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Bis[(μ -*O,O'*-salicylato)(2,2'-bipyridyl)-copper(II)] acetylsalicylic acid dihydrate

PASCALE LEMOINE,^a DUNG NGUYEN-HUY,^b BERNARD VIOSSAT,^b JEAN-MICHEL LÉGER^c AND ALAIN TOMAS^a

^aLaboratoire de Cristallographie et RMN biologiques, E.P. 2075-CNRS, Faculté des Sciences Pharmaceutiques et Biologiques de Paris V, 4, avenue de l'Observatoire, 75270 Paris CEDEX 06, France, ^bLaboratoire de Chimie Générale, Faculté de Médecine et de Pharmacie, 34, rue du Jardin des Plantes, BP199, 86005 Poitiers CEDEX, France, and ^cLaboratoire de Chimie Analytique, place de la Victoire, 33076 Bordeaux CEDEX, France. E-mail: lemoine@pharmacie.univ-paris5.fr

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Abstract

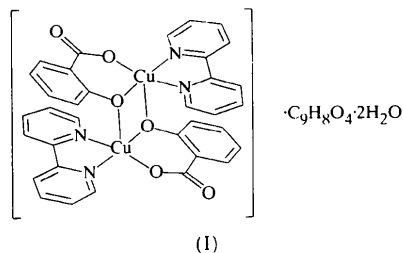
The asymmetric unit of the title compound, bis(μ -2-hydroxybenzoato-*O*¹, *O*²:*O*²)bis[(2,2'-bipyridyl-*N,N'*)copper(II)]-acetylsalicylic acid-water (1/1/2), [Cu₂(C₇H₄O₃)₂(C₁₀H₈N₂)₂].C₉H₈O₄.2H₂O, contains a binuclear copper complex, one acetylsalicylic acid molecule and two water molecules. Both crystallographically independent Cu^{II} atoms of the mixed binuclear unit show analogous distorted elongated square-pyramidal coordination (of the type 4+1). Each Cu^{II} atom is surrounded by one 2,2'-bipyridyl chelate and two salicylate

anions. The crystal packing is characterized by several intermolecular hydrogen bonds.

Comment

Copper(II) complexes with non-steroidal anti-inflammatory drugs (NSAIDs) have been studied extensively since Sorenson (1976) demonstrated that they are more active than their parent drugs and exhibit an anti-ulcer activity. Sorenson also showed that 3,5-diisopropylsalicylic acid which is an inactive agent becomes a potent anti-inflammatory compound when it chelates to copper(II). Moreover, binary complexes of Cu^{II} with 3,5-disubstituted salicylates and ternary complexes containing phenanthrolines have been prepared and characterized by Randford *et al.* (1993). These complexes have been tested for antiviral and cytotoxic activities; ternary complexes were ten times as cytotoxic as their binary analogues.

The crystal and molecular structure of the title compound, (I), has been determined in connection with investigations of binary complexes formed by Cu^{II} salts with some NSAIDs as indomethacin (Guessous *et al.*, 1998) and niflumic acid (Greenaway *et al.*, 1999) in our department. Following the work of Randford, we decided to synthesize and characterize ternary complexes of Cu^{II} with acetylsalicylic acid and heteroaromatic nitrogen bases (1,10-phenanthroline or bipyridine). Their biological activities will be tested and described elsewhere. The title compound consists of a binuclear copper complex, one acetylsalicylic acid and two water molecules. The two Cu atoms are crystallographically independent and present a similar environment. Each Cu^{II} atom is surrounded by one 2,2'-bipyridyl chelate *via N,N'* atoms, and two salicylate anions (obtained by deacetylation of acetylsalicylate during the synthesis). Each salicylate anion is bidentate *via* the carboxylate and hydroxyl groups [average bond length 1.895 (2) Å]; moreover, this hydroxyl group is bonded to the second Cu atom [average length 2.428 (3) Å] and so the salicylate anion acts as a bridging ligand between the Cu atoms [average angle Cu—O—Cu' 94.34 (9)°].



The Cu—N bond lengths are all equivalent [average 1.994 (2) Å]. So the coordination polyhedron around each Cu atom is a distorted square pyramid. The Cu and Cu' atoms are, respectively, 0.082 (1) Å below and

