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Crystal structure of catena-poly[dichlorido-(μ_2 -3-(2-pyridyl)-4-(4-pyridyl)-5-(3-pyridyl)-1,2,4-triazole- $\kappa^2 N:N'$)] copper(II), $C_{17}H_{12}N_6Cl_2Cu$

Table 1: Data collection and handling.

Crystal:	Green block
Size:	0.28 × 0.22 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.55 mm ⁻¹
Diffractometer, scan mode:	CCD, φ and ω
$\theta_{\max}$, completeness:	25.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	8812, 3137, 0.031
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2423
$N(\text{param})_{\text{refined}}$:	235
Programs:	CrysAlis ^{PRO} [1], Olex2 [2], SHELX [3]

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Abstract

$C_{17}H_{12}Cl_2CuN_6$, monoclinic, $P2_1/c$ (no. 14), $a = 13.113(3)$ Å, $b = 7.1325(4)$ Å, $c = 19.527(3)$ Å, $\beta = 103.628(2)^\circ$, $V = 1774.8(5)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0310$, $wR_{\text{ref}}(F^2) = 0.0682$, $T = 296(2)$ K.

CCDC no.: 1892724

The crystal structure is shown in the figure. 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

An aqueous solution (6 mL) of $CuCl_2 \cdot 2 H_2O$ (34 mg, 0.2 mmol) was added to a solution of 3-(2-pyridyl)-4-(4-pyridyl)-5-(3-pyridyl)-1,2,4-triazole (15 mg, 0.05 mmol) in CH_3OH (4 mL).

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After 20 min of vigorous mixing, the solution was filtered and left to stand at room temperature. Light green block single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent after 2 weeks in 47% yield (based on L ligand). Anal. Calc. for $C_{17}H_{12}N_6Cl_2Cu$: C, 46.96; H, 2.78; N, 19.33%. Found: C 46.69, H 2.83, N 19.17%.

Experimental details

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

Comment

The synthesis of coordination polymers (CPs) has received considerable attention in the past few decades not only for their beautiful structures but also because of their useful applications [4–6]. *N*-donor organic ligands such as pyridine and triazole have been widely used in the preparation of CPs for their strong chelating ability toward the metal ions [7]. 3-(2-Pyridyl)-4-(4-pyridyl)-5-(3-pyridyl)-1,2,4-triazole (denoted as L hereafter) is a ligand that combines the structural features of both pyridine and triazole and has been proved to be a good chelating ligand for the construction of a series of Zn(II) and Cd(II)-based CPs [8–10]. Our interest in the synthesis of Cu(II)-based CPs stems from their potential use as bioactive reagents [11, 12]. In this study, the self-assembly of the L ligand with $CuCl_2 \cdot 2 H_2O$ leads to the formation of a new Cu(II)-CP with a 1D chain-like network. According to the CCDC database, few

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

Atom	x	y	z	U _{iso} [*] /U _{eq}
Cu1	0.55522(3)	0.51829(4)	0.12524(2)	0.03391(11)
Cl1	0.39501(6)	0.64440(11)	0.08945(4)	0.0551(2)
Cl2	0.58712(8)	0.22187(11)	0.13810(4)	0.0651(3)
N1	0.63268(19)	0.6278(3)	0.22136(11)	0.0418(6)
N2	0.86801(19)	0.3503(3)	0.37745(11)	0.0436(6)
N3	0.91450(19)	0.2672(3)	0.44151(12)	0.0440(6)
N4	0.81882(16)	0.4998(3)	0.46337(10)	0.0315(5)
N5	0.8601(2)	0.3823(4)	0.60975(12)	0.0504(7)
N6	0.64231(17)	0.8459(3)	0.56462(11)	0.0324(5)
C1	0.6903(2)	0.5292(4)	0.27488(13)	0.0381(7)
H1	0.6930	0.3997	0.2699	0.046*
C2	0.6286(3)	0.8110(4)	0.22904(15)	0.0510(8)
H2	0.5884	0.8823	0.1927	0.061*
C3	0.6820(3)	0.8993(4)	0.28905(15)	0.0508(8)
H3	0.6787	1.0291	0.2925	0.061*
C4	0.7406(2)	0.7973(4)	0.34443(15)	0.0426(7)
H4	0.7756	0.8565	0.3857	0.051*
C5	0.7461(2)	0.6079(4)	0.33748(13)	0.0343(6)
C6	0.8103(2)	0.4876(4)	0.39146(13)	0.0345(6)
C7	0.8839(2)	0.3559(4)	0.49187(14)	0.0351(6)
C8	0.9106(2)	0.2984(4)	0.56642(14)	0.0350(6)
C9	0.9812(2)	0.1552(4)	0.58798(15)	0.0431(7)
H9	1.0157	0.0997	0.5567	0.052*
C10	0.9996(3)	0.0965(5)	0.65674(16)	0.0521(8)
H10	1.0465	−0.0008	0.6725	0.063*
C11	0.9487(3)	0.1813(5)	0.70224(16)	0.0547(9)
H11	0.9605	0.1439	0.7491	0.066*
C12	0.8802(3)	0.3224(5)	0.67657(16)	0.0566(9)
H12	0.8454	0.3804	0.7072	0.068*
C13	0.7591(2)	0.6226(3)	0.49741(12)	0.0297(6)
C14	0.6514(2)	0.6031(4)	0.48428(14)	0.0359(6)
H14	0.6169	0.5145	0.4521	0.043*
C15	0.5962(2)	0.7162(4)	0.51933(13)	0.0381(7)
H15	0.5238	0.7013	0.5110	0.046*
C16	0.7472(2)	0.8681(4)	0.57406(15)	0.0419(7)
H16	0.7796	0.9623	0.6044	0.050*
C17	0.8086(2)	0.7605(4)	0.54167(14)	0.0410(7)
H17	0.8806	0.7802	0.5494	0.049*

