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Coordination polymers incorporating Bi(III) and 2,4,6-pyridine tricarboxylic acid and its derivatives: synthesis, structure and topology

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Abstract

Bi(III) as its oxide combined with 2,4,6-pyridine tricarboxylic acid, H₂pdc-COOH, and various pyridine-derived additives in dimethylformamide (dmf) under solvothermal conditions produced three novel bismuth coordination polymers, {[Bi(μ -pdc-COO)₂][NH₂Me₂]₃, **1**, {[Bi(μ -pdc-COO)₂][C₃H₇N₂]₃·C₅H₆N₂}_n, **2**, and {[Bi₂(μ -pdc-COO)₂(μ -pdc-COOH)(pdc-COOH)][NH₂Me₂]₄·2dmf·NHMe₂}_n, **3**. The anionic coordination network topologies are two-dimensional chains-of-loops and ladders, respectively, but the local 8-coordinate environments about the bismuth(III) centres are in each case between that of a square antiprism and that of a hexagonal bipyramid. When the 4-carboxy substituent in H₂pdc-COOH is replaced by another potentially coordinating substituent to give 4-R-2,6-pyridine dicarboxylic acid, H₂pdc-R (R = OH, NH₂, Cl), the salts obtained contain discrete centrosymmetric dinuclear 8-coordinate bismuth anions with either double O-bridges between the metal centres, [Bi₂(μ -pdc-R)₂(pdc-R)₂(dmf)₂][NH₂Me₂]₂ (R = OH, NH₂), **4** and **5**, or double carboxylate bridges with one long Bi–O bond, [Bi₂(μ -pdc-NMe₂)₂(pdc-R)₂(dmf)₂][NH₂Me₂]₂, **6** (R = Cl, but replaced by dimethylamine during the reaction). The structures and supramolecular networks of **1-6** are described and compared as an exploration of alternatives to the conventional carboxylate-based organic linking units.

Keywords: Bismuth; 2,4,6-pyridine tricarboxylic acid; 2,6-pyridine dicarboxylic acid; Framework; MOF; structural characterization

1. Introduction

Reticular chemistry entails a 'building block' approach to developing porous compounds that extend infinitely in 1-3 dimensions [1]. Primarily explored using transition metal elements, such compounds have been researched extensively over the past two decades [2]. Although many potential applications have been touted over the lifetime of this field, research tends to be geared towards developing porous materials as tools for gas sorption, separation and catalysis; their capacity as a drug-delivery system receives less attention [3].

Bismuth is a non-toxic metal element of some medicinal value [4] – currently used to treat gastrointestinal problems. A small range of bismuth-based metal-organic framework (MOF) materials have been developed through the employment of the same carboxylate-based linkers frequently used in the synthesis of *d*-block MOFs [5]. Few instances of polymeric bismuth complexes utilising non-carboxylate organic linking ligands have been reported to date [6-9].

We are exploring the chemistry of extended bismuth structures by employing the tridentate 2,4,6-pyridine tricarboxylic acid, H₂pdc-COOH (Fig. 1), derivatives of which have been shown to be biodegradable in bacterial samples [10], in an attempt to find a stable structural building unit from which to construct multidimensional frameworks in a consistent and predictable manner. In this work, H₂pdc-COOH was employed alongside bismuth(III) oxide, Bi₂O₃, dmf and aminopyridine additives in solvothermal syntheses in order to synthesize a series of novel extended bismuth structures. Other 4-R-2,6-pyridine dicarboxylic acids, H₂pdc-R, in which the 4-carboxylic acid group of H₂pdc-COOH is replaced by another group (R = OH, NH₂, Cl), were also employed, but led only to dinuclear Bi(III) complexes. The resulting structures vary in overall topology and dimension, while possessing analogous connectivity around the bismuth cation.

Fig. 1. The organic acids H₂pdc-COOH (left) and H₂pdc-R (right; R = OH, NH₂, Cl).

2. Experimental

2.1. Materials and methods

Bi(NO₃)₃.5H₂O (97%) and Bi₂O₃ were purchased from Sigma-Aldrich; Chelidamic acid monohydrate (95%) and 4-chloro-2,6-pyridine dicarboxylic acid were purchased from TCI Deutschland GmbH. All chemicals were commercially available and used without further purification. ¹H and ¹³C NMR spectra were recorded on a Bruker Ascend 400 MHz NMR spectrometer. Solubility limitations precluded the recording of NMR spectra of the bismuth complexes.

2.1.1. Synthesis of 2,4,6-pyridine tricarboxylic acid (H₂pdc-COOH)

H₂pdc-COOH was synthesized according to the literature [11]. To 2,4,6-trimethylpyridine (4.84g, 0.04 mol) in H₂O (80 mL) in a 250 mL round-bottomed flask, KMnO₄ (50 g, 0.32 mol) was added over 4 hours while maintaining a temperature of 20-30°C. The resulting mixture was left to stir at room temperature for 16 hours. Increasing the temperature to 50°C, the reaction mixture was left to stir for a further 48 hours before cooling and filtering through fritted filter paper in order to remove solid MnO₂ from the reaction. The residue was washed with distilled water and the resulting filtrate evaporated to yield a white solid (3.24g, 38%). ¹H NMR (400 MHz, D₂O): δ 8.58 (s, 2H). ¹³C NMR (400 MHz, D₂O): δ 127.4, 142.2, 148.5, 166.5, 166.9.

2.1.2. Synthesis of 4-amino-2,6-pyridine dicarboxylic acid (H₂pdc-NH₂)

H₂pdc-NH₂ was synthesized according to the literature [18].

2.2. Preparation of Bi(III) complexes 1-6

2.2.1. { $[Bi(\mu-pdc-COO)_2][NH_2Me_2]_3$ }_n (1)

 H_2 pdc-COOH (50 mg, 0.2368 mmol) was dissolved in dimethylformamide (dmf, 6 mL) in a 15 mL screw-capped vial. Bi₂O₃ (110.3mg, 0.2368 mmol) was added, the cap screwed on tightly and the vial sonicated at room temperature for 10 minutes. The yellow suspension was heated at 120°C for 24 h before cooling in the oven to room temperature. Crystals of **1** were harvested by hand from atop a layer of grey-black crystalline powder.

