

Research Article

A New 3D Coordination Polymer of Bismuth with Nicotinic Acid *N*-Oxide

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The new three-dimensional coordination polymer $\{[\text{Bi}(\text{NNO})_2(\text{NO}_3)] \cdot 1.5\text{H}_2\text{O}\}_n$ (**1**, NNO^- = nicotinate *N*-oxide) was synthesized and characterized by elemental analysis, IR and $^1\text{H-NMR}$ spectroscopy, as well as single-crystal X-ray diffraction analysis. **1** crystallizes in the monoclinic space group $C2/c$. The crystal structure consists of a rectangular-shaped grid constructed with NNO linkers. Cavities of a diameter of $7.9\text{--}8.3 \text{ \AA}^2$ are filled with disordered water molecules. The thermal stability of the compound was evaluated by thermogravimetric analysis.

1. Introduction

Metal-organic frameworks (MOFs) have currently attracted ever-increasing attention because of their intriguing structural topologies and promising applications as functional materials in magnetism, sorption [1], separation, catalysis [2], and drug delivery [3]. Therefore, there are intense research efforts on the synthesis of such materials, and several metal-organic frameworks with zeolitic structures have been reported [4]. With their versatile bridging modes, carboxylates are often employed as building blocks to construct coordination polymers [5].

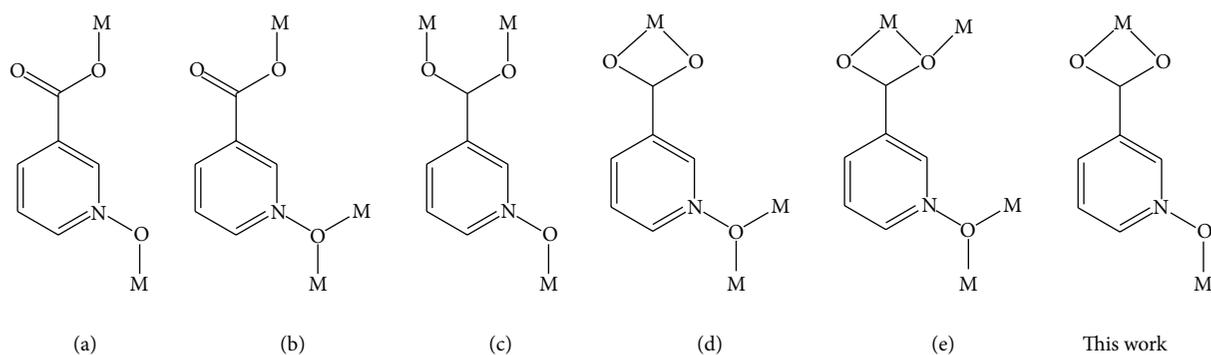
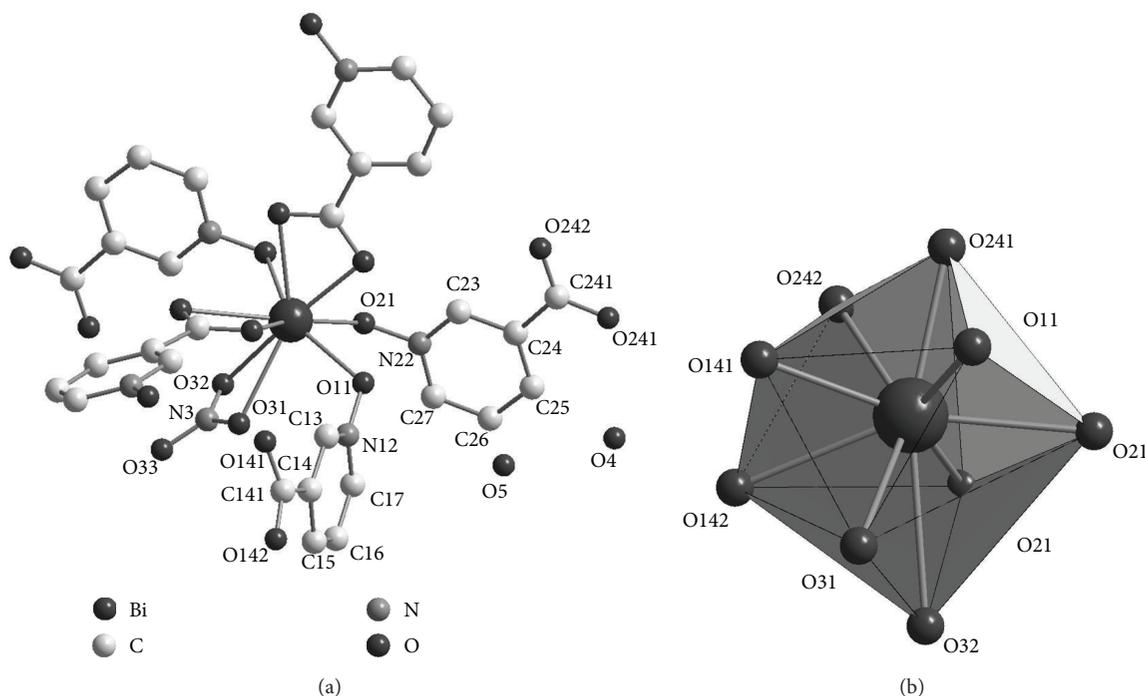
Pyridyl carboxylic acids and their *N*-oxide derivatives are especially useful in this regard, but the exploitation of the ligands in the construction of open framework materials is still in its infancy [6–8]. The anions of these acids may bond to metal centers via their *N*- and *O*- donor atoms. Thus, one would expect higher flexibility and more versatile coordination modes compared to the original ligand (Scheme 1). Furthermore, the separation of the bridging sites is definitely larger. However, studies on such ligand behavior toward coordination polymers are limited, and only a few transition metal-, lanthanide metal-, and main group metal-based coordination polymers incorporating pyridyl carboxylic acid *N*-oxides have been structurally examined [9, 10].

