

(2,2'-Bipyridyl- κ^2N,N')bis(salicylato- κ^2O,O')zinc(II)

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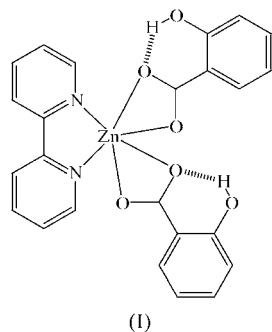
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The asymmetric unit of the title compound, $[\text{Zn}(\text{C}_7\text{H}_5\text{O}_3)_2(\text{C}_{10}\text{H}_8\text{N}_2)]$, contains one monomeric zinc complex. The Zn atom is coordinated to one 2,2'-bipyridyl ligand *via* both N atoms and to two salicylate anions (Hsal^-) in a bidentate chelating manner involving carboxylate O-atom coordination. The complex exhibits a distorted octahedral geometry about the Zn^{II} atom, with the 'apical' positions occupied by one of the two N atoms of the bipyridyl ligand and an O atom from one Hsal^- ligand; the Zn atom is 0.168 (1) Å out of the 'basal' plane. Two intramolecular six-membered hydrogen-bonded rings are present, generated from interactions between the carboxyl and hydroxyl groups of the salicylate ligands. The crystal packing is governed by weak $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\pi$ interactions.

Comment

Various zinc carboxylates are known to possess mild antiseptic and fungistatic properties. Complexes of Cu^{II} , Fe^{III} , Co^{II} , Ni^{II} , Ti^{IV} and Zn^{II} with 3,5-disubstituted salicylates (non-steroidal anti-inflammatory drugs or NSAIDs), and ternary complexes of Cu^{II} with added phenanthrolines, have been prepared and



characterized by Ranford *et al.* (1993). Continuing this work, we synthesized and characterized two ternary complexes of Zn^{II} with 3,5-diisopropylsalicylate and 1,10-phenanthroline or 2,9-dimethyl-1,10-phenanthroline (Lemoine *et al.*, 2004). Anticonvulsant and rotorod toxicity activities of these

complexes were determined to examine structure–anti-convulsant and structure–hypnotic activities of these Zn^{II} non-steroidal anti-inflammatory agent complexes. We describe here the synthesis and crystal structure of the title Zn^{II} complex, (I), with 2,2'-bipyridyl and salicylate ligands.

The asymmetric unit of (I) contains one monomeric six-coordinate zinc complex molecule. The Zn atom is surrounded by one bidentate 2,2'-bipyridyl ligand, coordinated *via* atoms N21 and N30, and two anionic bidentate salicylate (Hsal^-) ligands, coordinated *via* atoms O1, O2, O11 and O12 (Fig. 1). The complex exhibits a very distorted octahedral geometry around the Zn^{II} atom, with the 'apical' positions occupied by atoms O11 and N30. The Zn atom lies 0.168 (1) Å out of the 'basal' plane (O1/O2/O12/N21). The degree of deviation from an ideal octahedron is appreciable, with the angles subtended at the Zn atom ranging from 58.88 (9) to 105.0 (1)° (Table 1).

The chelation of Zn^{II} by the Hsal^- ligands in (I) leads to planar rings, denoted *P1* (O1/C1/O2/Zn) and *P2* (O11/C11/O12/Zn). The maximum out-of-plane deviation is 0.024 (2) Å for atom C11, with a dihedral angle (*P1/P2*) of 89.0 (1)°. The Zn–O distances range from 2.019 (3) to 2.365 (3) Å, compared with corresponding values in a similar environment in the compound (2,2'-bipyridyl)(methanol)(salicylato- κ^2O)-(salicylato- κ^2O,O')zinc of 2.022 (6)–2.305 (7) Å (Brownless *et al.*, 1999). The phenyl mean planes [*P3* (C2–C7) and *P4* (C12–C17)] of the salicylate ligands, with a maximum out-of-plane deviation of 0.013 (3) Å for atom C13, make a dihedral angle of 87.8 (2)°.

The Zn–N21 and Zn–N30 distances of 2.071 (3) and 2.100 (3) Å, respectively, are in agreement with those observed in the complex $[\text{Zn}(\text{3,5-diisopropylsalicylate})_2(1,10\text{-phenanthroline})]$ [2.056 (3) and 2.115 (3) Å, respectively; Lemoine *et al.*, 2004]. The bipyridyl moiety is essentially planar, with a maximum out-of-plane deviation of 0.037 (4) Å for atom C28, and the Zn^{II} atom is displaced from the least-squares plane *P5* (N21/C22–C29/N30/C31–C32) by 0.094 (3) Å. The dihedral angles between plane *P5* and planes *P3* and *P4* are 82.3 (1) and 71.4 (1)°, respectively.

