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The crystal structure of phenantroline-κ²*N*,*N*′-bis(6-phenylpyridine-2-carboxylato-κ²*N*,*O*) copper(II), $C_{36}H_{24}N_4O_4Cu$

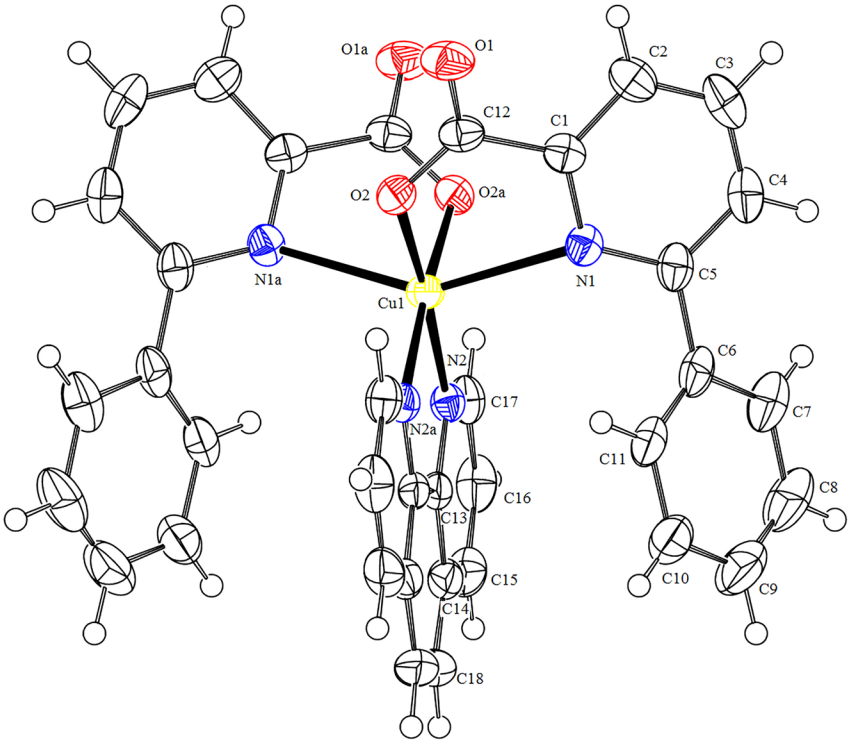

Figure 1: The molecular structure of title compound.

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Abstract

$C_{36}H_{24}N_4O_4Cu$, monoclinic, $I1_2/a1$ (no. 15), a = 16.5119(17) Å, b = 11.0747(7) Å, c = 17.6272(17) Å, β = 117.916(13)°, V = 2848.3(5) Å^3, Z = 4, $R_{gt}(F)$ = 0.0335, $wR_{ref}(F^2)$ = 0.0759, T = 200 K.

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The crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Ble block
Size:	0.13 × 0.12 × 0.1 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.82 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω-scans
θ_{max}, completeness:	25°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	5858, 2513, 0.028
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2156
$N(param)_{refined}$:	204
Programs:	Bruker programs [1], OLEX2 [2], SHELX [3], CrysAlis^{PRO}[4]

Source of materials

Synthesis of phenantroline-κ²*N*,*N*′-bis(6-phenylpyridine-2-carboxylate-κ²*N*,*O*)copper(II): a solution of $Cu(CH_3COO)_2.H_2O$ (100 mg, 0.5 mmol) in 5 mL distilled water was added to the solution of 6-phenylpyridine-2-carboxylic