Herein, we describe the synthesis and characterization of a new 3D coordination polymer with nicotinate *N*-oxide (NNO), $\{[\text{Bi}(\text{NNO})_2(\text{NO}_3)] \cdot 1.5\text{H}_2\text{O}\}_n$ (**1**). To the best of our knowledge, no systematic investigation of bismuth-based compounds [11] with nicotinic acid *N*-oxide has been documented [12].

2. Experimental Details

*Synthesis of $\{[\text{Bi}(\text{NNO})_2(\text{NO}_3)] \cdot 1.5\text{H}_2\text{O}\}_n$ (**1**).* All reagents were used as purchased without further purification. Nicotinic acid *N*-oxide (0.104 g, 0.75 mmol) was placed in one of the arms of a branched tube [13], whereas bismuth(III) nitrate pentahydrate (0.121 g, 0.25 mmol) was placed in the other arm. Methanol and water (ratio 3 : 1) were carefully added to fill both arms. The tube was sealed and the ligand-containing arm was immersed in a bath at 60°C , whereas the other maintained at ambient temperature. After two days, crystals that had been deposited in the cooler arm were filtered, washed with acetone and ether, and dried in air (yield: 85%).

Elemental analyses (C, H, and N) were performed using a Carlo Erba model EA 1108 analyzer: found: C: 20.54, H: 1.13, N: 6.58%. Calculated for $\text{C}_{12}\text{H}_{11}\text{BiN}_3\text{O}_{10.5}$: C: 20.82, H: 0.99, N: 6.94%. FT-IR (cm^{-1}): selected bands: 3443w, 3074w, 1617m, 1587m, 1557s, 1382s, 1287w, 1208m, 937m, 799s, 760m,

SCHEME 1: Coordination modes of the nicotinate *N*-oxide (NNO⁻) ligand.FIGURE 1: (a) Molecular structure of $\{[\text{Bi}(\text{NNO})_2(\text{NO}_3)] \cdot 1.5\text{H}_2\text{O}\}_n$ (**1**) and (b) the coordination sphere of the bismuth ion.