2.2.2. $\{[Bi(\mu - pdc - COO)_2][C_5H_7N_2]_3 \cdot C_5H_6N_2\}_n$ (2)

 H_2 pdc-COOH (50 mg, 0.2368 mmol) was dissolved in dmf (6 mL) in a 15 mL screw-capped vial. Bi₂O₃ (110.3 mg, 0.2368 mmol) and 4-aminopyridine (22.29 mg, 0.2368 mmol) were added and the vial sonicated at room temperature for 10 minutes. The vial was transferred to an oven and heated at 120°C for 24 h before cooling in the oven to room temperature. A layer of colourless needle-like crystals **2** could be observed atop a mass of green-black material; crystals were harvested by hand from the reaction mixture.

2.2.3. $\{[Bi_2(\mu-pdc-COO)_2(\mu-pdc-COOH)(pdc-COOH)][NH_2Me_2]_4 \cdot 2dmf \cdot NHMe_2\}_n$ (3)

H₂pdc-COOH (50 mg, 0.2368 mmol) was dissolved in dmf (6 mL) in a 15 mL screw-capped vial. Bi₂O₃ (110.3 mg, 0.2368 mmol) and either 3-aminopyridine, 2-aminopyridine, or 4,4'-bipyridine

(0.2368 mmol) were added and the vial sonicated at room temperature for 10 minutes. The vial was transferred to an oven and heated at 120°C for 24 h before cooling in the oven to room temperature. A layer of colourless needle-like crystals **3** could be observed atop a mass of green-black material; crystals were harvested by hand from the reaction mixture.

2.2.4. $[Bi_2(\mu - pdc - R)_2(pdc - R)_2(dmf)_2][NH_2Me_2]_2 [R = OH(4), NH_2(5)]$

 H_2 pdc-OH or H_2 pdc-NH₂ (50 mg) was dissolved in dmf (6 mL) in a 15 mL screw-capped vial. Bi₂O₃ (1 equiv.) was added and the vial sonicated at room temperature for 10 minutes. The vial was transferred to an oven and heated at 120°C for 24 h before cooling in the oven to room temperature. Colourless block-shaped crystals were harvested by hand from the reaction mixture.

2.2.5. $[Bi_2(\mu-pdc-NMe_2)_2(pdc-R)_2(dmf)_2][NH_2Me_2]_2$ (6)

 H_2 pdc-Cl (50 mg) was dissolved in dmf (6 mL) in a 15 mL screw-capped vial. Bi₂O₃ (1 equiv.) was added and the vial sonicated at room temperature for 10 minutes. The vial was transferred to an oven and heated at 120°C for 24 h before cooling in the oven to room temperature. Colourless block-shaped crystals of **6** were harvested by hand from the reaction mixture.

2.3. X-ray Crystallography

Single-crystal data for 1-6 were collected on a *Rigaku Oxford Diffraction SuperNova* areadetector diffractometer [13] using Mo K α radiation ($\lambda = 0.71073$ Å) from a micro-focus X-ray source and an *Oxford Instruments Cryojet XL* cooler set to 160 K. Data reduction was performed with *CrysAlisPro* [13]. Structure solutions were carried out using the *SHELXT-2018* [14] program, followed by refinement using *SHELXL-2018* [15]. The crystallographic data are listed in Table 1.

The dimethylammonium cations in **1** are disordered: two sets of positions were defined for each cation, with the site occupancy of the major component refining to 0.707(10) for the cation in the general position and being 0.5 by definition for the cation disordered about the two-fold axis. Similarity restraints were applied to all C–N bond lengths in the cations, while neighbouring atoms within and between each orientation of the disordered cations were restrained to have similar atomic displacement parameters (ADPs). Although none of the species in compound **1** has a stereogenic centre, it has crystallized in a chiral space group and the absolute structure parameter, determined by the method of *Parsons et al.* [16] using 1559 quotients, was -0.030(4). For **2**, the 4-aminopyridinium cation site shared with a neutral 4-aminopyridine molecule is disordered (see Section 3.2.2). The site occupation factor of the major orientation of the disordered cation refined to 0.779(17). Similarity restraints akin to those used for **1** were applied and, in addition, the disordered orientations were restrained to be planar. For **3**, there is complete disorder of the two tridentate ligands coordinating to

Bi2. Two sets of positions were defined for these ligands and the site occupation factor of the major conformation refined to 0.540(6). Similarity restraints were applied to the chemically equivalent bond lengths and angles, as well as the ADPs, involving all disordered atoms and each ligand was also restrained to be planar. The *SQUEEZE* procedure of the program *PLATON* [17] was applied; see Section 3.2.3. For **4** and **6**, the dmf ligand is disordered and the site occupation factor of the major conformation refined to 0.60(2) and 0.577(8), respectively. Similarity restraints, analogous to those described for **1**, were applied.

H-atoms were generally placed in calculated positions and allowed to ride on their parent atoms. The exceptions were the hydroxy H-atoms in **4**, the ligand amine H-atoms in **5** and the ammonium H-atoms in **6**, all of which were refined isotropically.

Table 1

Crystallographic data for 1-6.

3. Results and discussion

3.1. Syntheses

Compound 1 resulted from the solvothermal reaction between Bi_2O_3 and H_2pdc -COOH alone in dmf. The reactions that included various pyridines as additives were conducted to evaluate the role of the pK_a of the pyridine in structure direction. While compound 2 resulted from the use of 4aminopyridine ($pK_a = 9.17$), compound 3 was obtained consistently with 3-aminopyridine ($pK_a =$ 6.00), 2-aminopyridine ($pK_a = 6.86$), or 4,4'-bipyridine ($pK_a = 10.73$). The results from this limited selection of pyridines suggest that pK_a is not a sole or major contributor. The differences observed between the three products 1-3 could be related to the rate of the reaction. For 1, H₂pdc-COOH is slowly deprotonated by the oxidization of dmf to dimethylamine or dimethylammonium cations [18]. In 2 and 3, however, the H₂pdc-COOH at the start of the reaction will already be in a somewhat deprotonated state as a consequence of the added pyridine derivative: an increased rate of coordination ensues, potentially influencing the arrangement of the developing framework. In 2, the positioning of the H-donor/acceptor groups (1,4-position) of the base are such that extended chains are effectively tied together. Dimethylamine or dimethyl ammonium cations are not found in the crystals of 2, possibly because the more stable crystal lattice in terms of packing and hydrogen bonding arises when 4-aminopyridinium is incorporated.

The solvothermal syntheses of compounds 1-6 resulted in crystals of the reported compounds being isolated by hand from a further mass of material left after the reaction. X-ray powder diffraction of the bulk material indicated that it was predominantly unreacted Bi_2O_3 , which dominated the

background of the diffractograms and prevented their meaningful analysis. Attempts to isolate sufficient crystals by hand did not give enough material to obtain a clean diffractogram.

