Xia Li, Shangjun Liu*, Mingle Shen and Weihong Yan

Crystal structure of *catena*-poly[chlorido-(μ_2 -formato- $\kappa^2 O:O'$)-(1,10-phenanthroline- $\kappa^2 N,N'$)copper(II)], $C_{26}H_{18}Cl_2Cu_2N_4O_4$

Table 1: Data collection and handling.

Crystal:	Blue block
Size:	0.22 × 0.20 × 0.18 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	2.02 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	25.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	12033, 4257, 0.019
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3844
$N(\text{param})_{\text{refined}}$:	343
Programs:	Bruker [1], SHELX [2]

<https://doi.org/10.1515/ncrs-2020-0142>

Received March 14, 2020; accepted April 15, 2020; available online May 5, 2020

Abstract

$C_{26}H_{18}Cl_2Cu_2N_4O_4$, monoclinic, $P2_1/c$ (no. 14), $a = 9.5129(9)$ Å, $b = 17.8130(17)$ Å, $c = 15.2973(12)$ Å, $\beta = 110.975(5)^\circ$, $V = 2420.4(4)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0269$, $wR_{\text{ref}}(F^2) = 0.0929$, $T = 293(2)$ K.

CCDC no.: 1996958

The asymmetric unit of the title structure is shown in the figure ($A = 1 - x, y, z$; $B = 1 + x, y, z$). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of $CuCl_2 \cdot 2H_2O$ (1 mmol, 0.171 g), 1,10-phenanthroline (1 mmol, 0.198 g), $NaCO_2$ (1 mmol, 0.068 g), dimethylformamide (5 mL) and H_2O (5 mL) was stirred for half an hour at room temperature. The mixture was transferred in a 25 mL Teflon-lined steel reactor, heated to 423 K

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.6435(3)	0.14552(12)	0.24995(17)	0.0300(5)
H1	0.592240	0.138869	0.186097	0.036*
C2	0.1453(3)	0.14894(13)	0.24835(18)	0.0330(6)
H2	0.097118	0.134511	0.186335	0.040*
C3	0.5294(3)	−0.04367(15)	0.13251(19)	0.0416(6)
H3	0.510813	−0.004487	0.089682	0.050*
C4	0.6046(3)	−0.10743(17)	0.1188(2)	0.0484(7)
H4	0.635938	−0.110057	0.067819	0.058*
C5	0.6318(3)	−0.16584(16)	0.1804(2)	0.0481(7)
H5	0.680500	−0.208747	0.171278	0.058*
C6	0.5860(3)	−0.16069(14)	0.25739(19)	0.0379(6)
C7	0.5115(3)	−0.09452(13)	0.26636(17)	0.0305(5)
C8	0.4583(3)	−0.08637(13)	0.34251(16)	0.0283(5)
C9	0.4818(3)	−0.14367(14)	0.40929(18)	0.0361(6)
C10	0.5608(3)	−0.21024(15)	0.3993(2)	0.0465(7)
H10	0.579035	−0.248231	0.443698	0.056*
C11	0.6084(3)	−0.21852(14)	0.3276(2)	0.0470(7)
H11	0.657257	−0.262655	0.322720	0.056*
C12	0.4227(3)	−0.13163(16)	0.48026(19)	0.0425(6)
H12	0.435972	−0.167570	0.526626	0.051*
C13	0.3464(3)	−0.06742(16)	0.48092(18)	0.0414(6)
H13	0.306323	−0.059478	0.527391	0.050*
C14	0.3281(3)	−0.01298(15)	0.41133(17)	0.0337(5)
H14	0.274988	0.030645	0.412378	0.040*
C15	0.8465(3)	0.34422(13)	0.34078(17)	0.0314(5)
H15	0.790151	0.309736	0.360102	0.038*
C16	0.8915(3)	0.41018(14)	0.39099(18)	0.0385(6)
H16	0.865675	0.419266	0.443180	0.046*
C17	0.9738(3)	0.46184(14)	0.36402(19)	0.0395(6)
H17	1.006236	0.505609	0.398526	0.047*

*Corresponding author: Shangjun Liu, School of Biological and Chemical Engineering, Nanyang Institute of Technology, 473004, Nanyang, Henan, P.R. China, e-mail: shangjunliu66@163.com. <https://orcid.org/0000-0001-8577-1979>

Xia Li, Mingle Shen and Weihong Yan: School of Biological and Chemical Engineering, Nanyang Institute of Technology, 473004, Nanyang, Henan, P.R. China

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C18	1.0093(3)	0.44845(13)	0.28361(18)	0.0315(5)
C19	0.9604(2)	0.38024(12)	0.23727(16)	0.0263(5)
C20	0.9903(3)	0.36288(13)	0.15462(16)	0.0272(5)
C21	1.0638(3)	0.41568(14)	0.11723(17)	0.0334(6)
C22	1.1119(3)	0.48513(15)	0.1665(2)	0.0424(6)
H22	1.160661	0.520547	0.142793	0.051*
C23	1.0879(3)	0.50005(14)	0.2461(2)	0.0406(6)
H23	1.123247	0.544878	0.277457	0.049*
C24	1.0839(3)	0.39567(16)	0.03389(19)	0.0433(7)
H24	1.130721	0.428808	0.006003	0.052*
C25	1.0347(4)	0.32760(18)	−0.00641(19)	0.0494(7)
H25	1.046828	0.314376	−0.062109	0.059*
C26	0.9661(3)	0.27795(16)	0.03671(19)	0.0438(7)
H26	0.935908	0.231022	0.009917	0.053*
Cl1	0.27884(8)	0.09345(4)	0.08800(4)	0.03935(17)
Cl2	0.74963(9)	0.14912(4)	0.07118(5)	0.0483(2)
Cu1	0.37572(3)	0.05048(2)	0.23794(2)	0.02878(12)
Cu2	0.84669(3)	0.23167(2)	0.18980(2)	0.02763(11)
N1	0.4836(2)	−0.03706(11)	0.20437(14)	0.0313(5)
N2	0.3840(2)	−0.02185(11)	0.34428(13)	0.0282(4)
N3	0.8812(2)	0.32847(10)	0.26554(13)	0.0259(4)
N4	0.9425(2)	0.29553(11)	0.11463(14)	0.0309(4)
O1	0.5919(2)	0.11324(10)	0.30341(12)	0.0365(4)
O2	0.7580(2)	0.18629(9)	0.27363(12)	0.0369(4)
O3	0.2718(2)	0.12213(10)	0.28981(13)	0.0402(4)
O4	0.0773(2)	0.19252(10)	0.28079(13)	0.0398(4)