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.750000	0.66302 (3)	0.500000	0.02650 (13)
O1	0.91121 (12)	0.94971 (14)	0.60478 (10)	0.0427 (4)
O2	0.82833 (11)	0.78297 (14)	0.58435 (9)	0.0327 (4)
N1	0.86092 (12)	0.72077 (16)	0.45147 (11)	0.0293 (4)
N2	0.67609 (12)	0.52537 (16)	0.42456 (11)	0.0263 (4)
C1	0.87672 (15)	0.8348 (2)	0.48023 (14)	0.0298 (5)
C2	0.89685 (16)	0.9265 (2)	0.43810 (16)	0.0415 (6)
H2	0.909055	1.004462	0.460332	0.050*
C3	0.89831 (18)	0.8992 (3)	0.36246 (18)	0.0491 (7)
H3	0.909738	0.959355	0.331860	0.059*
C4	0.88277 (17)	0.7827 (3)	0.33271 (17)	0.0443 (7)
H4	0.883041	0.763399	0.281482	0.053*
C5	0.86662 (15)	0.6937 (2)	0.37956 (15)	0.0333 (6)
C6	0.85970 (16)	0.5637 (2)	0.35623 (16)	0.0362 (6)
C7	0.82686 (18)	0.5263 (3)	0.27118 (17)	0.0502 (7)
H7	0.806144	0.582853	0.227083	0.060*
C8	0.8253 (2)	0.4050 (3)	0.2530 (2)	0.0643 (9)
H8	0.802280	0.380233	0.196254	0.077*
C9	0.8572 (2)	0.3204 (3)	0.3171 (2)	0.0630 (9)
H9	0.856172	0.239028	0.303633	0.076*
C10	0.89069 (19)	0.3555 (2)	0.40155 (19)	0.0499 (7)
H10	0.912826	0.298447	0.445364	0.060*
C11	0.89085 (16)	0.4771 (2)	0.42005 (16)	0.0388 (6)
H11	0.912469	0.501054	0.476832	0.047*
C12	0.87197 (16)	0.8592 (2)	0.56290 (14)	0.0311 (5)
C13	0.70941 (15)	0.41606 (19)	0.45931 (13)	0.0268 (5)
C14	0.66877 (17)	0.3067 (2)	0.42096 (15)	0.0344 (6)
C15	0.58839 (17)	0.3152 (2)	0.34181 (16)	0.0419 (6)
H15	0.558510	0.245303	0.313159	0.050*
C16	0.55422 (17)	0.4248 (3)	0.30703 (16)	0.0417 (6)
H16	0.500917	0.430249	0.254928	0.050*
C17	0.59984 (15)	0.5292 (2)	0.35020 (14)	0.0336 (6)
H17	0.575995	0.603963	0.326050	0.040*
C18	0.7111 (2)	0.1964 (2)	0.46279 (17)	0.0472 (7)
H18	0.684151	0.123239	0.437851	0.057*

acid (99.6 mg, 0.5 mmol) and NaOH (20 mg, 0.5 mmol) in 10 mL distilled water under stirring. After the solution was heated to 75 °C, a solution of 1,10-phenanthroline (90 mg, 0.5 mmol) in 15 mL ethanol was added to the above mixture. The mixture was then continued to react for 4 h under stirring. When the solution was cooled to room temperature, some blue precipitation appeared and was filtered. The mother liquid was transferred to a small beaker and standed still until blue crystals of the title comound were received after 22 days. Anal. Calcd for $C_{36}H_{24}N_4O_4Cu$: C, 67.49; H, 3.75; N, 8.75%. Found: C, 67.27; H, 3.98; N, 8.56%.

Experimental details

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

Comment

Pyridine carboxylic acid or 1,10–phenanthroline and their derivatives were widely used to construct metal complexes owing to their abilities to form stable chelates [5]. And their metal complexes exhibited a wide range of potential applications including magnetic properties [6], neurotropic activity [7], fluorescence sensor [8], antimicrobial properties [9], and catalytic activity [10]. We have previously published some metal complexes of Co(II), Cu(II), Zn(II) and Pb(II) with 6-phenylpyridine-2-carboxylate as a bidentate primary ligand [11–16]. Continuing to enrich our studies on the synthesis of transition metal complexes using pyridine carboxylic acid derivative ligands, herein we used 6-phenylpyridine-2-carboxylic acid and 1,10–phenanthroline as excellent starting materials to construct a new Cu(II) complex.

The molecular structure is given in Figure 1. The Cu(II) complex contains a Cu(II) ion, two 6-phenylpyridine-2-carboxylate ligands and one neutral 1,10-phenanthroline ligand. The asymmetric unit is one half of a complex located on a twofold axis. The Cu(II) ion forms a distorted octahedral six-coordination geometry by coordinating to two N atoms (N1 and N1a) and two O atoms (O2 and O2a) of two 6-phenylpyridine-2-carboxylate ligands, and two N atoms (N2 and N2a) from one 1,10-phenanthroline ligand. The bond angle of both O2–Cu1–N2 and O2a–Cu1–N2a are 173.26(7)°, showing that O2 and N2 (or O2a and N2a) atoms located on the axial position, and other four atoms (O2a, N1, N2a and N1a, or O2, N1, N2 and N1a) located on the equatorial plane. The Cu–N and Cu–O bond distances are 2.0154(18) Å (Cu1–N2),2.0155(17) Å (Cu1–N2a), 2.4418(18) Å (Cu1–N1), 2.4418(17) (Cu1–N1a), 1.9615(15) (Cu1–O2 and Cu1–O2a), respectively, which agrees with the reports [12, 15]. The comlex molecules are further interconnected by π–π intercation of neighboring aromatic rings to form the 3D network structure.

