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Hydrothermal synthesis and crystal structure of poly[bis(μ_2 -3-(3,5-dicarboxyphenoxy)phthalato- $\kappa^3 O, O': O''$)-(μ_2 -1,2-di(pyridin-4-yl)ethane- $\kappa^2 N: N'$)copper(II)], $C_{22}H_{14}CuNO_9$

Table 1: Data collection and handling.

Crystal:	Blue block
Size:	0.33 × 0.28 × 0.23 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.14 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω -scans
$\theta_{\max}$, completeness:	25.5°, >85% (up to 25.2°: 99%)
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	10787, 3680, 0.029
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3252
$N(\text{param})_{\text{refined}}$:	300
Programs:	CyrsAlis ^{PRO} [1], SHELX [2, 3], OLEX2 [4]

on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The mixtures of 3-(3,5-dicarboxyphenoxy)phthalic acid (H_4L) (0.1 mmol, 36.0 mg), 1,2-di(pyridin-4-yl)ethane (bpa) (0.05 mmol, 10.0 mg), $Cu(NO_3)_2 \cdot 3H_2O$ (0.1 mmol, 24.0 mg), NaOH (0.1 mmol, 4.0 mg), and H_2O (6.0 mL) were sealed in a 23 mL Teflon-lined autoclave, heated to 433 K for 6 days, and then slowly cooled down to room temperature for crystallization. Blue block-shaped crystals of the title compound were obtained.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Discussion

Coordination polymers (CPs) have attracted more and more attention because of their potential use in many areas, such as catalysis [5], nonlinear optics [6], gas storage [7], molecular separation [8], luminescence [9], magnetism [10], sensors [11], electrochemistry [12], and so on. It has been still difficult to estimate the final structure because various factors, such as the geometries of the organic linkers, coordination modes of metal centers, pH, temperature, and solvents, have influence in the self-assembly process of CPs [13]. The semi-rigid multicarboxylate ligand 3-(3,5-dicarboxyphenoxy)phthalic acid has eight possible coordination sites which can supply more

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Abstract

$C_{22}H_{14}CuNO_9$, triclinic, $P\bar{1}$ (no. 2), $a = 7.9208(4)$ Å, $b = 10.2954(4)$ Å, $c = 13.1361(7)$ Å, $\alpha = 72.719(4)^\circ$, $\beta = 79.598(5)^\circ$, $\gamma = 85.190(4)^\circ$, $V = 1005.53(9)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0423$, $wR_{\text{ref}}(F^2) = 0.1051$, $T = 264(1)$ K.

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A part of the coordination polymer of the title crystal structure is shown in the figure. The asymmetric unit is shown with displacement ellipsoids. Tables 1 and 2 contain details

