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CRYSTAL STRUCTURE AND SPECTROSCOPIC CHARACTERIZATION OF A COORDINATION POLYMER OF COPPER(II) CHLORIDE WITH ETHYLENEDIAMINE AND THE 2-HYDROXYBENZOATE ION

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A new mixed-ligand one-dimensional copper(II) coordination polymer $[Cu(en)(sal)Cl]_n$ where en = ethylenediamine($C_2H_8N_2$) and Hsal = 2-hydroxybenzoic acid (salicylic acid; $C_7H_6O_3$) is synthesized and characterized by FTIR spectroscopy and single crystal X-ray diffraction. The structure contains Cu^{2+} ions in two different distorted octahedral coordination environments: an axially extended CuN_4Cl_2 moiety arising from a pair of bidentate en ligands and a CuO_4Cl_2 moiety arising from a pair of asymmetrically coordinated sal^- anions. The chloride ions bridge the copper ions into a zigzag chain propagating in [001]. The structure is consolidated by N—H···O and N—H···Cl hydrogen bonds which generate a layered network. Crystal data: $C_9H_{13}ClCuN_2O_3$, $M_r = 296.20$, monoclinic, $P2_1/c$, $a = 13.9179(10)$ Å, $b = 10.4900(8)$ Å, $c = 8.5181(6)$ Å, $\beta = 105.518(4)°$, $V = 1198.30(15)$ Å^3, $Z = 4$, $R(F) = 0.026$, $wR(F^2) = 0.068$.

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K e y w o r d s: copper(II) carboxylate, ethylenediamine, salicylate, coordination polymer.

INTRODUCTION

Copper is a part of many metallo-enzymes and plays a crucial role in biological processes. It also has pharmacological applications due to its anti-ulcer, anti-inflammatory (AI), anti-convulsant, anti-tremor, and SOD activities [1]. Salicylic acid (Hsal) $C_7H_6O_3$, also known as 2-hydroxybenzoic acid, has many biological properties including antipyretic, antiseptic, anti-bacterial, anti-fungal, keratolytic, and photoprotective activities and is used for skin treatments [2]. The biological properties of copper and salicylic acid are manifested with an increased activity in copper(II) salicylate that is a potent anti-oxidant, anti-inflammatory, anti-arthritic, and anti-epileptic agent [3]. It has anti-cancer, anti-tumor, anti-convulsant activities and ability to prevent chemically induced skin cancers [4, 5].

The presence of nitrogen-donor ligands in ternary copper carboxylates seems to further enhance their biological activities. Some of these act as mimics or model systems for copper(II)-containing metalloproteins, including tyrosinase, superoxide dismutase etc., and manifest a variety of pharmacological effects such as anticancer, anticarcinogenic, antimetastatic, and antimutagenic activities, suggesting their potential use as new therapeutically administered drugs [6—8]. These complexes also possess interesting magnetic properties [9].

Ethylenediamine ($H_2N—CH_2—CH_2—NH_2$; en) is the simplest example of an N-donor chelating ligand and in combination with copper(II) almost invariably forms a five-membered chelate ring.

When two such rings occur in the complex, they are almost always *trans* to each other. Many ternary copper(II)—carboxylate complexes with diamines contain $[Cu(en)_2(X)_2]^{2+}$ units where $X = H_2O$ or CH_3OH. The en ligands in the $[Cu(en)_2(X)_2]^{2+}$ di-cation usually form an equatorial square plane, while the two *trans* water (or methanol) molecules occupy axial positions, forming a Jahn—Teller tetragonally distorted octahedron. The carboxylate anions in these monomeric complexes usually take on the role of the counterion and intermolecular interactions, including O—H···O and N—H···O hydrogen bonds, and in some cases, aromatic π—π stacking interactions link the cations and anions into a supramolecular architecture. Examples of these salts include copper(II)—ethylenediamine/water complexes with 4-nitrobenzoate [10], 4-chlorobenzoate [11], 3-pyridyl-propionate [12], *o*-aminobenzoate [13], 2-chloro-5-flourobenzoate [14] and 4-fluorobenzoate [15], *p*-hydroxybenzoate [16]. A benzene-1,4-dicarboxylate complex has a similar structure but the two coordinated water molecule at the axial positions are replaced by methanol molecules [17].

