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STRUCTURAL CHARACTERIZATION OF A NEW COPPER(II) COMPLEX OF 1,10-PHENANTHROLINE AND BENZOATE [Cu(phen)($C_6H_5CO_2^-$)$_2$]

S.S. Batool[1], S. Ahmad[1], I.U. Khan[2], Ejaz[2], W.T.A. Harrison[3]

[1]*Department of Chemistry, University of Engineering and Technology, Lahore, Pakistan*
E-mail: saeed_a786@hotmail.com
[2]*Department of Chemistry, Government College University, Lahore, Pakistan*
[3]*Department of Chemistry, University of Aberdeen, Aberdeen, Scotland*
E-mail: w.harrison@abdn.ac.uk

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A new mixed-ligand copper(II) complex of 1,10-phenanthroline (phen) and benzoate ligands having the general formula [Cu(phen)($C_6H_5CO_2$)$_2$] is prepared and its crystal structure is determined by X-ray crystallography. The complex exists in the monomeric form; the coordination environment around the copper(II) ion is square planar, with the pair of monodentate benzoate ligands being in a *cis* disposition. In the crystal, the molecules are linked into [001] chains by weak C—H···O interactions; no aromatic π—π stacking occurs.

K e y w o r d s: copper(II) carboxylates, 1,10-phenanthroline, benzoic acid.

Copper containing enzymes perform a number of important functions such as growth, cell differentiation, mitochondrial oxidative phosphorylation (cytochrome C oxidase), catecholamine production (dopamine hydroxylase), pigmentation (tyrosinase), antioxidant protection (superoxide dismutase), anti-inflammatory activity (ceruloplasmin), iron metabolism, and copper transport [1—11]. Several copper(II) complexes of 1,10-phenanthroline and carboxylic acids are also known to possess antitumor and antimutagenic activity [10—19].

Keeping in view the biological importance of copper complexes, there has been a substantial increase in interest in the study of copper(II) complexes of bipyridine or phenanthroline and carboxylates [20—40]. These complexes exhibit a great structural diversity, including mononuclear, binuclear, or even polynuclear supramolecular complexes. In these complexes, carboxylate ions might involve monodentate [20—32] and bidentate chelating, including both symmetrical and asymmetrical, coordination modes [32—39]. Dicarboxylates usually form polymeric complexes exhibiting monodentate or chelating bridging modes [29, 30, 38, 39]. π—π Stacking interactions among the phenantroline ligands and with aromatic carboxylates, and the hydrogen bonding interactions play a very important role in the formation of supramolecular architectures [24, 27—30].

A considerable number of copper(II) complexes of phenanthroline and monocarboxylic acids (acetic, benzoic, 2-fluorobenzoic, formic, lactic, and propionic) have been reported [19, 27, 28, 31, 32, 34]. Except acetate and propionate complexes, the carboxylate ligand in these complexes coordinates in a monodentate terminal mode. The acetate and propionate ions behave as bridging ligands [19, 32]. In the present paper, we report the synthesis and crystal structure of a new heteroleptic copper(II) complex, using 1,10-phenanthroline and benzoate ($C_7H_5O_2^-$): [Cu(phen)(benzoate)$_2$] (**1**).

Experimental. ***Materials.*** $CuCl_2 \cdot 2H_2O$, 1,10-phenanthroline-dihydrate and benzoic acid were obtained from Merck Chemical Co., Germany.

Synthesis. A solution of 0.198 g (1.00 mmol) 1,10-phenanthroline in 15 ml of methanol was added to an aqueous solution (15 ml) of 0.170 g (1.00 mmol) of $CuCl_2 \cdot 2H_2O$. After stirring the sea-blue colored solution for half an hour at room temperature, 0.25 g (2 mmol) of a benzoic acid solution in 15 ml of methanol containing 20 drops of a NaOH solution (1 M) was added dropwise. The resulting blue solution was stirred for half an hour. The solution was then left to stand at room temperature. Dark blue crystals of **1** were obtained after one week. The crystals were washed with cold methanol, and dried in air. Yield = 15 % [m.p. 264 °C (decomp.)].

X-ray structure determination. Single crystal data collection for **1** was performed on a Bruker SMART APEX-II CCD diffractometer using graphite monochromated MoK_α radiation (λ = = 0.71073 Å) at 293 K. SAINT was used for the unit-cell refinement and data reduction [41]. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares against $|F|^2$ using SHELXL-97 [42]. The hydrogen atoms were geometrically placed (C—H = 0.93 Å) and refined as riding atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. Crystal data and details of the data collection are given in Table 1.