As Bi_2O_3 is only very slightly soluble in dmf, a clean stoichiometric reaction is considered unlikely. Reactions were attempted with various ligand:bismuth ratios (0.5:1, 1:1, 1:2, 1:3 and vice versa), along with different solvent quantities (3, 5, 6 and 8 mL) and temperatures (95, 120, 150 °C). None of these modifications made any significant difference to the reaction outcomes. The best crystals generally came from the 1:1 molar ratio of ligand:bismuth; crystals of **3** were very delicate when touched. A further advantage of using dmf as the solvent was that it avoided having water competing as a bismuth-coordinating ligand.

3.2. Bi(III) coordination polymers

3.2.1. { $[Bi(\mu-pdc-COO)_2][NH_2Me_2]_3$ } (1)

Reaction of H₂pdc-COOH with Bi₂O₃ (1:1) in dmf at 120°C yielded phase-pure colourless block crystals of **1** within 24 hours. Single crystal analysis of **1** revealed a 2-dimensional anionic framework with overall stoichiometry { $[Bi(\mu-pdc-COO)_2][NH_2Me_2]_3$ }, space group I2.

The asymmetric unit of 1 contains one fully deprotonated pdc-COO ligand, one half of a bismuth(III) cation (sits on a two-fold axis) and 1.5 dimethylammonium cations (one cation site is disordered about a two-fold axis and the other site is disordered in a general position). Expanding the structure reveals that each bismuth cation is 8-coordinated by two tridentate pdc-COO moieties and monodentate oxygen atoms from the 4-carboxy group of two further pdc-COO ligands (Fig. 2). The tridentate pdc-COO ligands lie in planes inclined to one another by 84.16(16)° and monodentate binding sites subtend an angle of 103.78(18)° at the Bi(III) centre. Interestingly, the Bi–O bond lengths in the chelated rings are unequal (Table 2). The 8-coordinate local topology is discussed further in Section 3.2.4.

Fig. 2. Displacement ellipsoid plot of the Bi(III) coordination environment in **1** (50% probability ellipsoids; symmetry codes: (i) $-\frac{3}{2}-x$, $\frac{1}{2}+y$, $-\frac{3}{2}-z$; (ii) $\frac{1}{2}+x$, $\frac{1}{2}+y$, $\frac{1}{2}+z$; (iii) -1-x, y, -1-z).

Table 2

Symmetry-unique bond distances (Å) around the central bismuth(III) centre in 1 and 2.

Each pdc-COO ligand bridges two Bi(III) cations and each Bi(III) is coordinated by four linkers to give extended 2-dimensional anionic sheets based on an oblique 9.62×6.62 Å grid having a (4,4) net by Wells notation [19] (Fig. 3). The point symbol for the net, calculated using ToposPro [20], is {8⁴.12²} {8}2, a 2-nodal 2,4 net with stoichiometry (2-c)2(4-c), and apparently a new topology

(Fig. S1). The sheets lie parallel to the $(10\overline{1})$ plane and the acute oblique angle defining the grid shape is 51.75(1)°. The shortest Bi···Bi distance across one grid unit is 8.3985(3) Å. Dimethylammonium cations sit in the spaces between the sheets, aligned roughly above the parallelepiped pores. In the crystal structure, the sheets stack slightly slipped relative to their normals, with the Bi(III) ions in successive sheets stacked along the [100] direction at a distance of 10.1017(2)Å. Nonetheless, open channels exist through the pores of the stacked sheets. Although there are no solvent accessible voids in the overall structure according to void space calculations run through *PLATON* [17], removing the dimethylammonium cations results in void spaces within the anionic lattice of 583 Å³ per unit cell (42% of the unit cell volume). Much of this space lies between the anionic layers, rather than within the grids of the layers. Interionic N–H···O hydrogen bonds between the cations and carboxylate Oatoms complete the three-dimensional supramolecular framework (Table 3).

Fig. 3. The square channels in 1 (left; viewed down the *c*-axis) formed by the layering of 2-dimensional sheets (right; viewed down the *b*-axis). Cation disorder not shown.

Table 3

Hydrogen-bond parameters for 1-6.

3.2.2. { $[Bi(\mu-pdc-COO)_2][C_5H_7N_2]_3 \cdot C_5H_6N_2\}_n$ (2)

With the addition of 1 molar equivalent of 4-aminopyridine to the reaction setup that produced 1, crystals of 2 were obtained as colourless needles.

Single crystal analysis of **2** revealed a space group of I2/a. The Bi(III) cation in {[Bi(μ -pdc-COO)₂][C₅H₇N₂]₃·C₅H₆N₂}_n lies on a two-fold axis and the asymmetric unit additionally includes one pdc-COO anion, one ordered 4-aminopyridinium cation and one disordered site occupied 50% by another 4-aminopyridinium cation and 50% by a neutral 4-aminopyridine molecule. The distinction between cation and neutral species at the disordered site in the structure model is unclear, but a required assumption for charge balance. Bismuth has a very similar 8-coordinate geometry to that observed in **1** (Fig. 4), but here the Bi–O distances in the chelating linkage are a more equivalent than in **1** (Table 2). Topological differences to that observed in **1** do, however, present themselves in the alignment of the pdc-COO ligands in **2** (Fig. 5): instead of adjacent tridentate and monodentate ligands at the same Bi(III) centre running off approximately at right angles to form two sides of the oblique grid, the same two ligands have twisted about their 4-carboxylate groups so that opposite ends bond to the same adjacent Bi(III) cation. These two ligands are then related across a centre of inversion and form a double pdc-COO bridge between adjacent Bi(III) centres which lie 8.6122(2) Å apart. The consequence of this is that the extended structure of **2** exists as one-dimensional ribbon-like chains directed along the [100] direction. A (2,4) net results according to Wells notation. The circuit

enclosed by one chain link measures approximately 8.61×3.27 Å. Each chain runs along a crystallographic two-fold axis and all chains in the structure are parallel with the shortest interchain Bi···Bi distances being 10.5547 (5) and 11.5660(9) Å. The 4-aminopyridinium cations and 4-aminopyridine solvent molecules are distributed within the channels that run parallel to the anionic chains. Void space calculations run through *PLATON* show that 59% of the unit cell volume (2125 Å³) is void upon removal of the cations and solvent molecules.

Fig. 4. Displacement ellipsoid plot of the Bi(III) coordination environment in **2** (50% probability ellipsoids; symmetry codes: (i) 1-*x*, 1-*y*, 1-*z*; (ii) $\frac{1}{2}+x$, 1-*y*, *z*; (iii) $\frac{3}{2}-x$, *y*, 1-*z*).

