

Mononuclear copper (II) salicylate imidazole complexes derived from copper (II) aspirinate. Crystallographic determination of three copper geometries in a unit cell

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Abstract

Complexes of the type $\text{Cu}(\text{Im})_n(\text{sal})_2$ (**1,2,3**) (where Im = imidazole, and sal = salicylate ion) have been prepared from the reaction of Im with tetrakis (aspirinato) dicopper (II) and were crystallographically and spectroscopically characterized. The three imidazole complexes **1** ($n = 2$), **2** ($n = 5$) and **3** ($n = 6$) co-crystallize and each complex is found in the unit cell. Crystals that contained **1**, **2** and **3** have unit cell parameters of $a = 12.772(5)$, $b = 13.078(4)$ and $c = 18.199(7)$ Å, $\alpha = 79.53(3)$, $\beta = 81.20(3)$ and $\gamma = 75.98(3)^\circ$ and belong to the space group $P\bar{1}$.

In **1** the copper ion is coordinated in a *trans* arrangement by two imidazole nitrogen atoms and two carboxylate oxygen atoms from the salicylate ligands. The second carboxylate atoms form weak interactions with the copper ion. For complex **2** the copper ion is in a distorted square pyramidal environment of nitrogen atoms from five imidazole ligands. There are two salicylate counterions. Complex **3** exists as tetragonally distorted octahedral copper (II) cation with six coordinated imidazole ligands and two salicylate counterions. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Copper (II); Salicylate; Imidazole; Crystal structure

1. Introduction

Salicylic acid and its derivatives, including aspirin, have been used for many years as anti-inflammatory, antipyretic and analgesic drugs. Copper (II) complexes with aspirin-like drugs are known to have a variety of pharmacological activities and are often more effective and desirable drugs than their parent ligands [1,2]. X-ray analysis of copper (II) complexes with salicylic-like acids has shown that these complexes can exist as mononuclear, dinuclear, or polynuclear species, depending on the reaction condition [3–5]. Copper (II) salicylate tetrahydrate, for example, is mononuclear [4] while the anhydrous complex can exist in the mononuclear and polynuclear forms [5]. Copper (II) aspirinate and its solvates with the weakly basic ligands DMF, H_2O , or CH_3OH contain binuclear units with bridging carb-

oxylates [6], thus, these complexes are similar to many other copper (II) carboxylate dimers [7].

Mononuclear copper (II) complexes of salicylate derivatives with basic ligands containing nitrogen donors have been previously reported [3,8–11], and were found to exist in a variety of structures, even when the added bases are of the same homologous series, such as imidazole and its derivatives. We and other researchers have reported the synthesis and spectral characterization of some mononuclear adducts of copper (II) aspirinate with imidazole and its derivatives [8–10]. While the complexes with imidazole and *N*-methylimidazole are known to exist as bis- and tetrakis-adducts [9,10], those of 1,2-dimethylimidazole and benzimidazoles are only known as bis-adducts [8,9]. This difference in behavior may be attributed, in part, to the steric restrictions imposed by the ligands in the latter bis-adducts. Few X-ray structures of mononuclear complexes of copper (II) salicylate with nitrogen donor ligands are known. The bis-adducts of 2-pyridylmethanol [12], *N*-methylimidazole [13], and nicotinamide [14] all contain essentially

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the CuN_2O_2 chromophore in a *trans* square-planar arrangement. The nitrogen donor atoms are from two pyridine or imidazole ligands and the oxygen donor atoms are from two salicylate carboxylate. In Cu (salicylato) (bipyridine) complex the copper ion is coordinated to two nitrogen donors of the 2,2'-bipyridine and chelated by the salicylate dianion via one carboxylate oxygen atom and the phenolate oxygen atom [15]. Herein we report the synthesis and X-ray structural characterization of a mixture of mononuclear complexes of the type $\text{Cu}(\text{imidazole})_n(\text{salicylate})_2$ (where $n = 2, 5$, or 6 for complexes **1**, **2** and **3**, respectively).

2. Experimental

2.1. Reagents and materials

All chemicals were of high purity grade (Aldrich or Sigma chemical) and were used without further purifications. Tetrakis- μ -aspirinato dicopper (II) $[\text{Cu}_2(\text{asp})_4]$ was prepared according to a published procedure [16].

