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A novel dimeric copper salicylate with an undissociated COOH group: Synthesis and crystal structure of $[Cu_2(HSal)(Sal)(2,2'\text{-bpy})_2](ClO_4)$

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Abstract

A dinuclear copper salicylate $[Cu_2(HSal)(Sal)(2,2'\text{-bpy})_2](ClO_4)$ (**1**) (H_2Sal = salicylic acid) has been synthesized and characterized with the aid of elemental analysis and infrared, ultraviolet and fluorescence spectroscopic studies. The molecular structure of **1**, determined by single-crystal X-ray diffraction studies, shows the presence of incompletely deprotonated salicylate ligands in the complex. Hydrogen bonding interactions and π–π aromatic stacking lead to the formation of 2D polymeric structure in the solid state.

Keywords: Copper salicylate; Hydrogen bonding; Crystal structure

Inorganic–organic hybrid compounds with extended structures are of current interest owing to their intriguing structural motifs and interesting electro-conductive, optical and magnetic properties [1]. Among these, metal carboxylates have been extensively studied because the carboxylate group can bind to metal ion in various modes, such as monodentate, bidentate and bridging [2]. From the coordination chemistry point of view, salicylic acid (H_2Sal) is a versatile ligand, since it offers two hard and strongly basic donor centers in a ligand geometry facilitating chelation and/or metal bridging for a medium- to large-size cation [3]. Furthermore, hydroxyl group in salicylate ligand can entertain intra- and/or intermolecular hydrogen bonding and assist the formation of multidimensional assemblies [4]. In particular, copper(II) complexes of salicylic acid are of interest from both structural and biological view points. Dinuclear copper(II) salicylates are biologically interesting because of their anti-inflammatory activity [5–7]. It has been reported that the copper(II) complex of aspirin is more active as an anti-inflammatory agent than the free ligand. The pyridine adduct $[Cu_2(asp)_4(py)_2]$ (asp = aspirin) has been found to be an effective anti-inflammatory, anticancer and anticonvulsant agent [5i].

Three different copper salicylate complexes have been studied so far in the literature: a pale-blue mononuclear copper(II) complex $[Cu(HSal_2)_2]$, a dark-green dinuclear copper(II) complex $[Cu_2(HSal)_4]$, and a yellow-brown polymeric copper(II) $[Cu(Sal)]_n$, (with or without solvents of crystallization) [8]. Combining a neutral chelating ancillary ligand such as 2,2′-bpy along with salicylic acid offers interesting structural variations in the resultant products. For example, 2,2′-bpy has been widely used to impede the aggregation of metal centers, owing to the excellent chelating mode of coordination of the ligand [9]. In the literature, there are a few reports concerning dinuclear copper complexes with salicylate and 2,2′-bpy ligands [7]. Among these $[Cu_2(Sal)_2(2,2'\text{-bpy})_2]\cdot 2H_2Sal$ (**A**) [7a] and $[Cu(Sal)(2,2'\text{-bpy})]\cdot C_2H_5OH\cdot H_2O$ (**B**) [7b] are structurally very similar to each other, while the structure of $[Cu_2(Sal)_2(2,2'\text{-bpy})_2]\cdot AcetylHSal\cdot 2H_2O$ (**C**) [7c] and $[Cu_2(DIPSA)_2(2,2'\text{-bpy})_2]\cdot 2DIPSA$ (**D**) [7d] have also been reported. In order to realize other structural types of Cu-salicylate com-

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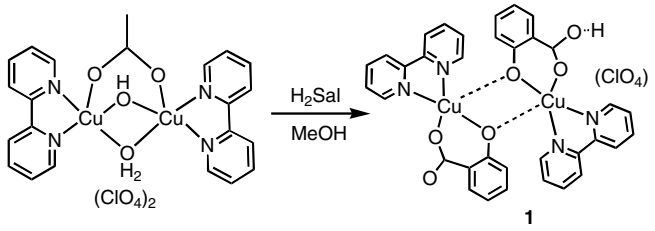
plexes containing 2,2-bpy ligand, we have studied the reactivity of the precursor complex $[Cu_2(OAc)(OH)(H_2O)(2,2'\text{-bpy})_2](ClO_4)_2$ [10] with salicylic acid and isolated a novel dimeric complex, where only 50% of the –COOH groups of the salicylate ligands are deprotonated while the other 50% of COOH remain intact. The details of the study are presented in this communication.