Most Cu(II)—en complexes are octahedral, but $[Cu(en)_2](sal)_2 \cdot 2H_2O$ [13] has a square-planar CuN_4 chromophore and $[Cu(en)_2(H_2O)](sy)_2(en)(H_2O)_2$(sy = syringate) has a unique square pyramidal structure [18]. In both these examples, however, the anions form a part of the outer sphere, acting only as counter ions. Our interest lies in the few cited cases in which the carboxylate ions are part of the metal coordination sphere, including $[Cu(hb)(en)_2(OH_2)](hb)$ (hb = benzilate) [19], $[Cu(isonic)(dien)(H_2O)1.5] \cdot 0.5SO_4 \cdot 2.5H_2O$ (isonic = isonicotinate; dien = diethylenediamine) [20] and $[Cu_3(pdc)_4(en)_2] \cdot en \cdot 4H_2O$ (pdc = pyridine-2,6-dicarboxylate, $C_7H_3NO_4^{2-}$) [21].

In order to extend this area of research, we now report the synthesis, spectroscopic characterization, and crystal structure of $[Cu(en)(sal)Cl]_n$, (**1**), a ternary copper(II) coordination polymer incorporating the salicylate ion and ethylenediamine.

EXPERIMENTAL

Materials and methods. All chemicals used were analytical reagents. Elemental analysis for C, H, and N was carried out using a Perkin—Elmer 2400 II elemental analyzer. The IR absorption spectrum was recorded on a FT/IR-4100 type A spectrometer in the range 4000—400 cm^{-1} using a KBr pellet.

Synthesis. $CuCl_2 \cdot 2H_2O$ (1 mmol = 0.170 g in 1 ml of H_2O) was taken in a 100 ml beaker. A solution of salicylic acid (2 mmol = 0.280 g in 40 ml methanol) was added to the copper solution in a drop-wise manner with stirring. Then, 20 drops of NaOH (0.1 M) were added and the resulting solution was stirred for 30 min at 60 °C. Next, the ethylenediamine solution (1mmol = 0.060 g in 1 ml water) was added in a drop-wise manner with stirring. The solution thus obtained was further stirred for half an hour at room temperature and filtered. The solution was kept undisturbed for one week, after which greenish-blue crystals of **1** were obtained. These crystals were harvested by vacuum filtration and rinsed with cold methanol. They appear to be indefinitely stable in air. The yield (based on Cu) was 32 %. Elemental analysis for $C_9H_{13}ClCuN_2O_3$; calculated (%): N 9.5, C 36.5, H 4.4; found: N 9.6, C 36.2, H 4.4.

X-ray structure determination. Intensity data for **1** were collected [22] 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 in the monoclinic space group $P2_1/c$ with SHELXS-97 and the atomic model optimized against $|F|^2$ with SHELXL-97 [23]. The O-bound H atom was located in a difference map and its position was freely refined. The other H atoms were geometrically placed (C—H = 0.93—0.97 Å, N—H = 0.90 Å) and refined as riding atoms. 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

IR spectroscopy. The FTIR spectrum of **1** is shown in Fig. 1. The strong broad peak centered around 3200 cm^{-1} probably corresponds to partial superposition of the N—H stretch and the phenolic

Table 1

Crystallographic parameters for **1**

Chemical formula	$C_9H_{13}ClCuN_2O_3$
M_r	296.20
Crystal system; space group	Monoclinic; $P2_1/c$ (No. 14)
Temperature, K	296
a, b, c, Å; β, deg.	13.9179(10), 10.4900(8), 8.5181(6); 105.518(4)
V, Å^3	1198.30(15)
Z	4
Radiation type; λ, Å	MoK_α; 0.71073
μ, mm^{-1}	2.04
Crystal size, mm	0.35×0.26×0.23
Data collection	
No. of measured and independent reflections	8951, 2351
Observed ([$I > 2\sigma(I)$] reflections	1898
R_{int}	0.028
$(\sin\theta/\lambda)_{max}$, Å^{-1}	0.617
Refinement	
$R(F)[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.026, 0.069, 1.05
No. of parameters	149
Min., max difference peak, e/Å^{-3}	–0.33, +0.22
CCDC deposition code	1045184

O—H vibration of the salicylate ion. The aromatic C—H vibration at 3138 cm^{-1} has been shifted significantly from the equivalent vibration in salicylic acid (3013 cm^{-1}). The asymmetric and symmetric C—H stretching bands due to the CH_2 groups in ethylenediamine appear at 2955 and 2889 cm^{-1}, respectively. The CH_2 group rocking vibrations occur at 822 cm^{-1} while its C—N stretch is observed at 1151 cm^{-1}. In the IR spectrum of free salicylic acid there is a strong absorption band at 1680 cm^{-1} for the CO_2H group, which is absent in the complex: the bands due to the asymmetric [$\upsilon_{asym}(CO_2^-)$] and symmetric [$\upsilon_{sym}(CO_2^-)$] stretching vibrations of the carboxylate group occur at 1591 and 1395 cm^{-1},

