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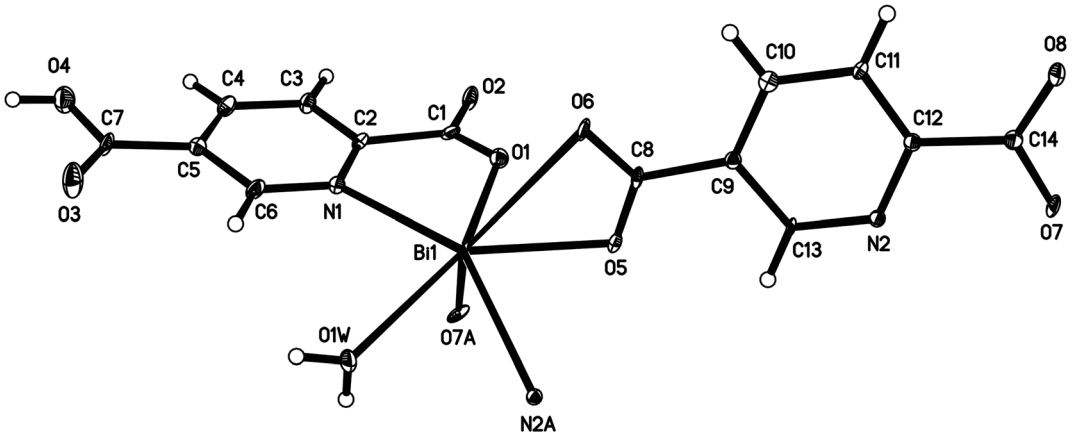
Crystal structure of *catena*-poly[aqua-(5-carboxypyridine-2-carboxylate-κ^2N,O)(2,5-pyridine-dicarboxylate-κ^4O,O′:N:O″)bismuth(III)], $C_{14}H_9BiN_2O_9$



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Abstract

$C_{14}H_9BiN_2O_9$, monoclinic, $P2_1/c$ (no. 14), a = 15.374(4) Å, b = 7.7838(18) Å, c = 12.694(3) Å, β = 109.525(4)°, V = 1431.7(6) Å^3, Z = 4, $R_{gt}(F)$ = 0.0378, $wR_{ref}(F^2)$ = 0.0965, T = 100 K.

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The molecular structure is shown in the figure. Table 1 contains the crystallographic data and the list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

1 Source of materials

The title polymer was synthesized through a hydrothermal method. The mixture of $Bi(NO_3)_3{\cdot}5H_2O$ (0.18 g, 0.38 mmol), 2,5-pyridine-dicarboxylic acid (0.09 g, 0.56 mmol), CH_3COOH (0.40 mL) and H_2O (2.60 g, 145 mmol) was stirred for 2 h, transferred into a 50 mL Teflon-lined stainless-steel autoclave, kept at 413 K for 120 h, and cooled down to room temperature at a rate of 5 K/h. The colorless rod crystals of the title compound were isolated (yield: ~63 % based on $Bi(NO_3)_3{\cdot}5H_2O$).

2 Experimental details

H atoms attached to C and O sites from the pdc^{2-} and $Hpdc^-$ ligand were positioned geometrically and refined using a riding model, with C–H = 0.95 Å and O–H = 0.84 Å, with U_{iso}(H) = 1.2 times U_{eq}(C) and 1.5 times U_{eq}(O), respectively. H atoms on the coordinated water molecule (O1W) were obtained by Fourier difference peaks. The restrictive orders of "dfix 0.83 H1WA O1W H1WB O1W" and "dang 1.37 H1WA H1WB" were applied to deal with the position of the H sites. The restrictive order of "isor" was employed to treat the slightly disordered sites in the structure.

3 Comment

The self-assembly of metal polymers using various N/O/S-containing multidentate ligands and metal cations with flexible coordination modes is an effective strategy in the synthesis of functional crystalline-phase materials.[4–9] These

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Table 1: Data collection and handling.

Crystal:	Colorless rod
Size:	0.32 × 0.28 × 0.25 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	12.4 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω scans
θ_{max}, completeness:	26.0°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7,480, 2,802, 0.056
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2,263
$N(param)_{refined}$:	241
Programs:	Bruker,[1] Olex2,[2] SHELX[3]

materials can demonstrate rich structural features, interesting topological architectures and multiple potential applications.[10–12] Herein, with the aid of the multidentate organic ligand 2,5-pyridine dicarboxylic acid (2,5-H_2pdc) and the metal Bi^{3+} cation, we synthesized a polymer $[Bi(C_7H_3NO_4)(C_7H_4NO_4)(H_2O)]_n$ ($C_7H_3NO_4$ = 2,5-pyridine-dicarboxylate, $C_7H_4NO_4$ = 5-carboxypyridine-2-carboxylate) by means of a hydrothermal method. X-ray single-crystal structural analysis indicates that the polymer exhibits a 3D supramolecular structure through O–H···O hydrogen bonds.