2.2. Preparation of $[\text{Cu}(\text{Im})_2(\text{sal})_2]$ (**1**); $[\text{Cu}(\text{Im})_5(\text{sal})_2]$ (**2**); $[\text{Cu}(\text{Im})_6(\text{sal})_2]$ (**3**)

A 0.50 g (0.59 mmol) sample of copper (II) aspirinate was stirred with 0.33 g (4.8 mmol) of imidazole dissolved in 50 ml of *n*-butanol in an ice bath for 4 h. The blue solution was left in the hood to evaporate. The blue oily product was dissolved in 15 ml of absolute ethanol. The blue solution was concentrated by slow evaporation in a hood to ca. 4 ml. Slow diffusion of anhydrous diethyl-ether into the blue solution produced dark blue crystals. *Anal. Calc.:* for $\text{Cu}_4\text{C}_{110}\text{H}_{112}\text{N}_{36}\text{O}_{24}$ (the mixture complexes contain one bis(imidazole) complex **1**, one hexakis(imidazole) complex **3** and two pentakis(imidazole) complexes **2** per unit cell) requires C, 51.28; H, 4.35; N, 19.58. Found: C, 50.98; H, 4.41; N, 19.5%.

2.3. Physical measurements

The procedures for obtaining IR, UV–visible, and magnetic moment measurements were as previously described [8]. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee, USA.

2.4. X-ray structure determination

A Siemens R3 mV diffractometer equipped with a highly oriented graphite crystal monochromator was used for data acquisition. Crystals covered with a viscous oil (Paratone N, Exxon) were mounted on a goniometer head and placed on the goniometer in a N_2 stream at -100°C . The intensities of three standard reflections were monitored for every 97 reflections and there were no significant variations in their intensities during the data

Table 1
Crystal data for $\text{Cu}(\text{Im})_n(\text{sal})_2$ (**1**, **2**, and **3**)

Chem formula	^a
fw	^a
Space group	$\text{P}\bar{1}$
Z	5
<i>a</i> , Å	12.772 (5)
<i>b</i> , Å	13.078 (4)
<i>c</i> , Å	18.199 (7)
α , deg	79.53 (3)
β , deg	81.20 (3)
γ , deg	75.98 (3)
<i>V</i> , Å ³	2881 (2)
<i>d</i> (calcd), g/cm ³	1.485
Radiation, λ , Å	Mo; 0.71073
Temp, °C	−100
Abs coeff, cm ^{−1}	8.14
^b <i>R</i> , %	6.38
^c <i>R</i> _w , %	7.64
GOF	1.68

^a Since the unit cell contains three different compounds, the chemical formula and formula weights have not been reported.

^b $R = \sum ||F_0| - |F_c|| / |F_0|$.

^c $R_w = [\sum w(|F_0| - |F_c|)^2 / \sum w|F_0|^2]^{1/2}$.

collection. All intensity data were collected using the 2θ scan type over a 2θ range $3.5\text{--}45^\circ$. Intensities were corrected for Lorentz and polarization effects and absorption corrections were applied [17]. The structures were solved with the use of the SHELXTL PLUS structure solution package [18]. The copper atoms were located from Patterson syntheses and all other non-hydrogen atoms were located in subsequent Fourier difference maps. All hydrogen atoms were included at their idealized positions ($d(\text{CH}) = 0.96 \text{ \AA}$) and were not refined, but were allowed to ride along with their attached atoms doing refinement. The data were corrected for extinction using procedures outlined in the SHELXTL PLUS structure solution package [18]. All non-hydrogen atoms were refined anisotropically except C21 and C30. A summary of the crystallographic data is given in Table 1.

Complexes **1,2** and **3** co-crystallized as blue rods in the space group $\text{P}\bar{1}$. The unit cell parameters were obtained from the least-squares fit of 25 reflections.

Data were collected between 2θ values of 3.5° and 40° which include the index ranged $0 \leq h \leq 13$, $\leq -13 \leq k \leq 13$, $-18 \leq l \leq 18$. Of the 5420 unique reflections measured, 3639 with $F_0 > 4.0 \sigma(F_0)$ were used during full-matrix least-squares refinement. The weighting scheme used was $w^{-1} = \sigma^2(F) + 0.001 F^2$. The largest peak in the final difference map was 0.60 \AA^{-3} .

