalates with novel structures have been widely synthesized and investigated in the presence of organic amines. Yet, the investigations about bismuth oxalates are less reported to the best of our knowledge [14,15]. With the features of highly variable coordination numbers from 3 to 10 and irregular coordination geometry, bismuth can form a range of coordination polymers with new and unusual network topologies [16], therefore bringing great interests to the coordination chemistry and the synthesis for new compounds.

We have begun to study the reactions of the rigid oxalate ligand with bismuth(III) salts by self-assembly in order to obtain coordination information on Bi atoms and to construct novel coordination polymers in the presence of organic amines [17,18]. In the present work, we introduce another two new Bi compounds with different combinations of oxalate ligands and Bi ions: $(C_3N_2H_5)_2[Bi_2(C_2O_4)_4(H_2O)_2] \cdot 2H_2O$ **1** and $[NH(C_2H_5)_3][Bi_3(C_2O_4)_5]$ **2**. They are both 3-D open-framework structure containing

*Corresponding author. Fax: +86 591 8789 3239.

E-mail address: zhanghh1840@hotmail.com (H. Zhang).

channels with guest molecules. The two compounds display strong fluorescent emissions at 419 nm for **1** and 442 nm for **2**, respectively, in the solid state at room temperature, implying that they may be excellent candidates for potential photoactive materials.

2. Experimental section

2.1. Materials and methods

All chemicals were of analytical reagent grade and commercially purchased, and used without further purification. The Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. The IR spectra were recorded in the 4000–400 cm^{-1} region on a Perkin-Elmer Spectrum 2000 spectrometer using KBr pellets. The fluorescent spectra were recorded on an Edinburgh Instrument FL/FS-920 fluorescent spectrometer using Xe lamp for steady fluorescent and H_2 nanosecond flash lamp for transient fluorescence. The TGA were performed on a Delta Series TGA7 instrument in N_2 atmosphere with heating rate of 10 $^\circ\text{C}/\text{min}$ from 25 to 800 $^\circ\text{C}$.

2.2. Synthesis of $(\text{C}_3\text{N}_2\text{H}_5)_2[\text{Bi}_2(\text{C}_2\text{O}_4)_4(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, **1**

A mixture of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.25 g, 0.52 mmol), $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (0.63 g, 5.00 mmol), imidazole (0.14 g, 2.06 mmol) and distilled water (3.50 mL) was stirred to homogeneity for 10 min in air. The mixture was loaded into a 15 mL Teflon-lined steel autoclave and heated at 120 $^\circ\text{C}$ for 2 days, and then cooled to room temperature. The colorless block crystals of **1** were collected. The product is stable in air and insoluble in water. Yield: 0.09 g (ca. 15% based on bismuth). $\text{Bi}_2\text{C}_{14}\text{N}_4\text{O}_{20}\text{H}_{18}$ (980.28): calcd. C 17.15, H 1.85, N 5.72; found C 17.09, H, 1.97 N, 5.68. IR (KBr): $\nu = 3476 \text{ cm}^{-1}$ (w), 3350 (m), 3153 (w), 2975 (w), 1592 (s), 1451 (w), 1303 (m), 1229 (w), 792 (s), 629 (w), 482 (w).

2.3. Synthesis of $[\text{NH}(\text{C}_2\text{H}_5)_3][\text{Bi}_3(\text{C}_2\text{O}_4)_5]$, **2**

A mixture of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.25 g, 0.52 mmol), $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (0.63 g, 5.00 mmol), triethylamine (0.10 mL) and distilled water (3.50 mL) was stirred to homogeneity for 10 min in air. The mixture was loaded into a 15 mL Teflon-lined steel autoclave and heated at 100 $^\circ\text{C}$ for 2 days, and then cooled to room temperature. The colorless block crystals of **2** were collected. The product is stable in air and insoluble in water. Yield: 0.06 g (ca. 12% based on bismuth). $\text{Bi}_3\text{C}_{16}\text{NO}_{20}\text{H}_{16}$ (1169.24): calcd. C 16.44, H 1.38, N 1.20; found C 16.53, H 1.45, N1.12. IR (KBr): $\nu = 3396 \text{ cm}^{-1}$ (m), 3168 (w), 1619 (s), 1439 (m), 1298 (w), 789 (w), 476 (w).