for 72 h. After cooled to room temperature, greenish-blue block crystals were obtained.

Experimental details

All hydrogen atoms were located in calculated positions (C–H = 0.93 Å) and refined as riding atoms. The *U*_{iso} values were constrained to be 1.2*U*_{eq} of the carrier atom.

Comment

Copper carboxylate complexes have been extensively studied and received continuous interest because of theory and diverse application for their coordination chemistry and physical properties [3–5]. The formate anion is the simplest carboxylate with the smallest steric effect, thus, widely used as an effective bridging ligand in coordination polymers [6–9] trivial.

The asymmetric unit of the title complex is made up of two Cu(II) ions, two chloride anions, two 1,10-phenanthroline, and two different formate anions (see the figure). Each Cu(II) ion is coordinated by two O atoms from two different formate ligands (Cu–O = 1.9452(16)–2.2473(19) Å), two N atoms from one 1,10-phenanthroline ligand (Cu–N = 2.0310(19)–2.0542(19) Å), and a chlorido

ligand (Cu–Cl = 2.2602(7)–2.2767(7) Å). Both Cu1 and Cu2 exhibit a distorted tetragonal pyramidal coordination geometry with the geometric index τ values of 0.257 and 0.161, respectively [10]. One O atom of a formate ligand, two N atoms of one 1,10-phenanthroline ligand and one Cl atom construct the basal position plane, while the axial coordination site is occupied by one O atom from another formate ligand.

It should be noted that the bidentate bridging formate groups exhibit *anti-anti* configurations and link the two Cu(II) atoms into a zigzag chain structure with the Cu–Cu distance of 5.779(4) Å along the *a* axis. In the solid, intermolecular weak C–H···Cl and C–H···O hydrogen bonds link chains into a three-dimensional framework.

Acknowledgements: This work was financially supported by Nanyang Institute of Technology.

References

1. Bruker. APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, WI, USA (2008).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
3. Zhu, J.; Wang, G.; Wu, D.: Crystal structure of (5,5'-bitetrazole-1,1'-diolate)-bis(1,10-phenanthroline)-copper(II), C₂₆H₁₆CuN₁₂O₂. *Z. Kristallogr. NCS* **235** (2020) 311–312.
4. Pasán, J.; Sanchiz, J.; Lloret, F.; Julve, M.; Ruiz-Pérez, C.: Magnetostructural relationships in polymorphic ethylmalonate-containing copper(II) coordination polymers. *CrystEngComm* **20** (2018) 7464–7472.
5. Carballo, R.; Castiñeiras, A.; Covelo, B.; Lago, A. B.; Vázquez-López, E. M.; Gómez-Paz, O.; Balboa, S.; Prieto, I.: Chiral and achiral 1D copper(II) coordination polymers based on glycolate and chelating aromatic diamine ligands. *CrystEngComm* **20** (2018) 2455–2464.
6. Xu, W.: *catena*-Poly[[aqua(formato- κ O)(1,10-phenanthroline- κ^2 N:N')manganese(II)]- μ -formato- κ^2 O:O'] monohydrate]. *Acta Crystallogr. E* **67** (2011) m893.
7. Yuan, P.-L.; Li, P.-Z.; Sun, Q.-F.; Liu, L.-X.; Gao, K.; Liu, W.-S.; Lu, X.-M.; Yu, S.-Y.: Synthesis, structure and magnetic property of a one-dimensional Co(II)-formate helical coordination polymer. *J. Mol. Struct.* **890** (2008) 112–115.
8. Boonmak, J.; Youngme, S.; Chotkhun, T.; Engkagul, C.; Chaitit, N.; van Albada, G. A.; Reedijk, J.: Polynuclear copper(II) carboxylates with 2,2'-bipyridine or 1,10-phenanthroline: synthesis, characterization, X-ray structures and magnetism. *Inorg. Chem. Commun.* **11** (2008) 1231–1235.
9. Wang, Z.; Zhang, B.; Zhang, Y.; Kurmoo, M.; Liu, T.; Gao, S.; Kobayashi, H.: A family of porous magnets, [M₃(HCOO)₆] (M = Mn, Fe, Co and Ni). *Polyhedron* **26** (2007) 2207–2215.
10. Addison, A. W.; Rao, T. N.; Reedijk, J.; Rijn, J. V.; Verschoor, G. C.: Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen-sulphur donor ligands; the crystal and molecular structure of aqua[1,7-bis(*N*-methylbenzimidazol-2'-yl)-2,6-dithiaheptane] copper(II) perchlorate. *J. Chem. Soc., Dalton Trans.* (1984) 1349–1356.