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The crystal structure of *catena*-poly[aqua-(4-iodopyridine-2,6-dicarboxylato- $\kappa^3 N, O, O'$)-copper(II)] monohydrate, $C_7H_6NO_6ICu$

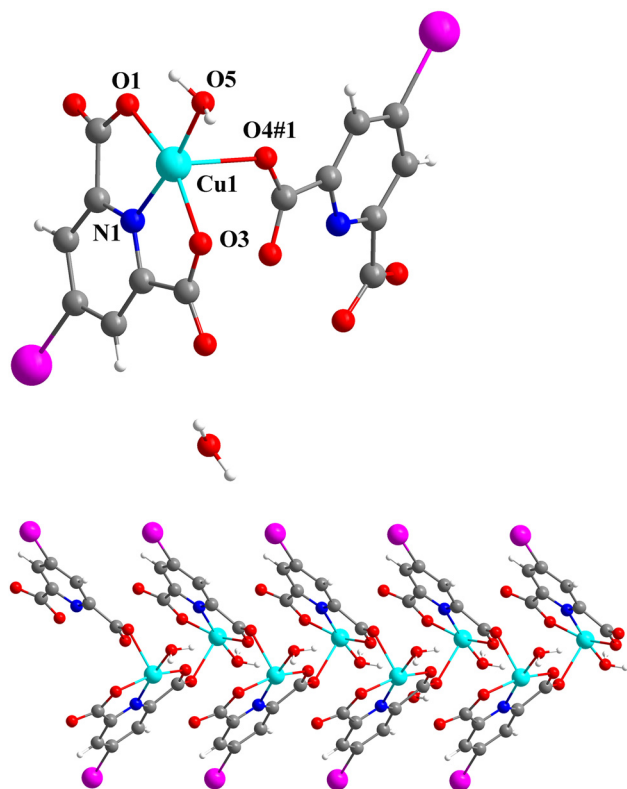


Table 1: Data collection and handling.

Crystal:	Green block
Size:	0.31 × 0.27 × 0.23 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	5.09 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω
$\theta_{\max}$, completeness:	25.0°, 98 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	9029, 1790, 0.036
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1642
$N(\text{param})_{\text{refined}}$:	149
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], Olex2 [4]

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

1 Source of material

All chemicals were purchased commercially and used without further purification. A mixture of $Cu(OAc)_2 \cdot H_2O$ (40.0 mg, 0.2 mmol), 4-iodopyridine-2,6-dicarboxylic acid (58.4 mg, 0.2 mmol), and deionized water (10 mL) was sealed in a 25 mL screw capped vial and heated at 90 °C for three days. After cooling to room temperature over 24 h, blue crystals were collected by filtration and washed with distilled water in 39 % yield.

2 Experimental details

Using OLEX2 [1], the structure was solved with the SHELXT [2] structure solution program and refined with the SHELXL [3] refinement package.

3 Comment

In the field of supramolecular chemistry, the rational design and synthesis of coordination polymers have obtained a growing attention due to potential applications [5–8]. In the self-assembly of coordination polymers, multidentate

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Abstract

$C_7H_6NO_6ICu$, monoclinic, $P2_1/n$ (no. 14), $a = 9.7229(4)$ Å, $b = 5.1728(2)$ Å, $c = 20.8336(8)$ Å, $\beta = 97.636(4)^\circ$, $V = 1038.52(7)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0287$, $wR_{\text{ref}}(F^2) = 0.0687$, $T = 293$ K.

