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Crystal structure of poly[(μ_2 -1-(1-imidazolyl)-4-(imidazol-1-ylmethyl)benzene- $\kappa^2 N:N'$)-(μ_3 -pyridazine-4,5-dicarboxylate- $\kappa^3 O:O':N$)]copper(II) hydrate, $C_{19}H_{16}CuN_6O_5$

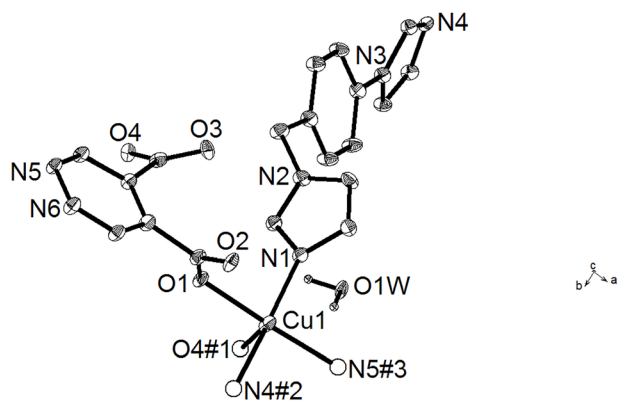


Table 1: Data collection and handling.

Crystal:	Blue block
Size:	0.35 × 0.29 × 0.22 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.22 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω -scans
$\theta_{\max}$, completeness:	26°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13,542, 3663, 0.023
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3462
$N(\text{param})_{\text{refined}}$:	280
Programs:	Olex2 [1], SHELX [2, 3], CrysAlis ^{PRO} [4]

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Abstract

$C_{19}H_{16}CuN_6O_5$, triclinic, $P\bar{1}$ (no. 2), $a = 9.0143(3)$ Å, $b = 9.2122(3)$ Å, $c = 11.8205(4)$ Å, $\alpha = 82.900(3)^\circ$, $\beta = 74.593(3)^\circ$, $\gamma = 83.612(3)^\circ$, $V = 935.90(5)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0284$, $wR_{\text{ref}}(F^2) = 0.0684$, $T = 293$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The mixture of pyridazine-4,5-dicarboxylic acid (H_2pda , 0.1 mmol, 16 mg), 1-(1-imidazolyl)-4-(imidazol-1-ylmethyl)benzene (iimb, 0.05 mmol, 11 mg), $Cu(OAc)_2 \cdot H_2O$ (0.2 mmol,

40 mg), H_2O (6.0 ml) was placed in a 23 ml Teflon lined stainless steel reactor. This reactor was placed in an oven and heated to 413 K under autogenous pressure for 96 h. Then the oven was cooled naturally to room temperature. Blue block crystals of the titled compound were obtained.

Experimental details

A suitable crystal of the titled compound was selected elaborately and mounted on a SuperNova diffractometer. The crystal was kept at 293 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT structure solution program and refined with the ShelXL refinement package [2, 3]. All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were modeled at their calculated positions and included in the refinement via the riding model. The U_{iso} of the H-atoms were constrained to 1.2 times U_{eq} of their bonding carbon atoms and 1.5 times U_{eq} of their bonding oxygen atoms for the hydrogen atoms in water molecules.

Discussion

A considerable number of coordination polymers based on divalent metal ions and well-chosen organic ligands have been synthesized by solvothermal methods, with charming