2.4. Single-crystal X-ray diffraction

Crystal data were performed at $293 \pm 2 \text{ K}$ with a Rigaku Weissenberg IP diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Lp correction and a Ψ empirical absorption correction were made for the intensity data. Structures were solved by direct methods using SHELXS-97 [19] and refined by full-matrix least-squares based on F^2 using SHELXL-97 program [20]. All non-hydrogen atoms in compounds **1** and **2** were refined anisotropically. The positions of hydrogen atoms of C and N atoms were generated geometrically, and hydrogen atoms of water molecules were generated for satisfying the charge requirements in compound **1**. In compound **2**, due to the disorder of C and N atoms positions of triethylamine, it was difficult to detect and refine the positions of the hydrogen atoms. The hydrogen atoms were generated for satisfying the charge requirements of the framework. The triethylamine cations are severely disordered in the lattice. The crystallographic data for compounds **1** and **2** are listed in Table 1. The atomic coordinates and equivalent isotropic displacement parameters are given in Table 2. The selected bond lengths are shown in Table 3. CCDC-294702 **1** and -294703 **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at: www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1
Crystallographic data for compounds **1** and **2**

| Compound | 1 | 2 |
|---|--|---|
| Formula | $\text{Bi}_2\text{C}_{14}\text{N}_4\text{O}_{20}\text{H}_{18}$ | $\text{Bi}_3\text{C}_{16}\text{NO}_{20}\text{H}_{16}$ |
| Molecular mass | 980.28 | 1169.24 |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | $P2_1/n$ | $Pbcn$ |
| a (\AA) | 9.7541(13) | 14.803(4) |
| b (\AA) | 17.7404(15) | 19.783(7) |
| c (\AA) | 14.6321(6) | 8.202(2) |
| β ($^\circ$) | 97.280(3) | 90 |
| V (\AA^3) | 2511.6(4) | 2401.8(12) |
| Z | 4 | 4 |
| $\rho_{\text{calcd.}}$ (g/cm^3) | 2.593 | 3.234 |
| μ (mm^{-1}) | 14.095 | 22.028 |
| T (K) | 293(2) | 293(2) |
| λ ($\text{MoK}\alpha$) (\AA) | 0.71073 | 0.71073 |
| Collected reflections | 10959 | 20767 |
| Independent reflections | 5749 ($R_{\text{int}} = 0.0464$) | 2662 ($R_{\text{int}} = 0.0373$) |
| Observed reflections ($> 2\sigma I$) | 4734 | 2472 |
| R_1, wR_2 (all data) | 0.0488, 0.0835 | 0.0260, 0.0699 |
| Largest diff. map peak and hole ($e \text{\AA}^{-3}$) | 1.007 and -1.379 | 1.200 and -1.293 |

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)} \right\}^{1/2}$$

$$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP], \text{ where } P = (F_o^2 + 2F_c^2)/3, \text{ where } a = 0.0423 \text{ and } b = 8.0490 \text{ for } \mathbf{1} \text{ and } a = 0.0394 \text{ and } b = 30.7312 \text{ for } \mathbf{2}.$$