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

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. Rigaku Oxford Diffraction. *CrysAlisPRO Software System (Version 1.171.38.43f)*; Rigaku Corporation: Oxford, UK, 2015.
5. Ghadermazi M., Derikvand Z., Mahmouidiazar Z., Shahnejat E., Rudbari H. A., Bruno G., Shokrollahi A., Nasiri S., Nader P. M. A comparison of solution and solid state coordination environments for calcium(II), zirconium(IV), cadmium(II) and mercury(II) complexes with dipicolinic acid and methylimidazole derivatives. *J. Coord. Chem.* 2015, *68*, 3982–4002.
6. Li J. P., Khan M. R., Liu B., Niu X. G., Li B. H., Hao Y. P., Liu Z. Y. Synthesis, structures and magnetic properties of Cu^{II} and Co^{II} compounds based on asymmetric 5-(1*H*-imidazole-1-yl)-3-pyridine carboxylic acid. *Eur. J. Inorg. Chem.* 2020, *2020*, 3786–3796.
7. Paronikyan E. G., Ogannisyan A. V., Paronikyan R. G., Dzhagatspanyan I. A., Nazaryan I. M., Akopyan A. G., Minasyan N. S. Synthesis and neurotropic activity of 4-phenylpyridine-3-carboxylic acid and 3-hydroxy-4-phenylthieno[2,3-*b*]-pyridine derivatives. *Pharm. Chem. J.* 2019, *52*, 839–843.
8. Song J. F., Wen H. F., Luo J. J., Jia Y. Y., Zhang X. Y., Su L. J., Zhou R. S. Five isomorphic lanthanide metal-organic frameworks constructed from 5-(3-carboxy-phenyl)-pyridine-2-carboxylic acid and oxalate: synthesis, crystal structures and selective fluorescence sensing for aniline. *J. Solid State Chem.* 2019, *269*, 43–50.
9. Omoregie1 H. O., Eseol A. O., Akong R. A. Mixed ligand complexes of copper(II) with benzoyltrifluoroacetone, 1,10-phenanthroline and 2,2′-bipyridine: structure, spectroscopic and antimicrobial properties. *J. Mol. Struct.* 2022, *1250*, 131826.
10. Wang L. H., Wang Z. J., Zhao M. L., Tai X. S., Ouyang J., Li Y. F., Zhang W., Jia W. L. Synthesis, crystal structure of tetra-nuclear macrocyclic Zn (II) complex and its application as catalyst for oxidation of benzyl alcohol. *Bull. Chem. React. Eng. Catal.* 2021, *16*, 839–846.
11. Tai X.-S., Wang Z.-J., Ouyang J., Li Y.-F., Zhang W., Jia W.-L., Wang L.-H. The crystal structure of [(phenantroline-κ^2*N, N″*)-bis(6-phenylpyridine-2-carboxylate-κ^2*N,O*) cobalt(II)] monohydrate, $C_{36}H_{26}N_4O_5Co$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 1309–1311.
12. Wang L.-H., Liang L., Li X.-T., Cao S.-H., Tai X.-S. The crystal structure of bis(6-phenylpyridine- 2-carboxylato-κ^2*N,O*) copper(II), $C_{24}H_{16}N_2O_4Cu$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 1251–1253.
13. Wang L.-H., Wang Z.-J., Ouyang J., Tai X.-S. The crystal structure of bis(6-phenylpyridine- 2-carboxylate-κ^2N,O)-(2,2′-bipyridine-κ^2N,N″) zinc(II) monohydrate, $C_{34}H_{26}N_4O_5Zn$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 1297–1299.
14. Tai X. S., Liang L., Li X. T., Cao S. H., Wang L. H. Crystal structure of diaqua-bis(μ_2 –6-phenylpyridine-2-carboxylate-κ^3*N,O:O*)-bis(6-phenylpyridine-2-carboxylato-κ^2N,O)lead(II)–N,N-dimethylformamide –water (1/2/4), $C_{54}H_{58}N_6O_{16}Pb_2$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 1199–1201.
15. Feng Y. M., Tai X. S., Xia Y. P. The crystal structure of [(2,2″-bipyridine-κ^2*N,N*)-bis(6-phenylpyridine-2-carboxylate-κ^2*N,O*)copper(II)], $C_{34}H_{24}N_4O_4Cu$. *Z. Kristallogr. N. Cryst. Struct.* 2022, *237*, 285–287.
16. Tai X. S., Xia Y. P. The crystal structure of [(2,2′-bipyridine-κ^2*N, N″*) -bis(6-phenylpyridine- 2-carboxylate-κ^2*N,O*)cobalt(II) monohydrate, $C_{36}H_{26}N_4O_5Co$. *Z. Kristallogr. N. Cryst. Struct.* 2022, *237*, 225–227.