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Synthesis and characteristics of a novel 3-D organic amine oxalate: $(enH_2)_{1.5}[Bi_3(C_2O_4)_6(CO_2CONHCH_2CH_2NH_3)]\cdot 6.5H_2O$

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Abstract

A novel 3-D compound of $(enH_2)_{1.5}[Bi_3(C_2O_4)_6(CO_2CONHCH_2CH_2NH_3)]\cdot 6.5H_2O$ has been hydrothermally synthesized and characterized by IR, ultraviolet–visible diffuse reflection integral spectrum (UV–Vis DRIS), fluorescence spectra, TGA and single crystal X-ray diffraction. It crystallizes in the monoclinic system, space group $C2/c$ with $a = 31.110(8)$ Å, $b = 11.544(3)$ Å, $c = 22.583(6)$ Å, $\beta = 112.419(3)^\circ$, $V = 7497(3)$ Å^3, $Z = 8$, $R_1 = 0.0463$ and $wR_2 = 0.1393$ for unique 7686 reflections $I > 2\sigma(I)$. In the title compound, the Bi atoms have eight-fold and nine-fold coordination with respect to the oxygen atoms, with the Bi atoms in distorted dodecahedron and monocapped square antiprism, respectively. The 3-D framework of the title compound contains channels and is composed of linkages between Bi atoms and oxalate units, forming honeycomb-like layers with two kinds of 6 + 6 membered aperture, and pillared by oxalate ligands and monamide groups. The channels have *N*-ethylamine oxalate monamide group $^{-}CO_2CONHCH_2CH_2NH_3^{+}$, which is formed by the in situ reaction of en and oxalate acid. At room temperature, the complex exhibits intense blue luminescence with an emission peak at 445 nm.

Keywords: Hydrothermal synthesis; Crystal structure; Oxalate; Luminescence

1. Introduction

In the past few years, compounds containing bismuth have been widely investigated due to their low toxicity, low cost, good stability [1–3] and applications in medical treatment, catalysts, luminescence and so on [4–7]. With the features of highly variable coordination numbers (3 $\bar{1}$ 0) and irregular coordination geometry, bismuth can form compounds with various structure [8], therefore bringing great interest on the coordination chemistry. On the other hand, in recent years, considerable efforts have been devoted to the design of open-framework inorganic materials other than silicates, phosphates, such as oxalates. Due to the multidentate character of oxalate group, some materials composed of it have been synthesized, in which the oxalate acts as a ligand, facilitating the formation of extended structures by bridging metal centers and therefore giving rise to a three-dimensional connectivity with channels or cavities [9–12]. In addition, some oxalates when thermally decomposed can yield porous materials with a high surface area, which makes them attractive as precursors for catalysts and some nanocrystalline oxides [13,14]. So far, more and more transition-metal, rare-earth-metal oxalates with novel structure have been widely synthesized and investigated. Yet, Bi oxalates are rarely reported to the best of our knowledge. The characteristics of Bi and oxalates provide wide-ranging potential for the synthesis of new compounds that may be useful in technology application.

We have made some attempts to synthesize bismuth oxalates in the presence of organic amine in the past few years [15]. In present work, a novel 3-D Bi oxalate: $(enH_2)_{1.5}[Bi_3(C_2O_4)_6(CO_2CONHCH_2CH_2NH_3)]\cdot 6.5H_2O$ with channels have been successfully synthesized by hydrothermal

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techniques. The IR, ultraviolet–visible diffuse reflection integral spectrum (UV–Vis DRIS), fluorescent spectra, and TGA of this compound were systematically investigated.

2. Experimental section

2.1. Materials and methods

All chemicals were of analytical regent 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 spectrum was recorded in the 4000–400 cm^{-1} region on a Perkin-Elmer Spectrum 2000 spectrometer using KBr pellet. The UV–Vis DRIS was measured by a Perkin-Elmer Lambda 900 UV–Vis spectrometer. 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 was performed on a Delta Series TGA7 instrument in N_2 atmosphere with heating rate of 10 °C/min from 25 to 800 °C.