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compounds **1** and **2**

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> (eq) | Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> (eq) |
|-------------------|----------|----------|----------|---------------|-------|-----------|----------|----------|---------------|
| <i>Compound 1</i> | | | | | | | | | |
| Bi(1) | 4917(1) | 6222(1) | 1589(1) | 23(1) | C(3) | 5574(7) | 5241(4) | −184(5) | 27(1) |
| Bi(2) | 5220(1) | 3360(1) | 4119(1) | 22(1) | C(4) | 2662(7) | 2339(4) | 3229(5) | 28(1) |
| O(1) | 6126(5) | 5004(3) | 2034(4) | 34(1) | C(5) | 2711(7) | 2227(4) | 4281(5) | 29(2) |
| O(2) | 3732(5) | 5453(3) | 2635(4) | 33(1) | C(6) | 7135(7) | 1969(4) | 3671(5) | 27(1) |
| O(3) | 6299(5) | 4919(3) | −713(4) | 35(1) | C(7) | 8179(7) | 2632(4) | 3829(5) | 26(1) |
| O(4) | 5675(6) | 5911(3) | 63(4) | 41(1) | C(8) | 4373(6) | 4858(4) | 5239(5) | 24(1) |
| O(5) | 1784(6) | 1974(3) | 2724(3) | 40(1) | N(1) | 1038(7) | 4909(5) | 3657(5) | 51(2) |
| O(6) | 1934(5) | 1745(3) | 4554(4) | 36(1) | N(2) | −1029(8) | 4969(8) | 3888(6) | 77(3) |
| O(7) | 7539(5) | 1365(3) | 3399(4) | 35(1) | C(9) | −39(11) | 4511(7) | 3784(7) | 64(3) |
| O(8) | 9402(5) | 2498(3) | 3710(4) | 39(1) | C(10) | 726(11) | 5652(7) | 3669(8) | 66(3) |
| O(9) | 5791(5) | 3852(3) | 2579(4) | 34(1) | C(11) | −577(14) | 5696(9) | 3804(9) | 84(4) |
| O(10) | 3585(5) | 4352(3) | 3318(4) | 32(1) | N(3) | −1004(14) | 4362(11) | 1348(9) | 137(7) |
| O(11) | 3509(5) | 2791(3) | 2952(3) | 36(1) | N(4) | 349(17) | 5237(8) | 1246(8) | 118(5) |
| O(12) | 3538(5) | 2628(3) | 4787(3) | 37(1) | C(12) | −849(11) | 5092(7) | 1389(8) | 58(3) |
| O(13) | 4153(5) | 4167(3) | 5263(3) | 31(1) | C(13) | 281(17) | 4099(8) | 1142(10) | 97(5) |
| O(14) | 3666(5) | 5360(3) | 5564(4) | 31(1) | C(14) | 1035(8) | 4676(7) | 1086(7) | 51(2) |
| O(15) | 7720(5) | 3254(3) | 4043(4) | 33(1) | OW1 | 5988(6) | 6639(3) | 3172(4) | 40(1) |
| O(16) | 5924(5) | 2092(3) | 3835(4) | 43(1) | OW2 | 6397(6) | 3037(4) | 5664(4) | 50(2) |
| C(1) | 5484(7) | 4527(4) | 2437(5) | 26(1) | OW3 | 7947(9) | 7733(5) | 3503(5) | 83(3) |
| C(2) | 4150(7) | 4805(4) | 2814(4) | 25(1) | OW4 | 3123(11) | 3092(7) | 1070(6) | 115(4) |
| <i>Compound 2</i> | | | | | | | | | |
| Bi(1) | 6956(1) | 8839(1) | 4032(1) | 11(1) | C(1) | 8219(4) | 7596(3) | 2461(8) | 15(1) |
| Bi(2) | 5000 | 8285(1) | 7500 | 10(1) | C(2) | 6590(4) | 9795(3) | 7368(8) | 16(1) |
| O(1) | 7453(3) | 7837(3) | 2272(7) | 26(1) | C(3) | 8828(4) | 7900(3) | 3799(8) | 16(1) |
| O(2) | 7764(3) | 10626(2) | 7059(6) | 19(1) | C(4) | 5234(4) | 8652(3) | 1647(8) | 15(1) |
| O(3) | 8569(3) | 7119(2) | 1636(6) | 21(1) | C(5) | 7471(4) | 10067(3) | 6558(8) | 15(1) |
| O(4) | 7832(3) | 9715(3) | 5496(7) | 25(1) | N(1) | 5234(13) | 6040(30) | 2040(40) | 170(20) |
| O(5) | 8558(3) | 8410(3) | 4523(7) | 24(1) | C(6) | 6438(13) | 6460(9) | 3637(19) | 88(6) |
| O(6) | 6059(3) | 8674(3) | 1571(6) | 23(1) | C(7) | 5000 | 5380(20) | 2500 | 154(16) |
| O(7) | 4707(3) | 8604(2) | 454(6) | 19(1) | C(8) | 5000 | 4718(15) | 2500 | 165(19) |
| O(8) | 6256(3) | 10141(2) | 8495(6) | 21(1) | C(9) | 5770(50) | 6160(30) | 4280(40) | 180(30) |
| O(9) | 6296(3) | 9250(2) | 6846(6) | 22(1) | C(10) | 5510(20) | 6658(14) | 3020(30) | 66(8) |
| O(10) | 9567(4) | 7597(3) | 4091(6) | 26(1) | | | | | |