667w, and 448w. Solution $^1\text{H-NMR}$ spectrum was recorded on a Bruker DRX-250 AVANCE spectrometer at 250 MHz using $[\text{D}_6]$ dimethylsulfoxide as the solvent: 8.45 (s, NNO, 1H), 8.40 (d, NNO, 1H), 7.75 (d, NNO, 1H), and 7.54 (dd, NNO, 1H) ppm.

Thermogravimetric analysis (TGA) was performed in N_2 atmosphere with a flow rate of 20 mL min^{-1} on a Seiko Instrument thermal analyzer from 20 to 800°C , with a heating rate of $10^\circ\text{C min}^{-1}$ in ceramic crucibles.

Data collection for X-ray diffraction single crystal structure determination was performed on a Stoe IPDS 2T diffractometer using graphite-monochromated $\text{MoK}\alpha$ radiation (0.71073 \AA). The data were corrected for Lorentz and polarization effects. A numerical absorption correction based on crystal-shape optimization was applied for all data [14]. The programs used in this work are Stoe's X-AREA [15], including X-RED and X-SHAPE for data reduction and

absorption correction [16], and the WINGX suite of programs [17], including SIR-92 [18] and SHELXL-97 [19] for structure solution and refinement. The hydrogen atoms were placed in idealized positions and constrained to ride on their parent atoms. The last cycles of refinement included atomic positions for all atoms, anisotropic displacement parameters for all nonhydrogen atoms, and isotropic displacement parameters for all hydrogen atoms. Full cif deposition, excluding structure factor amplitudes, was resided by the Cambridge Crystallography Data CCDC-906828 for **1**, and copies of the data can be obtained, free of charge, via <http://www.ccdc.cam.ac.uk/deposit>.

Crystal data of $[\text{Bi}(\text{NNO})_2(\text{NO}_3)] \cdot 1.5\text{H}_2\text{O}$ (**1**): $\text{C}_{12}\text{H}_{11}\text{BiN}_3\text{O}_{10.5}$, $574.22 \text{ g mol}^{-1}$; diffractometer IPDS-2T; $T = 120(2) \text{ K}$; $2\theta_{\text{max}} = 54.8^\circ$; $0^\circ \leq \omega \leq 180^\circ$, $\varphi = 0^\circ$; $0^\circ \leq \omega \leq 180^\circ$, $\varphi = 90^\circ \Delta\omega = 2^\circ$, 180 images; $-29 \leq h \leq 29$, $-16 \leq k \leq 16$, $-13 \leq l \leq 13$; $\rho_{\text{calc}} = 2.267 \text{ g cm}^{-3}$;

TABLE 1: Selected bond lengths/Å and angles/° for $\{[\text{Bi}(\text{NNO})_2(\text{NO}_3)] \cdot 1.5\text{H}_2\text{O}\}_n$ (**1**).