The green crystals of the title compound $[Cu_2(Sal)(HSal)(2,2'\text{-bpy})_2](ClO_4)$ (**1**) were obtained in 33% yield from the reaction between one equivalent of $[Cu_2(OAc)(OH)(2,2'\text{-bpy})_2(OH_2)](ClO_4)_2$ and two equivalents of H_2Sal in methanol (Scheme 1) [11]. The compound **1** has been characterized with the aid of analytical and spectroscopic studies. The single crystals of **1**, obtained directly from the reaction mixture, have been found to be analytically pure and suitable for X-ray diffraction studies [12]. The IR spectrum of **1** shows a broad absorption around 3460 cm^{-1} corresponding to the presence of undissociated –COOH group of salicylate ligand. The absorptions around 3100 cm^{-1} are due to aromatic C–H vibrations. The $\nu_{as}(COO^-)$ band is observed at around 1604 cm^{-1} while $\nu_{sym}(COO^-)$ is observed at 1383 cm^{-1}. Strong IR band observed at 1092 cm^{-1} indicates the presence of ClO_4^- anion in the complex. The UV–Vis spectrum exhibits a strong and a weak absorption at 344 and 629 nm, respectively. These absorptions could be assigned to the combination of LMCT/π–π^* transitions of 2,2′-bpy ligands and d–d transitions Cu^{2+} ion, respectively [13,14].

The emission spectrum of **1** in methanol at room temperature yields a strong emission at 406 nm ($\lambda_{ex} = 344$ nm). It is unlikely that this is an intra-ligand fluorescent emission but could be attributed to the charge transfer between the metal and ligand, since free 2,2′-bpy ligand does not show any luminescence in the range of 400–500 nm [15]. When excited at 344 nm, the electron transfers from the ground state E_0 to excited state E_2, then it non-radiatively decays to E_1, from where it comes back to the ground state with fluorescence emission (406 nm) [16]. The room temperature magnetic moment ($\mu_{found} = 1.714$ BM) for this complex matches well with the expected spin only value and hence implies a non-interacting Cu^{2+} dimer with no coupling at 25 °C. The ESR spectrum of polycrystalline powder of **1**, recorded at room temperature and 77 K (Fig. 1), gave a *g*-value of 2.098 which is consistent with the distorted square pyramidal CuN_2O_2O' chromophores and indicate a $d_{x^2-y^2}$ ground state for the Cu(II) ion [17].



Scheme 1.

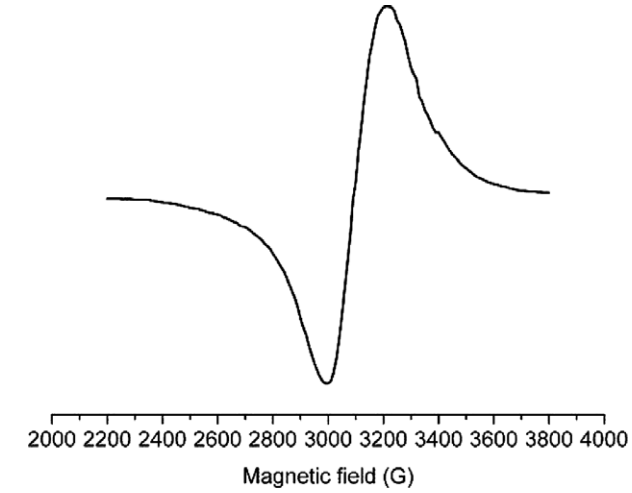


Fig. 1. ESR spectrum of $[Cu_2(HSal)(Sal)(2,2'\text{-bpy})_2](ClO_4)$ (**1**) at 77 K.

