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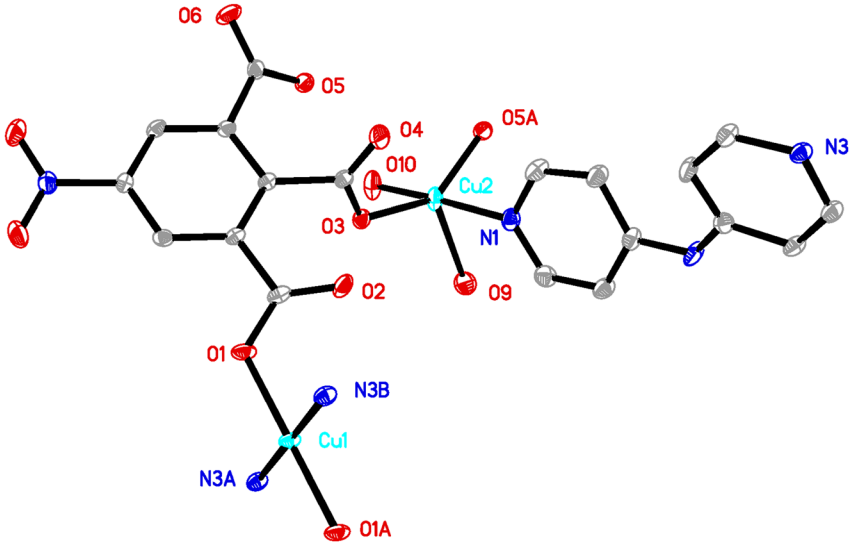
The crystal structure of poly[diaqua-(μ_3-5-nitrobenzene-1,2,3-tricarboxylato-$\kappa^3O:O':O'$)-(μ_2-4,4′-dipyridylamine-$\kappa^2N:N'$)copper(II)], $C_{38}H_{30}Cu_3N_8O_{20}$



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Abstract

$C_{38}H_{30}Cu_3N_8O_{20}$, triclinic, $P\bar{1}$ (no. 2), a = 7.2659(3) Å, b = 11.7245(3) Å, c = 12.6837(4) Å, α = 77.466(3)°, β = 73.915(3)°, γ = 75.794(3)°, V = 993.50(6) Å^3, Z = 1, $R_{gt}(F)$ = 0.0334, $wR_{ref}(F^2)$ = 0.0842, T = 291 K.

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A part of the polymeric title crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Violet block
Size:	0.32 × 0.27 × 0.23 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.69 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	25.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	12,847, 3694, 0.027
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 3279
$N(param)_{refined}$:	315
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], Olex2 [4]

Source of material

All chemicals were used without further purification. The title compound was prepared under the hydrothermal conditions by the following procedure: a mixture of 5-nitro-1,2,3-benzenetricarboxylic acid (0.1 mmol, 0.026 g), $Cu(OAc)_2 \cdot H_2O$ (0.1 mmol, 0.020 g), 4,4′-dipyridylamine (0.1 mmol, 0.017 g), and deionized water (6 mL) was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 413 K for three days. After cooling to room temperature at a

