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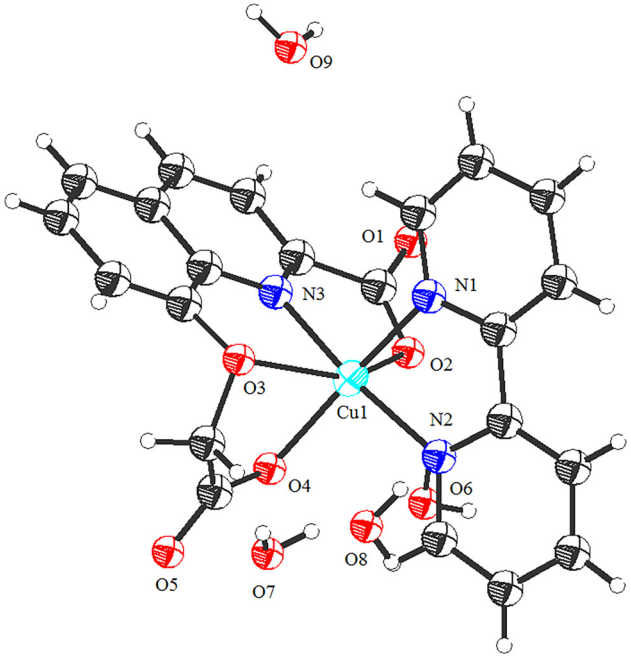
The crystal structure of [(8-carboxymethoxy-quinoline-2-carboxylate-κ^4N,O,O,O)-2,2′-bipyridine-κ^2N-copper(II)] tetrahydrate, $C_{22}H_{23}N_3O_9Cu$



https://doi.org/10.1515/ncrs-2023-0347
Received July 25, 2023; accepted October 20, 2023;
published online November 1, 2023

Abstract

$C_{22}H_{23}N_3O_9Cu$, triclinic, $P\bar{1}$ (no. 2), a = 9.0356(2) Å, b = 9.6247(3) Å, c = 14.2969(3) Å, α = 86.989(2)°, β = 86.414(2)°, γ = 66.913(2)°, V = 1140.98(5) Å^3, Z = 2, $R_{gt}(F)$ = 0.0405, $wR_{ref}(F^2)$ = 0.1172, T = 297.88(10) K.

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Table 1: Data collection and handling.

Crystal:	Blue block
Size:	0.15 × 0.13 × 0.12 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	1.88 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	77.6°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13,245, 4558, 0.039
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 4087
$N(param)_{refined}$:	329
Programs:	Bruker [1], Olex2 [2], SHELX [3], Diamond [4]

CCDC no.: 2302372

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

1 Source of materials

The synthesis of Cu(II) complex proceeds as following method: 0.2471 g 8-carboxymethoxy-quinoline-2-carboxylic acid (1.0 mmol), 0.1997 g cupric acetate monohydrate (0.50 mmol), 0.1562 g 2,2′-bipyridine (1.0 mmol), and 0.080 g NaOH (2.0 mmol) were added to 25 mL of ethanol-water solution (v:v = 3:2) with stirring. The mixture immediately became cloudy, and continued to react at 75 °C for 5 h. After cooling to room temperature, it is filtered, and the filtrate remains still placed. The blue block crystals of the title Cu(II) complex were obtained in 18 days.