 U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3

The selected bond lengths (\AA) for compounds **1** and **2**

| | | | |
|-------------------------------|----------|---------------|----------|
| <i>Compound 1^a</i> | | | |
| Bi(1)–O(8)#1 | 2.414(5) | Bi(2)–O(12) | 2.398(5) |
| Bi(1)–O(2) | 2.447(5) | Bi(2)–O(11) | 2.450(5) |
| Bi(1)–O(7)#1 | 2.492(5) | Bi(2)–OW2 | 2.470(6) |
| Bi(1)–O(1) | 2.508(5) | Bi(2)–O(14)#4 | 2.533(5) |
| Bi(1)–O(3)#3 | 2.601(5) | Bi(2)–O(10) | 2.557(5) |
| Bi(1)–O(5)#2 | 2.443(5) | Bi(2)–O(16) | 2.404(5) |
| Bi(1)–O(6)#2 | 2.480(5) | Bi(2)–O(15) | 2.462(5) |
| Bi(1)–O(4) | 2.500(5) | Bi(2)–O(13) | 2.525(5) |
| Bi(1)–OW1 | 2.528(5) | Bi(2)–O(9) | 2.543(5) |
| <i>Compound 2^b</i> | | | |
| Bi(1)–O(2)#1 | 2.275(5) | Bi(2)–O(10)#3 | 2.271(5) |
| Bi(1)–O(6) | 2.437(5) | Bi(2)–O(3)#3 | 2.372(5) |
| Bi(1)–O(7)#2 | 2.539(5) | Bi(2)–O(7)#5 | 2.540(5) |
| Bi(1)–O(1) | 2.560(5) | Bi(2)–O(9) | 2.758(5) |
| Bi(1)–O(8)#1 | 2.311(5) | Bi(2)–O(10)#4 | 2.271(5) |
| Bi(1)–O(4) | 2.476(5) | Bi(2)–O(3)#4 | 2.372(5) |
| Bi(1)–O(5) | 2.551(5) | Bi(2)–O(7)#2 | 2.540(5) |
| Bi(1)–O(9) | 2.635(5) | Bi(2)–O(9)#6 | 2.758(5) |

^aSymmetry transformations used to generate equivalent atoms: #1: $-x+3/2, y+1/2, -z+1/2$; #2: $-x+1/2, y+1/2, -z+1/2$; #3: $-x+1, -y+1, -z$; #4: $-x+1, -y+1, -z+1$.^bSymmetry transformations used to generate equivalent atoms: #1: $x, -y+2, z-1/2$; #2: $-x+1, y, -z+1/2$; #3: $x-1/2, -y+3/2, -z+1$; #4: $-x+3/2, -y+3/2, z+1/2$; #5: $x, y, z+1$; #6: $-x+1, y, -z+3/2$.

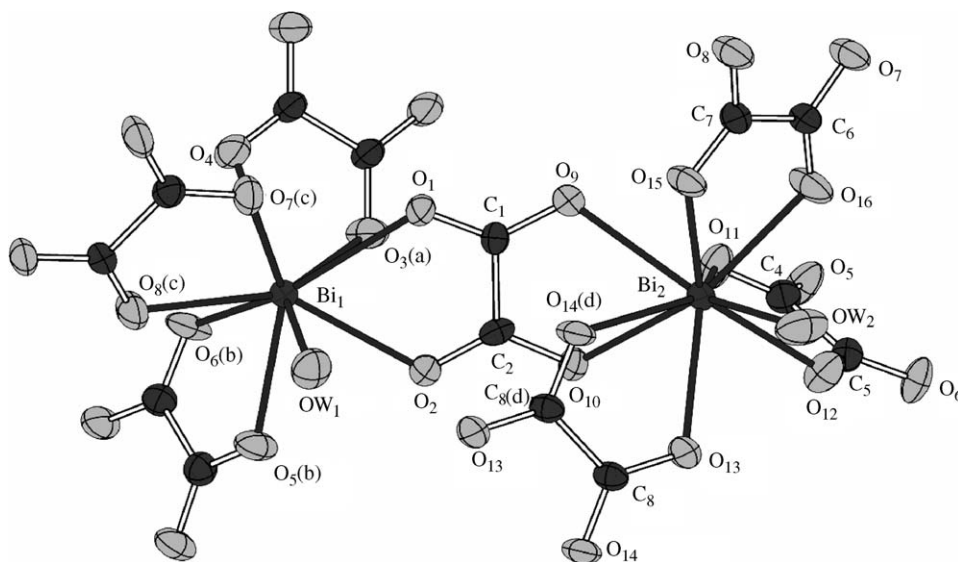


Fig. 1. Coordination environment of Bi atoms in **1** showing the atom labeling scheme (thermal ellipsoid plot). Symmetry codes for the generated atoms: (a) $1-x, 1-y, -z$; (b) $0.5-x, 0.5+y, 0.5-z$; (c) $1.5-x, 0.5+y, 0.5-z$; and (d) $1-x, 1-y, 1-z$.