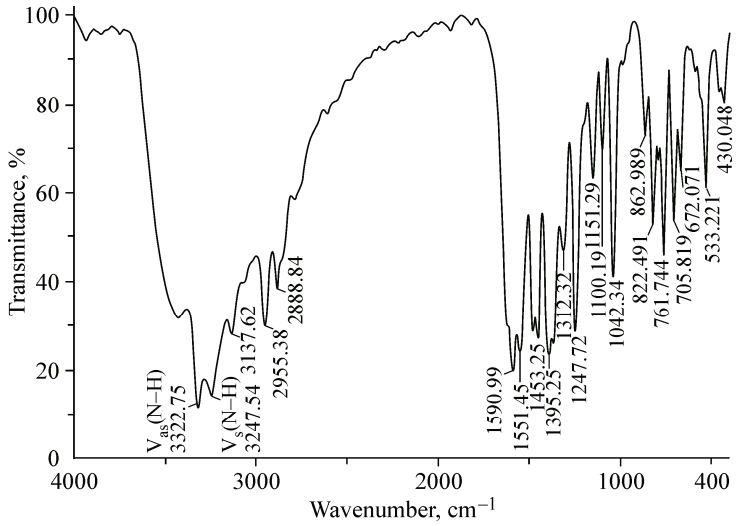

Fig. 1. IR spectrum of **1**

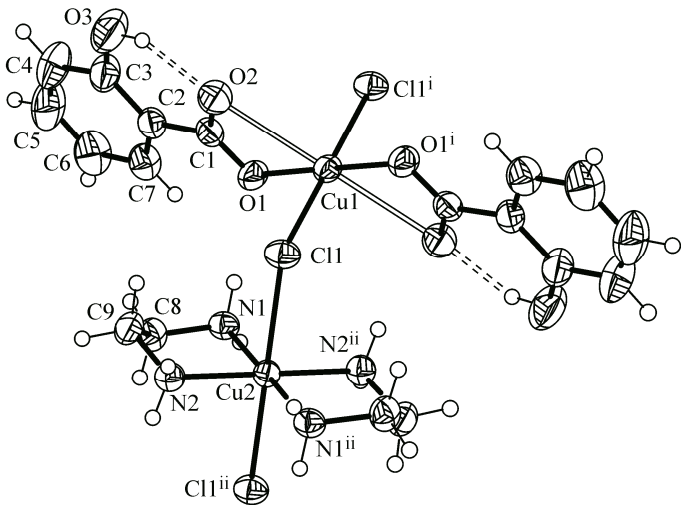

Fig. 2. Building units in **1** showing 50 % displacement ellipsoids. The O—H···O hydrogen bonds are indicated by double-dashed lines and the long Cu1—O2 bonds by open lines.
Symmetry codes: ^{i} –*x*, 1–*y*, 1–*z*; ^{ii} –*x*, 1–*y*, –*z*

respectively. The frequency difference between these bands ($\Delta\nu$ = 196 cm^{-1}) suggests an asymmetric chelating coordination mode of the carboxylate group to the metal ion [24, 25]. The Cu—N stretching band for ethylenediamine appears at 430 cm^{-1} while the Cu—O peak for the salicylate moiety appears at 533 cm^{-1}. These spectroscopic features imply the coordination of both ligands to the copper(II) ion(s) [26] as confirmed by the crystal structure.

Crystal structure. The crystal structure of **1** shows that it contains two distinct copper(II) ions (both lying on crystallographic inversion centers) with different distorted octahedral coordination environments comprised by $Cu1O_4Cl_2$ and $Cu2N_4Cl_2$ chromophores (Fig. 2). Selected geometrical data are presented in Table 2.