Complex **1** was further characterized by a single-crystal X-ray diffraction study [11]. The crystal structure of the complex consists of a discrete dimeric $[Cu_2(HSal)(Sal)(2,2'\text{-bpy})_2]^+$ cation and a perchlorate anion (Fig. 2). The compound **1** crystallizes in the monoclinic $P2_1/c$ space group. A comparison of key structural parameters with those of related copper complexes are listed in Table 1. The molecular structure of **1** is considerably different from other Cu-Sal-2,2′-bpy complexes **A**–**D**. Although like **A**–**D**, complex **1** is also dimeric, there are fundamental differences. For example, the former four compounds are neutral species while compound **1** is cationic with a perchlorate

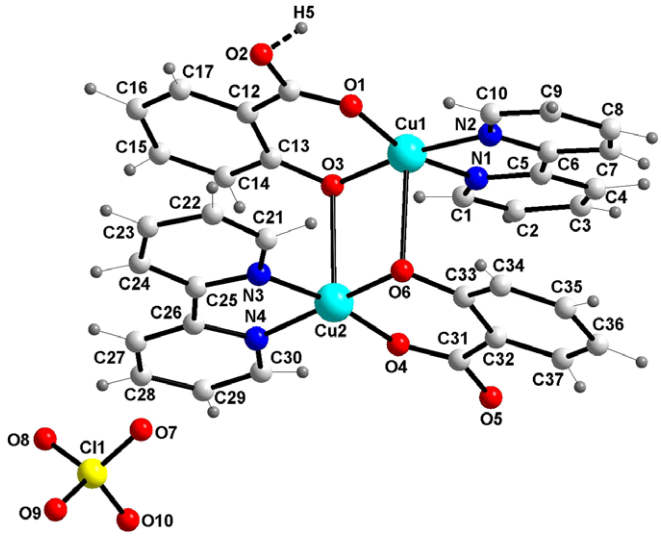


Fig. 2. Molecular structure of $[Cu_2(HSal)(Sal)(2,2'\text{-bpy})_2](ClO_4)$ (**1**). Selected bond lengths (Å): Cu(1)–N(1) 1.990(6), Cu(1)–N(2) 1.993(6), Cu(2)–N(3) 1.981(6), Cu(2)–N(4) 1.982(6), Cu(1)–O(1) 1.908(5), Cu(1)–O(3) 1.900(5), Cu(1)–O(6) 2.56(3), Cu(2)–O(4) 1.902(5), Cu(2)–O(6) 1.885(5), Cu(2)–O(3) 2.50(3). Bond angles (°): N(1)–Cu(1)–N(2) 81.5(2), N(3)–Cu(2)–N(4) 81.0(3), N(1)–Cu(1)–O(1) 164.3(3), N(1)–Cu(1)–O(3) 94.5(2), N(2)–Cu(1)–O(1) 91.7(2), N(2)–Cu(1)–O(3) 171.5(2), N(3)–Cu(2)–O(4) 170.3(3), N(3)–Cu(2)–O(6) 93.6(2), N(4)–Cu(2)–O(4) 92.2(2), N(4)–Cu(2)–O(6) 173.6(2), O(1)–Cu(1)–O(3) 93.9(2), O(4)–Cu(2)–O(6) 92.7(2).