3. Results and discussion

3.1. Spectroscopic results

The mixture of complexes **1**, **2** and **3** is the product of the slow reaction of copper (II) aspirinate with imidazole.

ole derivatives. During the reaction and/or recrystallization, the acetoxy group of the aspirinate ligand undergoes hydrolysis to give the salicylate ligand. This mixture of complexes contains coordinated and uncoordinated salicylate ions. The stretching frequency of the acetoxy carbonyl moiety of the aspirinate ligands occurs near 1750 cm^{-1} for mononuclear copper (II) aspirinate complexes and at 1758 and 1725 cm^{-1} for the dinuclear copper (II) aspirinate [8,9,11]. The complexes do not exhibit a C=O stretching frequency in this region, suggesting that the acetoxy group has been lost. This is confirmed by the solid-state structures (vide infra).

The mixture of **1**, **2** and **3** exhibits IR frequencies at 1595 and 1395 cm^{-1} which are assigned to ν_{as} (COO) and ν_{s} (COO), respectively, of the coordinated salicylate ligand in **1**. The positions of these carboxylate stretching vibrations and the separation between them are in the range expected for carboxylate groups that act essentially as a monodentate ligand [19] and comparable to those reported for mononuclear copper (II) and zinc (II) salicylate complexes [15,20]. The IR frequencies of the non-coordinated salicylate ions in complexes **2** and **3** found at 1624 , 1590 , and 1574 cm^{-1} are assigned to (CC) + ν_{as} (COO) vibrations. The vibrations at 1385 and 1255 cm^{-1} are assigned to ν_{s} (COO) and to the bending of C—OH of the salicylate monoanion [21].

The mixture has a magnetic moment of 1.90 BM/Cu atom. This value is consistent with the presence of one unpaired electron in mononuclear copper (II) complexes. The electronic spectrum for the mixture in methanol exhibits a very broad asymmetric d–d absorption transitions centered at 636 nm ($\epsilon = 210\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$). It

is probably due to the overlap of bands due to the chromophores $\text{CuN}_2\text{O}_2 \dots \text{O}_2$ of **1** and CuN_5 of **2** and the chromophore $\text{CuN}_4 \dots \text{N}_2$ of **3**. The spectrum also exhibits a band at 406 nm ($\epsilon = 225\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) and it is assigned to ligand-to-metal charge transfer. A similar band between 400 and 450 nm previously reported for mononuclear copper (II) salicylate compounds was ascribed to a ligand-to-metal charge transfer transition [3].

3.2. Crystal structure of **1**, **2** and **3**

The mixture of complexes **1**, **2** and **3** has the general formula $\text{Cu}(\text{Im})_n(\text{sal})_2$. Selected bond distances and angles for **1**, **2** and **3** are deposited in Table 2. Complex **1** has the formula $\text{Cu}(\text{Im})_2(\text{sal})_2$ and crystallizes with a *trans* geometry in which the imidazole and salicylate ligands are both coordinated to the copper ion (Fig. 1). The copper ion is located on an inversion center. The Cu—N distance is $1.961(11)\text{ \AA}$ and the Cu—O distance is $2.042(8)\text{ \AA}$. These distances compare favorably with analogous distances in other mononuclear imidazole derivatives of copper (II) carboxylates [22,23]. One carboxylate oxygen atom from each salicylate anion together with two imidazole nitrogen atoms forms the square-planar inner coordination sphere about the copper atom. The second carboxylate oxygen atom from each salicylate anion is at a distance of 2.86 \AA from the copper atom and thus would be considered weakly coordinating at best. The dihedral angle between the plane of the carboxylate group and the six-membered ring of the salicylate ligand is 8.3° which indicates that the

Table 2
Selected bond angles ($^\circ$) and bond lengths (\AA) for **1**, **2**, and **3**