2.2. Hydrothermal synthesis

In a typical synthesis, a mixture of $Bi(NO_3)_3 \cdot 5H_2O$ (0.24 g, 0.49 mmol), $H_2C_2O_4 \cdot 2H_2O$ (0.63 g, 0.50 mmol), en (0.25 mL) and distilled water (4.00 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 °C for 2 days, and then cooled to room temperature. The colorless block crystals of the title compound and white powder were filtered off and washed with distilled water. A yield of 61% (based on bismuth) was observed. The crystal is a stable crystalline solid in water and can be kept in a dry atmosphere for extended periods of time. Anal. Found: C, 15.11; H, 2.69; N, 4.55. Calc.: C, 15.24; H, 2.42; N, 4.68%.

2.3. Single-crystal X-ray diffraction

A single crystal with dimensions of $0.20 \times 0.08 \times 0.05\,mm^3$ was mounted on a glass fiber. The reflection intensities were collected on a Siemens Smart CCD diffractometer equipped with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) using the ω-scan mode. A total of 29 230 reflections (independent 8574, $R_{int} = 0.0463$) with unique 7686 reflections $I > 2\sigma(I)$ were measured. The structure was solved by direct methods using SHELXS-97 [16] and refined by full-matrix least-squares based on F^2 using SHELXL-97 program [17]. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms of C and N atoms were generated geometrically, and of water molecules were located from different Fourier maps. A summary of crystal data and structure refinement for the title compound is provided in Table 1. The atomic coordinates and equivalent isotropic displacement parameters are given in Table 2. The Selected bond lengths and angles are listed in Table 3.

Table 1
Summary of crystal data and refinement results

Empirical formula	$Bi_3C_{19}N_5O_{33.5}H_{36}$
Formula weight ($g\,mol^{-1}$)	1497.47
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	31.110(8)
b (Å)	11.544(3)
c (Å)	22.583(6)
β (°)	112.419(3)
V (Å^3)	7497(3)
Z	8
D_{cal} ($g\,cm^{-3}$)	2.653
M (mm^{-1})	14.173
Temperature (K)	293(2)
Final R factors ($I > 2\sigma(I)$)^a	$R_1 = 0.0463^a$, $wR_2 = 0.1393^b$
Final R factors (all data)	$R_1 = 0.0554$, $wR_2 = 0.1463$
Gof	1.000
Largest diff. map peak and hole e Å^{-3}	1.116 and −1.612

$w = 1/[\sigma^2(F_o^2) + (0.0990P)^2 + 109.4840P]$, where $P = (F_o^2 + 2F_c^2)/3$.

[a] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}$.

3. Results and Discussion

3.1. Structure description

The structure of this compound consists of $[Bi_3(C_2O_4)_6(CO_2CONHCH_2CH_2NH_3)]^{3-}$ anions, en cations, and lattice water molecules. A view of the anion is shown in Fig. 1. There are three crystallographically unique Bi atoms in the asymmetric unit. The Bi(1) center displays a distorted dodecahedron geometry, which is completed by eight oxygen atoms from oxalate groups. The Bi(2) and Bi(3) centers represent distorted monocapped square antiprism rounding by nine oxygen atoms of which the eight are from oxalate ligands and the other is from the monamide groups. The Bi–O distances are in the range of 2.315(7)–2.921(8) Å. The O–Bi–O angles range from 66.2(3)° to 157.6(3)°. The irregularity of the Bi-donor atom distances appears to be a common feature in the citrate complexes [18–21] and complexes with nitrilotriacetic acid [22]. The feature may be related to the requirement that the bond valence sum (BVS) [23] must be 3 and the question of the stereochemical activity of the lone pair on the Bi(III) ion [24]. In the title compound, BVS indicate that both Bi atoms are in the +3 oxidation state: the calculated bond valences for the Bi atoms are in the range of 2.935–3.161. However, it is complicated because of a lone electron pair on Bi(III), which could be stereochemically active and the formation of a complex of any metal ion with a multidentate ligand representing a compromise between the steric interactions in the ligand and the steric and electronic requirements of the metal [22]. So, the distorted