Results and discussion. ***Synthesis and spectroscopy.*** The reaction of $CuCl_2 \cdot 2H_2O$ with 1,10-phenanthroline and benzoic acid in a 1:1:2 molar ratio resulted in a product of the empirical composition [Cu(phen)(benzoate)$_2$] (**1**). The selected IR frequencies of the free ligands and copper(II) complex **1** are given in Table 2. The band around 1600 cm^{-1} is due to the asymmetric vibration of a coordinated

Table 1

Crystal data and details of the structure refinement for compound **1**

Formula	$C_{26}H_{18}CuN_2O_4$
Formula weight	485.90
Crystal system	Monoclinic
Space group; Z	$C2/c$; 4
a, b, c, Å	21.2662(7), 9.9266(3), 10.9599(3)
β, deg.	115.575(1)
V, Å^3	2086.96(11)
ρ_{calc}, g/cm^3	1.547
$F(000)$	996
μ, mm^{-1}	1.085
T, K	293(2)
λ, Å	0.71073
θ range, deg.	2.77—28.30
Limiting indices h, k, l	$-28 \rightarrow 27$, $-13 \rightarrow 12$, $-14 \rightarrow 14$
Reflections: collected/uniq.	9910/2601 [R_{Int} = 0.019]
Observed data [$I > 2\sigma(I)$]	2346
Data / restraints / parameters	2601 / 0 / 150
R_1, wR_2, S [$I > 2\sigma(I)$]	0.026, 0.076, 1.10
$\Delta\rho_{min,max}$, e/Å^3	–0.26, +0.33

Table 2

Selected IR frequencies (cm^{-1}) *of the free ligands and the title complex*

Species	ν(C=N)	ν(C=C)	ν(CO_2, asym)	ν(CO_2, sym)
Phen	1562, 1618	1423, 1446, 1505	—	—
Benzoic acid	—	1555	1689	1603
[Cu(phen)(benzoate)$_2$]	1564, 1600	1422, 1513	1600	1361

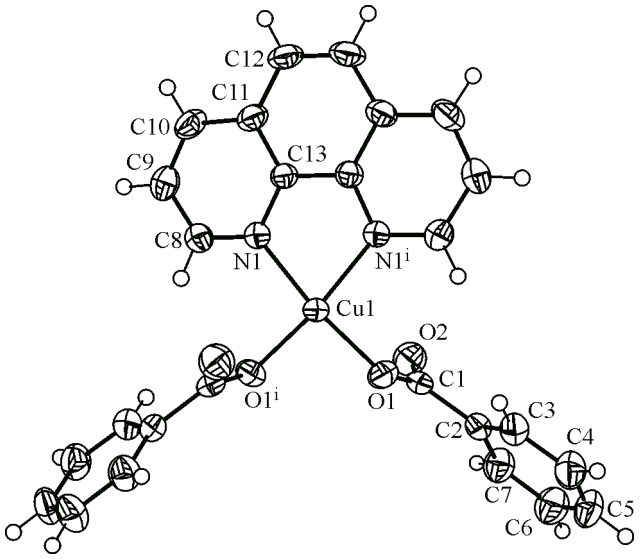

Fig. 1. Molecular structure of **1** (50 % displacement ellipsoids).
Symmetry code: i = 1–*x*, *y*,1/2–*z*

carboxylate group ($\nu_{asym}(CO_2^-)$), while the band in the region of 1370 cm^{-1} may be attributed to the symmetric stretching vibration of a carboxylate group ($\nu_{sym}(CO_2^-)$). The large difference in $\nu_{sym}(CO_2^-)$ and $\nu_{asym}(CO_2^-)$ frequencies ($\Delta\nu > 230$ cm^{-1}) is indicative of the monodentate coordination of the carboxylate groups to the metal [34, 43]. These bands are typical of monodentate carboxylate ligands and are similar to those found for other copper(II) carboxylato/1,10-phenanthroline complexes [22, 34]. The C—H stretching bands are observed at 3063 cm^{-1}. The peak at 452 cm^{-1} is due to Cu—N stretching vibrations. The presence of ν(C=N) and ν(C=C) bands of phen around 1600 cm^{-1} and 1400 cm^{-1} respectively, also indicates the coordination of the phenanthroline ligand to the metal.

Crystal structure description. The molecular structure of the monomeric, neutral complex of **1** is shown in Fig. 1, and selected geometrical data are listed in Table 3. The Cu^{2+} ion lies on a crystallographic two-fold axis and the asymmetric unit corresponds to half of the molecular formula. The metal ion is coordinated by two nitrogen atoms of the phenanthroline ligand and two oxygen atoms of two monodentate carboxylate ions in a slightly distorted *cis*-CuN_2O_2 square planar geometry. The pucker angle between Cu1/N1/N1^i and Cu1/O1/O1^i (i = 1–*x*, *y*, 1/2–*z*) is 1.58(16)° and the dihedral angle between the outer rings of the phen ligand is 1.49(14)°.

