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STRUCTURAL CHARACTERIZATION OF A MIXED-LIGAND COMPLEX OF COPPER(II) WITH 1,10-PHENANTHROLINE AND THE *m*-AMINOBENZOATE ION

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A new copper(II) complex of 1,10-phenanthroline ($C_{12}H_8N_2$) and the *meta*-aminobenzoate ion (*m*-amb; $C_7H_6NO_2^-$), having the formula $Cu(C_{12}H_8N_2)(C_7H_6NO_2)Cl\cdot 0.5H_2O$, is prepared and characterized by elemental analysis, IR spectroscopy, and single crystal X-ray diffraction. The structure is built up from monomeric units in which the coordination environment around the metal ion is a square plane arising from a bidentate 1,10-phenanthroline molecule, a monodentate *m*-amb anion, and a chloride ion. A very long (Cu—N = 2.856(5) Å) bond to the nitrogen atom of an adjacent *m*-amb ion generates [101] polymeric chains in the crystal. The crystal structure is consolidated by N—H···O and O—H···O hydrogen bonds and C—H···O, C—H···Cl, and aromatic π—π stacking interactions. Crystal data: $C_{19}H_{15}ClCuN_3O_{2.5}$, $M_r = 424.33$, monoclinic, $P2_1/n$ (No. 14), $a = 9.8200(5)$, $b = 10.9291(7)$, $c = 16.3803(9)$ Å, $\beta = 105.293(3)°$, $V = 1695.74(17)$ Å^3, $Z = 4$, $R(F) = 0.043$, $wR(F^2) = 0.122$.

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Keywords: synthesis, copper(II), 1,10-phenanthroline, *m*-aminobenzoate ion, coordination polymer.

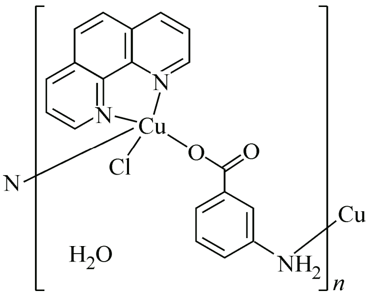
INTRODUCTION

Copper is a bio-essential trace element, being an important part of various metalloenzymes. It controls many metabolic processes in biological systems, including mitochondrial oxidative phosphorylation, iron metabolism, and synthesis of neurotransmitter, cell growth and differentiation, dioxygen transport, free radical detoxification *etc*. The fact that enables copper to act as a catalytic cofactor is its ability to manifest biological copper(I)—copper(II) redox interconversions. The Cu—Zn SOD enzyme is one of nearly thirty known copper-containing metallo-enzymes (e.g., tyrosinase, cytochrome C oxidase, ceruloplasmin, dopamine hydroxylase, *etc*.) that acts as a natural antioxidant and catalyzes the dismutation of toxic superoxide (O_2^-) ions, which are being continuously produced *in vivo*, into less toxic hydrogen peroxide (H_2O_2) and dioxygen (O_2) under physiological conditions in the body [1]. The synthesis of copper(II) complexes of phenanthroline and carboxylates and the study of their function as SOD-biomimetics is a focal point in the field of bioinorganic chemistry [2—5].

Copper(II) phenanthroline/carboxylato complexes possess a wide range of pharmacological applications due to their antiviral [6], antimicrobial [7—9], antimycobacterial [10, 11], anti-inflammatory, and anticandida [12] activities. Their relatively low molecular weights make their use attractive as drugs [13].

Mixed-ligand complexes of copper(II) with diamines and carboxylates exhibit great structural diversity and coordination versatility, owing to the variable ligation of the carboxylate moiety. Copper(II) carboxylates exhibit monodentate [6, 14] and bidentate [15, 16], coordination modes resulting in supramolecular metal-organic frameworks. Aromatic π—π stacking interactions involving the phenanthroline ligands with aromatic carboxylates and hydrogen bonding interactions appear to play an important role in both formation and consolidation of these supramolecular architectures [17—18].

As part of our studies in this area, we now report the synthesis and structural characterization of $Cu(C_{12}H_8N_2)(C_7H_6NO_2)Cl\cdot 0.5H_2O$ (**1**): a new coordination polymer containing copper(II),1,10-phenanthroline and the *meta*-aminobenzoate anion.



Scheme 1

EXPERIMENTAL

Materials and methods. $CuCl_2\cdot 2H_2O$ and 1,10-phenanthroline were purchased from Merck Chemical Company, Germany, while *m*-aminobenzoic acid, methanol, and NaOH were purchased from Sigma-Aldrich Chemical Company. Elemental analyses for C, H, and N were carried out using a Perkin-Elmer 2400 II elemental analyzer. The infrared spectrum of **1** was recorded on a FT/IR-4100 type A spectrometer in the range 4000—400 cm^{-1}.