Table 1
Comparison of structural features of Cu-bipyridine complexes with –O and –N coordination. (Sal = salicylato, DIPSA = diisopropylsalicylato)

Compound	Space group	Geometry around Cu	Cu–O (Å) (carboxylato)	Cu–O (Å) (phenoxo)	Cu–O(Cu) (Å) (phenoxo)	Cu–N (Å)	Cu–Cu (Å)	N–Cu–N (°)	O–C–O (°)	Ref.
$[Cu_2(Sal)(HSal)(2,2'\text{-bpy})_2]\,ClO_4$ (**1**)	$P2_1/c$	Square pyramidal				1.990(6)	3.265(4)			This work
			1.908(5)	1.885(7)	2.56(3)	1.993(6)		81.5(2)	118.7(7)	
			1.902(5)	1.900(6)	2.50(3)	1.981(6)		81.0(3)	119.0(7)	
						1.982(6)				
$[Cu_2(Sal)_2(2,2'\text{-bpy})_2]\cdot 2H_2Sal$ (**A**)	$P2_1/a$	Square pyramidal	1.906(2)	1.883(2)	2.53(6)	1.991(2)	3.24(7)	81.8(1)	120.4(5)	[7a]
			1.882(2)			2.002(3)				
$[Cu_2(Sal)_2(2,2'\text{-bpy})_2]\cdot C_2H_5OH\cdot H_2O$ (**B**)	$P\bar{1}$	Square pyramidal	1.897(2)	1.90(1)	2.445(2)	1.998(2)	3.240(1)	89.80(8)	119.9(2)	[7b]
$[Cu_2(Sal)_2(2,2'\text{-bpy})_2]\cdot AcetylHSal\cdot 2H_2O$ (**C**)	$P\bar{1}$	Square pyramidal				1.993(2)	3.188(3)			[7c]
			1.891(2)	1.891(1)	2.423(3)	1.987(2)		80.9(4)	120.3(7)	
			1.896(2)	1.890(2)	2.433(3)	2.001(2)		80.8(8)	119.8(3)	
						1.995(2)				
$[Cu_2(DIPSA)_2(2,2'\text{-bpy})_2]\cdot 2DIPSA$ (**D**)	$P\bar{1}$	Square pyramidal	1.884(4)	1.922(1)	2.28(3)	2.003(2)	3.168(1)	80.6(3)	119.8(5)	[7d]
			1.920(2)			2.010(2)				

anion. Quite surprisingly, the carboxylate proton of one of the Sal ligands in **1** remains intact on the COO^- group. However protonated carboxylato group of salicylate has been observed in Mo and W complexes [18,19]. Each copper ion in **1** is coordinated by two N atoms from the chelating 2,2′-bipyridine molecule, one carboxylate oxygen and one phenolato oxygen in a square planar arrangement. The phenolato O atom further forms a weak bridge to the adjacent Cu ion in the axial direction with a longer Cu–O bond (2.56(3) and 2.50(3) Å). With this bridging phenoxide oxygen linking the second [Cu(HSal)(2,2′-bpy)] unit, square pyramidal coordination geometry is achieved around each copper with the formation of a Cu_2O_2 four-membered ring.

Unlike the other dimers **A**–**D** [7], the cationic part of **1** does not possess an center of inversion in the center of Cu_2O_2 ring due to the presence of the extra H^+ ion on the salicylate carboxylic groups. The additional proton actually resides between the two different carboxylate oxygens O2 and O5 and is somewhat equidistant from both the oxygen (1.204(1) and 1.324(1) Å). The binding modes of both carboxylates are monodenate. The Cu–O (carboxylato and phenoxo) and Cu–N bonds in **1** are comparable to those found for **A**–**D**. However, within **1**, the Cu–O and Cu–N distances involving Cu(2) are slightly shorter than the corresponding distances involving Cu(1). The Cu···Cu distance (3.265(4) Å) is comparable to those found in related copper dimers [7]. This distance rules out any appreciable magnetic interaction between the two copper metal centers at room temperature, which is also consistent with the measured magnetic moment for **1** at 25 °C (*vide supra*). The N–Cu–N bond angles (81.2(5) and 81.0(3)°) are comparable to corresponding dimers $[Cu_2(Sal)_2(2,2'\text{-bpy})_2]\cdot 2H_2Sal$ (81.1°) [7a] and $[Cu_2(DIPSA)_2(2,2'\text{-bpy})_2]\cdot 2H_2DIPSA$ (80.6°) [7d]. The two rings in the 2,2′-bipyridine ligand are slightly twisted relative to each other, with dihedral angles N1–C5–C6–N2 of −5.39(1)° and N3–C25–C26–N4 of 0.68(1)°, respectively.