Each ordered 4-aminopyridinium cation cross-links three anionic chains of **2** through N– H···O hydrogen-bonds (Table 3) between all available N–H donors and adjacent pdc-COO carboxylate O-atoms (two coordinating and one non-coordinating O-atom). Pairs of 4-aminopyridine cations sit either side of centres of inversion with their amine groups facing inwards, thereby forming a R⁴₄(12) graph set motif [21] with the carboxylate O-atoms from two chains. The disordered cations also congregate in pairs across centres of inversion and each of these cations cross-links two anionic chains. Overall, the classic hydrogen-bonding interactions complete a three-dimensional framework of cations and anionic chains (Fig. 5). There are $\pi \cdots \pi$ interactions between the parallel pyridine rings within each centrosymmetric double pdc-COO bridge (see Table 4 for the parameters). Short centrosymmetric stacks of four 4-aminopyridinium cations also show $\pi \cdots \pi$ interactions; the inner pair have significant slippage of their centres of gravity, while the outer pair are aligned with little slippage, but the ring planes are tilted by 12.8(7)°.

Fig. 5. Graphical representation of 2: 1-dimensional ribbons are interconnected through a hydrogen-bonding network. Cation disorder not shown.

Table 4

Geometric parameters of the $\pi \cdots \pi$ interactions in 2–6.

3.2.3. { $[Bi_2(\mu-pdc-COO)_2(\mu-pdc-COOH)(pdc-COOH)][NH_2Me_2]_4$ ·2dmf·NHMe₂}_n(3)

Replacing 4-aminopyridine, as used to produce **2**, with either of 2-aminopyridine, 3aminopyridine or 4,4'-bipyridine yielded colourless needles of **3** in each instance. Single crystal analysis revealed a space group of I2/a.

The model for the asymmetric unit of **3** contains two symmetry-independent Bi(III) cations two pdc-COO and two monoprotonated pdc-COOH anions, two dimethylammonium cations and a dmf molecule. The carboxylic acid group at the 4-position of the pyridine ring of the pdc-COOH ligand coordinated to Bi1 is non-coordinating and the H-atom could be located. The C–O distances in

this group also support the presence of carboxylic acid and not carboxylate. The corresponding Hatom of the pdc-COOH ligand could not be located, because of complete disorder of the tridentate ligands coordinating to Bi2, but is assumed to be there; that carboxylic acid group is also noncoordinating. The C–O distances are less indicative in this case, because of restraints used for the disorder modelling. No additional species were unambiguously discernible in difference electron density maps, but four void spaces of 682 Å³ remain per unit cell, which equates to 341 Å³ per asymmetric unit. Application of the *SQUEEZE* procedure [17] revealed 119 e per asymmetric unit. Given that the species described above leave a charge imbalance, it is assumed that there are two more dimethylammonium cations in the void space in the asymmetric unit and the void-space electron count is matched if one assumes one additional dimethylamine molecule and one additional dmf molecule are also in the asymmetric unit. Thus the overall composition of **3** is proposed as being $\{[Bi_2(\mu-pdc-COO)_2(\mu-pdc-COOH)(pdc-COOH)][NH_2Me_2]_4\cdot 2dmf\cdotNHMe_2\}_n$.

The two symmetry-independent Bi(III) centres each have similar atomic connectivity to that observed in each of **1** and **2**: bismuth is 8-coordinated by two tridentate pdc-COO ligands, one of which is pdc-COOH, and two monodentate carboxylate oxygen atoms from two further pdc-COO ligands (Fig. 6). However, the origins of the monodentate oxygen atoms differ for each Bi centre. At Bi1, the monodentate interactions are with an oxygen atom of the 4-carboxy-position of two different pdc-COO ligands. At Bi2, one monodentate interaction is with the second oxygen atom of the 4-carboxy-position of one of the monodentate pdc-COO ligands interacting with Bi1, so that this carboxylate group is ditopic and links Bi1 to Bi2, while the other monodentate interaction is with one of the ortho-carboxylate groups of the pdc-COOH ligand of Bi1 thereby forming an additional O-atom bridge between Bi1 and Bi2. This connectivity results in a highly distorted 6-membered Bi₂CO₃ ring; a motif that is not present in the structures of **1** and **2**. The Bi–O and Bi–N bond distances (Table Bi–O distances involving oxygen atoms involved in the bridges within the Bi₂CO₃ ring tend to be slightly longer than otherwise.

Fig. 6. Displacement ellipsoid plot of the Bi(III) coordination environment in **3** (50% probability ellipsoids; major disorder conformation; symmetry codes: (i) x, 1+y, z; (ii) x, -1+y, z).

Table 5

Bond distances (Å) around each of the two bismuth(III) environments in 3^a.

The supramolecular anionic structure is that of ladders extending in the [010] direction (Fig. 6). The uprights in the ladder are composed solely of Bi1 centres on one side and Bi2 centres on the other side, with adjacent Bi-centres along each upright being linked by a single pdc-COO ligand

through its head and tail. The rungs of the ladder are formed by the cross-linking effect of the Bi_2CO_3 ring. The pdc-COOH ligands act as decoration protruding from the ladder as terminal extensions of the rungs. The Wells notation for the ladder motif is (4,3). The Bi \cdots Bi distance across the ladder rung is 4.4630(16) Å, while the Bi \cdots Bi distance along each upright is 9.5592(6) Å. The resultant pore between the roughly antiparallel pdc-COO ligands in the rungs of the ladder is extremely distorted.

It is difficult to be definitive about the dimensionality of the supramolecular network generated by the hydrogen-bonding interactions, because not all cations and solvent molecules could be included in the model. The two defined dimethylammonium cations reinforce the ladder motif through their hydrogen bonds (Table 3). The carboxylic acid group of one pdc-COOH ligand cross-links adjacent ladders via the free oxygen atom of a carboxy group involved in the tridentate coordination to a bismuth cation to give a two-dimensional network of sheets that lies parallel to the (001) plane. Although the H-atom of the other pdc-COOH ligand could not be located, the O···O distances suggest there is an interaction here which links two adjacent sheets related by a centre of inversion into pairs. These double sheets then stack along [001] with dimethylammonium cations and dmf solvent molecules between them (Fig. 7). There are weak $\pi \cdots \pi$ interactions between the N4-pyridine rings of disordered non-bridging pdc-COOH ligand and the pdc-COO ligand are not involved in such interactions.

Fig. 7. The extended chains in 3 sandwiching a channel of hydrogen-bonded dimethylammonium counterions and dmf molecules (the minor component of the anion disorder and the upper part of the unit cell box are not shown).