Bi1-O141 ⁱ	2.323(2)	Bi1-O241 ⁱⁱ	2.326(2)
Bi1-O11	2.333(2)	Bi1-O21	2.476(2)
Bi1-O242 ⁱⁱ	2.557(2)	Bi1-O21 ⁱⁱⁱ	2.573(2)
Bi1-O142 ⁱ	2.584(2)	Bi1-O31	2.611(3)
Bi1-O32	2.816(3)	O242 ⁱⁱ -Bi1-O31	141.81(8)
O141 ⁱ -Bi1-O21	158.87(8)	O241 ⁱⁱ -Bi1-O21	81.81(8)
O11-Bi1-O21	77.77(8)	O141 ⁱ -Bi1-O242 ⁱⁱ	75.83(8)
O241 ⁱⁱ -Bi1-O242 ⁱⁱ	53.30(8)	O11-Bi1-O242 ⁱⁱ	121.46(8)
O21-Bi1-O242 ⁱⁱ	109.84(8)	O141 ⁱ -Bi1-O21 ⁱⁱⁱ	133.78(7)
O241 ⁱⁱ -Bi1-O21 ⁱⁱⁱ	98.58(8)	O11-Bi1-O21 ⁱⁱⁱ	143.28(7)
O21-Bi1-O21 ⁱⁱⁱ	65.67(8)	O242 ⁱⁱ -Bi1-O21 ⁱⁱⁱ	71.12(8)
O141 ⁱ -Bi1-O142 ⁱ	53.40(8)	O241 ⁱⁱ -Bi1-O142 ⁱ	120.95(8)
O11-Bi1-O142 ⁱ	129.15(8)	O21-Bi1-O142 ⁱ	147.33(7)
O242 ⁱⁱ -Bi1-O142 ⁱ	74.19(8)	O21 ⁱⁱⁱ -Bi1-O142 ⁱ	86.58(7)
O141 ⁱ -Bi1-O31	73.64(9)	O241 ⁱⁱ -Bi1-O31	144.30(8)
O11-Bi1-O31	76.15(8)	O21-Bi1-O31	106.92(8)
O21 ⁱⁱⁱ -Bi1-O31	116.71(8)	O142 ⁱ -Bi1-O31	69.35(8)

i: $-x, y, -z + 1/2$, ii: $x, -y, z - 1/2$, iii: $-x + 1/2, -y + 1/2, -z$.

and 25057 measured reflections of which 3574 were symmetrically independent; $R_{\text{int}} = 0.0832$; $F(000) = 2168$; $\mu = 10.543 \text{ mm}^{-1}$. Monoclinic, $C2/c$ (no. 15), $a = 23.468(1)$, $b = 13.334(1)$, $c = 10.912(1) \text{ \AA}$, $\beta = 99.762(3)^\circ$, $V = 3364.9(2) \times 10^6 \text{ \AA}^3$, and $Z = 8$; R values: R_1/wR_2 for 3387 reflections with $[I_0 > 2\sigma(I_0)]$: 0.0205/0.0456, for all data: 0.0219/0.0462; $S_{\text{all}} = 1.076$.

3. Results and Discussion

Colourless block-shaped crystals of $\{[\text{Bi}(\text{NNO})_2(\text{NO}_3)] \cdot 1.5\text{H}_2\text{O}\}_n$ (**1**) were obtained by slow interdiffusion of solutions of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and nicotinic acid N -oxide (HNNO) in aqueous methanol under ambient conditions. The crystal structure of **1** may be regarded as a three-dimensional coordination polymer. The coordination environment around the Bi^{3+} ion is shown in Figure 1 together with the asymmetric unit of the crystal structure; selected interatomic distances are summarized in Table 1. The bismuth ions center slightly distorted tricapped trigonal prisms with two oxygen atoms of one nitrate anion and seven oxygen atoms of five nicotinate N -oxide anions with Bi-O distances between 2.323(2) and 2.816(3) Å [20] (sum of the ionic radii Bi^{3+} and O^{2-} is 2.43 Å).

The distorted $[\text{Bi-O}_9]$ polyhedra is hemidirected subject to stereochemically active lone pairs [20], and the presence of stereochemically active lone pairs is commonly observed in bismuth-based coordination compounds [21]. In **1**, there are, therefore, relatively short Bi-O distances ranging from 2.207(8) to 2.367(8) Å and rather long Bi-O distances ranging from 2.592(8) to 2.743(9) Å, as well as bond angles of less than 90° (ranging from 53.30(8) to 86.58(7)°, see Table 1).