Complex 1			
Cu(1)—N(1)	1.961 (11)	Cu(1)—O(1)	2.042 (8)
O(1)—C(4)	1.290 (17)	O(2)—C(4)	1.260 (13)
Cu(1)—O(2)	2.87		
N(1)—Cu(1)—O(1)	90.8 (4)	Cu(1)—O(1)—C(4)	112.5 (7)
O(1)—C(4)—O(2)	121.9 (12)	O(1)—C(4)—C(5)	118.5 (9)
O(2)—C(4)—C(5)	119.5 (12)		
Complex 2			
Cu(2)—N(3)	2.157 (9)	Cu(2)—N(5)	2.034 (9)
Cu(2)—N(7)	2.021 (8)	Cu(2)—N(9)	2.036 (9)
Cu(2)—N(11)	2.003 (9)		
N(3)—Cu(2)—N(5)	92.6 (3)	N(3)—Cu(2)—N(7)	103.6 (3)
N(5)—Cu(2)—N(7)	87.2 (4)	N(3)—Cu(2)—N(9)	105.0 (3)
N(5)—Cu(2)—N(9)	88.9 (4)	N(7)—Cu(2)—N(9)	151.2 (3)
N(3)—Cu(2)—N(11)	90.5 (3)	N(5)—Cu(2)—N(11)	176.5 (3)
N(7)—Cu(2)—N(11)	90.3 (4)	N(9)—Cu(2)—N(11)	92.2 (4)
Complex 3			
Cu(3)—N(13)	2.130 (10)	Cu(3)—N(15)	2.448 (10)
Cu(3)—N(17)	2.025 (9)		
N(13)—Cu(3)—N(15)	91.8 (3)	N(13)—Cu(3)—N(17)	89.2 (4)
N(15)—Cu(3)—N(17)	91.6 (4)		

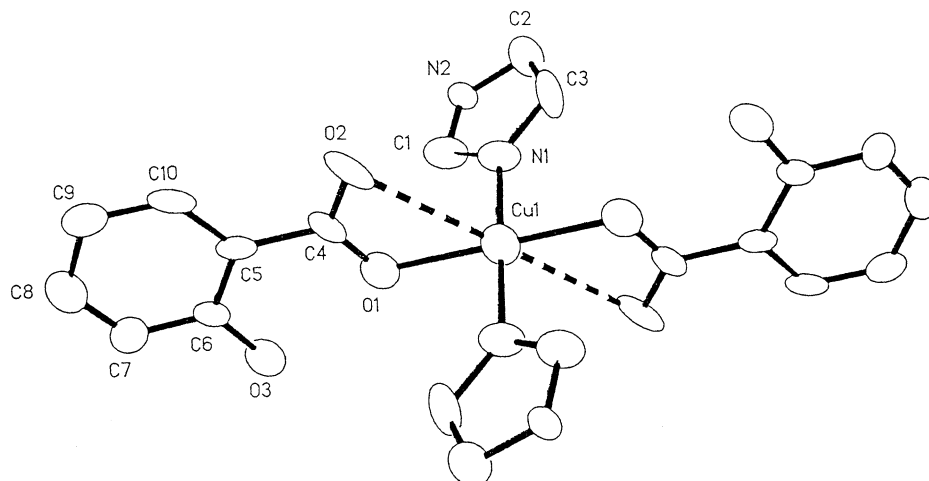


Fig. 1. Structure of $[\text{Cu}(\text{Im})_2(\text{sal})_2]$, **1**. Hydrogen atoms have been omitted for clarity.

ligand is nearly planar. The least-squares plane of the salicylate ligand makes an angle of 86.5° with the square plane of the copper ion. The imidazole ligands are rotated about the Cu—N bonds out of the copper square plane by 18.5° . Because the hydroxy substituent is on the opposite side of the ring, the only type of hydrogen bonding available to the hydroxy group in **1** is intermolecular hydrogen bonding involving imidazole N—H groups of neighboring molecules. These hydrogen bonding interactions are evident in plots of the unit cell.

The second geometric form that is exhibited for the imidazole adducts is that of **2**, a square pyramid slightly distorted toward a trigonal bipyramid. In this structure

the salicylate groups are strictly counterions but are extensively hydrogen-bonded to imidazole ligands of other molecules or complex cations. The structure of the cation of **2** is shown in Fig. 2. The copper ion is coordinated to five imidazole ligands. One Cu—N distance is $2.157(9)$ Å while the other four fall in the range 2.003 – 2.036 Å (Table 2). If the cation is viewed in a square pyramidal geometry, the longer Cu—N(3) distance involves the apical imidazole whose donor atom N(3) is $92.6(3)^\circ$ and $90.5(3)^\circ$ from the two basal donor atoms N(5) and N(11), respectively. The angles between N(3) and the other two basal atoms N(7) and N(9) are 103.4° and 105.3° , respectively. The $103.6(3)$ and $105.0(3)^\circ$ angles reflect the slight distortion towards a trigonal bipyramidal structure.