3.2.4. Comparison of the structures of the Bi(III) coordination polymers

Each of the structures **1-3** possesses the same bis-tridentate $Bi(pdc-COO)_2$ core, with a dihedral angle between the pdc-COO planes of approximately 85-90°. The Bi(III) centres are always 8-coordinate with the two remaining bonding interactions arising from either the 4-carboxylate group of adjacent pdc-COO ligands or, as in the case of **3** only, a bridging interaction involving one of the tridentate-binding carboxylate oxygen atoms. No solvent molecules or non-pdc-COO entities are bound directly to Bi(III). **1** and **2** are identical in the sense of coordination environment at each bismuth centre. Differences in topology in this case arise from the relative orientation of the pdc-COO ligands: in **1**, chains of ligands intersect at the Bi(III) centres to give an oblique two-dimensional grid pattern with sides strictly parallel (Fig. 3). In **2**, adjacent Bi(III) centres are linked via a centrosymmetric double-bridge through two antiparallel pdc-COO moieties to give a chain-of-rings motif. Each successive link in the chain is approximately orthogonal to its neighbour, giving rise to the ribbon-like topology. The structure of **3** also contains a comparable sub-structure chain motif to that found in **1**, but additional bridging modes not observed in **1** are present, leading to the anionic

ladder structure (Fig. 6).

The local coordination topology of the Bi(III) centres in all structures, including the structures of **4-6** discussed below, can be analysed in terms of the ideas of Kepert for 8-coordinate bis(tridentate ligand) bis(monodentate ligand) metal complexes [22]. The angle subtended at the Bi(III) centre for the formally monodentate connections lie between 95 and 126°. The higher end of this range (116-126°) is adopted by monodentate connections where at least one of the connections is part of a bridge between Bi(III) centres, while 103-106° occurs when there are two monodentate non-bridging ligands, as only found in **1** and **2**. An outlier of 95° occurs at Bi2 in **3** where both monodentate ligands are O-or carboxylate-bridging. All N–Bi–N angles between tridentate ligands are tightly clustered between 125 and 134° across all structures, while the O···N···O angles (the ABC definition of Kepert) range from 112-116°. The normalized bite of a tridentate ligand, the *b*-value of Kepert, is defined as the (mean) distance between the donor atoms of the chelate divided by the (mean) metal-donor atom distance [22]. The *b*-values for **1-6** have a very narrow range of 1.04 to 1.09. The values from the structures reported here are thus consistent with the examples of Kepert, which are attributed to a coordination topology that lies between that of a square antiprism and that of a hexagonal bipyramid.

3.3. Discrete Bi(III) anionic complexes: substituting the 4–COOH group

The effect on the Bi-coordinating and framework-building properties of pdc-COO was investigated by replacing the carboxylic acid at the 4-position of the pdc-COO ring with another potentially coordinating substituent, namely 4-hydroxy, 4-amino and 4-chloro.

3.3.1. $[Bi_2(\mu - pdc - R)_2(pdc - R)_2(dmf)_2][NH_2Me_2]_2 [R = OH (4), NH_2 (5)]$

The reaction of Bi₂O₃ with the 4-hydroxy-2,6-pyridine dicarboxylic acid and 4-amino-2,6pyridine dicarboxylic acid derivatives, H₂pdc-OH and H₂pdc-NH₂, under the same conditions used for the synthesis of **1-3** gave rise to discrete centrosymmetric dinuclear Bi(III) anions as their dimethylammonium salts, **4** (Fig. 8) and **5** (Fig. S2), respectively. Each of these complexes crystallized as colourless blocks with space group $P\overline{1}$ and their structures are essentially isostructural. Each has the general formula [Bi₂(μ -pdc-R)₂(pdc-R)₂(dmf)₂][NH₂Me₂]₂, wherein the asymmetric unit contains a single bismuth centre coordinated by two pdc-R ligands in a tridentate pincer-like manner, a disordered dmf ligand coordinating via its O-atom and a discrete dimethylammonium counter-ion. One of the carboxylate O-atoms coordinating to the bismuth centre also coordinates to the other, centrosymmetrically-related, bismuth centre in the anion. This completes the 8-coodination of each bismuth centre and the two Bi(III) centres are thus bridged by two O-atoms to give a Bi₂O₂ core (Table 6). The pdc-R ligand not involved in the O-bridge and the dmf ligand lie roughly perpendicular to the Bi₂O₂ plane. A similar dinuclear anion has been observed in the structure of the 2-amino-3ammoniopyridinium salt of [Bi₂(µ-pdc)₂(pdc)₂(H2O)₂] [23].

Fig. 8. Displacement ellipsoid plot of the dinuclear Bi(III) anion and Bi₂O₂ core in **4** (50% probability ellipsoids; major disorder conformation of the dmf ligand; symmetry code: (i) 1-*x*, 1-*y*, 1-*z*). The anion in **5** is almost identical in appearance.

Table 6

Bond distances (Å) around the unique bismuth(III) centre in 4-6.

In 4, N–H···O hydrogen bonds from pairs of dimethyl ammonium cations link adjacent anions into a supramolecular chain, which runs parallel to the $[01\overline{1}]$ direction. The hydrogen-bond acceptors are non-coordinating carboxylate O-atoms of pdc-OH ligands (Table 3). The hydroxy group of one symmetry-independent pdc-OH ligand forms a hydrogen bond with a non-coordinating carboxylate O-atom of an anion from a different supramolecular chain, while the other hydroxy group interacts with a coordinating carboxylate O-atom of an anion in a third chain. Taken together, the hydrogen-bonding interactions link all species in the crystal into a three-dimensional supramolecular framework, which consists of alternating layers of cations and anions lying parallel to (001) (Fig. 9). The pattern of hydrogen bonding interactions in **5** is very similar (Fig. S3), except that one of the unique amine groups hydrogen-bonds to non-coordinating O-atoms of two other anions from separate supramolecular chains, while the other amine group hydrogen-bonds to two coordinating O-atoms of a single neighbouring anion of a fourth chain.

There are weak $\pi \cdots \pi$ interactions between centrosymmetrically-related bridging pdc-OH ligands in adjacent dinuclear anions of **4**, which link the anions into stepped chains running parallel to the [100] direction (Table 4). There are additional weak $\pi \cdots \pi$ interactions between centrosymmetrically-related but quite offset pyridine rings of non-bridging pdc-OH ligands, so that these pendant ligands from adjacent chains of anions in the [010] direction interdigitate and form stack of molecules through these rings. Despite the long distances between the centres of gravity of the rings and the slippage values, it has been argued that such interactions are still energetically relevant [24]. The $\pi \cdots \pi$ interactions in **5** are similar, but the ring slippages and α angles (Table 4) indicate an even greater offset as a consequence of the spatial influence of the amine group of the pdc-NH₂ ligands.