In **1**, the second O atom of the carboxylate group lies 2.7255(15) Å away from Cu1 and an alternative description of the metal-ion coordination would be a grossly distorted octahedron. The N—Cu—N bite angle of the phen ligand is 81.52(7)°, which is comparable with a mean value of 81.04° (s.d. = 1.49°) for Cu-phen complexes [19—36]. The C—O bond lengths of the carboxylate group (Table 3) differ by about 0.057 Å and the Cu^{2+} ion deviates from the C1/O1/O2 plane by –0.16 (6) Å.

The dihedral angles between the CuN_2O_2 mean plane and the carboxylate group and the benzene ring are 87.61(11)° and 58.25(6)°, respectively; that between the carboxylate group and its benzene ring is 34.50(17)°. The dihedral angle between the symmetry-related benzene rings of the benzoate groups is 87.49(4)°. In the crystal, the molecules are linked by weak C9—H9···O2^{ii} (ii = –*x*, 1–*y*, 1–*z*) interactions, with H···O = 2.57 Å, C···O = 3.204 (2) Å, and C—H···O = 126°, with the uncoordinated carboxylate O atom acting as the acceptor. Crystal symmetry generates [001] chains incorporating centrosymmetric $R_2^2(16)$ loops between each pair of molecules (Fig. 2). Despite the preponderance of aromatic rings, there is no aromatic π—π stacking present in the crystal of **1**.

T a b l e 3

Selected bond distances (Å) *and bond angles* (deg.) *for compound* **1**

Cu1—O1	1.9414(10)	O1—Cu1—N1	172.64(5)
Cu1—N1	2.0192(12)	O1—Cu1—O1^i	96.08(7)
C1—O1	1.2824(18)	N1—Cu1—N1^i	81.52(7)
C1—O2	1.2256(19)	C1—O1—Cu1	108.90(10)

Symmetry code: i = 1–*x*, *y*, 1/2–*z*.

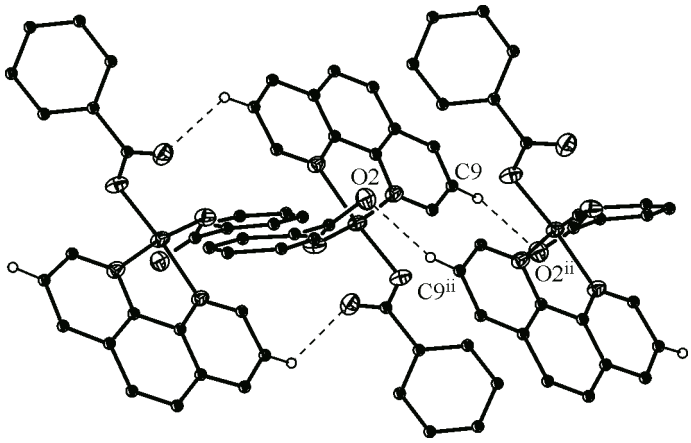

Fig. 2. Fragment of a [001] hydrogen-bonded chain of molecules incorporating $R_2^2(16)$ loops in the crystal of **1** with C—H···O links shown as double-dashed lines.
Symmetry code: ii = –*x*, 1–*y*, 1–*z*

Compound **1** is essentially isostructural with the known structure of the cinnamate ligand [Cu(phen)(cinnamate)$_2$] (*i.e.*, a similar unit cell and equivalent packing, taking into account the different space-filling requirements of the ligands) [44]. The uncoordinated O atom in [Cu(phen)(cinnamate)$_2$] lies 2.5660(15) Å from the metal ion; the phen bite angle is 81.5(7)°, and the metal ion deviates from the carboxylate plane by –0.12(6) Å. The difference in C—O bond lengths is 0.042 Å, which is somewhat less than the equivalent value in **1**.

Conclusions. The synthesis and crystal structure of [Cu(phen)(benzoate)$_2$] (**1**) has been described. In **1**, the copper atom has a distorted square planar geometry and the benzoate ion coordinates as a monodentate ligand. Conversely, chelating bidentate [33—35] or bridging carboxylate groups [32, 38] have been observed in some other complexes. Weak C—H···O interactions link the molecules of **1** into chains in the crystals, but no aromatic π—π stacking occurs.

Supplementary material. Crystallographic data for **1** has been deposited with the Cambridge Crystallographic Center under CCDC Nos. 865466. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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