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for the title compound

Atom	*x*	*y*	*z*	*U*(eq)	Atom	*x*	*y*	*z*	*U*(eq)
Bi(1)	6295(1)	5819(1)	9021(1)	14(1)	N(2)	1308(4)	5210(10)	7303(5)	39(3)
Bi(2)	7094(1)	5077(1)	6911(1)	15(1)	N(3)	1446(3)	5515(9)	5731(5)	28(2)
Bi(3)	5471(1)	780(1)	8970(1)	13(1)	N(4)	5352(4)	5511(11)	6336(6)	43(3)
O(1)	5589(3)	4614(7)	8814(4)	29(2)	N(5)	5906(3)	6495(9)	5585(5)	26(2)
O(2)	6462(3)	3750(7)	9148(4)	31(2)	C(1)	5632(3)	3541(8)	8871(4)	16(2)
O(3)	5308(2)	2828(6)	8794(4)	26(2)	C(2)	6134(3)	3046(9)	9076(5)	17(2)
O(4)	6180(2)	1980(6)	9152(4)	24(2)	C(3)	5609(3)	8102(8)	8674(5)	17(2)
O(5)	5576(3)	7019(6)	8562(4)	24(2)	C(4)	6120(3)	8530(8)	9048(4)	15(2)
O(6)	6445(3)	7848(7)	9152(4)	32(2)	C(5)	6925(4)	5518(11)	8171(4)	22(2)
O(7)	5286(2)	8815(6)	8522(4)	22(2)	C(6)	6423(3)	5579(10)	7650(5)	22(2)
O(8)	6164(2)	9585(6)	9217(4)	21(2)	C(7)	6465(4)	5965(9)	10487(5)	20(2)
O(9)	6967(3)	5683(9)	8746(4)	36(2)	C(8)	6957(4)	5869(9)	10486(5)	20(2)
O(10)	6107(3)	5913(8)	7818(4)	37(2)	C(9)	7315(4)	2588(10)	7523(5)	24(2)
O(11)	7252(2)	5298(8)	8001(3)	25(2)	C(10)	7794(3)	3044(9)	7582(4)	18(2)
O(12)	6372(2)	5291(7)	7094(3)	21(2)	C(11)	6639(3)	7409(9)	5766(5)	20(2)
O(13)	6131(3)	6091(9)	9953(4)	34(2)	C(12)	6097(3)	7468(9)	5520(5)	20(2)
O(14)	6995(3)	5823(7)	9950(4)	26(2)	C(13)	5243(3)	861(8)	7480(5)	16(2)
O(15)	6423(3)	5890(7)	11010(4)	28(2)	C(14)	4824(3)	496(9)	9870(4)	15(2)
O(16)	7290(3)	5791(7)	11017(3)	25(2)	C(15)	2398(4)	3012(10)	4778(5)	24(2)
O(17)	6964(2)	3249(6)	7229(4)	22(2)	C(16)	1208(4)	5052(10)	6609(6)	29(3)
O(18)	7798(2)	4084(6)	7387(4)	21(2)	C(17)	1527(4)	5774(10)	6392(5)	26(2)
O(19)	7278(3)	1639(7)	7743(4)	25(2)	C(18)	5400(4)	6293(11)	5353(6)	30(3)
O(20)	8133(3)	2386(7)	7815(4)	33(2)	C(19)	5194(4)	6393(13)	5827(7)	42(3)
O(21)	6815(2)	6404(7)	5878(4)	25(2)	O*W*1	1840(3)	4720(9)	3663(4)	36(2)
O(22)	6848(3)	8338(7)	5823(4)	28(2)	O*W*2	2123(3)	6542(10)	5414(5)	54(3)
O(23)	5887(3)	8364(7)	5285(4)	31(2)	O*W*3	5000	5758(11)	7500	53(4)
O(24)	4834(3)	1059(7)	9400(3)	24(2)	O*W*4	5554(4)	3382(11)	5958(7)	76(4)
O(25)	4549(3)	675(6)	10138(4)	23(2)	O*W*5	689(4)	3271(10)	7253(7)	73(4)
O(26)	5589(2)	847(7)	7994(3)	22(2)	O*W*6	1300(5)	7573(12)	7700(8)	88(5)
O(27)	5254(2)	869(6)	6927(3)	18(2)	O*W*7	5428(5)	3534(15)	7374(7)	94(5)
N(1)	2240(3)	2555(8)	4102(4)	26(2)					

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

dodecahedron and monocapped square antiprism are reasonable polyhedra in this compound.