Intermolecular hydrogen bondings and π–π aromatic stacking interactions play an important role in stabilizing **1** in the solid state (Table 2, Fig. 3). In addition to the very strong symmetric O···H···O intermolecular hydrogen bonding that exists between the O(2) and O(5) oxygen atoms of the two carboxylate groups, additional C–H···O interactions listed in Table 2 are also observed. For example, a strong C–H···O interaction was observed between carboxylic O(2) and a 2,2′-bpy –CH group of a

Table 2
Observed hydrogen bonds in **1**

D–**H**···**A**	**D**–**H** (Å)	**H**···**A** (Å)	**D**···**A** (Å)	**D**–**H**···**A** (°)
O(2)···H(5)···O(5)[b]	1.204(1)	1.324(1)	2.47(7)	155.3(10)
C(4)–H(4)···O(10)[a]	1.042(7)	2.250(7)	3.224(1)	154.9 (7)
C(15)–H(15)···O(10)[c]	0.99(3)	2.714(5)	3.63(1)	155.0(4)
C(23)–H(23)···O(8)[d]	0.991(1)	2.461(8)	3.259(1)	137.3(7)
C(30)–H(30)···O(2)[b]	0.86(7)	2.717(2)	3.484(1)	149.4(8)

Equivalent positions: (a) $1-x$, $1/2+y$, $3/2-z$, (b) x, $1/2-y$, $z-1/2$, (c) $-x$, $1/2+y$, $3/2-z$, and (d) $-x$, $-y$, $2-z$.

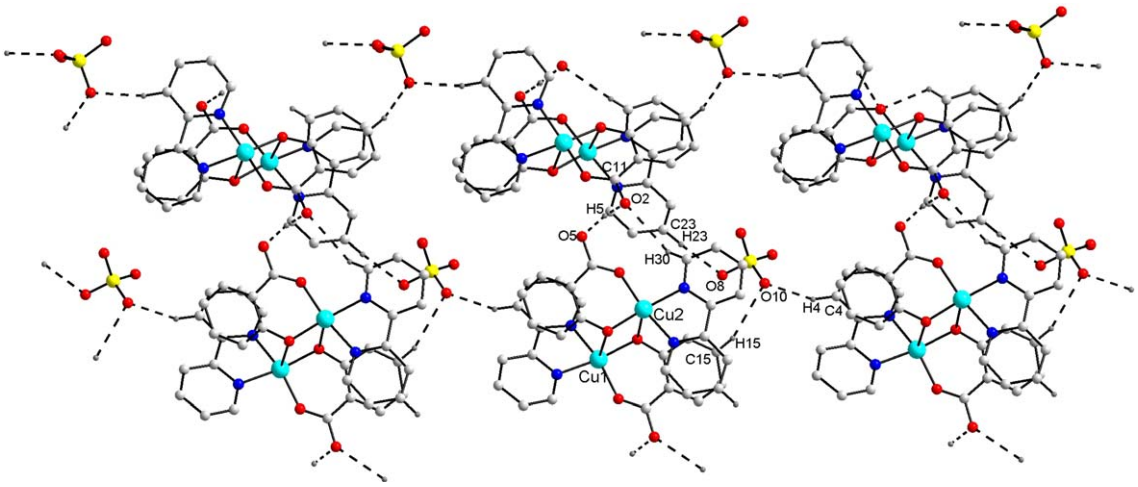


Fig. 3. Observed H-bonding scheme and π–π stacking in **1**.