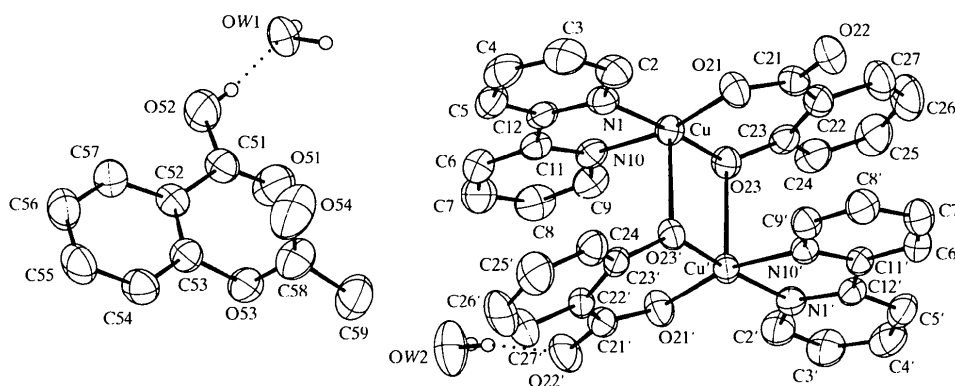


Fig. 1. Perspective view of the asymmetric unit of (I) showing the atomic numbering, with hydrogen bonds as dashed lines. Ellipsoids are at the 50% probability level for non-H atoms.

0.098 (1) Å above the approximate basal plane P(1) (O21, O23, N1, N10) or P(2) (O21', O23', N1', N10'), toward the apical atom (O23' or O23) belonging to the hydroxyl groups of the salicylate anions. The bonds Cu—O23' and Cu'—O23 only deviate by 6.0 (1)° from the perpendicular to the mean planes P(1) and P(2). The outlines O21—C21—C22—C23—O23, P(3), and O21'—C21'—C22'—C23'—O23', P(4), have planar geometries with a dihedral angle of 6.3 (1)°; Cu and Cu' are displaced 0.316 (3) and 0.460 (3) Å, respectively, out of these planes. The dihedral angles between P(1) or P(2) and their benzene ring are 20.5 (1) and 28.7 (1)°. The distances and angles within the 2,2'-bipyridyl ligands do not differ from those found in the literature. Their mean planes are quasi-parallel [dihedral angle 4.50 (8)°]. The distances and angles within the acetylsalicylic acid solvate are analogous to those observed in the molecule of aspirin (Wheatley, 1964), the largest difference involving C51—O51 [1.235 (4) Å in aspirin itself and 1.194 (4) Å in (I)]. The crystal packing is characterized by several intermolecular hydrogen bonds, the shortest involving the acid hydrogen of the aspirin and one of the two water molecules [O52—H52...OW1 2.541 (3) Å and 168 (3)°]. In addition, the crystalline cohesion is likewise ensured by many van der Waals contacts, the shortest being 3.234 (5) Å.

Experimental

The sodium salt of acetylsalicylic acid was prepared by dissolving acetylsalicylic acid (0.1 mol) in H₂O with NaOH so that the final pH of the solution was about 9; bipyridine (0.1 mol) was then dissolved in it. This mixture was added to a stirred aqueous solution of CuCl₂ (0.1 mol). After heating (<343 K) and stirring for 2 h, the precipitate was separated. Single crystals were obtained by slow evaporation of the filtrate under ambient pressure.

Crystal data

[Cu₂(C₇H₄O₃)₂(C₁₀H₈N₂)₂]_n·
C₉H₈O₄·2H₂O
M_r = 927.84
Triclinic
P $\bar{1}$
a = 12.949 (4) Å
b = 13.031 (8) Å
c = 13.97 (1) Å
α = 66.08 (7)°
β = 85.89 (5)°
γ = 69.08 (3)°
V = 2005 (2) Å³
Z = 2
D_x = 1.537 Mg m⁻³
D_m = 1.51 Mg m⁻³
D_m measured by flotation in
CCl₄/CHCl₃

Data collection

Enraf–Nonius CAD-4
diffractometer
ω–2θ scans
Absorption correction:
ψ scans (North *et al.*,
1968)
T_{min} = 0.778, T_{max} = 0.858
6605 measured reflections
6591 independent reflections

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.034
wR(F²) = 0.094
S = 1.037
6590 reflections
647 parameters
H atoms treated by a
mixture of independent
and constrained refinement

Cu Kα radiation
λ = 1.54180 Å
Cell parameters from 25
reflections
θ = 13.6–22.2°
μ = 1.912 mm⁻¹
T = 293 (2) K
Prism
0.45 × 0.12 × 0.08 mm
Blue