It is noteworthy that in the title compound the oxalate acid in the reaction mixture reacts with en to form the unusual fragments *N*-ethylamine oxalate monamide. The forming of amide compound may be caused by the Bi(III) using as a catalyst and through self-assembly in hydrothermal conditions. The amide compound is linked to some Bi atoms through the oxygen atoms.

The 3-D open-framework structure of this compound can be understood in terms of building units formed by the linkages between the Bi atoms, oxalate ligands and monamide groups. The connectivity between Bi(1), Bi(3) atoms and oxalate units form Bi(1)···Bi(3) oxalate zigzag chains. Bi(2) atoms and oxalate units form Bi(2)···Bi(2) oxalate zigzag chains. Then the oxalate units link zigzag chains to give a honeycomb-like layer, with two kinds of 6 + 6 membered aperture (Fig. 2). The layers are connected through oxalate ligands and monamide groups, creating the 3-D structure with 1-D channels as shown in Fig. 3. While the monamide groups lay between the layers. The water molecules and diprotonated en cations were all located in the channels.

In addition, there exists N–H···O, O*W*–H···O and O*W*–H···N hydrogen bond effect (N···O distances and O*W*···O distances are in the range of 2.650–3.308 Å and 2.756–3.466 Å, respectively. O*W*(1)···N(2) distance is 2.882 Å). These hydrogen bonds enhance the stability of the title compound.

3.2. Spectroscopy

The IR spectrum of the title compound shows characteristic of protonated en and oxalate. The peaks at 3286, 3049 cm^{-1} are attributed to O–H of water and N–H of en molecules asymmetric stretching vibrations, respectively. Bands in the region of 1599–1725 cm^{-1} are characteristic of acid carbonyl groups and of asymmetric stretching vibrations of RCO_2^- groups. The bands at 1448 and 1228 cm^{-1} can be attributed to the absorption of CH_2 bending and C = O stretching vibrations, moreover, the 1228 cm^{-1} band can also be attributed to the C–N stretching vibration. The bands from 713 to 1060 cm^{-1} are due to O–C = O in plane bending. The peak at 493 cm^{-1} is ascribed to Bi–O stretching vibrations and O–C = O out-of-plane bending vibrations.