neighboring molecule (∠C(30)–H(30)···O(2) 149.4(8)°). Oxygen atoms of perchlorate anion form additional bridges between the cationic dimers (∠C(4)–H(4)···O(10) 154.9(7)°, ∠C(23)–H(23)···O(8) 137.3(7)°, ∠C(15)–H(15)···O(10) 155.0(4)°) The dimeric cations are further stabilized by π–π aromatic stacking interactions between the 2,2′-bpy and salicylate ligand (interplanar distances d(C(10)···C(34)) = 3.390(6) Å and d(C(14)···C(30)) = 3.915(1) Å) [20]. As a result of all these secondary interactions a 3D supramolecular assembly is formed in the solid state as shown in Fig. 3.

In conclusion, we have shown in this communication that use of a Cu-2,2′-bpy-perchlorate precursor for the preparation of copper-Sal-2,2′-bpy complex leads to the isolation of an ionic complex. The complex can also be considered as $[Cu_2(H)(Sal)_2(2,2'\text{-bpy})]$, due to the presence of the extra proton, equidistant from the two uncoordinated carboxyl oxygen centers of two different salicylate ligands. The complex remains paramagnetic at room temperature with no magnetic interaction between the two copper ions although the fairly short Cu···Cu separation could lead to interesting magnetic interaction between the metal ions at lower temperatures.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.05.025.

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[11] $[Cu_2(OAc)(OH)(H_2O)(2,2'\text{-bpy})_2](ClO_4)]$ (186 mg, 0.25 mmol) was dissolved in methanol (30 mL). To this, a clear solution of salicylic acid (70 mg in 10 mL of methanol, 0.5 mmol) was added. The solution became deep blue to dark green. The resulting solution was stirred for 2 hours and filtered. To this filtrate 2 mL of dichloromethane was added and kept at room temperature for crystallization. X-ray quality crystals were formed from solution after one week. Yield: 0.066 g (35%); m.p. >260 °C (dec). Anal. Calcd for $C_{34}H_{24}N_4O_{10}Cu_2Cl$: C 50.2; H 3.1; N 6.9. Found: C 50.0; H 2.9; N 7.2. IR (KBr, cm^{-1}): 3436(br), 3078(m), 1601(vs), 1567(s), 1496(s), 1474(s), 1446(vs), 1318(m), 1252(w), 1090(vs), 1031(m), 1015(m), 773(s), 731(m), 660(m), 623(s). UV–Vis (MeOH, nm, ε, $cm^{-1}\,M^{-1}$): 629 (151) and 344 (2023). Fluorescence: ($\lambda_{ex} = 344$ nm, MeOH): 406 nm. $\Phi = 0.0224$. $\mu_{eff} = 1.714$ BM, $\mu_S = 1.713$ BM.

[12] Crystal data for **1**: crystal dimensions: $0.30 \times 0.15 \times 0.15$ mm, formula weight = 812.11, monoclinic, space group $P2_1/c$, $a = 13.6670(8)$ Å, $b = 13.4110(8)$ Å, $c = 17.713(3)$ Å, $\alpha = 90°$, $\beta = 95.930(8)°$, $\gamma = 90°$, $V = 3229.2(6)$ $Å^3$, $Z = 4$, $D(\text{calc}) = 1.670$ mg/m^3, $\mu = 1.468$ mm^{-1}, $F(000) = 1648$, GOF = 0.980, data/restraints/parameters = 5652/0/560, $R_1[I > \sigma(I)] = 0.0612$, $R_2[I > \sigma(I)] = 0.1148$. X-ray diffraction data were collected on a Nonius MACH-3 diffractometer equipped with a graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structure solution was achieved by direct methods as implemented in SHELXS-97. The final refinement of the structures was carried using full least-squares methods on F^2 using SHELXL-97. The positions of hydrogen atoms were identified from the successive difference Fourier maps and were included in further calculations and refinement. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms isotropically.

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