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(-pdc-COO)2][NH2Me2]3n, 1, [Bi(-pdc-COO)2][C5H7N2]3·C5H6N2n, 2, and [Bi2(-pdc-COO)2(pdc-COOH)(pdc-COOH)][NH2Me2]4·2dmf·NHMe2n, 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(-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(-pdc-NMe2)2(pdc-NMe2)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.

DOI: https://doi.org/10.1016/j.poly.2020.114564

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ZORA URL: https://doi.org/10.5167/uzh-187695
Journal Article
Published Version

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Originally published at:
Senior, Levi; Linden, Anthony (2020). Coordination polymers incorporating Bi(III) and 2,4,6-pyridine tricarboxylic acid and its derivatives: Synthesis, structure and topology. Polyhedron, 184:114564.
DOI: https://doi.org/10.1016/j.poly.2020.114564
Coordination polymers incorporating Bi(III) and 2,4,6-pyridine tricarboxylic acid and its derivatives: Synthesis, structure and topology

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A R T I C L E   I N F O

Article history:
Received 5 March 2020
Accepted 14 April 2020
Available online 18 April 2020

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

A B S T R A C T

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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, dimethylformamide (dmf) and aminopyridine additives in solvothermal syntheses in order to synthesise 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.

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. $^1$H and $^{13}$C 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 (H$_2$pdcooH)

H$_2$pdcooH was synthesized according to the literature [11]. To 2,4,6-trimethylpyridine (4.84 g, 0.04 mol) in H$_2$O (80 mL) in a 250 mL round-bottomed flask, KMnO$_4$ (50 g, 0.32 mol) was added over 4 h while maintaining a temperature of 20–30 °C. The resulting mixture was left to stir at room temperature for 16 h. Increasing the temperature to 50 °C, the reaction mixture was left to stir for a further 48 h before cooling and filtering through fritted filter paper in order to remove solid MnO$_2$ from the reaction. The residue was washed with distilled water and the resulting filtrate evaporated to yield a white solid (3.24 g, 38%). $^1$H NMR (400 MHz, D$_2$O): δ 8.58 (s, 2H). $^{13}$C NMR (400 MHz, D$_2$O): δC 127.4, 142.2, 148.5, 166.5, 166.9.

2.1.2. Synthesis of 4-amino-2,6-pyridine dicarboxylic acid (H$_2$pdco-NH$_2$)

H$_2$pdco-NH$_2$ was synthesized according to the literature [12].

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

2.2.1. [Bi$_2$([μ-pdc-COO])$_2$][NH$_3$Me$_2$]$_2$ (1)

H$_2$pdcooH (50 mg, 0.2368 mmol) was dissolved in dimethylformamide (dmf, 6 mL) in a 15 mL screw-capped vial. Bi$_2$O$_3$ (110.3 mg, 0.2368 mmol) was added, the cap screwed on tightly and the vial sonicated at room temperature for 10 min. 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 a layer of grey-black crystalline powder.

2.2.2. [Bi$_2$([μ-pdc-COO])$_2$][C$_3$H$_7$N$_2$]$_2$C$_5$H$_5$N$_2$]$_2$ (2)

H$_2$pdcooH (50 mg, 0.2368 mmol) was dissolved in dmf (6 mL) in a 15 mL screw-capped vial. Bi$_2$O$_3$ (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 min. 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$_2$([μ-pdc-COO])$_2$([μ-pdc-COOH])[pdc-COOH]][NH$_3$Me$_2$]$_2$2dmf[NHMe$_2$]$_2$ (3)

H$_2$pdcooH (50 mg, 0.2368 mmol) was dissolved in dmf (6 mL) in a 15 mL screw-capped vial. Bi$_2$O$_3$ (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 min. 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$_2$([μ-pdc-R])$_2$([μ-pdc-R])[pdc-R])][NH$_3$Me$_2$]$_2$ [R = OH (4), NH$_2$ (5)]

H$_2$pdco-OMe or H$_2$pdco-NH$_2$ (50 mg) was dissolved in dmf (6 mL) in a 15 mL screw-capped vial. Bi$_2$O$_3$ (1 equiv.) was added and the vial sonicated at room temperature for 10 min. 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$_2$([μ-pdc-NMe$_2$])$_2$([μ-pdc-NMe$_2$])[pdc-NMe$_2$])][NH$_3$Me$_2$]$_2$ (6)