In the $Cu_1O_4Cl_2$ moiety, the copper(II) ion, which lies at the (0, 1/2, 1/2) special position, is coordinated by four oxygen atoms from the two salicylate anions and by two chloride ions. The Cu1—O2 bond is much longer (2.6455(14) Å) than Cu1—O1 (1.9569(13) Å), indicating an asymmetric bidentate coordination mode for the sal^{-1} anion. Indeed, this Cu1—O2 bond length is significantly longer than the Cu1—Cl1 separation of 2.2872(5) Å: overall, the Cu1 coordination geometry could be described as an extremely distorted octahedron or alternately as a CuO_2Cl_2 square plane with ″secondary″ Cu1—O2 bonds. The bite angle for O1—Cu1—O2 is 55.30(5)° and an intramolecular O—H···O hydrogen bond (Table 3) occurs within the sal^{-1} anion, which generates an S(6) ring.

In the $Cu_2N_4Cl_2$ grouping, the copper(II) ion, which lies at the (0, 1/2, 0) special position, is coordinated by four N atoms from two ethylenediamine ligands, each forming a five-membered chelate

T a b l e 2

Selected geometrical data (Å, deg.) *for* **1**

Bond lengths				Bond angles	
Cu1—O1	1.9569(13)	Cu1—Cl1	2.2872(5)	O1—Cu1—Cl1	90.91(4)
Cu1—O2	2.6454(14)	Cu2—N2	2.0302(15)	N2—Cu2—N1	83.82(6)
Cu2—N1	2.0377(15)	Cu2—Cl1	2.7780(5)	N1—Cu2—Cl1	93.05(5)
C1—O1	1.276(2)	C1—O2	1.265(2)	O1—Cu1—O2	55.30(5)
C3—O3	1.356(3)			N2—Cu2—Cl1	87.11(5)
				Cu1—Cl1—Cu2	114.11(2)

Table 3

Hydrogen bonds (Å, deg.) *for* **1**

O3—H3···O2	0.86(3)	1.78(3)	2.567(2)	152(3)
N1—H1A···O1	0.90	2.25	3.138(2)	168
N1—H1B···Cl1^{iii}	0.90	2.77	3.3389(16)	122
N2—H2A···O2^{iv}	0.90	2.25	3.124(2)	163
N2—H2B···Cl1^{v}	0.90	2.69	3.2768(16)	124
N2—H2B···O2^{v}	0.90	2.61	3.353(2)	140

Symmetry codes: ^{iii} $-x$, $y-1/2$, $1/2-z$; ^{iv} x, y, $z-1$; ^{v} x, $1.5-y$, $z-1/2$.

ring. These define the CuN_4 equatorial plane of a distorted octahedron,with Cu2—N1 and Cu2—N2 distances of 2.0377(15) and 2.0302(15) Å, respectively, which are distinctly shorter than those of the octahedral copper (II) complex with ethylenediamine (Cu—N = 2.150(2) Å) [27]. The N1—Cu2—N2 bite angle of the en ligand is 83.82(6)°, which is comparable with literature values [28].

The conformation of the chelate ring in **1** is well-described as being twisted about the C8—C9 bond: C8 is displaced by –0.341(2) Å and C9 by +0.369(2) Å from the plane of N1/Cu1/N2. The axial positions are occupied by chloride ligands (Cu2—Cl1 = 2.7780(5) Å). This bond is long, but still by about 0.37 Å shorter than the van der Waals separation of 3.15 Å for these atoms. The coordination environment around Cu2 is therefore a Jahn—Teller distorted octahedron.

The chloride ion in **1**establishes a connection between the metal centers forming a $[—Cu—Cl—]_n$ chain propagating in the [001] direction with a zigzag *motif*: the Cu1—Cl1—Cu2 bond angle is 114.11(2)° and the Cu1 and Cu2 ions alternate in the chain. The dihedral angle between any pair of adjacent CuO_2Cl_2 and CuN_4 planes is 36.93(5)°. The structure of **1** is consolidated by N—H···O and N—H···Cl hydrogen bonds (Table 3). These link the polymeric chains into (100) sheets.

CONCLUSIONS

The reaction of $CuCl_2 \cdot 2H_2O$ with salicylic acid and ethylenediamine in the molar ratios of 1:2:1 in the presence of NaOH yielded the product $[Cu(sal)(en)Cl]_n$. The crystal structure presented in this study is unique in the respect that it is the only known copper—en—carboxylate in which a chloride ion bridges two copper(II) ions, producing a one-dimensional polymeric chain.

It also contains salicylate ions that do not merely act as counterions, but are coordinated to the metal ion, which is an unprecedented structural feature for these complexes. In addition to the Cu—Cl backbone, the structure is consolidated by N—H···O and N—H···Cl hydrogen bonds which generate a layered network.

Crystallographic data for **1** have been deposited with the Cambridge Crystallographic Center (ref. CCDC 1045184). These 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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