Table 3
The selected bond lengths (Å) and angles (°) for the title compound

Bi(1)–O(13)	2.368(8)	Bi(1)–O(14)	2.378(8)
Bi(1)–O(6)	2.384(8)	Bi(1)–O(9)	2.403(8)
Bi(1)–O(2)	2.439(8)	Bi(1)–O(1)	2.489(8)
Bi(1)–O(5)	2.495(7)	Bi(1)–O(10)	2.554(8)
Bi(2)–O(17)	2.315(7)	Bi(2)–O(11)	2.333(7)
Bi(2)–O(18)	2.338(8)	Bi(2)–O(12)	2.446(7)
Bi(2)–O(16)#1	2.527(7)	Bi(2)–O(15)#1	2.551(8)
Bi(2)–O(19)#2	2.553(7)	Bi(2)–O(21)	2.645(8)
Bi(2)–O(20)	2.884 (7)	Bi(3)–O(26)	2.369(7)
Bi(3)–O(27)#3	2.391(7)	Bi(3)–O(3)	2.419(7)
Bi(3)–O(8)#4	2.437(7)	Bi(3)–O(7)#4	2.461(7)
Bi(3)–O(4)	2.501(7)	Bi(3)–O(24)	2.537(8)
Bi(3)–O(25)#5	2.643(8)	Bi(3)–O(23)	2.921 (8)
O(1)–C(1)	1.247(12)	O(2)–C(2)	1.266(12)
O(3)–C(1)	1.260(12)	O(4)–C(2)	1.243(13)
O(5)–C(3)	1.272(12)	O(6)–C(4)	1.234(12)
O(7)–C(3)	1.243(12)	O(8)–C(4)	1.269(12)
O(9)–C(5)	1.270(12)	O(10)–C(6)	1.243(13)
O(11)–C(5)	1.243(12)	O(12)–C(6)	1.250(12)
O(13)–C(7)	1.266(13)	O(14)–C(8)	1.264(12)
O(15)–C(7)	1.240(13)	O(16)–C(8)	1.253(13)
O(17)–C(9)	1.289(13)	O(18)–C(10)	1.280(12)
O(19)–C(9)	1.227(13)	O(20)–C(10)	1.242(12)
O(21)–C(11)	1.268(13)	O(22)–C(11)	1.235(13)
O(23)–C(12)	1.231(13)	O(24)–C(14)	1.257(12)
O(23)–C(12)	1.231(13)	O(24)–C(14)	1.257(12)
O(25)–C(14)	1.236(12)	O(26)–C(13)	1.247(13)
O(27)–C(13)	1.263(12)		
O(14)–Bi(1)–O(10)	134.3(3)	O(6)–Bi(1)–O(10)	92.5(3)
O(9)–Bi(1)–O(10)	66.2(3)	O(2)–Bi(1)–O(10)	96.8(3)
O(1)–Bi(1)–O(10)	89.8(3)	O(5)–Bi(1)–O(10)	74.3(2)
O(17)–Bi(2)–O(11)	76.3(3)	O(17)–Bi(2)–O(18)	69.7(2)
O(11)–Bi(2)–O(18)	77.5(2)	O(17)–Bi(2)–O(12)	76.1(3)
O(11)–Bi(2)–O(12)	69.4(2)	O(18)–Bi(2)–O(12)	136.9(2)
O(17)–Bi(2)–O(16)#1	90.6(3)	O(11)–Bi(2)–O(16)#1	150.2(2)
O(18)–Bi(2)–O(16)#1	72.9(2)	O(12)–Bi(2)–O(16)#1	133.7(2)
O(17)–Bi(2)–O(15)#1	70.2(3)	O(11)–Bi(2)–O(15)#1	131.9(3)
O(18)–Bi(2)–O(15)#1	119.4(3)	O(12)–Bi(2)–O(15)#1	69.7(2)
O(16)#1–Bi(2)–O(15)#1	64.1(2)	O(17)–Bi(2)–O(19)#2	138.8(2)
O(11)–Bi(2)–O(19)#2	76.8(3)	O(18)–Bi(2)–O(19)#2	74.5(2)
O(12)–Bi(2)–O(19)#2	121.5(2)	O(16)#1–Bi(2)–O(19)#2	97.8(2)
O(15)#1–Bi(2)–O(19)#2	148.4(2)	O(17)–Bi(2)–O(21)	139.9(2)
O(11)–Bi(2)–O(21)	137.2(3)	O(18)–Bi(2)–O(21)	128.6(2)
O(12)–Bi(2)–O(21)	94.4(2)	O(16)#1–Bi(2)–O(21)	67.9(2)
O(15)#1–Bi(2)–O(21)	69.9(2)	O(19)#2–Bi(2)–O(21)	79.4(2)
O(26)–Bi(3)–O(27)#3	69.0(2)	O(26)–Bi(3)–O(3)	85.0(3)
O(27)#3–Bi(3)–O(3)	75.4(2)	O(26)–Bi(3)–O(8)#4	78.1(3)
O(27)#3–Bi(3)–O(8)#4	133.2(2)	O(3)–Bi(3)–O(8)#4	134.6(2)
O(26)–Bi(3)–O(7)#4	75.1(3)	O(27)#3–Bi(3)–O(7)#4	72.2(2)
O(3)–Bi(3)–O(7)#4	146.3(3)	O(8)#4–Bi(3)–O(7)#4	67.7(2)
O(26)–Bi(3)–O(4)	72.3(3)	O(27)#3–Bi(3)–O(4)	127.1(2)
O(3)–Bi(3)–O(4)	66.6(2)	O(8)#4–Bi(3)–O(4)	68.2(2)
O(7)#4–Bi(3)–O(4)	129.2(2)	O(26)–Bi(3)–O(24)	140.5(2)
O(27)#3–Bi(3)–O(24)	72.3(2)	O(3)–Bi(3)–O(24)	78.1(2)
O(8)#4–Bi(3)–O(24)	137.4(2)	O(7)#4–Bi(3)–O(24)	100.3(3)
O(4)–Bi(3)–O(24)	129.4(3)	O(26)–Bi(3)–O(25)#5	141.9(2)
O(27)#3–Bi(3)–O(25)#5	112.6(2)	O(3)–Bi(3)–O(25)#5	133.0(2)
O(8)#4–Bi(3)–O(25)#5	75.1(2)	O(7)#4–Bi(3)–O(25)#5	70.0(2)
O(4)–Bi(3)–O(25)#5	120.2(2)	O(24)–Bi(3)–O(25)#5	62.6(2)