H$_2$pdco-CI (50 mg) was dissolved in dmf (6 mL) in a 15 mL screw-capped vial. Bi$_2$O$_3$ (1 equiv.) was added and the vial sonicated at room temperature for 10 min. 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 area-detector diffractometer [13] using Mo Kα radiation ($λ = 0.71073$ 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 occupancy 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.
3. Results and discussion

3.1. Syntheses

Compound 1 resulted from the solvothermal reaction between Bi$_2$O$_3$ and H$_2$pdC-COOH alone in dmf. The reactions that included various pyridines as additives were conducted to evaluate the role of the pdc$_2$ of the pyridine in structure direction. While compound 2 resulted from the use of 4-amino pyridine (pK$_a$ = 9.17), compound 3 was obtained consistently with 3-amino pyridine (pK$_a$ = 6.00), 2-amino pyridine (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, H$_2$pdC-COOH is slowly deprotonated by the oxidation of dmf to dimethylamine or dimethylammonium cations [18]. In 2 and 3, however, the H$_2$pdC-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$_2$O$_3$, 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$_2$O$_3$ 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 M 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(μ-pdc-COO)$_2$]$_2$][NH$_2$Me$_2$]$_2$ (1)

Reaction of H$_2$pdC-COOh with Bi$_2$O$_3$ (1:1) in dmf at 120 °C yielded phase-pure colourless block crystals of 1 within 24 h. Single crystal analysis of 1 revealed a 2-dimensional anionic framework with overall stoichiometry [[Bi(μ-pdc-COO)$_2$]$_2$][NH$_2$Me$_2$]$_2$], space group I2.

The asymmetric unit of 1 contains one fully deprotonated pdc$_2$-COOH 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.

Each pdc-COO ligand bridges two Bi(III) cations and each Bi(III) is coordinated by four linkers to give extended 2-dimensional
3.2.2. \([\{\text{Bi(III-pdc-COO)}\}_2\text{C}_7\text{H}_2\text{N}_2\text{C}_6\text{H}_6\text{N}_2\_n\} (2)\]

With the addition of 1 M 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 \(\{\text{Bi(III-pdc-COO)}\}_2\text{C}_7\text{H}_2\text{N}_2\text{C}_6\text{H}_6\text{N}_2\_n\}\) lies on a two-fold axis and the asymmetric unit additionally includes one pdc-COO anion, one ordered 4-aminopyridination 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 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 \([8^4.12^2] (8^2)\), a 2-nodal 2,4 net with stoichiometry \(2\text{-c}\)\(2\text{-c}\), and apparently a new topology (Supplementary fig. S1). The sheets lie parallel to the \((1 0 0)\) plane. The point symbol for the net by 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 Bi–Bi distance 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.

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-aminopyridinium cations sit either side of centres of inversion with their amine groups facing inwards, thereby forming a \(R_2^\infty(12)\) 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 \(\pi...\pi\) interactions between the parallel pyridine rings within each centrosymmetric double

**Table 2**

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

Symmetry codes for O4 in 1: -3/2 - x, 1/2 + y, -3/2 - z; in 2: 1 - x, 1 - y, 1 - z.

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

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.