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

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
I1	0.79457 (3)	0.69797 (6)	0.48485 (2)	0.03385 (14)
Cu1	0.50749 (5)	0.18515 (8)	0.73115 (2)	0.01738 (15)
O1	0.3717 (3)	0.4815 (5)	0.70608 (13)	0.0223 (6)
O2	0.3524 (3)	0.8389 (5)	0.64428 (15)	0.0313 (7)
O3	0.6642 (3)	−0.0708 (5)	0.72716 (12)	0.0182 (6)
O4	0.8640 (3)	−0.1049 (5)	0.68501 (12)	0.0229 (6)
O5	0.4024 (3)	0.0298 (5)	0.79305 (13)	0.0253 (6)
H5A	0.4211	−0.1339	0.7975	0.038*
H5B	0.3145	0.0313	0.7785	0.038*
N1	0.5878 (3)	0.3302 (5)	0.66067 (14)	0.0156 (7)
C1	0.4062 (4)	0.6298 (8)	0.66128 (19)	0.0226 (9)
C2	0.5289 (4)	0.5347 (7)	0.63043 (18)	0.0170 (8)
C3	0.5832 (4)	0.6435 (7)	0.57866 (19)	0.0221 (9)
H3	0.5408	0.7844	0.5564	0.027*
C4	0.7045 (4)	0.5340 (8)	0.56084 (17)	0.0214 (9)
C5	0.7663 (4)	0.3218 (7)	0.59436 (19)	0.0203 (9)
H5	0.8473	0.2490	0.5832	0.024*
C6	0.7032 (4)	0.2229 (7)	0.64477 (18)	0.0175 (9)
C7	0.7494 (4)	−0.0023 (7)	0.68929 (17)	0.0176 (8)
O6	1.0927 (3)	0.0919 (6)	0.63485 (14)	0.0295 (7)
H6A	1.1660	0.0025	0.6441	0.044*
H6B	1.0269	−0.0131	0.6385	0.044*

carboxylate derivatives could provide not only various coordination modes such as terminal monodentate, chelating to one metal center, bridging bidentate in syn-syn, syn-anti, or anti-anti configuration to two metal centers, but also noncovalent interactions such as hydrogen bonding, $\pi\cdots\pi$ stacking, van der Waals, halogen bonding, as well as electrostatic or dipole interaction [9–12].

However, the multidentate N-heterocyclic ligands are very limited. The rigid 4-iodopyridine-2,6-dicarboxylate (ipydc) ligand [13], which has a 120° angle between the six-membered pyridyl ring and the two adjacent carboxylate groups, could potentially provide various coordination modes to synthesize both discrete and consecutive coordination polymers under appropriate conditions [14–17]. Note, the 4-positional iodine atom on the pyridyl ring of ipydc ligand could be involved in the formation of a halogen bond.

In the asymmetric unit of the title structure, there are one crystallographically independent Cu(II) centre, one deprotonated ipydc ligand, one coordinated water molecule and one isolated water molecule (upper part of the figure). The Cu(II) centre is in a square-pyramidal geometry with the CuO₄N chromophore. The Cu(II) centre is coordinated by two carboxylate oxygen atoms and one pyridyl nitrogen atom from one ipydc ligand (O1, O3 and N1) and one oxygen atom of the coordinated water molecule in the equatorial plane,

one carboxylate oxygen atom from one ipydc ligand (O4#1) in the apical position. The Cu–O/N distances associated with Cu(II) centre vary in the range of 1.906(3)–2.283(3) Å and the bond angles about the Cu(II) center range from 79.91 (11)° to 171.46 (12)°. These values are normal and match with previously reported Cu(II) compounds [16, 17]. In the compound, the ipydc ligand link Cu(II) centers to result to a one-dimensional infinite chain-like structure (lower part of the figure).

It is worth mentioning that the compound contains coordinated and isolated water molecules, which could form abundant hydrogen bonds. A number of O–H $\cdots$ O hydrogen bonds in the compound is present, involving coordinated/isolated water molecules and the carboxylate oxygen atoms of ipydc. There is an iodine-based halogen bond because the distance between iodine atom and the isolated water molecule is 3.054(3) Å, which is shorter than the sum of the van der Waals radii of the two atoms (ca. 3.5 Å).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

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References

- Agilent Technologies. *CrysAlis^{PRO} Software System, Version 1.171.38.41r*; Agilent Technologies UK Ltd: Oxford, UK, 2015.
- Sheldrick G. M. *SHELXTL* – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
- Sheldrick G. M. Crystal structure refinement with *SHELXL*. *Acta Crystallogr.* 2015, *C71*, 3–8.
- Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* 2009, *42*, 339–341.
- Zhang X., Wang W., Hu Z., Wang G., Uvdal K. Coordination polymers for energy transfer: preparations, properties, sensing applications, and perspectives. *Coord. Chem. Rev.* 2015, *284*, 206–235.
- Liu J. Q., Luo Z. D., Pan Y., Singh A. K., Trivedi M., Kumar A. Recent developments in luminescent coordination polymers: designing strategies, sensing application and theoretical evidences. *Coord. Chem. Rev.* 2020, *406*, 213145.
- Mirzaei M., Eshtiahi-Hosseini H., Alfi N., Aghabozorg H., Gharamaleki J. A., Beyramabadi S. A., Syntheses K. E., Salimi A. R., Shokrollahi A., Aghaei R. Crystal, molecular structures, and solution studies of Cu(II), Co(II), and Zn(II) coordination compounds containing pyridine-2, 6-dicarboxylic acid and 1, 4-pyrazine-2, 3-dicarboxylic acid: comparative computational studies of Cu(II) and Zn(II) complexes. *Struct. Chem.* 2011, *22*, 1365–1377.