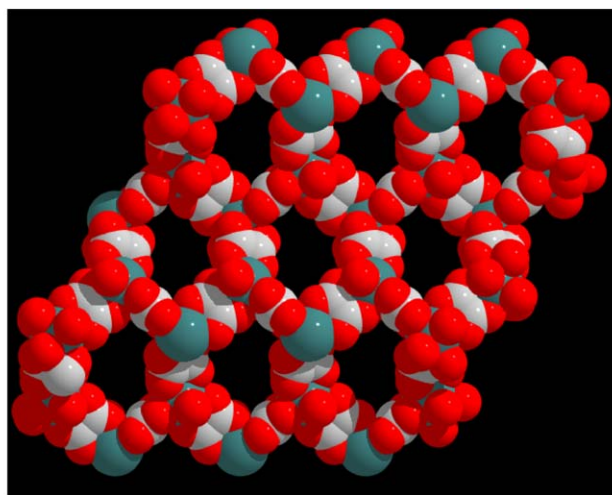
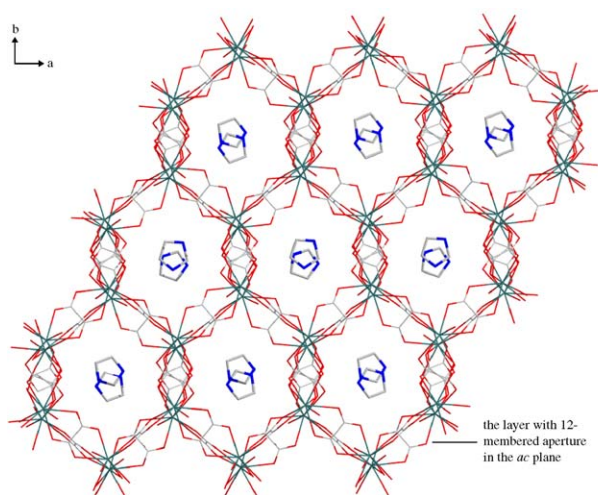


Fig. 2. View of the 3-D structure with channels of **1** along the c -axis: wires/sticks model (left), space-filling model (right; guest molecules were omitted for clarity). Color scheme: Bi, teal; C, gray; N, blue; O, red.

3. Results and discussion

3.1. Structure description

The crystal structure of **1** consists of $[\text{Bi}_2(\text{C}_2\text{O}_4)_4(\text{H}_2\text{O})_2]^{2-}$ anions, protonated imidazole cations and water molecules. There are two crystallographically unique Bi atoms in the asymmetric unit. All the Bi centers display a distorted monocapped square antiprism surrounded by nine oxygen atoms of which the eight are from oxalate units and the other is from a water molecule (Fig. 1). The Bi–O distances are in the range of 2.398(5)–2.601(5) Å. The O–Bi–O angles range from 63.39(25)° to 143.00(18)°. The BiO_9 coordination polyhedron is relatively less distorted compared to that in $[\text{Bi}_3(\text{C}_2\text{O}_4)_6(\text{CO}_2\text{CONHCH}_2\text{CH}_2\text{NH}_3)] \cdot 6.5\text{H}_2\text{O}$ [18], indi-

cating that the lone electron pair on the Bi^{3+} ion become less evident.

The 3-D framework structure of **1** can be understood in terms of building units formed by the linkages between the Bi atoms and oxalate units. The connectivity between Bi and three oxalates gives rise to a honeycomb-like layer, with a 12-membered aperture in the ac plane. Then the layers are also connected through oxalate ligands, creating the 3-D structure with a channel along the c -axis as shown in Fig. 2. The channel has a $5.0 \times 5.0 \text{ \AA}^2$ pore, which is carried out by a combination of the space-filling structure. The uncoordinated water molecules and protonated imidazole molecules were located in the channels. When these extraframework species are not considered, the accessible volume within the crystal is calculated to be 48.2% by using the program PLATON [21].