| D-H  | A     | Symmetry code for A | D-H (Å) | H - A (Å) | D - A (Å) | D-H  | A     |
|------|-------|---------------------|---------|-----------|-----------|------|-------|
| N2-H2A O3 | -1/2 + x, 1/2 + y, 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 - x, -1 + y, -1 - z | 0.91 | 1.97 | 2.77(9) | 147 |
| N3-H3B O5 | 0.91 | 2.06 | 2.96(11) | 174 |
| N2-H2 O1 | 3/2 - x, 1/2 - y, 1/2 - z | 0.88 | 1.90 | 2.76(12) | 167 |
| N3-H31 O6 | 3/2 - x, y, 1 - z | 0.88 | 2.14 | 2.99(3) | 163 |
| N3-H32 O5 | x, 3/2 - y, -1/2 + z | 0.88 | 2.13 | 2.98(9) | 164 |
| N4-H4 O2 | x, 3/2 - y, 1/2 + z | 0.88 | 1.91 | 2.71(17) | 151 |
| N5-H51 O5 | 1/2 - x, y, 1 - z | 0.88 | 2.43 | 3.06(4) | 130 |
| N5-H52 O3 | 0.88 | 2.37 | 3.08(3) | 139 |
| O9-H9 O17 | 1/2 + x, -y, z | 0.84 | 1.70 | 2.52(14) | 168 |
| N5-H5A O17 | 0.91 | 1.89 | 2.77(2) | 164 |
| N5-H5B O1 | 0.91 | 1.82 | 2.71(11) | 169 |
| N6-H6A O3 | x, 1 + y, z | 0.91 | 1.99 | 2.83(11) | 153 |
| N6-H6B O25 | 0.91 | 2.06 | 2.89(9) | 151 |
| O8-H8 O5 | 2 - x, 1 - y, 1 - z | 0.85(7) | 1.80(7) | 2.64(5) | 171(7) |
| O3-H3 O7 | -1 + x, 1 + y, z | 0.92(7) | 1.67(7) | 2.58(5) | 172(7) |
| N4-H4A O2 | 1 - x, 2 - y, -z | 0.91 | 1.97 | 2.82(6) | 155 |
| N4-H4B O9 | 0.91 | 1.88 | 2.78(5) | 175 |
| N3-H3A O7 | 1 + x, -1 + y, z | 0.88(6) | 2.00(6) | 2.87(5) | 169(5) |
| N3-H3B O9 | 1 - x, -y, 1 - z | 0.79(5) | 2.44(6) | 3.19(6) | 160(5) |
| N4-H4A O5 | -x, 1 - y, 1 - z | 0.87(5) | 2.10(5) | 2.94(5) | 164(5) |
| N4-H4B O1 | -1 + x, y, z | 0.88(6) | 2.40(7) | 3.14(5) | 143(6) |
| N6-H6A O2 | 1 - x, -y, 2 - z | 0.91 | 1.91 | 2.78(5) | 160 |
| N6-H6B O9 | 0.91 | 1.91 | 2.81(5) | 175 |
| N5-H5A O9 | 0.88(3) | 1.89(3) | 2.76(3) | 171(3) |
| N5-H5B O4 | x, 1 + y, z | 0.88(3) | 2.08(4) | 2.88(3) | 152(3) |
| N5-H5B O5 | x, 1 + y, z | 0.88(3) | 2.34(4) | 3.10(3) | 147(3) |

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

3.2.3. [Bi(µ-pdc-COOH)]$_2$[µ-pdc-COOH]$_2$[NH$_4$]$_2$[2dmf-NHMe$_2$]$_2$ (3)

Replacing 4-aminopyridine, as used to produce 2, with either of 2-aminopyridine, 3-aminopyridine 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 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 H-atom 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 non-coordinating. 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 Å$^3$ remain per unit cell, which equates to 341 Å$^3$ 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 \([\text{Bi}_2\mu\text{pdc-COOH}]_2[\text{pdc-COOH}][\text{NH}_2\text{Me}_2]_4\text{2dmfNHMe}_2\). 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 \(\text{Bi}_2\text{CO}_3\) ring; a motif that is not present in the structures of 1 and 2. The Bi–O and Bi–N bond distances (Table 5) are in similar ranges to those found in structures 1 and 2, with a slightly wider variation because the Bi–O distances involving oxygen atoms involved in the bridges within the \(\text{Bi}_2\text{CO}_3\) ring tend to be slightly longer than otherwise.
The supramolecular anionic structure is that of ladders extending in the [0 1 0] 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 $\text{Bi}_2\text{CO}_3$ 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–Bi distance across the ladder rung is 4.4630(16) Å, while the Bi–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 (0 0 1) 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 [0 0 1] with dimethylammonium cations and dmf solvent molecules between them (Fig. 7). There are weak π–π interactions between the N4-pyridine rings of disordered non-bridging pdc-COOH ligand in adjacent ladders, so that these pendant ligands interdigitate (Table 4). The other pdc-COOH ligand and the pdc-COO ligand are not involved in such interactions.

### 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-mdc-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 2, but additional bridging modes not observed in 2 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 a 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 to 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-aminoo and 4-chloro.