Synthesis. A solution of 0.198 g (1.00 mmol) 1,10-phenanthroline in 15 ml methanol was slowly added to an aqueous solution (15 ml) of 0.170 g (1.00 mmol) $CuCl_2\cdot 2H_2O$, with constant stirring. The dark blue solution thus obtained was stirred for half an hour at room temperature. Then, 0.275 g (nearly 2 mmol) of an *m*-aminobenzoic acid solution in 15 ml methanol containing 20 drops of a NaOH solution (1 M) was added dropwise to the above solution. The resulting green solution was stirred for half an hour at 50 °C and filtered. The filtrate was then left to stand at room temperature. Green crystals of **1** were obtained after one week; they were washed with cold methanol and dried in air. Yield = 50 % based on copper; m.p. 221 °C (decomposes). Microanalysis (%) for $C_{19}H_{15}ClCuN_3O_{2.50}$. Calculated: N 9.90, C 53.78, H 3.56, found: N 9.37, C 53.49, H 3.87.

X-ray structure determination. The 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 296 K. The structure was solved by direct methods and the atomic model was optimized by the refinement against $|F|^2$ with SHELXL-97 [19]. The O3 atom of the water molecule of crystallization was found to be statistically disordered over two adjacent sites related by inversion symmetry (O3···O3′ = 2.11 Å). The C-bound H atoms were geometrically placed (C—H = 0.93 Å) and refined as riding atoms. The N- and O-bound H atoms were located in difference maps: the positions of the N-bonded H atoms were freely refined and the O-bonded H atoms were refined as riding atoms in their as-found relative positions. The constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) was applied in all cases. Crystal data and details of the structure determination are summarized in Table 1.

RESULTS AND DISCUSSION

Infrared spectroscopy. The selected IR frequencies of **1** are shown in Table 2. The O—H stretch [20] appears as a strong, broad band extending approximately from 3500 to 2500 cm^{-1}. This broad band partially obscures other peaks like the C—H and N—H bands. The band at 3061 cm^{-1} is proba-

Table 1

Crystal data for complex **1**

Empirical formula	$C_{19}H_{15}ClCuN_3O_{2.5}$
Formula weight	424.33
Temperature, K	296(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$ (No.14)
a, *b*, *c*, Å; β, deg.	9.8200(5), 10.9291(7), 16.3803(9); 105.293(3)
V, Å^3	1695.74(17)
Z	4
ρ_{calc}, g/cm^3	1.662
μ, mm^{-1}	1.469
$F(000)$	864
Crystal size, mm	0.33×0.25×0.23
2θ range for data collection, deg.	5.56—53.0
h k l ranges	$-12 \to 9$; $-13 \to 13$; $-19 \to 20$
Reflections scanned / independent	12658 / 3493 ($R_{Int} = 0.047$)
Data / restraints / parameters	3493 / 0 / 259
$R(F)$ $[I > 2\sigma(I)]$	0.043
$wR(F^2)$	0.122
Min., max. Δρ, e/Å^3	–0.60, +0.37

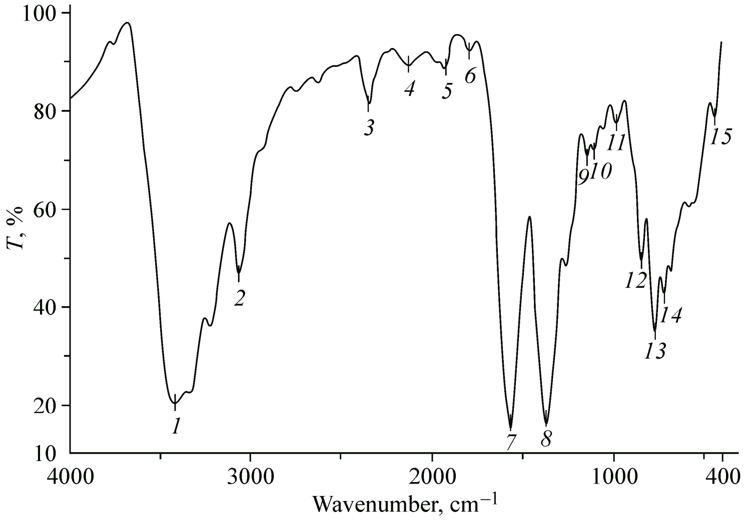
Table 2

Selected IR *frequencies* (cm^{-1}) *of complex* **1**

Compound	ν(O—H)	ν(N—H)	$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	ν(Cu—O)	ν(Cu—N)
$Cu(C_{12}H_8N_2)(C_7H_6NO_2)Cl \cdot 0.5H_2O$ (**1**)	3420	3216	1570	1367	584	441