X-ray diffraction analysis shows that compound **2** is also a 3-D polymer with channels. There are 23 non-hydrogen atoms in the asymmetric unit, of which Bi(2) is in the special position and N(1), C(7), C(8), C(9), and C(10) are disordered. There are two crystallographically unique Bi atoms in the asymmetric unit. As shown in Fig. 3, all the Bi centers are coordinated in a distorted dodecahedral sphere by eight oxygen atoms from oxalate units adopting bidentate and tricoordinate coordination modes. The Bi–O distances are in the range of 2.271(5)–2.758(5) Å. The O–Bi–O angles range from 61.59(15)° to 155.83(16)°. The BiO₈ polyhedron in compound **2** is more distorted than that in K[Bi(C₂O₄)₂]·5H₂O [22] and Bi(NH₄)(C₂O₄)₂·xH₂O [23].

In compound **2**, four Bi(1) and two Bi(2) atoms connect oxalate units with bidentate and tricoordinate coordination modes to form a Bi₆(C₂O₄)₆⁶⁺ cationic cluster unit. Then each cluster unit connects to two close ones through bridging oxalate ligands to create linear cluster chain

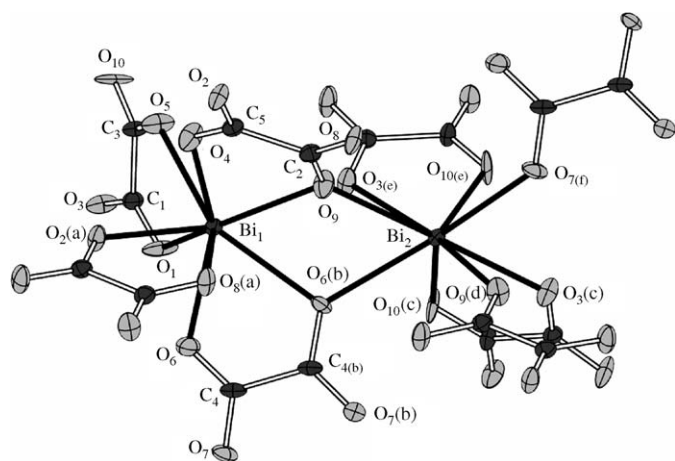


Fig. 3. Coordination environment of Bi atoms in **2** showing the atom labeling scheme (thermal ellipsoid plot). Symmetry codes for the generated atoms: (a) $x, 2-y, -0.5+z$; (b) $1-x, y, 0.5-z$; (c) $-0.5+x, 1.5-y, 1-z$; (d) $1-x, y, 1.5-z$; (e) $1.5-x, 1.5-y, 0.5+z$; and (f) $x, y, 1+z$.

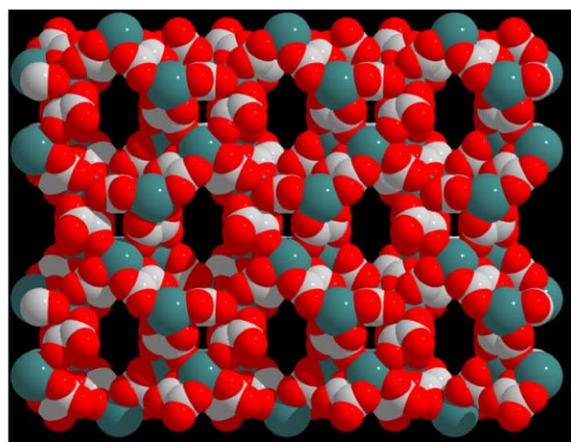
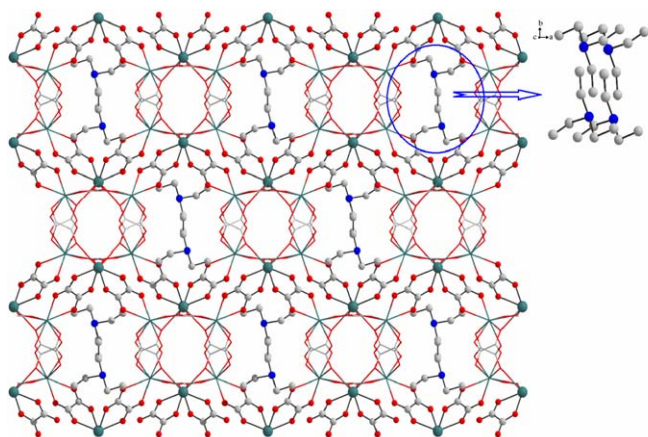