Fig. 9. Alternating layers of hydrogen-bonded cations and anions in 4 (major disorder conformation of the dmf ligand; 5 is almost identical).

3.3.2. $[Bi_2(\mu-pdc)_2(pdc-NMe_2)_2(dmf)_2][NH_2Me_2]_2$ (6)

Although the reaction between Bi2O3 and H2pdc-Cl was carried out under the same conditions

that were used for the synthesis of **4** and **5**, the carboxylate ligand (pdc-Cl) undergoes substitution with dimethylamine derived from the dmf solvent to form pdc-NMe₂. Crystallising in space group $P\overline{1}$ as a colourless plate, the product of the reaction is a crystalline salt, which can be formulated as $[Bi_2(\mu-pdc)_2(pdc-NMe_2)_2(dmf)_2][NH_2Me_2]_2$, **6**. The anion is a centrosymmetric dinuclear species with the same distribution of ligands to those in **4** and **5**, but it does not contain the Bi₂O₂ bridge. Instead, the two Bi(III) centres are loosely joined *via* a carboxylate bridge, in which one of the Bi–O bonds is quite long at 2.9689(17) Å (Fig. 10, Table 6). The altered arrangement possibly results from the presence and exchange of chloride anions in the reaction mixture; dimethylamine has larger spatial requirements and lacks the hydrogen-bonding capacity exhibited by the 4-substituents associated with **4** and **5**.

The discrete dimethylammonium cations form hydrogen bonds with carboxylate O-atoms in adjacent anions of **6** and thereby link the anions in an alternating fashion into extended chains, which run parallel to the [010] direction and can be described by a graph set motif of $C_2^2(8)$ (Fig. 11, Table 3). There are weak very offset $\pi \cdots \pi$ interactions between the pdc-NMe₂ ligands containing atom N2, which are involved in the bridging between the Bi(III) centres (Table 4). Each of these pdc pyridine rings has a further weak centrosymmetric $\pi \cdots \pi$ interaction on the other side with its symmetry-related counterpart from a neighbouring anion and so the anions are linked into slanted stacks, which run parallel to the [100] direction. Additionally, adjacent stacks in the [010] direction are linked by weak centrosymmetric offset $\pi \cdots \pi$ interactions between the non-bridging pdc-NMe₂ ligands containing atom N1.

Fig. 10. Displacement ellipsoid plot of the dinuclear Bi(III) anion in **6** (50% probability ellipsoids; symmetry code: (i) 1-*x*, 1-*y*, -*z*).

Fig. 11. The hydrogen-bonded chains of cations and anions in 6.

4. Conclusion

Bismuth coordination polymers were obtained in each case where the pdc-COO ligand was used, but not when the 4-carboxylate group of the ligand was replaced by the less strongly coordinating 4-hydroxy, 4-amino and 4-chloro substituents. The underlying net topology of the bismuth coordination polymers can be altered through varying reaction additives without altering the local connectivity. Additionally, the use of bismuth oxide as a metal source yields Bi_2O_2 metal clusters which provide a promising lead in the further development of extended bismuth-organic structures.

CRediT authorship contribution statement

Levi Senior: Conceptualisation, Investigation, Methodology, Visualisation, Validation, Writing original draft. Anthony Linden: Conceptualisation, Supervision, Visualization, Validation, Writing review & editing, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

CCDC 1988080–1988085 contain the supplementary crystallographic data for **1–6**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/structures. Supplementary data to this article can be found online at ...

References

- [1] H. Furukawa, K.E. Cordova, M.O'Keeffe, O.M. Yaghi, Science 341 (2013) 6149.
- [2] M.J. Kalmutzki, N. Hanikel, O.M. Yaghi, Sci. Adv. 4 (2018) eaat9180.

[3] Y. Yang, R. Ouyang, L. Xu, N. Guo, W. Li, K. Feng, L. Ouyang, Z. Yang, Y. Miao, J. Coord. Chem. 68 (2015) 379.

- [4] H.L. Dupont. Drug Intell. Clin. Pharm. 21 (1987) 687.
- [5] G. Wang, Y. Liu, B. Huang, X. Qin, X. Zhang, Y. Dai, Dalton Trans. 44 (2015) 16238.
- [6] T. Rhauderwiek, C. Cunha, H. Terraschke, N. Stock, Eur. J. Inorg. Chem. (2018) 3232.
- [7] X.-P. Zhang, H.-R. Tian, G.-F. Yan, Y. Su, Y.-L. Feng, J.-W. Cheng, Dalton Trans. 42 (2013) 1088.

- [8] A.C. Wibowo, M.D. Smith, H-C. Loye, Cryst. Growth Des. 11 (2011) 4449.
- [9] Y.-Q. Sun, S.-Z. Ge, Q. Liu, J.-C. Zhong, Y.-P. Chen, CrystEngComm 15 (2013) 10188.
- [10] B. Seyfried, B. Schink, Biodegradation 1 (1990) 1.
- [11] L. Syper, K. Kloc, J. Mkochowski, Tetrahedron 36 (1980) 123.
- [12] J.B. Lamture, Z.H. Zhou, A.S. Kumar, T.G. Wensel, Inorg. Chem. 34 (1995) 864.

[13] Rigaku Oxford Diffraction, CrysAlisPro Software System, Version 1.171.40.53, Rigaku Corporation, Oxford, UK, 2019.

[14] G.M. Sheldrick, Acta Crystallogr. A: Found. Adv. 71 (2015) 3.

[15] G.M. Sheldrick, Acta Crystallogr. C: Struct. Chem. 71 (2015) 3.

- [16] S. Parsons, H. D. Flack, T. Wagner, Acta Crystallogr. B: Struct. Sci., Cryst. Eng. Mater. 69 (2013) 249.
- [17] A.L. Spek, Acta Crystallogr. C: Struct. Chem. 71 (2015) 9.

[18] A.D. Burrows, K. Cassar, R.M.W. Friend, M.F. Mahon, S.P. Rigby, J.E. Warren, CrystEngComm 7 (2005) 548.

[19] A.F. Wells, Acta Crystallogr. 7 (1954) 534.

[20] V.A. Blatov, A.P. Shevchenko, D.M. Proserpio, Cryst. Growth Des. 14 (2014) 3576.

[21] J. Bernstein, R.E. Davis, L. Shimoni, N.-L. Chang, Angew. Chem. Int. Ed. Engl. 34 (1995) 1555.

