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Crystal structure of dodecaqua-bis(μ_2 -4,4'-bipyridine- $\kappa^2N:N'$)-bis(4,4'-((5-carboxylato-1,3-phenylene)bis(oxy))dibenzoato- κ^1O)tricopper(II) - water (1/4), $C_{62}H_{70}Cu_3N_4O_{32}$

Table 1: Data collection and handling.

Crystal:	Green block
Size:	0.32 × 0.28 × 0.26 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.03 mm ⁻¹
Diffractometer, scan mode:	Xcalibur, Eos, ω
$\theta_{\max}$, completeness:	26.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	19105, 6864, 0.068
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3826
$N(\text{param})_{\text{refined}}$:	477
Programs:	CrysAlis ^{PRO} [1], SHELX [2], Olex2 [3]

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Abstract

$C_{62}H_{70}Cu_3N_4O_{32}$, monoclinic, $C2/c$ (no. 15), $a = 44.710(7)$ Å, $b = 12.8847(17)$ Å, $c = 11.9901(18)$ Å, $\beta = 102.286(13)^\circ$, $V = 6749.0(17)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0618$, $wR_{\text{ref}}(F^2) = 0.1978$, $T = 293(2)$ K.

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The crystal structure is shown in the figure (the asymmetric unit is labelled). Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

$Cu(NO_3)_2 \cdot 3H_2O$ (0.048 g, 0.2 mmol), 4,4'-[(5-carboxy-1,3-phenylene)-bis(oxy)]dibenzoic acid (H_3L , 0.0394 g, 0.1 mmol), and 4,4'-bipyridine (bpy, 0.0156 g, 0.1 mmol) were mixed in 10 mL aqueous solution, and the pH value was adjusted to 5.5 with a sodium hydroxide solution (1 M).

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After stirring the mixture for 30 min at room temperature, the resulting mixture was transferred and sealed in a 25 mL Teflon-lined stainless steel vessel, which was sealed and heated at 140 °C for 48 h. Green block crystals of the title compound obtained after cooling the vessel to room temperature. The yield was 56% based on the H_3L ligand.

Experimental details

H atoms bonded to C atoms from organic ligands were positioned geometrically and refined using a riding model, with $C-H = 0.93$ Å, with $U_{\text{iso}}(H) = 1.2$ times $U_{\text{eq}}(C)$.

Comment

The multicarboxylic acid/ carboxylate and N -donor bipyridine ligands are two most widely used kinds of linkers in the construction of coordination polymers [4, 5]. Polycarboxyl (ate) ligands may take the anionic or protonated form to provide various coordination modes upon binding to metals. On the one hand, the neutral bipyridine ligands normally bind to the metal ions as the rod-like bidentate tectons. The recently reported studies show that the combination of multicarboxylic acid and N -donor co-ligands is a good choice for building CPs with high porosity and interesting structural diversity [6], and some of them even show promising cytotoxicity toward the human lung cancer cell lines [7]. However, the formation of coordination polymers is highly influenced by many factors such as temperature and solvents [8].

The asymmetric unit of the title structure is composed of one and a half $Cu(II)$ ion, one L^{3-} anion, one bpy ligand, six coordinated water molecules, and two lattice water