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.98971 (5)	0.46012 (3)	0.67007 (3)	0.02904 (12)
Cu2	0.5000	0.0000	1.0000	0.02065 (13)
O1	0.8797 (3)	0.32333 (16)	0.67205 (15)	0.0266 (4)
O2	0.6156 (4)	0.42361 (19)	0.60852 (19)	0.0476 (6)
O3	0.5864 (3)	0.02127 (17)	0.83849 (14)	0.0299 (5)
O4	0.5375 (3)	0.22050 (18)	0.81274 (15)	0.0314 (5)
O5	0.9523 (3)	0.38562 (16)	0.41512 (15)	0.0284 (4)
O6	0.8209 (4)	0.3406 (2)	0.29458 (17)	0.0493 (7)
O7	1.2280 (3)	0.38774 (19)	0.56804 (19)	0.0437 (6)
H7A	1.2557	0.4372	0.5075	0.066*
H7B	1.2058	0.3289	0.5459	0.066*
O8	1.2015 (3)	0.4228 (2)	0.79244 (18)	0.0424 (5)
H8A	1.2484	0.4838	0.7880	0.064*
H8B	1.3028	0.3707	0.7722	0.064*
O9	0.7941 (4)	−0.0814 (2)	0.35523 (17)	0.0445 (6)
O10	0.7030 (4)	−0.17260 (19)	0.52149 (19)	0.0462 (6)
N1	0.7795 (3)	0.5413 (2)	0.78330 (19)	0.0282 (5)
N2	−0.2345 (3)	0.9066 (2)	1.00702 (17)	0.0231 (5)
N3	0.3448 (3)	0.7372 (2)	1.0063 (2)	0.0343 (6)
H3	0.3812	0.7448	1.0630	0.041*
N4	0.7493 (3)	−0.0857 (2)	0.4555 (2)	0.0281 (5)
C1	0.7399 (4)	0.3342 (2)	0.6261 (2)	0.0253 (6)
C2	0.7378 (4)	0.2217 (2)	0.5839 (2)	0.0194 (5)
C3	0.6750 (4)	0.1219 (2)	0.6555 (2)	0.0197 (5)
C4	0.6822 (4)	0.0202 (2)	0.6141 (2)	0.0216 (5)
H4	0.6445	−0.0468	0.6618	0.026*
C5	0.7465 (4)	0.0202 (2)	0.5004 (2)	0.0215 (5)
C6	0.8026 (4)	0.1179 (2)	0.4281 (2)	0.0228 (6)
H6	0.8415	0.1166	0.3520	0.027*
C7	0.8007 (4)	0.2188 (2)	0.4695 (2)	0.0210 (5)
C8	0.5927 (4)	0.1239 (3)	0.7786 (2)	0.0228 (6)
C9	0.8624 (4)	0.3236 (2)	0.3851 (2)	0.0247 (6)
C10	0.7851 (4)	0.5321 (3)	0.8903 (2)	0.0326 (7)
H10	0.8881	0.4793	0.9154	0.039*
C11	0.6457 (4)	0.5972 (3)	0.9636 (2)	0.0331 (7)
H11	0.6560	0.5884	1.0366	0.040*
C12	0.4887 (4)	0.6763 (3)	0.9289 (2)	0.0274 (6)
C13	0.4908 (4)	0.6914 (3)	0.8165 (2)	0.0340 (7)
H13	0.3960	0.7485	0.7875	0.041*
C14	0.6340 (4)	0.6215 (3)	0.7492 (2)	0.0351 (7)
H14	0.6294	0.6305	0.6752	0.042*
C15	0.1519 (4)	0.7872 (2)	1.0055 (2)	0.0260 (6)
C16	0.0599 (4)	0.7793 (3)	0.9251 (2)	0.0296 (6)
H16	0.1253	0.7332	0.8697	0.036*
C17	−0.1286 (4)	0.8405 (3)	0.9287 (2)	0.0275 (6)
H17	−0.1863	0.8357	0.8733	0.033*
C18	−0.1501 (4)	0.9055 (2)	1.0895 (2)	0.0251 (6)
H18	−0.2234	0.9456	1.1480	0.030*
C19	0.0376 (4)	0.8485 (3)	1.0919 (2)	0.0267 (6)
H19	0.0888	0.8505	1.1508	0.032*

rate of 5 Kh^{-1}, purple block crystals were collected by filtration and washed with distilled water in 37% yield (based on Cu).

Experimental details

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

Comment

The design and construction of coordination polymers is of current interest in the fields of crystal engineering and supramolecular chemistry, not only for their structural diversities and intriguing topologies, but also for their applications as functional materials [5–8]. In the processes of synthesizing desired coordination polymers, the choice of organic ligands, central metal ions, the temperature, the ratio of solvent, and counterions are important factors in construction of target coordination polymers. It is worth mentioned that aromatic multicarboxylates such as 1,3-benzenedicarboxylate, 1,4-benzenedicarboxylate, 1,3,5-benzenetricarboxylic acid, and 5-nitro-1,2,3-benzenetricarboxylate (nbta) as organic ligands have been widely used to construct various coordination polymers [9–12]. On the other hand, 4,4′-dipyridylamine (dpa), as a flexible dipyridyl coligand, has attracted significant attention during the construction of coordination polymers [13–15]. Here, we present a new Cu(II) coordination polymer based on nbta and dpa.

The title compound was prepared under mild hydrothermal conditions. Single crystal X-ray structural analysis shows that the compound is a layered structure and crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit consists of one and half Cu(II) centers, one dpa ligand, one fully deprotonated nbta ligand, and two coordinated water molecules. The five-coordinated Cu1 atom is in a distorted square-pyramidal environment coordinated by two carboxylate oxygen atoms rom two different nbta ligands, one pyridyl nitrogen atom from one dpa ligand and two coordinated water molecules. The four-coordinated Cu2 atom is in an almost perfect square-planar environment with the CuO_2N_2 chromophore satisfied by carboxylate oxygen atoms from two nbta ligands and two pyridyl nitrogen atoms from two dpa ligands. The Cu–O/N distances associated with central Cu atoms are in the range of 1.9481(17)–2.381(2) Å, which are within the normal ranges. The Cu(II) ions are interconnected by carboxylate groups of μ_3-bridging nbta ligands, giving a chain structure. Interestingly, these chains are further linked by dpa ligands to generate a layered structure.

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