The molecular structure of the title compound is shown in figure. In order to better confirm the valence state of Bi site in the structure, we further calculated it by using the method of bond-valence calculations (BVS).[13] The results reveal that the valence state of Bi site is +III (+2.81). Its molecular structural unit consists of one Bi^{3+} cation, one $Hpdc^-$ anion, one pdc^{2-} anion and one water molecule. Within the molecular structure, the Bi(1) site is coordinated with the surrounding five O atoms and two N atoms, generating a seven-coordinated capped octahedral $\{BiO_5N_2\}$ geometric configuration. Among them, four O atoms come from one $Hpdc^-$ and two different pdc^{2-} anions, two N atoms come from one $Hpdc^-$ and one pdc^{2-} ligand, and one O atom belongs to one coordinated water molecule. The coordination mode of Bi^{3+} in the title compound can be compared with the previously reported Bi^{3+}-containing polymer $\{Bi_4(\mu_3\text{-}O)_2(\mu_4\text{-}O)_2(C_7H_3NO_4)_2\}_n$ (A),[14] although the qualities of coordinated atoms are different (the title compound: $\{BiO_5N_2\}$, A: $\{BiO_6N\}$), the Bi^{3+} cation displays seven-coordinated capped octahedral geometric configuration in the two polymers. In addition, compared with the two known polymers based on Bi^{3+} cation $\{[Bi(H_2O)]_2(C_7H_3NO)_2(C_{12}H_8N)_2(N_3)_2{\cdot}2H_2O\}_n$ (B)[15] and $\{[Bi^{III}Cu^{II}(C_7H_3NO_4)_2(NO_3)(C_{12}H_8N_2)(H_2O)]2H_2O\}_n$ (C),[16] the coordination geometric configurations of Bi^{3+} cations are different: the Bi^{3+} cation exhibits a $\{BiO_3N_5\}$ eight-coordinated dicapped trigonal prismatic geometry in polymer B, while in polymer C, the Bi^{3+} cation shows a $\{BiO_7N_2\}$ nine-coordinated tricapped trigonal prismatic geometric configuration. The bond distances of Bi–O and Bi–N span in the ranges of 2.208(6)–2.861(6) Å and 2.526(6)–2.542(7) Å, respectively. The angles of O–Bi–O and O–Bi–N fall in the scopes of 72.04(19)–139.0(2)°, 67.18(19)–140.17(19)°, respectively. The angle of N–Bi–N is 137.1(2)°. The above mentioned bond lengths and angles fall in their normal scopes and can be compared with the previously reported complexes based on Bi^{3+} cation.[8,14–16] Adjacent molecular structural units are interconnected through O(7) and N(2) atoms, extending into a 1D zigzag-chain structure. In this 1D zigzag-chain, each pdc^{2-} anion provides four coordination sites (one N and three carboxyl O atoms), while each $Hpdc^-$ anion only provides two coordination sites (one N and one carboxyl O atom), which leads to the distribution of two tetra-dentate pdc^{2-} ligands and one bidentate $Hpdc^-$ ligand around each Bi^{3+} cation. Each pdc^{2-} ligand is connected to two Bi^{3+} cations, and each $Hpdc^-$ ligand is linked to one Bi^{3+} cation by means of one O atom and one N atom. Under this connection mode, the formed distance of $Bi^{3+}\cdots Bi^{3+}$ is 8.250 Å. These neighboring chains are linked by the O–H···O hydrogen bonds [O1W–H1WA···O6, 2.760(8) Å, 174(9)°, x, 3/2 – y, –1/2 + z; O1W–H1WB···O2, 2.634(8) Å, 170(9)°, x, –1 + y, z; O4–H4A···O7, 2.995(8) Å, 120.8°, –1 + x, –1 + y, –1 + z; O4–H4A···O8, 2.695(8) Å, 166.6°, –1 + x, –1 + y, –1 + z] and $\pi\cdots\pi$ stacking effect [*Cg*1–*Cg*1^{i}, 3.300(3) Å, *Cg*1: C2–C6/N1, i = –x, 2 – y, 1 – z; *Cg*2–*Cg*2^{ii}, 3.426(3) Å, *Cg*2: C9–C13/N2, ii = 1 – x, 2 – y, 2 – z; *Cg*2–*Cg*2^{iii}, 3.300(3) Å, iii = 1 – x, 3 – y, 2 – z], resulting in the formation of a 3D supra-molecular structure.

The IR spectrum of the title compound was measured on a Perkin–Elmer FTIR spectrometer between 400 and 4,000 cm^{-1}. The peaks of 3,411 and 1,625 cm^{-1} are attributed to –OH units from the coordinated water molecules[17,18] and $Hpdc^-$ ligands. The peaks of 1,399, 1,361 and 1,284 cm^{-1} are belonged to the –COO groups from pdc^{2-} and $Hpdc^-$ ligands. The peaks of 3,102, 3,036 and 1,484 cm^{-1} and a series of peaks in the range of 1,239 and 640 cm^{-1} (1,239, 1,161, 1,136, 1,026, 814, 756, 685 and 640 cm^{-1}) can be assigned to the C–H vibrations from the pyridine rings.[19,20] In addition, the peaks of 524 and 446 cm^{-1} can prove the existence of Bi–O and Bi–N bonds.[15]

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