examples of CPs incorporating the L ligand have been previously reported in the literature. The crystal structure of the title compound is isomorphous with that of its Zn(II)-based counterpart [9].

Single-crystal X-ray diffraction analysis reveals that the title complex belongs to the monoclinic space group $P2_1/c$ with one Cu(II) ion, one ligand and two coordinated Cl[−] ion in the asymmetric unit. The distorted tetrahedral coordination environment of the center Cu(II) is composed of two pyridyl nitrogen atoms from two different L ligands and two coordinated Cl[−] ions. The L ligand shows a bidentate-bridging coordination mode *via* 3-pyridyl and 4-pyridyl with a transoid

conformation. Thus, the Cu(II) ions are connected by the L bridges to generate a 1D polymeric chain along the *c* axis with a Cu(II)-Cu(II) separation of 10.308(2) Å.

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References

- Agilent. CrysAlis^{PRO}. Agilent Technologies, Yarnton, Oxfordshire, England (2011).
- 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. Crystallogr.* **42** (2009) 339–341.
- Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
- Huang, C.-H.; Gao, L.-L.; Wu, W.-N.: Crystal structure of catena-poly[(2-(5-chloroquinolin-8-yloxy)-1-(pyrrolidin-1-yl)ethan-1-one- κ^3N,O,O')-(dinitrato- κ^2O,O')mercury(II)], C₁₅H₁₅N₄O₈ClHg. *Z. Kristallogr. NCS* **233** (2018) 1073–1074.
- Zhang, H.; Zou, X.; Feng, Q.; Xu, B.; Pang, H.: Crystal structure of catena-poly[diodido-(μ_2 -1,5-dimethyl-2-phenyl-4-((pyridin-3-ylmethylene)amino)-1,2-dihydro-3H-pyrazol-3-one- $\kappa^2N:O$)zinc(II)], C₁₇H₁₆N₄OZn. *Z. Kristallogr. NCS* **233** (2018) 1061–1062.
- Robin, A. Y.; Fromm, K. M.: Coordination polymer networks with *O*- and *N*-donors: what they are, why and how they are made. *Coord. Chem. Rev.* **250** (2006) 2127–2157.
- Zhang, J.-P.; Zhang, Y.-B.; Lin, J.-B.; Chen, X.-M.: Metal azolate frameworks: from crystal engineering to functional materials. *Chem. Rev.* **112** (2012) 1001–1033.
- Wang, X.; Guo, W.; Guo, Y.-M.: Controllable assemblies of Cd(II) supramolecular coordination complexes based on a versatile tripyridyltriazole ligand and halide/pseudoanions. *J. Mol. Struct.* **1096** (2015) 136–141.
- Wang, X.; Guo, Y.-M.: Diverse structures and physicochemical properties of four zinc-tripyrilidyltriazole coordination polymers regulated by counter-ions. *Aust. J. Chem.* **1096** (2015) 136–141.
- Shi, D.-W.; Li, H.-Y.; Lei, J.-B.; Huang, F.-P.; Qin, X.-H.; Yu, Q.; Bian, H.-D.: 1*H*-3-(2-Pyridyl)-5-(3-pyridyl)-1,2,4-triazole (2, 3'-Hbpt) as ligand in Cd(II) complexes: synthesis, crystal structures, and fluorescence. *J. Coord. Chem.* **68** (2015) 1957–1969.
- Santini, C.; Pellei, M.; Gandin, V.; Porchia, M.; Tisato, F.; Marzano, C.: Advances in copper complexes as anticancer agents. *Chem. Rev.* **114** (2014) 815–862.
- Li, X.-J.; Zheng, K.; Li, Y.-T.; Yan, C.-W.; Wu, Z.-Y.; Xuan, S.-Y.: Synthesis and structure of a 1-D copper(II) coordination polymer bridged both by oxamido and carboxylate: *in vitro* anticancer activity and reactivity toward DNA and protein BSA. *J. Coord. Chem.* **68** (2015) 928–948.