2 Experimental details

The hydrogen atoms were positioned geometrically (C–H = 0.93–0.97 Å, O–H = 0.85 Å). Their U_{iso} values were set to $1.2U_{eq}$ or $1.5U_{eq}$ of the parent atoms.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	−0.0680 (3)	0.6665 (2)	0.75667 (16)	0.0466 (5)
H1	−0.017981	0.702609	0.708113	0.056*
C2	−0.2242 (3)	0.7539 (3)	0.7845 (2)	0.0573 (6)
H2	−0.279368	0.846994	0.755059	0.069*
C3	−0.2970 (3)	0.7009 (3)	0.8567 (2)	0.0625 (7)
H3	−0.402438	0.757956	0.876959	0.075*
C4	−0.2126 (3)	0.5621 (3)	0.89921 (19)	0.0560 (6)
H4	−0.260180	0.525087	0.948538	0.067*
C5	−0.0569 (3)	0.4794 (2)	0.86742 (15)	0.0416 (4)
C6	0.0458 (3)	0.3294 (2)	0.90766 (14)	0.0423 (5)
C7	−0.0040 (3)	0.2596 (3)	0.98322 (17)	0.0557 (6)
H7	−0.106847	0.304420	1.010974	0.067*
C8	0.1037 (4)	0.1211 (3)	1.01626 (19)	0.0633 (7)
H8	0.073508	0.071422	1.066710	0.076*
C9	0.2551 (4)	0.0576 (3)	0.97419 (19)	0.0646 (7)
H9	0.328422	−0.035164	0.995934	0.077*
C10	0.2969 (3)	0.1327 (3)	0.89971 (18)	0.0572 (6)
H10	0.399427	0.089693	0.871280	0.069*
C11	0.3354 (3)	0.6365 (3)	0.81864 (16)	0.0488 (5)
C12	0.3314 (2)	0.6416 (2)	0.71201 (15)	0.0423 (5)
C13	0.3660 (3)	0.7501 (3)	0.65585 (18)	0.0506 (5)
H13	0.396170	0.820311	0.682879	0.061*
C14	0.3549 (3)	0.7512 (3)	0.56175 (18)	0.0525 (6)
H14	0.379141	0.821728	0.523842	0.063*
C15	0.3069 (3)	0.6461 (3)	0.52081 (16)	0.0458 (5)
C16	0.2895 (3)	0.6408 (3)	0.42348 (17)	0.0582 (6)
H16	0.310379	0.709627	0.382234	0.070*
C17	0.2427 (4)	0.5359 (3)	0.39017 (17)	0.0628 (7)
H17	0.231864	0.533945	0.326044	0.075*
C18	0.2101 (3)	0.4301 (3)	0.45006 (17)	0.0555 (6)
H18	0.177607	0.359486	0.425571	0.067*
C19	0.2262 (2)	0.4309 (2)	0.54490 (14)	0.0414 (4)
C20	0.2756 (2)	0.5389 (2)	0.58185 (14)	0.0390 (4)
C21	0.2931 (3)	0.1775 (3)	0.60016 (18)	0.0537 (6)
H21A	0.322089	0.154278	0.534669	0.064*
H21B	0.235956	0.115767	0.624921	0.064*
C22	0.4453 (3)	0.1377 (3)	0.65315 (16)	0.0499 (5)
Cu1	0.24617 (3)	0.39114 (3)	0.76500 (2)	0.03891 (13)
N1	0.0152 (2)	0.5306 (2)	0.79716 (12)	0.0396 (4)
N2	0.1935 (2)	0.2667 (2)	0.86674 (12)	0.0438 (4)
N3	0.2891 (2)	0.53944 (19)	0.67594 (12)	0.0378 (4)
O1	0.3328 (3)	0.7512 (2)	0.85545 (14)	0.0748 (6)
O2	0.3376 (2)	0.5178 (2)	0.86003 (11)	0.0530 (4)
O3	0.18771 (18)	0.33480 (17)	0.60691 (11)	0.0451 (3)
O4	0.44274 (19)	0.22149 (18)	0.72007 (11)	0.0474 (4)
O5	0.5635 (3)	0.0249 (2)	0.62955 (15)	0.0767 (6)
O6	0.5905 (3)	0.3070 (3)	0.95692 (16)	0.0831 (6)
H6A	0.508609	0.382446	0.939031	0.125*
H6B	0.596455	0.322175	1.014362	0.125*
O7	0.7470 (3)	0.1554 (5)	0.8035 (2)	0.1204 (12)
H7A	0.710738	0.217715	0.847541	0.181*
H7B	0.664147	0.164423	0.774618	0.181*
O8	0.0612 (5)	0.0233 (5)	0.7446 (3)	0.1287 (11)
H8A	0.115716	−0.014590	0.792587	0.193*
H8B	−0.030172	0.089099	0.761473	0.193*
O9	−0.0714 (5)	0.9267 (4)	0.5844 (3)	0.1298 (12)
H9A	−0.052639	0.986184	0.619243	0.195*
H9B	−0.094777	0.968119	0.530334	0.195*