[22] D.L. Kepert, in: S.J. Lippard (Ed.), Progress in Inorganic Chemistry, John Wiley & Sons, Inc., New York, 1978, Vol. 24, pp. 179-249.

[23] H. Aghabozorg, S. Kazemi, A.A. Agah, M. Mirzaei, B. Notash, Acta Crystallogr. E: Struct. Rep. Online 67 (2011) m360.

[24] R. Kruszynski, T. Sierański, Cryst. Growth Des. 16 (2016) 587.

Crystallographic data for 1–6.

Structure	1	2	3	4	5
Empirical formula	C22H28BiN5O12	C ₃₆ H ₃₁ BiN ₁₀ O ₁₂	$C_{48}H_{63}Bi_2N_9O_{26}\\$	$C_{38}H_{42}Bi_2N_8O_{22}\\$	C ₃₈ H ₄₀
CCDC no.					
$M_{\rm r}$ (g/mol)	763.47	1004.69	1600.03	1380.75	1376.8
T (K)	160(2)	160(2)	160(2)	160(2)	160(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclir
Space group	<i>I</i> 2	I2/a	I2/a	$P\overline{1}$	$P\overline{1}$
Ζ	2	4	8	1	1
<i>a</i> (Å)	10.1017(2)	17.2134(3)	20.8376(3)	8.9911(3)	9.6056
<i>b</i> (Å)	8.39850(10)	11.5660(3)	9.55920(10)	11.8703(4)	12.109
<i>c</i> (Å)	16.8625(3)	18.0478(4)	58.5817(8)	12.0770(4)	12.123
α (°)	90	90	90	72.149(3)	69.554
β (°)	104.716(2)	91.009(2)	95.5360(10)	69.948(3)	67.031
γ(°)	90	90	90	72.692(3)	73.066
$V(Å^3)$	1383.67(4)	3592.58(14)	11614.5(3)	1125.52(7)	1196.8
Radiation, λ (Å)	Μο Κα, 0.71073	Μο Κα, 0.71073	Μο Κα, 0.71073	Μο Κα, 0.71073	Mo Ke
μ (mm ⁻¹)	6.441	4.990	6.145	7.902	7.427
D _{calc} (Mg m ⁻³)	1.832	1.858	1.830	2.037	1.910
Colour, habit	Colourless, block	Colourless, needle	Colourless, needle	Colourless, block	Colou
Crystal size (mm)	$0.26 \times 0.10 \times 0.05$	$0.12 \times 0.04 \times 0.03$	$0.20\times 0.07\times 0.04$	$0.18 \times 0.10 \times 0.06$	0.09 ×
θ range (°)	2.7–29.5	3.1–29.3	2.1-28.5	2.7–29.5	2.5-29
Absorption correction	Numerical	Spherical harmonics	Spherical harmonics	Numerical	Spheri
T_{\min}, T_{\max}	0.681, 1.000	0.913, 1.000	0.661, 1.000	0.760, 1.000	0.753,
Reflections measured	15131	20971	103887	24870	26563
Unique reflections	3472	4470	13517	5643	5970
R _{int}	0.035	0.059	0.082	0.061	0.057
Observed reflections $[I > 2\sigma(I)]$	3472	3950	11019	5085	5053
Data, parameters, restraints	3472, 229, 82	4470, 307, 202	13517, 936, 1279	5641, 358, 73	5970,
Goodness-of-fit on F^2	1.047	1.132	1.154	1.085	1.069
$R[F^2 > 2\sigma(F^2)]$	0.0218	0.0902	0.0702	0.0351	0.0349
$wR(F^2)$ (all data)	0.0512	0.2148	0.1551	0.0833	0.0646
$\Delta ho_{ m max}, \Delta ho_{ m min}$ (e Å ⁻³)	1.48, -0.86	10.37, -2.51	2.00, -1.96	2.40, -1.54	1.55, -

Symmetry-unique bond distances (Å) around the central bismuth(III) centre in 1 and 2.

	1	2
Bi1–O1	2.516(4)	2.466(9)
Bi1–O4 ⁱ	2.529(5)	2.495(8)
Bi1–O6	2.334(5)	2.411(9)
Bi1–N1	2.455(4)	2.480(9)

Symmetry codes for O4ⁱ in 1: $\frac{1}{2}+x$, $\frac{1}{2}+y$, $\frac{1}{2}+z$; in 2: 1-*x*, 1-*y*, 1-*z*.

Hydrogen-bond parameters for 1-6.

D–H···A	Symmetry code for A	D-H (Å)	$\mathrm{H}^{\ldots}A$ (Å) ^c	$D \cdots A$ (Å)	D–H···A (°)
1 ^a					
N2–H2A····O3	$-\frac{1}{2}+x$, $\frac{1}{2}+y$, $\frac{1}{2}+z$	0.91	2.01	2.76(2)	140
N2-H2B…O3	-3/2-x. $1/2+y$, $-3/2-z$	0.91	1.84	2.73(2)	166
N3–H3A…O1	-1- <i>x</i> , -1+ <i>y</i> , -1- <i>z</i>	0.91	1.97	2.775(9)	147
N3–H3B…O5		0.91	2.06	2.969(11)	174
2 ^a					
N2-H2…O1	$\frac{3}{2}-x$. $\frac{1}{2}-y$, $-\frac{3}{2}-z$	0.88	1.90	2.763(12)	167
N3–H31…O6	$^{3}/_{2}$ -x. y, 1-z	0.88	2.14	2.993(13)	163
N3–H32…O5	$x, \frac{3}{2}-y, -\frac{1}{2}+z$	0.88	2.13	2.989(13)	164
N4–H4…O2	$x, \frac{3}{2}-y, \frac{1}{2}+z$	0.88	1.91	2.711(17)	151
N5–H51…N5	¹ / ₂ - <i>x</i> . <i>y</i> , 1- <i>z</i>	0.88	2.43	3.06(4)	130
N5–H52…O3		0.88	2.37	3.08(3)	139
3 ^a					
09–Н9…017	¹ / ₂ + <i>x</i> , - <i>y</i> , <i>z</i>	0.84	1.70	2.528(14)	168
N5–H5A…O17		0.91	1.89	2.772(14)	164
N5–H5B…O1		0.91	1.82	2.717(11)	169
N6–H6A…O3	<i>x</i> , 1+ <i>y</i> , <i>z</i>	0.91	1.99	2.835(11)	153
N6–H6B…O25		0.91	2.06	2.889(11)	151
4					
O8–H8…O5	2- <i>x</i> , 1- <i>y</i> , 1- <i>z</i>	0.85(7)	1.80(7)	2.642(5)	171(7)
O3–H3…O7	-1+ <i>x</i> , 1+ <i>y</i> , <i>z</i>	0.92(7)	1.67(7)	2.584(5)	172(7)
N4–H4A…O2	1- <i>x</i> , 2- <i>y</i> , - <i>z</i>	0.91	1.97	2.822(6)	155
N4–H4B…O9		0.91	1.88	2.782(5)	175
5					
N3–H3A…O7	1+x, -1+y, z	0.88(6)	2.00(6)	2.871(5)	169(5)
N3–H3B…O9	1- <i>x</i> , - <i>y</i> , 1- <i>z</i>	0.79(5)	2.44(6)	3.196(6)	160(5)
N4–H4A…O5	- <i>x</i> , 1- <i>y</i> , 1- <i>z</i>	0.87(5)	2.10(5)	2.944(5)	164(5)
N4–H4B…O1	-1+x, y, z	0.88(6)	2.40(7)	3.148(5)	143(6)
N6–H6A…O2	1- <i>x</i> , - <i>y</i> , 2- <i>z</i>	0.91	1.91	2.783(5)	160
N6–H6B…O9		0.91	1.91	2.816(5)	175
6					
N5–H5A…O9		0.88(3)	1.89(3)	2.763(3)	171(3)
N5–H5B…O4	<i>x</i> , 1+ <i>y</i> , <i>z</i>	0.88(3)	2.08(4)	2.886(3)	152(3)
N5–H5B…O5	<i>x</i> , 1+ <i>y</i> , <i>z</i>	0.88(3)	2.34(4)	3.109(3)	147(3)

