

Electronic Supplementary Information (ESI)

## New 3D Bismuth-Oxo Coordination Polymers Containing Terephthalate-Based Ligands: Observation of Bi<sub>2</sub>O<sub>2</sub>-Layer and Bi<sub>4</sub>O<sub>3</sub>-Chain Motifs

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X-ray Crystallography details of compound **1** and **2**.

**Table 1.** Crystal data and structure refinement of compound **1** and **2**.

**Figure S1.** Stereochemically active lone pair formation of compound **1** with ligand's oxygen disorder, the arrows show the approximate location of lone pair electrons. Bi = blue, O = red.

**Figure S2.** Bi<sub>2</sub>O<sub>2</sub> layer of compound **1**, which consists of repeating unit of AA'B chains propagated in the x and y directions. Bi= blue polyhedra, O = red.

**Figure S3.** Stereochemically active lone pair formation of compound **2**, the arrows show the approximate location of lone pair electrons. Bi = blue, O = red.

**Figure S4.** Le Bail profile fitting using Jana Software on X-Ray Powder pattern of compound **1**.

**Figure S5.** Diffuse-reflectance (UV/vis) spectra of as received TA ligand and compound **1**.

### X-ray Crystallography details of compound **1** and **2**.

X-ray intensity data from a colorless needle crystal (**1**) and colorless plate crystals (**2**) were measured at 150(2) K and 295(2) K, respectively, using a Bruker SMART APEX diffractometer (Mo K $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ).<sup>1</sup> Raw area detector data frame reduction and correction for absorption effects were performed with the SAINT+ and SADABS programs.<sup>1</sup> Final unit cell parameters were determined by least-squares refinement of 5335 and 6252 reflections from the data set for compound **1** and **2**, respectively. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against  $F^2$  were performed with SHELXTL.<sup>2</sup>

Compound **1** crystallizes in the monoclinic system. The space group P2<sub>1</sub>/m was determined by examination of the pattern of systematic absences in the intensity data, and by obtaining a reasonable structure solution and refinement. The asymmetric unit consists of four bismuth atom sites, four bridging oxygen (oxide) atom sites, and two independent terephthalato ligands. Bismuth atoms Bi3 and Bi4 and bridging oxo-atoms O3 and O4 are located on crystallographic mirror planes; Bi1, Bi2, O1 and O2 are located on general positions. Disorder of both terephthalato ligands was observed. All atoms of ligand C1-C8/O5-O8 except for phenyl ring atoms C3, C4, C6 and C7 are located on a mirror plane; C3, C4, C6 and C7 are disordered across the mirror. Ligand C9-C16/O9-O12 is disordered equally over two orientations (labels suffixed A or B) on general positions. Both independent disordered ligands were restrained to adopt chemically reasonable geometries with 36 distance restraints, and all ligand atoms were refined isotropically. The bismuth and bridging oxo-atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized

positions and included as riding atoms. The disorder was also observed in space group  $P2_1$ , and therefore is not artificially imposed by the additional symmetry of  $P2_1/m$ .

For compound **2**, there is extensive disorder in the crystal, affecting three of the four crystallographically independent ligands and the interstitial water molecules. Because of this disorder, the data are moderate quality and only general structural features should be considered reliable. The compound crystallizes in the triclinic system. The structure was obtained in the space group  $P\bar{1}$  (# 2). The asymmetric unit consists of four bismuth atoms, three bridging oxygen (oxide) atoms (O23, O24, O25), two  $C_8H_3NO_6^{2-}$  ligands located on general positions (associated with nitrogen atoms N1 and N4/N5) and half each of two ligands located on inversion centers (N2 and N3), a coordinated water molecule (O26) and two interstitial water molecules (O27, O28). The ligand N4/N5 is disordered on its general position, with the effect that the nitro groups are scrambled over two positions. Populations were fixed at  $N4/O19/O20 = 0.75$  and  $N5/O21/O22 = 0.25$ , to give sensible displacement parameter values. A similar disorder is imposed on the two ligands on inversion centers. The two interstitial water molecules were refined with a fixed isotropic displacement parameter of  $0.10 \text{ \AA}^2$ , and their populations refined freely. All other atoms affected by disorder were refined isotropically. Several geometric restraints were used to maintain chemically reasonable geometries. The four bismuth atoms, three bridging oxides, coordinated water O26 and ligand N1 were refined with anisotropic displacement parameters. Interstitial water O28 is disordered commensurate with nitro group N3/O13/O14. Hydrogen atoms bonded to carbon were placed in geometrically idealized positions and included as riding atoms. Hydrogen of the water molecules were not located or calculated. The same ligand and