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
Cu1	0.26503(5)	0.84893(4)	1.06017(3)	0.02604(14)
O1	0.1625(3)	0.7975(2)	0.95555(16)	0.0239(5)
O2	0.3210(3)	0.9545(2)	0.83259(17)	0.0288(5)
O3	−0.0578(3)	1.0490(2)	0.89152(18)	0.0323(5)
O5	0.3099(3)	0.7003(2)	0.74662(18)	0.0360(6)
O9	0.5755(3)	0.9024(2)	0.35639(19)	0.0422(6)
H9	0.6194	0.9514	0.2976	0.063*
O4	−0.2936(3)	1.0607(3)	0.8280(2)	0.0405(6)
O6	0.8012(3)	0.3631(2)	0.79222(19)	0.0397(6)
N1	0.4972(3)	0.7688(3)	1.0359(2)	0.0259(6)
O8	0.8079(4)	0.7749(3)	0.3311(2)	0.0576(8)
O7	0.9025(4)	0.3593(3)	0.6224(2)	0.0571(8)
H7	0.9836	0.3159	0.6487	0.086*
C14	−0.1402(4)	1.0172(3)	0.8303(3)	0.0260(7)
C8	0.0983(4)	0.8623(3)	0.7781(2)	0.0215(6)
C7	0.2002(4)	0.8751(3)	0.8610(2)	0.0213(6)
C17	0.6821(4)	0.5184(3)	0.6471(3)	0.0278(7)
C16	0.5421(4)	0.5559(3)	0.7147(3)	0.0276(7)
H16	0.5165	0.5055	0.7869	0.033*
C15	0.4417(4)	0.6696(3)	0.6727(2)	0.0263(7)
C1	0.6124(4)	0.7782(4)	1.0957(3)	0.0349(8)
H1	0.5875	0.8361	1.1394	0.042*
C9	−0.0587(4)	0.9306(3)	0.7611(3)	0.0269(7)
C3	0.8076(4)	0.6175(3)	1.0338(3)	0.0269(7)
C13	0.1647(4)	0.7768(3)	0.7156(3)	0.0278(7)
C18	0.7190(4)	0.5932(3)	0.5396(3)	0.0301(7)
H18	0.8093	0.5657	0.4939	0.036*
C19	0.6205(4)	0.7098(3)	0.5001(2)	0.0276(7)
C20	0.4811(4)	0.7485(3)	0.5663(3)	0.0281(7)
H20	0.4150	0.8262	0.5398	0.034*
C21	0.6767(4)	0.7978(3)	0.3874(3)	0.0320(8)
C2	0.7661(4)	0.7062(4)	1.0957(3)	0.0362(8)
H2	0.8431	0.7173	1.1379	0.043*
C22	0.7994(4)	0.4053(3)	0.6963(3)	0.0340(8)
C6	0.9654(4)	0.5290(4)	1.0426(3)	0.0339(8)
H6A	1.0545	0.5818	1.0518	0.041*
H6B	0.9423	0.4548	1.1085	0.041*
C5	0.5408(5)	0.6897(4)	0.9703(3)	0.0407(9)
H5	0.4656	0.6861	0.9245	0.049*
C4	0.6908(5)	0.6137(4)	0.9675(3)	0.0430(9)
H4	0.7148	0.5593	0.9210	0.052*
C12	0.0840(5)	0.7613(4)	0.6353(3)	0.0417(9)
H12	0.1309	0.7033	0.5944	0.050*
C10	−0.1400(4)	0.9162(4)	0.6805(3)	0.0402(9)
H10	−0.2439	0.9625	0.6689	0.048*
C11	−0.0682(5)	0.8339(4)	0.6171(3)	0.0499(11)
H11	−0.1224	0.8271	0.5618	0.060*

varied patterns (monodentate, bridging, chelating) to construct coordination polymers. The ancillary ligands are introduced to construct the coordination polymers, the final

structures have more tunability [10]. With the above consideration, we chose 3-(3,5-dicarboxyphenoxy)phthalate 1,2-bis(4-pyridyl)ethane to assemble with Cu(II) ions under hydrothermal conditions.

The crystal structure of the compound shows a one-dimensional chain structure. The asymmetric unit contains crystallographically one Cu(II) cation, one incompletely deprotonated H₂L^{2−} anion ligand and one half bpa as shown in the Figure. In this complex, each copper cation is four-coordinated [CuNO₃] by one N atom from one bpa ligand, three oxygen atoms from two H₂L^{2−} anions ligands. The Cu—O bond lengths are 1.933(2), 1.983(2) and 2.010(2) Å for Cu1—O1, Cu1—O3A and Cu1—O4A, and the Cu—N bond length is 1.963(2) Å for Cu1—N1, respectively. Two adjacent [CuNO₃] tetragona are connected by two H₂L^{2−} dianion ligands adopting a monodentate and chelating coordination mode to form a [Cu₂(CO₂)₄N₂] unit with a Cu···Cu distance of 5.2046(6) Å. The [Cu₂(CO₂)₄N₂] are extended by one bpa ligand to produce an infinite one-dimensional chain. The structure of the compound extends into 3D supermolecular through hydrogen bonds.

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