bly a =C—H stretch. The band around 1570 cm^{-1} is due to the asymmetric vibration of a coordinated carboxylate group [$\nu_{asym}(CO_2^-)$], while the band at 1367 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 ($\Delta\nu = 203$ cm^{-1}) is indicative of the monodentate-O coordination of carboxylate groups to the metal [20, 21]. Overall, these bands are similar to those found for other copper(II)—1,10-phenanthroline complexes incorporating carboxylate moieties [22]. The bands at 1144 and 1106 cm^{-1} are assigned to C—O and C—N stretches, respectively. The low-energy peaks at 584 and 441 cm^{-1} might be due to Cu—O and Cu—N stretching modes, respectively [23]. Two strong vibrations at 845 and 722 cm^{-1} correspond to out of plane (oop) C—H deformations of the 1,10-phenanthroline molecule [24]. This indicates that both ligands are coordinated to the metal ion, as confirmed by the crystal structure.

Crystal structure. The molecular structure of $Cu(C_{12}H_8N_2)(C_7H_6NO_2)Cl \cdot 0.5H_2O$ (**1**) is shown in Fig. 1. Selected bond lengths and angles are presented in Table 3. The copper ion is coordinated to a bidentate phen molecule (Cu—N = 2.018(3) and 2.020(3) Å), a monodentate carboxylate O atom (Cu—O = 1.936(2) Å), and a chloride ion (Cu—Cl = 2.2416(12) Å) in a square planar (r.m.s. deviation of the bonded atoms from the metal ion = 0.040 Å) arrangement. The N—Cu—N bite angle is 81.64(11)° and the *trans* N—Cl—O and N—Cu—Cl angles are 169.43(12)° and 169.38(8)°, respectively. These geometrical data are in good accordance with previous results for similar materials [25, 26].



Scheme 2

The refinement of U_{ij} values for the uncoordinated O2 atom of the carboxylate group led to an unrealistically anisotropic ellipsoid and the atom was modelled as being disordered over two adjacent sites (O2···O2 = 1.15 Å), which may correlate with the positional disorder of the water molecule of crystallization. The dihedral angle between the phen and benzene ring planes is 79.78(16)°.

Table 3

Selected bond lengths (Å) *and angles* (deg.) *for complex* **1**

Bond lengths		Bond angles			
Cu1—O1	1.936(2)	O1—Cu1—N1	90.61(11)	O1—Cu1—Cl1	93.59(9)
Cu1—N1	2.018(3)	O1—Cu1—N2	169.43(12)	N1—Cu1—Cl1	169.38(8)
Cu1—N2	2.020(3)	N1—Cu1—N2	81.64(11)	N2—Cu1—Cl1	92.88(9)
Cu1—Cl1	2.2416(12)	O1—Cu1—N3^{i}	110.58(11)	N1—Cu1—N3^{i}	83.44(12)
Cu1—N3^{i}	2.856(5)	N2—Cu1—N3^{i}	75.81(11)	Cl1—Cu1—N3^{i}	104.12(9)

Symmetry code: ^{i} x–1/2, 1/2–y, z–1/2.

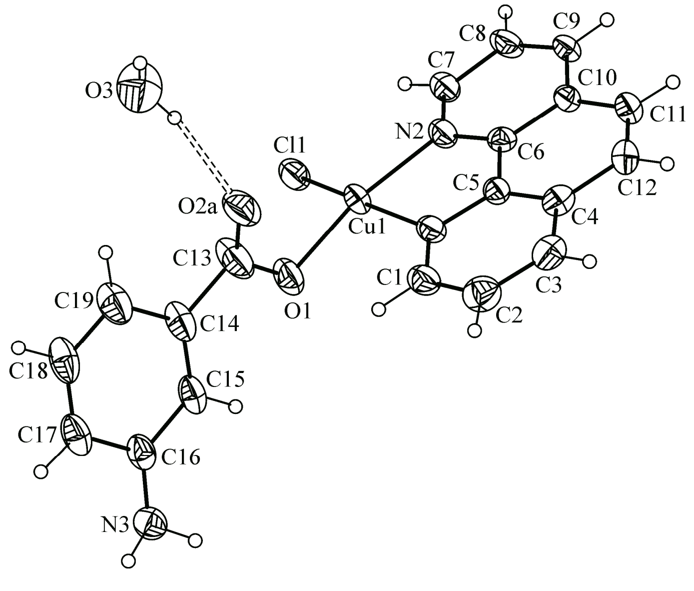


Fig. 1. Molecular structure of **1** showing 50 % displacement ellipsoids.
Only one disorder component of O2 and O3 is shown. The O—H···O hydrogen bond is indicated by a double-dashed line