Symmetry transformations used to generate equivalent atoms: $\sharp 1x, -y+1, z-1/2$; $\sharp 2 -x+3/2, y+1/2, -z+3/2$; $\sharp 3 -x+1, y, -z+3/2$; $\sharp 4x, y-1, z$; $\sharp 5 -x+1, -y, -z+2$.

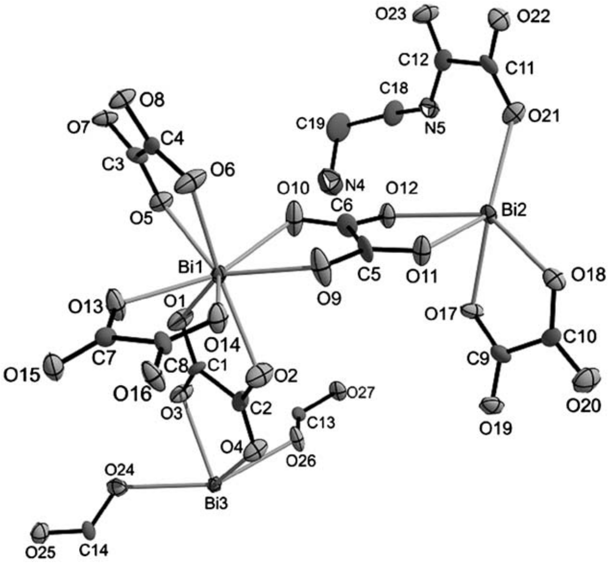

Fig. 1. Thermal ellipsoid plot and atomic labeling scheme of the $[Bi_3(C_2O_4)_6(CO_2CONHCH_2CH_2NH_3)]^{3-}$ anion. The hydrogen atoms are omitted for clarity.

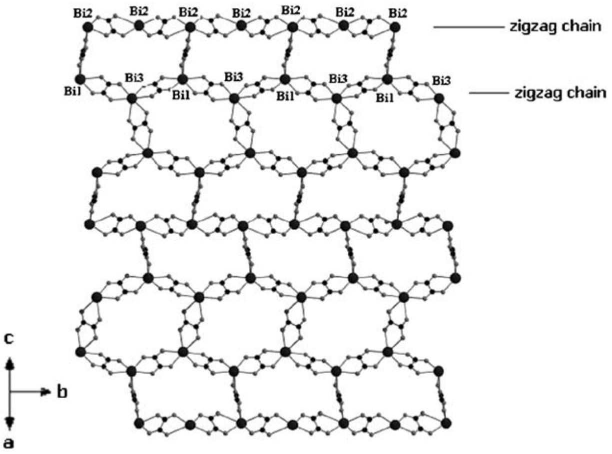

Fig. 2. View of 2-D layer structure with two kinds of 6 + 6 membered aperture.