3 Comment

Recently, the studies on the structure and property of copper(II) complexes has been of one interest to chemists. Because they show novel structures [5] and excellent properties in anticancer properties [6], DNA binding and cleavage properties [7], magnetic property [8], etc. 8–carboxymethoxy-quinoline-2-carboxylic acid is an excellent polydentate ligand with four carboxylate-oxygen, one ether-oxygen and one pyridine-nitrogen atom. And it is known that it forms Mn(II), Co(II), Ni(II), and Cu(II) complexes as tetradentate O,O,N,O-chelates [9, 10]. Our research group has also been studying the synthesis, structural characterization and properties of copper complexes [11–13]. To continue the structure of the copper complexes, we have synthesized a copper complex using 8-carboxymethoxy-quinoline-2-carboxylic acid, cupric acetate monohydrate, 2,2′-bipyridine, and NaOH as materials. The coordination environment of the title Cu(II) complex is shown in Figure. As shown in Figure, the title Cu(II) complex is composed of one copper(II) ion, one 8-carboxymethoxy-quinoline-2-carboxylate ligand, one 2,2′-bipyridine ligand, and four uncoordinated water molecules. The copper(II) ion is six-coordinated with three carboxylate oxygen atoms (O2 and O4), one ether oxygen atom (O3) and one nitrogen atom (N3) from the same deprotonated 8-carboxymethoxy-quinoline-2-carboxylate ligand, and two nitrogen atoms (N1 and N2) of 2,2′-bipyridine ligand, forming a distorted octahedron geometry with N2 and N3 atoms at axial position. The 8-carboxymethoxy-quinoline-2-carboxylate ligand is tetradentate coordination mode, however its two deprotonated carboxylate groups adopt monodentate coordination mode. The bond lengths of Cu–O are 1.9816(16)–2.2619(17) Å, and the Cu–N bond lengths are 1.9883(17)–2.0286(17) Å, and the coordination angles around Cu(II) ion are in the range of 77.67(7)–171.87(7)°. The 8-carboxymethoxy-quinoline-2-carboxylate ligand coordinates with the copper(II) ion through the N and O atoms, forming three stable five-membered rings (ring 1: Cu1–O2–C11–C12–N3–Cu1, ring 2: Cu1–O3–C19–C20–N3–Cu1, ring 3: Cu1–O3–C21–C22–O4–Cu1). And the dihedral angles of ring 1 and ring 2, ring 2 and ring 3 are 3.92° and 73.79°, respectively, indicating that the copper(II) complex molecule is non-planar. The copper(II) complex molecules form 1D chain by the O–H···O hydrogen bonds.

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.

Research funding: This project was supported by the Talent Training Support of Henan Academy of Sciences (No. 220608086, 230608020, and 220208005), the National Natural Science Foundation of China (No. 21171132, http://dx.doi.org/10.13039/501100001809), and Science Foundation of Weifang (2020ZJ1054).

References

1. Bruker. *SAINT and SADABS*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2000.
2. 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.* 2009, *42*, 339–341.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Brandenburg K. *DIAMOND. Visual Crystal Structure Information System. Ver. 3.2*; Crystal Impact: Bonn, Germany, 2012.
5. Kan S. J., Ma Y. W., Chen C. J., Qian J. Crystal structure of poly[bis(μ_2-2,6-bis(1-imidazoly)pyridine-κ^2N:N') copper(II)] diperchlorate dihydrate, $C_{22}H_{22}Cl_2CuN_{10}O_{10}$. *Z. Kristallogr. N. Cryst. Struct.* 2023, *238*, 693–695.
6. Hou L. X., Jia X. Y., Wu Y. R., Li J. L., Yao D., Gou Y., Huang G. J. Aroylhydrazone Cu(II) complexes: syntheses, crystal structures, and anticancer properties. *J. Mol. Struct.* 2021, *1239*, 130469.
7. Kumar M. P., Tejaswi S., Rambabu A., Kalalbandi V. K. A., Shivaraj. Synthesis, crystal structure, DNA binding and cleavage studies of copper(II) complexes with isoxazole Schiff bases. *Polyhedron* 2016, *102*, 111–120.
8. Glaser T., Liratzis I., Frohlich R., Weyhermuller T. A trinucleating ligand based on 1,8-naphthalenediol: synthesis, structural and magnetic properties of a linear Cu–II Cu–II Cu–II complex. *Chem. Commun.* 2007, *4*, 356–358.
9. Zhang Y. P., Yang J. J., Lu J. Y., Gao C. Y., Zhao J. Z. Syntheses, structures, DNA/BSA binding and DNA cleavage of mononuclear manganese(II) and cobalt(II) complexes with *N,O*-chelating quinoline derivative ligand. *Chin. J. Inorg. Chem.* 2016, *32*, 2172–2182.
10. Lou H. D., Yin L., Zhang B. Q., Ouyang Z. W., Li B., Wang Z. X. Series of single-ion and 1D chain complexes based on quinolinic derivative: synthesis, crystal structures, HF–EPR, and magnetic properties. *Inorg. Chem.* 2018, *57*, 7757–7762.
11. Wang L. H., Liang L., Li X. T., Cao S. H., Tai X. S. The crystal structure of bis(6-phenylpyridine-2-carboxylato-κ^2N,O)copper(II), $C_{24}H_{16}N_2O_4Cu$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 1251–1253.
12. Cao S. H., Li X. Z., Gao Y., Li F. H., Li K. X., Cao X. X., Dai Y. W., Mao L. R., Wang S. S., Tai X. S. A simultaneously GSH-depleted bimetallic Cu(II) complex for enhanced chemodynamic cancer therapy. *Dalton Trans*. 2020, *49*, 11851–11858.
13. Tai X. S., Li P. F., Liu L. L. Preparation, characterization, and catalytic property of a Cu(II) complex with 2-carboxybenzaldehyde-*p*-toluenesulfonyl hydrazone ligand. *Bull. Chem. React. Eng. Catal.* 2018, *13*, 7–13.