#### 3.3.1. [B_{12}(\mu-pdc-R_2)(\mu-pdc-R_2)(dmf)_2][NH_2Me_2]_2 [R = OH (4), NH_2 (5)]

The reaction of Bi$_2$O$_3$ with the 4-hydroxy-2,6-pyridine dicarboxylic acid and 4-aminoo-2,6-pyridine dicarboxylic acid derivatives, H$_2$pdch–OH and H$_2$pdch–NH$_2$, 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 (Supplementary fig. S2), respectively. Each of these complexes crystallized as colourless blocks with space group $P\bar{T}$ and their structures are essentially isosstructural. Each has the general formula $[B_{12}(\mu-pdc-R_2)(\mu-pdc-R_2)(dmf)_2][NH_2Me_2]_2$, wherein the asymmetric unit contains a single bismuth centre coordinated by two pdc-R ligands in a trigonate 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-coordination of each bismuth centre and the two Bi(III) centres are thus bridged by two O-atoms to give a Bi$_2$O$_2$ core (Table 6). The pdc-R ligand not involved in the O-bridge and the dmf ligand lie roughly perpendicular to the Bi$_2$O$_2$ plane. A similar dinuclear anion has been observed in the structure of the 2-amino-3-ammoniopyridinium salt of $[B_{12}(\mu-pdc-R_2)(\mu-pdc-R_2)(H_2O)_2]$ [23].

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 [0 1 0] 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

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**Table 5**

| Bond distances (Å) around each of the two bismuth(III) environments in 3'. |
|-----------------------------------|
| B1–O1                            | 2.484(6) |
| B1–O4a                           | 2.450(6) |
| B1–O6                            | 2.345(6) |
| B1–O7                            | 2.603(8) |
| B1–O12                           | 2.242(7) |
| B1–O16a                          | 2.729(12)|
| B1–N1                            | 2.459(7) |
| B1–N2                            | 2.481(8) |

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

*a Only the distances for the major disorder conformation of Bi2 are shown; those from the minor conformation are similar (restraints applied).*
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 (0 0 1) (Fig. 9). The pattern of hydrogen bonding interactions in 5 is very similar (Supplementary 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.

Table 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 | 2.666(3) | 2.609(3) | 2.2636(16) |
| Bi1–O6' | 2.663(3) | 2.558(3) | – |
| Bi1–O9' | – | – | 2.9689(16) |
| 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.

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).

Fig. 8. Displacement ellipsoid plot of the dinuclear Bi(III) anion and Bi$_2$O$_2$ 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.

Fig. 9. Alternating layers of hydrogen-bonded cations and anions in 4 (major disorder conformation of the dmf ligand; 5 is almost identical).
There are weak π⋯π 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 [1 0 0] direction (Table 4). There are additional weak π⋯π 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 [0 1 0] direction interdigitate and form stacks 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 π⋯π 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.

3.3.2. \([\text{Bi}_2(\mu-\text{pdc-NMe}_2\gamma)(\text{pdc-NMe}_2\delta)(\text{dmf})_2][\text{NH}_3\text{Me}_2\gamma_2](6)\)

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 \(\text{P} \overline{1} \text{C} \overline{1} \text{C} \overline{1} \text{C} \overline{1} \text{C} \overline{1} \text{C}\) as a colourless plate, the product of the reaction is a crystalline salt, which can be formulated as \([\text{Bi}_2(\mu-\text{pdc-NMe}_2\gamma)(\text{pdc-NMe}_2\delta)(\text{dmf})_2][\text{NH}_3\text{Me}_2\gamma_2]\). 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 [0 1 0] direction and can be described by a graph set motif of \(\text{C}^2_1(8)\) (Fig. 11, Table 3). There are weak very offset π⋯π 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 π⋯π 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 [1 0 0] direction. Additionally, adjacent stacks in the [0 1 0] direction are linked by weak centrosymmetric offset π⋯π interactions between the non-bridging pdc-NMe₂ ligands containing atom N₁.

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 coordination geometry. Additionally, the use of bismuth oxide as a metal source yields Bi₂O₃ metal clusters which provide a promising lead in the further development of extended bismuth-organic structures.

CRediT authorship contribution statement

**Levi Senior:** Conceptualization, Investigation, Methodology, Visualization, Validation, Writing - original draft. **Anthony Linden:** Conceptualization, 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.

Acknowledgements

This work was supported by the Department of Chemistry, University of Zurich, Switzerland.
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 https://doi.org/10.1016/j.poly.2020.114564.

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