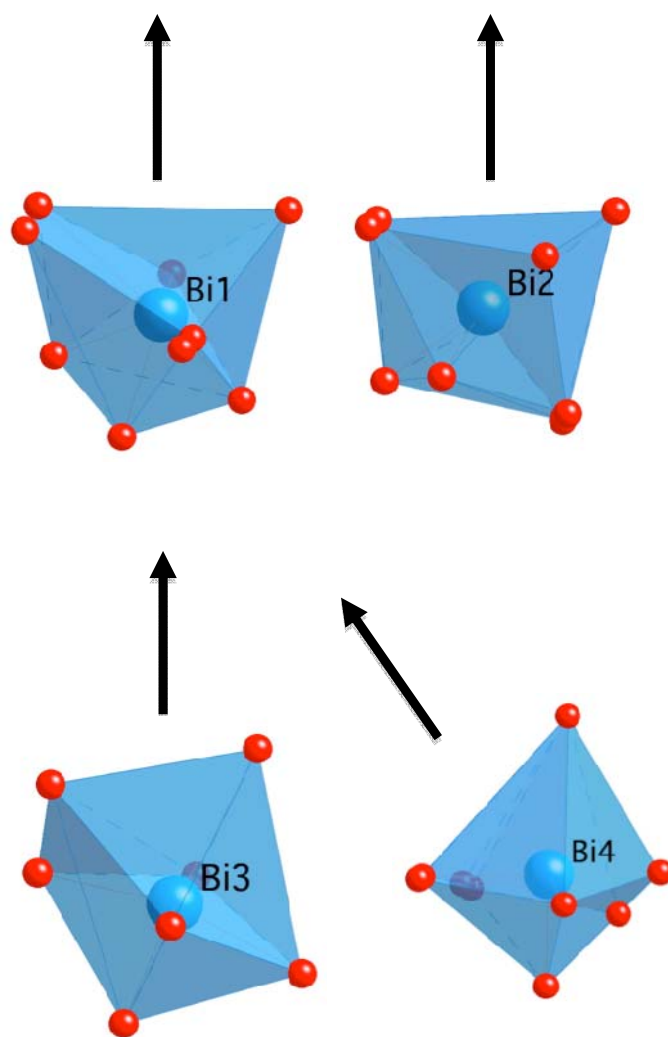
water disorder was observed during trial refinements in the space group P1 (#1), and therefore is not imposed by an incorrect space group choice.

1 SMART Version 5.630, SAINT+ Version 6.45 and SADABS Version 2.05. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2003.

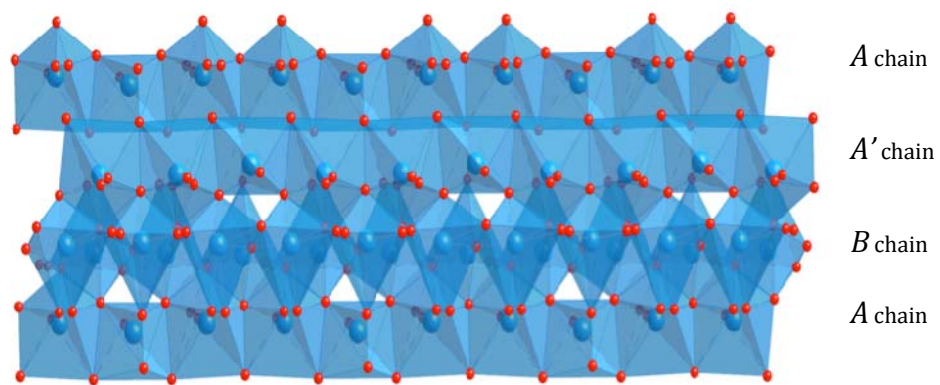
2 Sheldrick, G. M. SHELXTL Version 6.14; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2000.