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Cu1	0.79348 (3)	1.00882 (3)	0.28659 (2)	0.02048 (8)
O1	0.56355 (15)	1.01692 (16)	0.30344 (12)	0.0249 (3)
O2	0.59351 (17)	0.91484 (19)	0.13580 (13)	0.0349 (4)
O3	0.3917 (2)	0.73446 (19)	0.43801 (15)	0.0404 (4)
O4	0.2168 (2)	0.8764 (2)	0.55538 (13)	0.0396 (4)
N1	0.77637 (19)	0.81486 (19)	0.37953 (15)	0.0253 (4)
N2	0.6745 (2)	0.6574 (2)	0.52779 (15)	0.0271 (4)
N3	0.7616 (2)	0.35833 (19)	1.03905 (15)	0.0248 (4)
N4	0.80148 (18)	0.19302 (19)	1.18051 (14)	0.0228 (4)
N5	0.02946 (18)	0.99068 (19)	0.26511 (14)	0.0212 (4)
N6	0.12523 (19)	1.0411 (2)	0.16322 (14)	0.0245 (4)
C1	0.5151 (2)	0.9645 (2)	0.22764 (17)	0.0219 (4)
C2	0.3416 (2)	0.9699 (2)	0.24836 (16)	0.0191 (4)
C3	0.2746 (2)	1.0307 (2)	0.15706 (17)	0.0230 (4)
H3	0.3403	1.0665	0.0867	0.028*
C4	0.0857 (2)	0.9329 (2)	0.35528 (16)	0.0210 (4)
H4	0.0162	0.9008	0.4249	0.025*
C5	0.2422 (2)	0.9173 (2)	0.35219 (16)	0.0178 (4)
C6	0.2911 (2)	0.8354 (2)	0.45839 (17)	0.0204 (4)
C7	0.8479 (3)	0.6776 (3)	0.3593 (2)	0.0387 (6)
H7	0.9268	0.6554	0.2935	0.046*
C8	0.7855 (3)	0.5796 (3)	0.4502 (2)	0.0426 (6)
H8	0.8129	0.4792	0.4582	0.051*
C9	0.6727 (2)	0.7974 (2)	0.48160 (18)	0.0259 (4)
H9	0.6066	0.8731	0.5170	0.031*
C10	0.5585 (3)	0.6001 (3)	0.63072 (19)	0.0309 (5)
H10A	0.5090	0.5244	0.6076	0.037*
H10B	0.4799	0.6787	0.6557	0.037*
C11	0.6216 (2)	0.5368 (2)	0.73426 (18)	0.0261 (4)
C12	0.7319 (3)	0.6004 (3)	0.7691 (2)	0.0373 (6)
H12	0.7748	0.6832	0.7248	0.045*
C13	0.7800 (3)	0.5425 (3)	0.8692 (2)	0.0359 (6)
H13	0.8550	0.5857	0.8915	0.043*
C14	0.7151 (2)	0.4202 (2)	0.93494 (17)	0.0254 (4)
C15	0.6035 (3)	0.3560 (2)	0.90218 (19)	0.0290 (5)
H15	0.5586	0.2748	0.9476	0.035*
C16	0.5590 (3)	0.4135 (2)	0.80126 (18)	0.0288 (5)
H16	0.4859	0.3687	0.7781	0.035*
C17	0.8149 (3)	0.4303 (3)	1.11279 (19)	0.0307 (5)
H17	0.8312	0.5294	1.1050	0.037*
C18	0.8391 (3)	0.3266 (2)	1.20017 (19)	0.0303 (5)
H18	0.8756	0.3436	1.2635	0.036*
C19	0.7556 (2)	0.2164 (2)	1.08286 (17)	0.0246 (4)
H19	0.7231	0.1443	1.0484	0.030*
O1W	0.8977 (2)	0.7951 (3)	0.07393 (18)	0.0650 (6)
H1WA	0.8994	0.8369	0.0054	0.098*
H1WB	0.8035	0.8259	0.0989	0.098*

architectures, tailored properties [5–8]. The organic ligands can be aromatic carboxylates, aliphatic carboxylates, N-heterocyclic carboxylates or other species [9, 10]. Especially, N-heterocyclic carboxylates (pyridine carboxylates, imidazole carboxylates, pyrazine carboxylates and so on)

possess inherently two different functional groups, namely carboxyl group and N-heterocyclic ring [11–14]. On the one hand, the oxygen atoms of carboxyl groups can ligate to different metal ions, honored with strong coordination abilities and versatile coordination modes. On the other hand, the nitrogen atoms in the heterocyclic rings can also bind to metal ions because they maybe have lone electron pairs for donation. Thereby, N-heterocyclic carboxylates enable to be one kind of reliable building units to construct coordination polymers. Up to now, there are only few cases using pyridazine-4,5-dicarboxylate (pda) as organic ligand [15–17]. In these rare reports, the pda ligand exhibits μ_1 -O, μ_2 -O: O' and μ_2 -O coordination modes, respectively. And the nitrogen atoms of pyridazine moiety make no contribution. Inspired by the mixed organic ligand strategy and the inherent properties of pda, we introduced pda and 1-(1-imidazolyl)-4-(imidazol-1-ylmethyl)benzene (iimb) to built related coordination polymers.

The title complex is a neutral polymer with a two-dimensional bilayer structure. As illustrated in the figure, the asymmetric unit is comprised of one Cu(II) cation, one pda dianion, one iimb ligand and one lattice water molecule. Each Cu1 atom exhibits a tetragonal pyramidal configuration by two oxygen atoms (O1, O4#1) from two symmetry-related pda dianions, one nitrogen atom (N5#3) from another pda dianion and two nitrogen atoms (N1, N4#2) from two symmetry-related iimb ligands (symmetry codes: #1: $-x, 2-y, 1-z$; #2: $x, 1+y, -1+z$; #3: $1+x, y, z$). In this [CuO₂N₃] unit, the basal plane is defined by O1, N1, N4#2 and N5#3, while the apical site is occupied by O4#1 atom. The Cu–O distances are 2.0226(13) Å and 2.2337(16) Å. The Cu–N distances range from 1.9772(17) Å to 2.0645(16) Å. And the average separation of Cu–O and Cu–N bonds are consistent with other reported data [18–20].

Every pda dianions adopt μ_3 -O: O': N coordination mode and bind to three Cu(II) ions, which is distinct from those aforementioned examples. In this manner, the adjacent Cu atoms are propagated by the μ_3 -pda dianions to generate a double-strand chain structure along the *a* direction. These chains are further bridged by μ_2 -iimb molecules to form a two-dimensional bilayer structure lying in the *ab* plane. In the layer motifs, there are relative weak π – π stacking interactions between the benzene rings of iimb molecules with the centroid-centroid distance of 4.2898(2) Å.

Furthermore, there are two kinds of hydrogen-bonding interactions between the pda dianions and the unligated water molecules. For O1W–H1WA...N6#1, $d = 3.061(2)$ Å, $\theta = 172.8^\circ$. And the values are 2.781(2) Å and 172.0° for O1W–H1WB...O2. Both hydrogen bonds participate in

connecting discrete bilayers to create the final three-dimensional supramolecular structure.

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