In **1**, five unique NNO^- anions adopted two different types of coordination modes, as shown in Figure 2. See Scheme 1 for the known coordination modes of NNO^- in

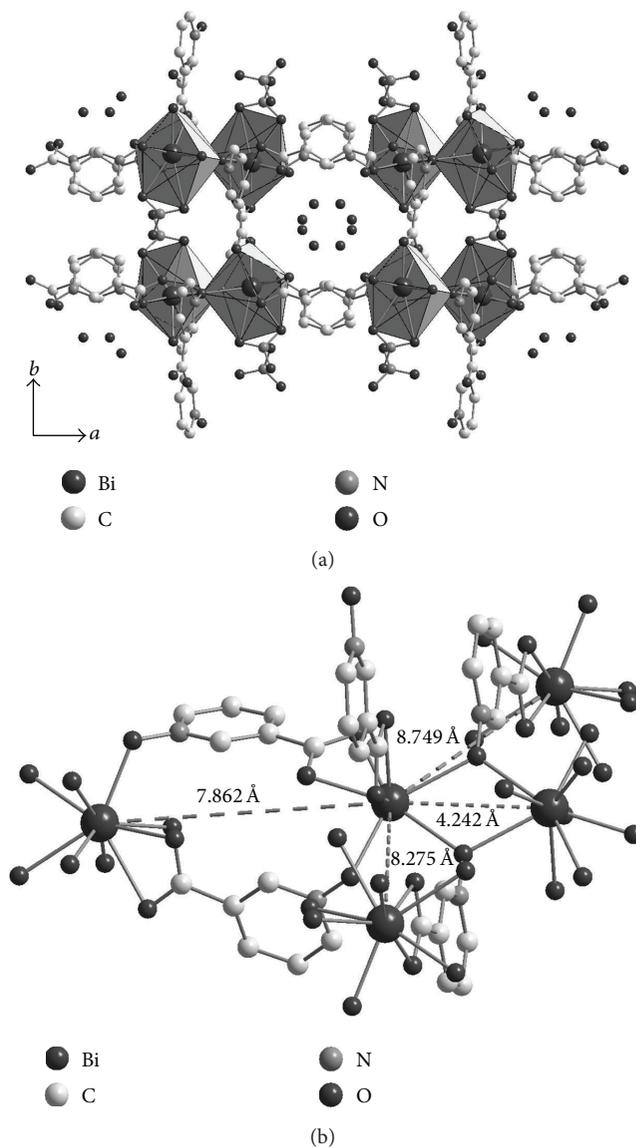


FIGURE 2: (a) View of the three-dimensional coordination polymer in the crystal structure of **1** along the crystallographic b axis. The guest water molecules are located within the rectangular channels. (b) Bi-Bi distances and the coordination modes of the NNO^- anions in **1**.

structurally characterized coordination polymers [22]. One type of the NNO^- anions (three NNO^- anions) in **1** bridges three Bi(III) ions. In particular, the N -oxide moiety bridges two bismuth ions (μ -O) with distances of 4.242 Å, whereas the carboxylate group forms two bonds, chelating to one Bi(III) ion (Scheme 1(d)). The other type of the NNO^- anions (two NNO^- anions) bridges two bismuth ions through chelating of the carboxylate and coordinating of the N -oxide groups to Bi(III). The interconnection of the bismuth ions by the NNO^- ligands results in the formation of a 3D network with Bi-Bi separations of 4.242, 7.862, 8.275, and 8.749 Å (Figure 2(b)). One nitrate anion coordinates to Bi(III) as a chelating anion.