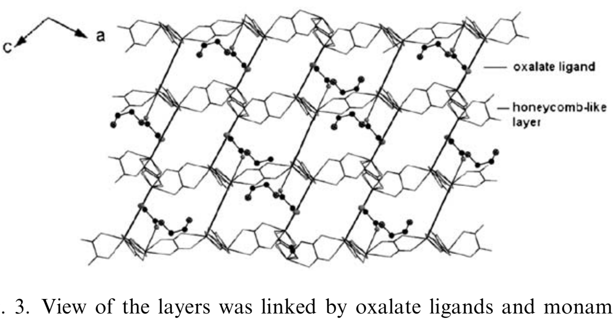

Fig. 3. View of the layers was linked by oxalate ligands and monamide groups. The oxalate ligands are represented by black lines, and en and water molecules are omitted for clarity.

In UV–Vis spectrum of the title compound, it shows two absorption bands at 205 and 264 nm which can be assigned to $\pi \rightarrow \pi^*$ transfer transition of ligand and L → M transfer transition, respectively [25]. The emission spectrum of the title compound was detected in the solid state at room temperature and depicted in Fig. 4. It can be observed that upon excitation at 375 nm the intense emission peak occurred at 445 nm, which may be assigned to the ligand-to-metal-charge transfer (LMCT) or the $^1P_1 \rightarrow {}^1S_0$ and $^3P \rightarrow {}^1S_0$ transitions of the s^2 electron of Bi^{3+} ion [26,27]. The fluorescence lifetime of it is $\tau_1 = 6.49\,ns$ (66.32%) and $\tau_2 = 2.55$ ns (33.68%). Recently, non-doped light-emitting materials have attracted great attention due to the advantage of the control of deposition rate and dopant concentration and the potential application in flat panel displays [28]. The title compound, with blue emission as one of the three basic colors, may be useful for developing new blue-light-emitting devices.

3.3. *Thermal analysis*

TG curve of the title compound can be divided into a two-step mass loss. The weight loss of 7.1% at 100–171 °C corresponds to the release of solvent water molecules (calc. 7.8%). The weight loss of 47.1% at 202–432 °C arises from the decomposition of en, amide and oxalate molecules (calc. 46.7%).

4. Conclusions

In summary, a novel compound, $(enH_2)_{1.5}[Bi_3(C_2O_4)_6(CO_2CONHCH_2CH_2NH_3)] \cdot 6.5H_2O$ has been successfully synthesized by hydrothermal techniques. It takes a 3-D open-framework structure composing of Bi atoms, oxalate units and monamide fragments. The oxalate monamide groups are formed by the insitu reaction of en and oxalate acid. And the monamide fragments, water molecules and diprotonated en were trapped in the channels. The solid state of this compound is luminescent with a peak

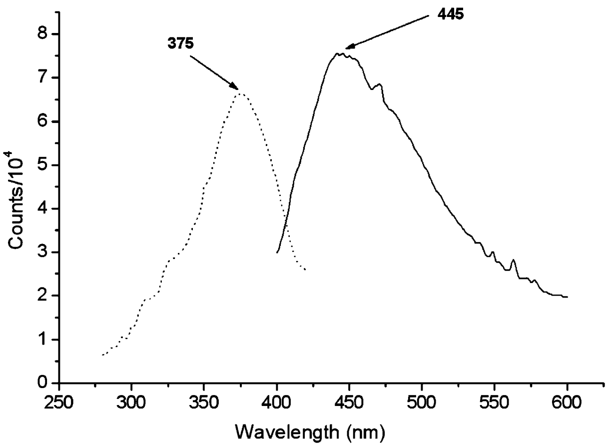

Fig. 4. The excitation (left) and emission (right) spectra of the title compound in the solid state at room temperature.

maximum at 445 nm upon excitation at 375 nm at room temperature. Synthesis of compounds with deferent Bi and oxalate ratios to generate novel framework is underway.

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