**Table 1.** Crystal data and structure refinement of compound **1** and **2**.

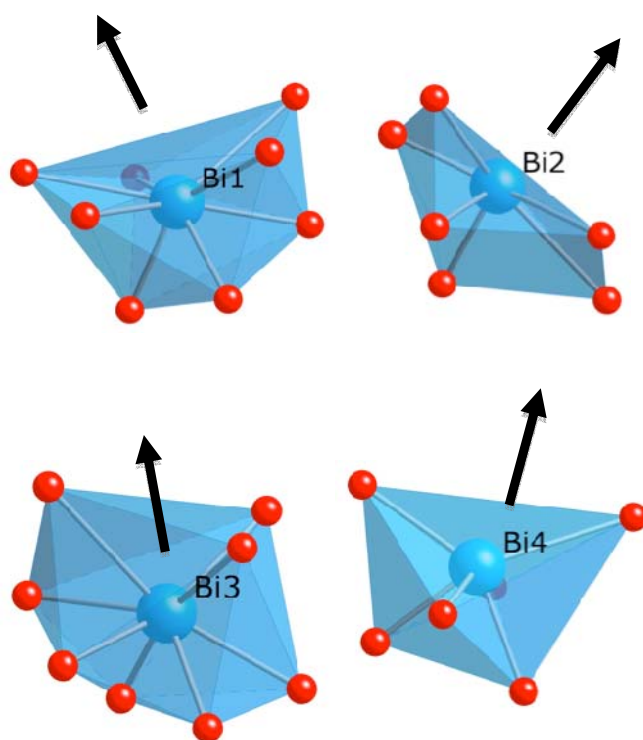
Compound	<b>1</b>	<b>2</b>
Empirical formula	C <sub>8</sub> H <sub>4</sub> Bi <sub>2</sub> O <sub>6</sub>	C <sub>24</sub> H <sub>12.36</sub> Bi <sub>4</sub> N <sub>3</sub> O <sub>22.68</sub>
Formula weight	614.07	1541.52
Temperature	150(2) K	295(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	P2 <sub>1</sub> /m	P $\bar{1}$
Unit cell dimensions	a = 10.0998(7) Å $\alpha$ = 90° b = 12.1043(8) Å $\beta$ = 98.582(10)° c = 11.8472(8) Å $\gamma$ = 90°	a = 11.6396(17) Å $\alpha$ =101.04(3)° b = 11.7565(17) Å $\beta$ =93.708(3)° c = 13.0034(19) Å $\gamma$ =114.402(2)°
Volume	1432.12(17) Å <sup>3</sup>	1569.7(4) Å <sup>3</sup>
Z	6	2
Density (calculated)	4.272 Mg/m <sup>3</sup>	3.261 Mg/m <sup>3</sup>
Absorption coefficient	36.822 mm <sup>-1</sup>	22.460 mm <sup>-1</sup>
F(000)	1596	1382
Crystal size	0.08 x 0.05 x 0.04 mm <sup>3</sup>	0.12 x 0.08 x 0.03 mm <sup>3</sup>
Theta range for data collection	1.74 to 26.39°.	1.62 to 27.64°
Index ranges	-12<=h<=12, -15<=k<=15, -14<=l<=14	-15<=h<=15, -15<=k<=15, -16<=l<=16
Reflections collected	23035	23150
Independent reflections	3075 [R(int) = 0.0429]	7269 [R(int) = 0.0487]
Completeness to theta	99.9 %	99.5 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.5519	1.0000 and 0.4831
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameter	3075 / 36 / 184	7269 / 31 / 360
Goodness-of-fit on F <sup>2</sup>	1.021	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0256, wR2 = 0.0585	R1 = 0.0401, wR2 = 0.0870
R indices (all data)	R1 = 0.0328, wR2 = 0.0619	R1 = 0.0539, wR2 = 0.0929
Largest diff. peak and hole	2.275 and -1.267 e.Å <sup>-3</sup>	1.854 and -1.476 e.Å <sup>-3</sup>



**Figure S1.** Stereochemically active lone pair formation of compound **1** with ligand's oxygen disorder, the arrows show the approximate location of lone pair electrons. Bi = blue, O = red.