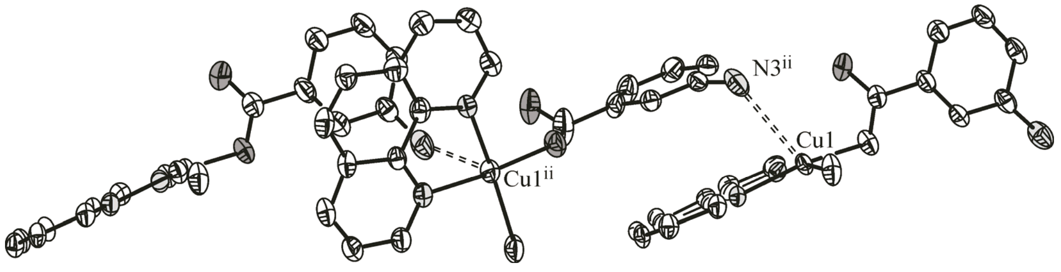


Fig. 2. Fragment of a [101] polymeric chain in the structure of **1** with the long Cu1—N3 bond shown as a double-dashed line.
Symmetry code: (ii) *x*–1/2, 1/2–*y*, *z*–1/2

A very long (2.855(5) Å) Cu—N contact to the amine group of an adjacent $C_7H_8NO_2^-$ ion completes a highly distorted square-based pyramidal arrangement for the metal ion. If this contact is regarded as a bond, polymeric chains (Fig. 2) arise, which propagate in the [101] direction, with adjacent molecules in the chain being related by *n*-glide symmetry.

The structure of **1** is consolidated by various hydrogen bonds (Table 4) as well as aromatic π—π stacking. One of the H atoms of the amine —NH_2 group forms an N—H···O link to both disordered components (O2a and O2b) of the uncoordinated carboxylate oxygen atom. Another H atom forms a bifurcated N—H···(O, Cl) bond to the chloride ion of an adjacent chain and the uncoordinated water molecule (O3). The disordered water molecule (O3) crosslinks the polymeric chains by O—H···O hydrogen bonds to the uncoordinated carboxylate O2 atom, which possibly correlates with the disorder observed for this species. Finally, a C—H···O and a C—H···Cl interaction are observed, although their structural role in the relatively complex packing in this structure is not clear. Aromatic π—π stacking appears to play a significant role in determining the packing in **1**, with a number of short centroid—centroid contacts observed (3.479(2) Å between the N1 and N2 rings, 3.511(2) Å between the C11 and C14 rings, 3.771(2) Å between the N1 and C14 rings, and 3.787(2) Å between the N1 and C11 rings).

CONCLUSIONS

The synthesis and crystal structure of $Cu(C_{12}H_8N_2)(C_7H_8NO_2)Cl\cdot 0.5H_2O$(**1**) have been described. The phenanthroline molecule acts in its usual fashion as a chelating bidentate ligand and the *m*-amino-

Table 4

Bond separations (Å) *and bond angles* (deg.) *in the complex* **1**

Donor—H…Acceptor	D—H	H…A	D…A	D—H…A
N3—H3A…O2A^{i}	0.80(5)	2.42(5)	3.087(7)	141(4)
N3—H3A…O3^{ii}	0.80(5)	2.58(5)	3.291(8)	149(5)
N3—H3B…Cl1^{iii}	0.90(5)	2.56(5)	3.447(4)	168(4)
O3—H3C…O2A	0.80	2.01	2.788(12)	165
O3—H3D…O2B^{iv}	0.81	1.92	2.718(10)	171
C8—H8…O3^{v}	0.93	2.39	3.066(8)	129
N3—H3A…O2B^{i}	0.80(5)	2.45(5)	3.128(8)	144(5)
C9—H9…Cl1	0.93	2.75	3.554(4)	145

Symmetry codes: ^{i} *x*+1/2, 1/2–*y*, *z*+1/2; ^{ii} 1.5–*x*, *y*–1/2, 1.5–*z*; ^{iii} 1/2–*x*, *y*–1/2, 1.5–*z*; ^{iv} 1–*x*, 1–*y*, 1–*z*; ^{v} –*x*, 1–*y*, 1–*z*. The four values for the hydrogen bonds refer to the D—H, H···A, D···A separations (Å) and the D—H···A bond angle (deg.), respectively.

benzoate anion coordinates as a monodentate-O ligand. Similar coordination modes have been observed in many other mixed-ligand Cu(II)—phenanthroline/carboxylate complexes, for example with the benzoate [14], acetate [27], and adipate anions [28].

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Crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1042555). 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; e-mail: deposit@ccdc.cam.ac.uk.

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