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Cu1	0.250000	0.250000	0.000000	0.0237(2)
Cu2	0.50082(2)	0.25034(4)	−0.00355(5)	0.0274(2)
O1	0.24778(6)	0.4108(2)	−0.0139(3)	0.0300(8)
H1A	0.233171	0.436030	0.016507	0.045*
H1B	0.264254	0.439225	0.027748	0.045*
O2	0.26261(7)	0.2670(2)	0.1747(3)	0.0297(8)
O3	0.25765(8)	0.1052(3)	0.2316(3)	0.0441(9)
O4	0.44122(8)	0.5210(3)	0.8109(3)	0.0545(11)
O5	0.41630(8)	0.5925(3)	0.9321(3)	0.0565(12)
O6	0.44125(8)	−0.0056(3)	0.8260(3)	0.0484(11)
O7	0.42016(7)	−0.0737(3)	0.9592(3)	0.0476(10)
O8	0.29975(6)	0.1040(3)	0.6501(3)	0.0331(8)
O9	0.30318(7)	0.4606(3)	0.5412(3)	0.0363(8)
O11	0.50908(8)	0.1362(3)	0.1169(4)	0.0570(12)
H11A	0.511400	0.162964	0.183998	0.085*
H11B	0.526558	0.108186	0.117126	0.085*
O12	0.50884(8)	0.3623(3)	0.1174(4)	0.0657(14)
H12A	0.495255	0.412549	0.102401	0.099*
H12B	0.526084	0.394702	0.116388	0.099*
O13	0.54603(7)	0.2484(2)	−0.0132(3)	0.0384(9)
H13A	0.554979	0.191875	0.016859	0.058*
H13B	0.556016	0.297232	0.029257	0.058*
O14	0.49416(9)	0.3594(4)	−0.1306(4)	0.0872(18)
H14A	0.483005	0.335144	−0.195315	0.131*
H14B	0.482810	0.411322	−0.114650	0.131*
O15	0.49098(8)	0.1415(4)	−0.1312(4)	0.0730(15)
H15A	0.506630	0.100884	−0.128329	0.110*
H15B	0.476726	0.099095	−0.120248	0.110*
N1	0.29670(8)	0.2498(3)	−0.0035(3)	0.0220(8)
N2	0.45494(8)	0.2536(3)	0.0028(3)	0.0246(9)
C1	0.44516(10)	0.2458(3)	0.1011(4)	0.0288(11)
H1	0.459606	0.239902	0.169176	0.035*
C2	0.41506(11)	0.2461(4)	0.1047(4)	0.0328(12)
H2	0.409239	0.240412	0.174462	0.039*
C3	0.39281(10)	0.2548(3)	0.0042(4)	0.0295(11)
C4	0.40296(11)	0.2648(4)	−0.0947(4)	0.0357(13)
H4	0.388953	0.272460	−0.163667	0.043*
C5	0.43369(11)	0.2637(4)	−0.0932(4)	0.0328(12)
H5	0.439995	0.270214	−0.161908	0.039*
C6	0.35952(10)	0.2535(3)	0.0019(4)	0.0279(11)
C7	0.34724(10)	0.1902(4)	0.0750(4)	0.0383(13)
H7	0.360025	0.148381	0.127854	0.046*
C8	0.31635(10)	0.1896(4)	0.0689(4)	0.0347(12)
H8	0.308593	0.145314	0.117084	0.042*
C9	0.30864(10)	0.3106(4)	−0.0725(4)	0.0301(11)
H9	0.295496	0.352487	−0.124101	0.036*
C10	0.33930(10)	0.3145(4)	−0.0715(4)	0.0298(11)
H10	0.346430	0.358960	−0.121088	0.036*
C11	0.41661(12)	0.5497(4)	0.8410(5)	0.0418(14)
C12	0.38682(11)	0.5261(4)	0.7596(4)	0.0338(12)
C13	0.38516(11)	0.4562(4)	0.6716(5)	0.0377(13)
H13	0.402955	0.424291	0.660446	0.045*
C14	0.35778(11)	0.4327(4)	0.6002(5)	0.0396(13)
H14	0.357124	0.384751	0.541759	0.047*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C15	0.33126(11)	0.4800(4)	0.6146(4)	0.0307(12)
C16	0.33213(11)	0.5533(4)	0.6975(4)	0.0378(12)
H16	0.314444	0.588365	0.704645	0.045*
C17	0.36019(12)	0.5747(4)	0.7718(5)	0.0434(14)
H17	0.360859	0.622543	0.830372	0.052*
C18	0.41813(11)	−0.0265(4)	0.8684(4)	0.0327(12)
C19	0.38722(11)	0.0087(4)	0.8056(4)	0.0290(11)
C20	0.36206(11)	−0.0131(4)	0.8502(5)	0.0379(13)
H20	0.364665	−0.051057	0.917559	0.046*
C21	0.33324(11)	0.0192(4)	0.7986(5)	0.0379(13)
H21	0.316560	0.002461	0.830052	0.046*
C22	0.32917(10)	0.0770(4)	0.6989(4)	0.0281(11)
C23	0.35426(10)	0.1010(4)	0.6526(4)	0.0323(12)
H23	0.351797	0.140359	0.586260	0.039*
C24	0.38291(10)	0.0659(4)	0.7059(4)	0.0325(12)
H24	0.399649	0.080965	0.674123	0.039*
C25	0.26435(9)	0.1979(4)	0.2499(4)	0.0279(11)
C26	0.27729(9)	0.2298(4)	0.3722(4)	0.0248(11)
C27	0.28405(9)	0.3330(4)	0.4021(4)	0.0256(10)
H27	0.279928	0.385093	0.347358	0.031*
C28	0.29670(9)	0.3562(4)	0.5121(4)	0.0262(10)
C29	0.30222(10)	0.2816(4)	0.5980(4)	0.0277(11)
H29	0.310241	0.299454	0.673574	0.033*
C30	0.29530(9)	0.1805(4)	0.5661(4)	0.0276(11)
C31	0.28263(9)	0.1535(4)	0.4558(4)	0.0250(10)
H31	0.277648	0.084676	0.436982	0.030*
O10	0.46375(8)	0.0021(3)	0.6339(3)	0.0414(9)
H10A	0.448925	0.010843	0.577036	0.062*
H10B	0.4541(11)	0.005(4)	0.687(3)	0.037(16)*
O16	0.46051(8)	0.4990(3)	0.6132(4)	0.0416(9)
H16A	0.449288	0.476597	0.551668	0.062*
H16B	0.4509(12)	0.508(4)	0.666(4)	0.050(19)*

molecules (*cf.* the figure). Cu1 ion, sitting on the 2-fold axis, is six-coordinated with two pyridyl N atoms, two carboxylato O atoms and two aqua ligands, resulting in a [CuN₂O₄] distorted octahedral geometry. Cu2 ion reveals a similar coordination environment with Cu1, which is shaped by one pyridyl N atom and five coordinated water molecules. Although this compound is isostructural to the Ni(II) and Co(II)-compound, respectively, it has different lattice water arrangements which gives rise to different H-bonding interactions. Both water molecules form H-bonding interactions with two adjacent carboxylate groups (*cf.* the figure) and one neighboring coordinated water while this was not the case for the Ni(II) and Co(II)-based compounds, indicating the different synthesis might result in different lattice guest agreement [9]. The title complex is further assembled into a 3D supramolecular framework by the hydrogen bond interactions.

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