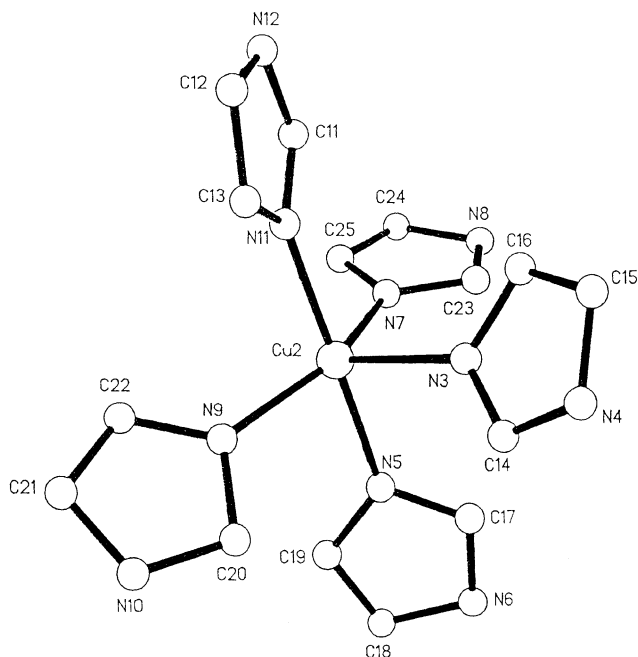


Fig. 2. Structure of the cation of $[\text{Cu}(\text{Im})_5(\text{sal})_2]$, **2**. Hydrogen atoms have been omitted for clarity.

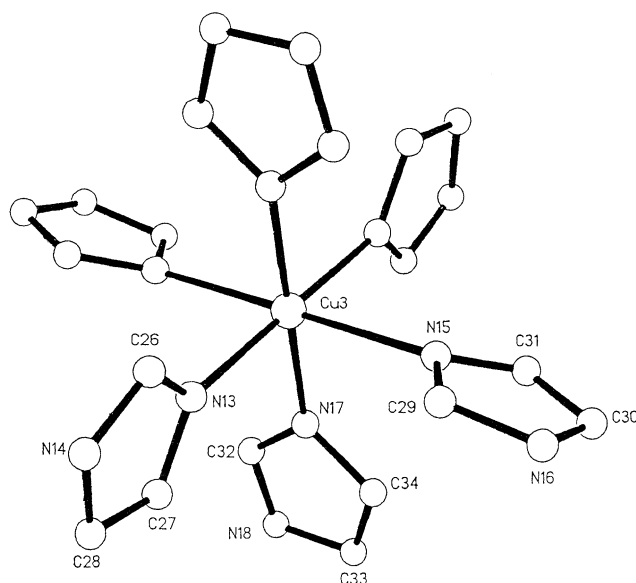


Fig. 3. Structure of the cation of $[\text{Cu}(\text{Im})_6(\text{sal})_2]$, **3**. Hydrogen atoms have been omitted for clarity.

The third geometric form that exists for the imidazole adducts is the tetragonally distorted octahedron for **3** (Fig. 3). It consists of centrosymmetric $\text{Cu}(\text{Im})_6^{2+}$ cations and non-coordinated salicylate anions. It is closely related to $[\text{Cu}(\text{Im})_6](\text{HCO}_2)_2$ [24], where hexakis (imidazole) copper (II) entities are also present. Because of crystallographically imposed symmetry, there are two short distances for the imidazole nitrogen donor atoms in the square plane. The $\text{Cu}(3)\text{—N}(13)$ distance is 2.130(10) Å and the $\text{Cu}(3)\text{—N}(17)$ distance is 2.03(1) Å. The planes of the two sets of symmetry-related imidazole ligands form the square planar core having a dihedral angle of 94.2°. The two elongated Cu—N bond distances, $\text{Cu}(3)\text{—N}(15)$ and $\text{Cu}(3)\text{—N}(15A)$, are 2.448(10) Å.

4. Conclusion

Imidazole reacts with binuclear copper (II) aspirinate to form bis-, pentakis-, and hexakis(imidazole) mononuclear copper (II) complexes that contain the salicylate ions. The complexes co-crystallize with one bis(imidazole) complex, one hexakis(imidazole) complex, and two pentakis(imidazole) complexes per unit cell. The bis(imidazole) complex lies on the special position 1/2, 0, 1/2, the hexakis(imidazole) complex lies on the special position 0, 0, 0, and the pentakis(imidazole) complex occupies general positions. It is likely that in solution there is interconversion among these various copper geometries.

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