Fig. 4. View of the 3-D structure with channels of **2** along the c -axis: ball-and-stick and wires/sticks models (left), space-filling model (right; guest molecules were omitted for clarity). Color scheme: Bi, teal; C, gray; N, blue; O, red.

producing an aperture along the c -axis. Then cationic cluster chains are connected through bidentate bridging oxalate ligands, therefore resulting the 3-D framework with a 12-membered channel along the c -axis as shown in Fig. 4. The channel has a $4.6 \times 4.6 \text{ \AA}^2$ pore, which is carried out by a combination of the space-filling structure. The disordered triethylamine molecules were located in the channels. Such disorder of the triethylamine molecules had been reported in nonanuclear lanthanide complexes [24]. When the guests are removed, the accessible volume within the crystal is calculated to be 58.6%.

3.2. Fluorescent properties

To study the fluorescent properties of these two polymeric solids, the emissions of **1** and **2** were detected at room temperature in the solid-state and the results are depicted in Fig. 5. Intense fluorescent emissions at 419 nm ($\lambda_{\text{exc}} = 375 \text{ nm}$) for **1** and 442 nm ($\lambda_{\text{exc}} = 380 \text{ nm}$) for **2** were observed, which may be assigned to the ligand-to-metal-charge transfer (LMCT) or the $^1P_1 \rightarrow ^1S_0$ and $^3P_1 \rightarrow ^1S_0$ transitions of the s^2 electron of Bi³⁺ ion [25,26]. And, compound **1** exhibits a quenching of the fluorescence with $\tau = 2.73 \text{ ns}$.

3.3. Thermal analysis

The TG curve of **1** can be divided into a two-step mass loss. The first weight loss of 7.4% (calc. 7.8%) observed from 81 to 118 °C corresponds to the release of water molecules. The second weight loss of 45.5% (calc. 46.1%) observed from 212 to 296 °C arises from the decomposition of imidazole and oxalate molecules. The TG curve of **2** shows a weight loss of 58.2% in the range of 233–289 °C, corresponding to the release of triethylamine and oxalate molecules (calc. 59.8%). From the TG curves, the framework of **1** and **2** both collapsed during the loss processes of organic amines.

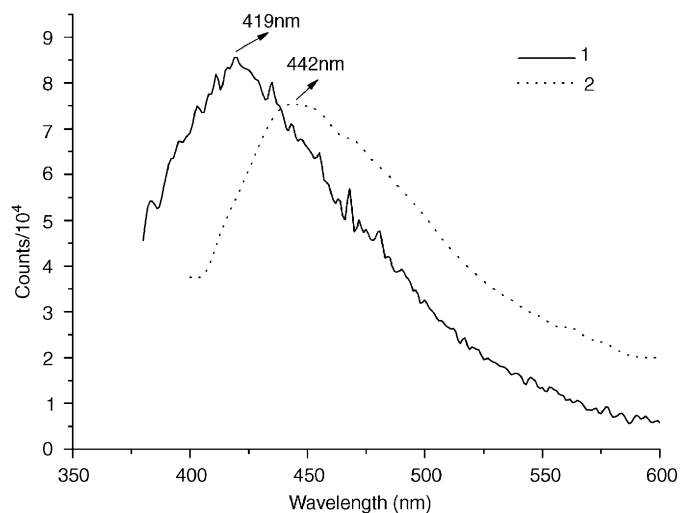


Fig. 5. The emission spectra of **1** and **2** in the solid state at room temperature.

4. Conclusions

In the present study, two novel 3-D oxalate-containing bismuth(III) compounds with open-framework structures containing channels with guest molecules were obtained in the presence of organic amines by hydrothermal synthesis. In compound **1**, the coordination number of Bi^{3+} is 9 and the oxalate act as bidentate ligands. In compound **2**, the coordination number of Bi^{3+} is 8, while the oxalate adopt bidentate and tricoordinate coordination modes. Compounds **1** and **2** exhibit intense blue luminescence with emission peaks at 419 and 442 nm, respectively, in the solid state at room temperature, suggesting the potential application in photoactive materials. The unique coordination environments of Bi(III) as well as the Bi(III) oxalate-amine structures described here indicate that it would be profitable to explore this lead further by investigating other Bi(III) carboxylates synthesized under similar conditions.