4979 reflections with
I > 2σ(I)
R_{int} = 0.007
θ_{max} = 64.95°
h = -14 → 15
k = 0 → 15
l = -14 → 16
2 standard reflections
frequency: 90 min
intensity decay: none

w = 1/[σ²(F_o²) + (0.0474P)²
+ 0.9012P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} = -0.016
Δρ_{max} = 0.373 e Å⁻³
Δρ_{min} = -0.347 e Å⁻³
Extinction correction: none
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu—O23	1.891 (2)	Cu'—O21'	1.896 (2)
Cu—O21	1.901 (2)	Cu'—N1'	1.987 (2)
Cu—N1	1.993 (2)	Cu'—N10'	1.995 (2)
Cu—N10	2.001 (2)	Cu'—O23	2.443 (3)
Cu—O23'	2.413 (3)	Cu—Cu'	3.188 (3)
Cu'—O23'	1.890 (2)		
O23—Cu—O21	93.91 (9)	O23'—Cu'—N1'	174.09 (8)
O23—Cu—N1	174.37 (9)	O21'—Cu'—N1'	92.05 (9)
O21—Cu—N1	91.72 (10)	O23'—Cu'—N10'	93.28 (9)
O23—Cu—N10	93.56 (9)	O21'—Cu'—N10'	165.63 (9)
O21—Cu—N10	167.55 (9)	N1'—Cu'—N10'	80.93 (9)
N1—Cu—N10	80.92 (10)	O23'—Cu'—O23	85.22 (9)
O23—Cu—O23'	86.06 (9)	O21'—Cu'—O23	102.4 (1)
O21—Cu—O23'	101.06 (9)	N1'—Cu'—O23	93.66 (9)
N1—Cu—O23'	92.71 (9)	N10'—Cu'—O23	90.60 (9)
N10—Cu—O23'	89.38 (9)	Cu—O23'—Cu'	94.85 (9)
O23'—Cu'—O21'	93.85 (9)	Cu—O23—Cu'	93.83 (9)

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O52—H52...OW1 ⁱ	0.87 (4)	1.69 (4)	2.541 (3)	168 (3)
OW1—H1A...O22	0.95	1.81	2.737 (3)	168
OW1—H1B...O22 ⁱⁱ	0.95	1.82	2.766 (3)	174
OW2—H2B...O22 ⁱⁱⁱ	0.93	1.90	2.816 (3)	169
OW2—H2A...O22 ^{iv}	0.95	2.20	3.140 (4)	174

Symmetry codes: (i) $x, 1 + y, z$; (ii) $-x, -y, 1 - z$; (iii) $x, y, z - 1$; (iv) $-x, 1 - y, 1 - z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *Nonius* (unpublished). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *CAMERON* (Watkin *et al.*, 1996). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1051). Services for accessing these data are described at the back of the journal.

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3-Hydroxyphthalide and its adduct with dibutyltin oxide

LIAN EE KHOO^a AND ALAN HAZELL^b

^a*School of Science, Nanyang Technological University, 469 Bukit Timah Road, Singapore 25976, Singapore, and* ^b*Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Århus C, Denmark. E-mail: ach@kemi.aau.dk*

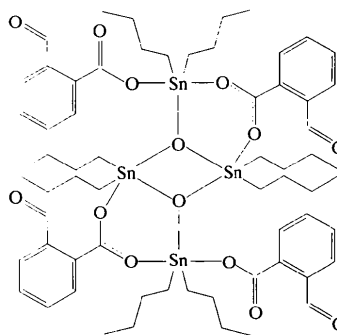
(Received 9 June 1999; accepted 31 August 1999)

Abstract

3-Hydroxyphthalide, C₈H₆O₃, reacts with dibutyltin oxide to give bis{μ₃-oxo-(μ-2-formylbenzoato-*O*:*O'*)-(2-formylbenzoato-*O*)bis[dibutyltin(IV)]}, [Sn₄(C₄H₉)₈-(C₈H₅O₃)₄(μ-O)₂], in which the four Sn atoms are all five-coordinated to three O and two C atoms arranged at the corners of a distorted trigonal bipyramid. The equatorial Sn—μ₃-O distances are in the range 2.039 (2)–2.048 (2) Å and are significantly shorter than the axial Sn—μ₃-O distances of 2.170 (3) and 2.182 (2) Å. The Sn—O_{carboxylate} bonds are all axial and have distances in the range 2.204 (3)–2.271 (3) Å, which are inversely correlated with the respective C—O bond distances. The mean Sn—C distance is 2.136 (6) Å. 3-Hydroxyphthalide undergoes ring opening to give the anion of 2-formylbenzoic acid which bonds to the Sn atoms. The structure of 3-hydroxyphthalide is stabilized by O—H...O hydrogen bonds [O...O = 2.766 (1) Å] which link the molecules in a zigzag chain parallel to *b*.

Comment

The reaction between *o*-substituted aromatic carboxylic acids with diorganotin oxide yields two types of diorganotin carboxylate, *i.e.* with a 2:1 or a 1:1 ligand–tin ratio (Gielen *et al.*, 1992, 1993). As a continuation of our studies of the structure–activity relationship (Goh *et al.*, 1998), we report the structures of the prod-



(I)