8. Abdolmaleki S., Ghadermazi M., Ashengroph M., Saffari A., Sabzkohi S. M. Cobalt (II), zirconium (IV), calcium (II) complexes with dipicolinic acid and imidazole derivatives: X-ray studies, thermal analyses, evaluation as in vitro antibacterial and cytotoxic agents. *Inorg. Chim. Acta* 2018, 480, 70–82.
9. Henwood A. F., Hegarty I. N., McCarney E. P., Lovitt J. I., Donohoe S., Gunnlaugsson T. Recent advances in the development of the btp motif: a versatile terdentate coordination ligand for applications in supramolecular self-assembly, cation and anion recognition chemistries. *Coord. Chem. Rev.* 2021, 449, 214206.
10. Thanasekaran P., Lee C. H., Lu K. L. Neutral discrete metal–organic cyclic architectures: opportunities for structural features and properties in confined spaces. *Coord. Chem. Rev.* 2014, 280, 96–175.
11. Zhao Y. H., Xu H. B., Fu Y. M., Shao K. Z., Yang S. Y., Su Z. M., Hao X. R., Zhu D. X., Wang E. B. A series of lead(II)-organic frameworks based on pyridyl carboxylate acid N-oxide derivatives: syntheses, structures, and luminescent properties. *Cryst. Growth Des.* 2008, 8, 3566–3576.
12. Mukherjee A., Tothadi S., Desiraju G. R. Halogen bonds in crystal engineering: like hydrogen bonds yet different. *Acc. Chem. Res.* 2014, 47, 2514–2524.
13. Lv B. Crystal structure of [aqua-(4-iodopyridine-2,6-dicarboxylato- κ^3O,N,O')-(1,10-phenanthroline- κ^2N,N')copper(II)]dihydrate, $C_{19}H_{16}O_7N_3CuI$. *Z. Kristallogr. N. Cryst. Struct.* 2021, 236, 891–893.
14. Lv B. Crystal structure of *catena*-poly[aqua-(4-iodopyridine-2,6-dicarboxylato- κ^3N,O,O')-(μ_2 -4-amino-4*H*-1,2,4-triazole- $\kappa^2N:N'$)copper(II)], $C_9H_8N_5O_5CuI$. *Z. Kristallogr. N. Cryst. Struct.* 2021, 236, 873–875.
15. Lv B. Crystal structure of bis(μ_2 -4-iodopyridine-2,6-dicarboxylato- $\kappa^3O:N:O'$)-bis(4-iodopyridine-2,6-dicarboxylato- $\kappa^3O:N:O'$)-bis(μ^2 -1-(4-pyridyl)piperazine- $\kappa^2N:N'$)-hexa-aqua-tetra-copper(II), $C_{46}H_{46}Cu_4I_4N_{10}O_{22}$. *Z. Kristallogr. N. Cryst. Struct.* 2021, 236, 957–959.
16. Ruiz-Pérez C., Sanchiz J., Molina M. H., Lloret F., Julve M. Ferromagnetism in malonato-bridged copper(II) complexes. Synthesis, crystal structures, and magnetic properties of $\{[Cu(H_2O)_3][Cu(mal)_2(H_2O)]\}_n$ and $\{[Cu(H_2O)_4]_2[Cu(mal)_2(H_2O)]\}[Cu(mal)_2(H_2O)_2]\{[Cu(H_2O)_4][Cu(mal)_2(H_2O)_2]\}(H_2mal = \text{malonic acid})$. *Inorg. Chem.* 2000, 39, 1363–1370.
17. Brudenell S. J., Spiccia L., Bond A. M., Comba P., Hockless D. C. Structural, EPR, and electrochemical studies of binuclear copper(II) complexes of bis(pentadentate) ligands derived from bis(1,4,7-triazacyclonane) macrocycles. *Inorg. Chem.* 1998, 37, 3705–3713.