^a For disordered structures, only the parameters of the major conformation are listed.

Ring 1 ^a	Ring 2	Cg···Cg (Å) ℃	Distance	Slippage (Å)	α (°) ^d
			between ring		
			planes (Å)		
2 ^b					
N1	N1(1- <i>x</i> , 1- <i>y</i> , 1- <i>z</i>)	3.485(6)	3.275(4)	1.191	20.0
N2	$N2(^{3}/_{2}-x, \frac{1}{2}-y, \frac{1}{2}-z)$	4.169(7)	3.233(5)	2.632	39.1
N2	$N3(\frac{1}{2}+x, -\frac{1}{2}+y, -\frac{1}{2}+z)$	3.625(8)	3.471(5)	0.745	11.9
3 ^b					
N4	N4(1- <i>x</i> , 1- <i>y</i> , 1- <i>z</i>)	4.618(6)	3.827(5)	2.583	34.0
4					
N1	N1(- <i>x</i> , 2- <i>y</i> , 1- <i>z</i>)	4.822(3)	3.257(2)	3.566	47.5
N1	N1(1- <i>x</i> , 2- <i>y</i> , 1- <i>z</i>)	4.627(3)	3.429(2)	3.106	42.2
N2	N2(2- <i>x</i> , 1- <i>y</i> , 1- <i>z</i>)	3.972(2)	3.240(2)	2.298	35.4
5					
N1	N1(1- <i>x</i> , - <i>y</i> , 1- <i>z</i>)	4.991(3)	3.684(2)	3.366	42.4
N1	N1(2- <i>x</i> , - <i>y</i> , 1- <i>z</i>)	5.321(3)	2.970(2)	4.415	56.1
N2	N2(- <i>x</i> , 1- <i>y</i> , 1- <i>z</i>)	4.139(2)	3.278(2)	2.527	37.6
6					
N1	N1(1- <i>x</i> , - <i>y</i> , 1- <i>z</i>)	4.6271(12)	3.3512(9)	3.191	43.6
N2	N2(1- <i>x</i> , 1- <i>y</i> , - <i>z</i>)	5.5964(13)	3.1172(9)	4.648	56.2
N2	N2(2- <i>x</i> , 1- <i>y</i> , - <i>z</i>)	4.8590(13)	3.4305(9)	3.441	45.1

Geometric parameters of the $\pi \cdots \pi$ interactions in 2–6.

^a The first two columns list the label of the N atom of the pyridine ring involved.

^b For disordered structures, only the parameters of the major conformation are listed.

^c Cg is the centre of gravity of a pyridine ring.

^d α is the angle between the Cg···Cg vector and the normal to the ring planes.

Table 5		

Bi1–O1	2.483(6)	Bi2–O7	2.540(8)
Bi1-O4 ⁱ	2.450(6)	Bi2013	2.472(6)
Bil-O6	2.345(6)	Bi2–O15 ⁱⁱ	2.531(12)
Bil-O7	2.603(8)	Bi2–O18	2.487(5)
Bi1–O12	2.242(7)	Bi2–O19	2.470(6)

Bi2-024

Bi2-N3

Bi2-N4

Bond distances (Å) around each of the two bismuth(III) environments in 3^a.

2.481(8) Symmetry codes: (i) x, 1+y, z; (ii) x, -1+y, z.

2.729(12)

2.459(7)

^a Only the distances for the major disorder conformation of Bi2 are shown; those from the minor conformation are similar (restraints applied).

2.474(6)

2.500(7)

2.484(7)

Table 6

Bi1-O16ii

Bi1-N1

Bi1-N2

Bond distances (Å) around the unique bismuth(III) centre in 4-6.

	4	5	6
Bi1–O1	2.464(3)	2.548(3)	2.2396(15)
Bi1–O5	2.339(3)	2.281(3)	2.5995(17)
Bi1–O6	2.686(3)	2.609(3)	2.2636(16)
Bi1–O6 ⁱ	2.663(3)	2.558(3)	_
Bi1–O9 ⁱⁱ	-	_	2.9689(17)
Bi1-O10	2.289(3)	2.336(3)	2.6677(16)
Bi1–O11	2.566(4)	2.645(4)	2.5793(16)
Bi1–N1	2.387(4)	2.366(3)	2.3662(18)
Bi1–N2	2.489(4)	2.442(3)	2.4334(19)

Symmetry codes: (i) 1-x, 1-y, 1-z; (ii) 1-x, 1-y, -z.

CRediT authorship contribution statement

Levi Senior: Conceptualisation, Investigation, Methodology, Visualisation, Validation, Writing - original draft. Anthony Linden: Conceptualisation, Supervision, Visualization, Validation, Writing - review & editing, Project administration.

Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Three 1- and 2-dimensional bismuth-organic-frameworks have been synthesized from Bi_2O_3 and 2,4,6-pyridine tricarboxylic acid in the presence of a variety of additives. In contrast, replacement of the 4-carboxy group with weaker donor groups results in discrete dinuclear anions.