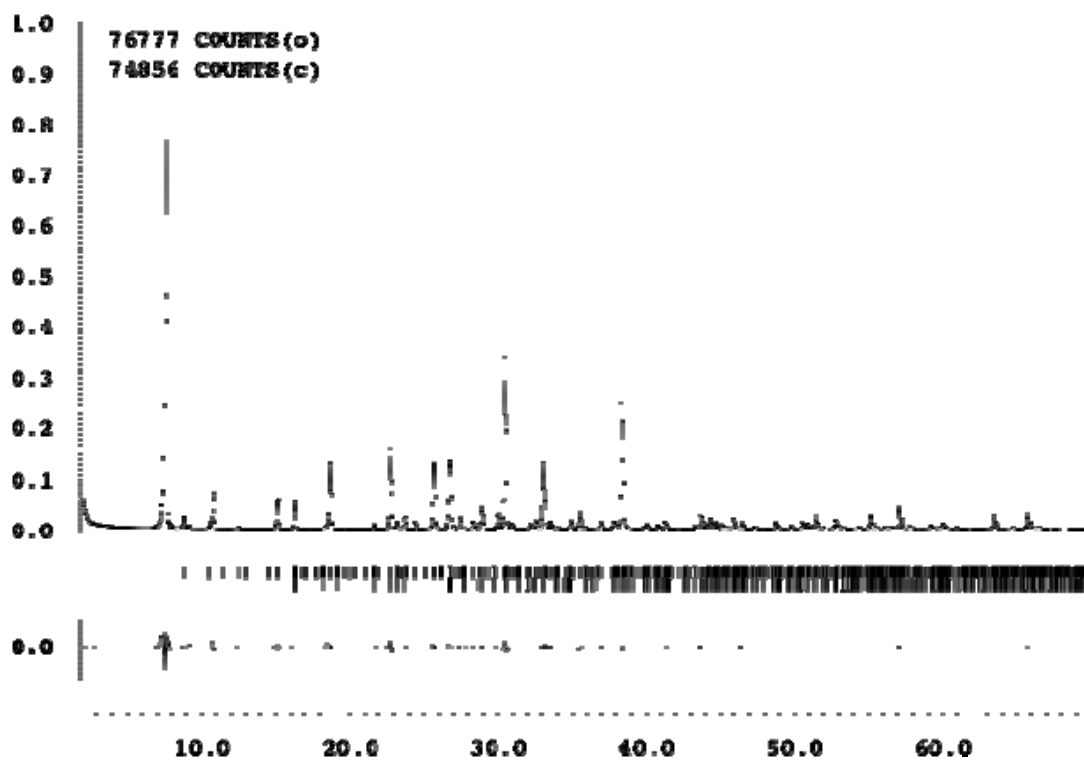


**Figure S2.**  $\text{Bi}_2\text{O}_2$  layer of compound **1**, which consists of repeating unit of  $AA'B$  chains propagated in the x and y directions. Bi= blue polyhedra, O = red.



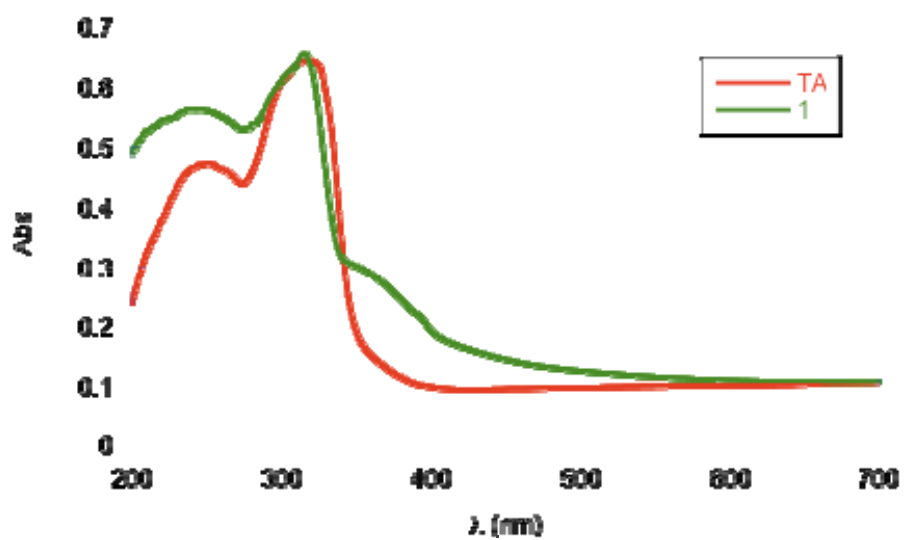
**Figure S3.** Stereochemically active lone pair formation of compound **2**, the arrows show the approximate location of lone pair electrons. Bi = blue, O = red.





**Figure S4.** Le Bail profile fitting using Jana2000® Software on X-Ray Powder

Diffraction pattern of compound 1.



**Figure S5.** Diffuse-reflectance (UV/vis) spectra of as received TA ligand and of compound **1**.