Acknowledgments

This work was supported by the Natural Science Foundation of Fujian Province (Project no. K02028) and the Foundation of Education Committee of Fujian Province (Project no. JB04049).

References

- [1] P.N. Trikalitis, K.K. Rangan, T. Bakas, M.G. Kanatzidis, *J. Am. Chem. Soc.* 124 (2002) 12255.
- [2] A.C. Sudik, A.R. Millward, N.W. Ockwig, A.P. Cote, J. Kim, O.M. Yaghi, *J. Am. Chem. Soc.* 127 (2005) 7110.
- [3] Y. Kubota, M. Takata, R. Matsuda, R. Kitaura, S. Kitagawa, K. Kato, M. Sakata, T.C. Kobayashi, *Angew. Chem. Int. Ed.* 44 (2005) 920.
- [4] M. Yoshizawa, M. Tamura, M. Fujita, *J. Am. Chem. Soc.* 126 (2004) 6846.
- [5] M. Fujita, K. Umamoto, M. Yoshizawa, N. Fujita, T. Kusukawa, M. Kawano, *Chem. Commun.* (2001) 509.
- [6] G.J. Halder, C.J. Kepert, B. Moubaraki, K.S. Murray, J.D. Cashion, *Science* 298 (2002) 1762.
- [7] K. Uemura, S. Kitagawa, M. Kondo, K. Fukui, R. Kitaura, H.C. Chang, T. Mizutani, *Chem. Eur. J.* 8 (2002) 3587.
- [8] M.C. Munoz, M. Julve, F. Lloret, J. Faus, M. Andruh, *J. Chem. Soc. Dalton Trans.* (1998) 3125.
- [9] P.A. Prasad, S. Neeraj, S. Natarajan, C.N.R. Rao, *Chem. Commun.* (2000) 1251.
- [10] E. Jeanneau, N. Audebrand, D. Louër, *Chem. Mater.* 14 (2002) 1187.
- [11] R. Vaidyanathan, S. Natarajan, C.N.R. Rao, *Inorg. Chem.* 41 (2002) 4496.
- [12] S. Mandal, S. Natarajan, *J. Solid State Chem.* 178 (2005) 2376.
- [13] M.E. Davis, R.F. Lobo, *Chem. Mater.* 4 (1992) 756.
- [14] A.A. Udovenko, L.M. Volkova, S.S. Sergienko, R.L. Davidovich, V.Ya. Shevchenko, *Koordinats. Khim.* 9 (1983) 711.
- [15] U. Kolitsch, *Acta Crystallogr. C* 59 (2003), m501.
- [16] M.N. Sokolov, T.V. Mitkina, O.A. Gerasko, V.P. Fedin, A.V. Virovets, R. Llusar, *Z. Anorg. Allg. Chem.* 629 (2003) 2440.
- [17] W.J. Guo, H.H. Zhang, C.C. Huang, R.Q. Sun, Y.P. Chen, Y.N. Cao, *Chinese J. Struct. Chem.* 7 (2005) 846.
- [18] X.H. Yu, H.H. Zhang, Y.N. Cao, Y.P. Chen, Z. Wang, *J. Solid State Chem.* 179 (2006) 247.
- [19] G.M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Solution, University of Göttingen, Germany, 1997.
- [20] G.M. Sheldrick, SHELXL-97, Program for X-ray Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- [21] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2003.
- [22] U. Heinl, P. Hinse, R. Mattes, *Z. Anorg. Allg. Chem.* 627 (2001) 2173.
- [23] G. Vanhoyland, A.L. Bail, J. Mullens, L.C.V. Poucke, *Inorg. Chem.* 43 (2004) 785.
- [24] G. Xu, Z.M. Wang, Z. He, C.S. Liao, C.H. Yan, *Inorg. Chem.* 41 (2002) 6802.
- [25] A.M. Srivastava, W.W. Beers, *J. Lumin.* 81 (1999) 293.
- [26] H.F. Folkerts, J. Zuidema, G. Blasse, *Chem. Phys. Lett.* 249 (1996) 59.