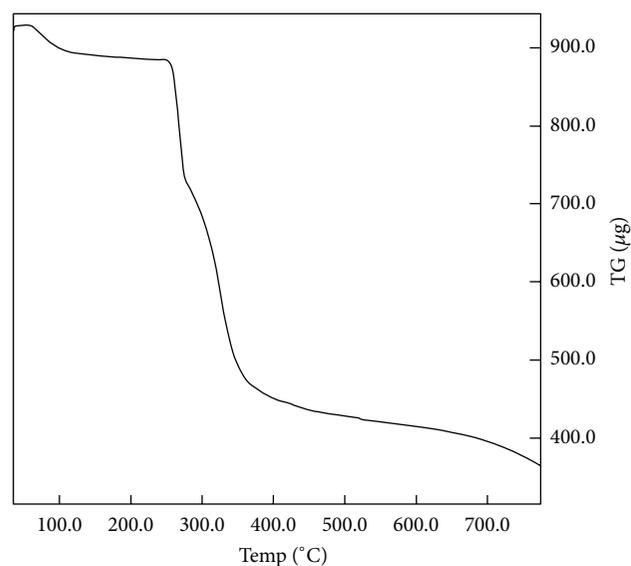


FIGURE 3: Thermogravimetry curve of $\{[\text{Bi}(\text{NNO})_2(\text{NO}_3)] \cdot 1.5\text{H}_2\text{O}\}_n$ (**1**).

TABLE 2: Hydrogen bonding in the crystal structure of (**1**).

A···B	D(A···B)/Å
O4···O4 (1 - x, 1 - y, -z)	2.574(1)
O241···O11 (x, 1 - y, -1/2 + z)	2.739(3)
O4···O5 (x, 1 - y, -1/2 + z)	2.775(2)
O4···O241 (1 - x, y, 1/2 - z)	2.983(8)

Encapsulated in the Bi(III)-NNO framework, there are uncoordinated, disordered water molecules in the crystal structure of **1**. The bridging NNO^- ligands are arranged in conjunction with weak π - π stacking interactions of the pyridine rings (distances between the rings are 3.440 Å) [23]. The rectangular-shaped grid, formed by NNO^- anions and bismuth ions, gives rise to the large rectangular cavities known among noninterpenetrating structures [24], with approximate cavity sizes of 7.9–8.3 Å². One and a half crystallographically unique water molecules are trapped within these channels. As shown in Figure 2, uncoordinated water molecules and the carboxylate oxygen atoms of the NNO^- ligands are involved in hydrogen bonding interactions (Table 2). The topology of the three-dimensional bismuth(III)-coordination polymer may be characterized (by TOPOS program) by the point symbol for the net as follows: $\{3^3 \cdot 4^5 \cdot 5^6 \cdot 6\}$.

Thermogravimetric analysis (TGA) was performed applying polycrystalline samples under nitrogen atmosphere to get an idea of the thermal stability of $\{[\text{Bi}(\text{NNO})_2(\text{NO}_3)] \cdot 1.5\text{H}_2\text{O}\}_n$ (**1**), see (Figure 3). The first weight loss at 85–115°C in the TG curve corresponds to the loss of water molecules (calcd. 4.70%). Decomposition of the framework is characterized by an intense exothermic peak (270°C) followed by another weak exothermic peak (320°C). Accordingly, a rapid mass loss occurs between 270 and 350°C in the TG curve corresponding to 50% of the original

sample mass. Coordination polymer **1** appears to decompose completely during this transition, presumably leaving a final residue of Bi_2O_3 (found 41.20%, calcd. 40.59%). The mass loss calculations as well as the microanalyses (atomic absorption) of the solid residues suggest that the residue left as a final decomposition product of the complexes is Bi_2O_3 . IR analysis of the final residue (at 700°C) revealed none of the characteristic absorption bands of **1**. In addition, the presence of absorption peaks at 421, 500, 541, and 845 cm^{-1} in the IR spectrum provides evidence for the identity of the residue as Bi_2O_3 [25].

4. Conclusions

In this paper, with $\{[\text{Bi}(\text{NNO})_2(\text{NO}_3)] \cdot 1.5\text{H}_2\text{O}\}_n$ ($\text{NNO}^- =$ nicotinate *N*-oxide, **1**), a new three-dimensional coordination polymer is reported. Channels are formed by bridging of the NNO^- ligands, representing a new coordination mode. Uncoordinated and disordered water molecules are trapped within the rectangular channels. These water molecules and the carboxylate O-atom of the NNO^- ligands are involved in hydrogen bonding interactions. This three-dimensional coordination polymer appears to represent the first crystal structure of bismuth(III) with nicotinic acid *N*-oxide.

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