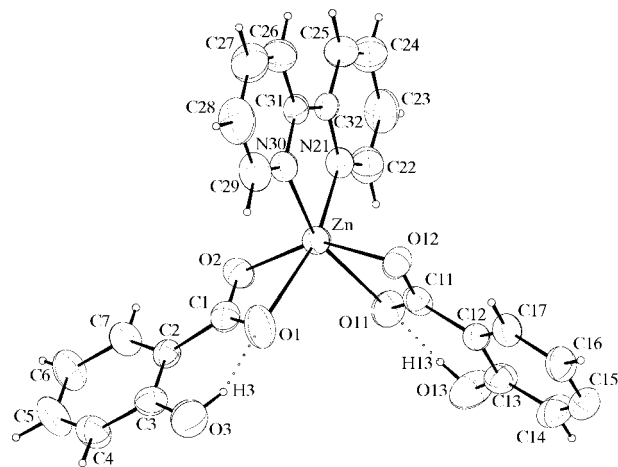


Figure 1
A perspective view of the asymmetric unit of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

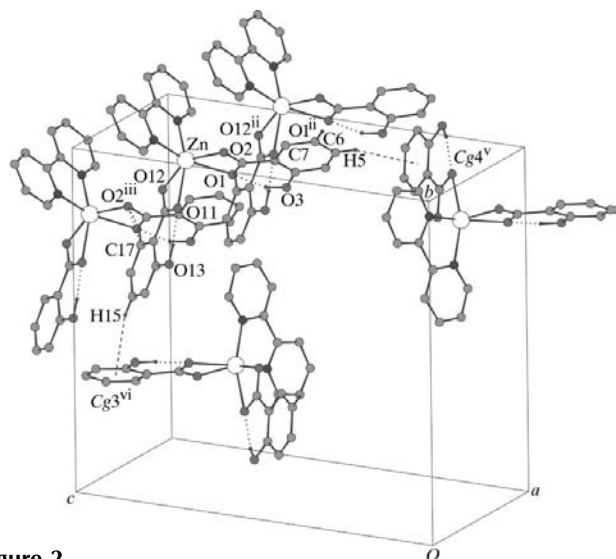


Figure 2
Part of the crystal structure of (I), showing the packing interactions; Cg3 and Cg4 are defined in Table 2. [Symmetry codes: (ii) 1 + x, y, z; (iii) x - 1, y, z; (v) x - 1, 1/2 - y, 1/2 + z; (vi) 1 - x, 1/2 + y, 1/2 - z.]

The H atoms attached to atoms O3 and O13 are involved in intramolecular hydrogen bonding *via* atoms O1 and O11, respectively (Table 2), thus contributing to the lengthening of the O1—Zn and O11—Zn bond distances and the planarity of the rings O1/C1—C3/O3/H3 and O11/C11—C13/O13/H13; the maximum out-of-plane deviation for these planes is 0.07 (2) Å for atom H13.

The crystal packing of (I) is governed by four C—H...O interactions with C...O < 3.41 Å and τ > 144°, and two C—H...Cg(π-ring) interactions with H...Cg < 3 Å and τ < 30° (Table 2). The C—H...O interactions lead to chains approximately along the [100] direction, while the C—H...π(arene) interactions complete a three-dimensional network (Fig. 2). In addition, crystalline cohesion is ensured by numerous van der Waals contacts, the shortest being O2...C25^{vii} of 3.147 (5) Å [symmetry code: (vii) 2 - x, 2 - y, 2 - z].

Experimental

Compound (I) was prepared by mixing aqueous solutions of sodium salicylate (1.601 g, 10 mmol) and zinc chloride (0.680 g, 5 mmol). The resulting precipitate was collected by filtration, washed with water and dried overnight. The title complex was obtained by reaction of this zinc(II) complex with 2,2'-bipyridyl (bipy-Zn 1:1) in methanol. The reaction mixture was stirred for 30 min. Colourless parallelepipedic crystals of (I) were obtained by slow evaporation of this solution under ambient air pressure.

Crystal data

[Zn(C₇H₅O₃)₂(C₁₀H₈N₂)]
M_r = 495.77
Monoclinic, P2₁/c
a = 7.642 (4) Å
b = 16.635 (3) Å
c = 17.354 (3) Å
β = 101.20 (2)°
V = 2164 (2) Å³
Z = 4
D_x = 1.522 Mg m⁻³
D_m = 1.51 (1) Mg m⁻³

D_m measured by flotation in
CCl₄—CHCl₃
Mo Kα radiation
Cell parameters from 25
reflections
θ = 1.7–8.9°
μ = 1.18 mm⁻¹
T = 293 (2) K
Parallelepiped, colourless
0.45 × 0.35 × 0.10 mm

Table 1
Selected geometric parameters (Å, °).

Zn—O2	2.019 (3)	Zn—O1	2.366 (3)
Zn—O12	2.040 (3)	O2—C1	1.261 (4)
Zn—N21	2.071 (3)	O1—C1	1.254 (4)
Zn—N30	2.099 (3)	C3—O3	1.352 (4)
Zn—O11	2.313 (3)		
O2—Zn—O12	146.17 (10)	N30—Zn—O11	157.76 (10)
O2—Zn—N21	102.49 (12)	O2—Zn—O1	58.89 (10)
O12—Zn—N21	105.02 (11)	O12—Zn—O1	93.68 (10)
O2—Zn—N30	104.49 (11)	N21—Zn—O1	161.04 (10)
O12—Zn—N30	99.83 (11)	N30—Zn—O1	101.28 (11)
N21—Zn—N30	78.86 (12)	O11—Zn—O1	89.95 (10)
O2—Zn—O11	97.74 (9)	C1—O2—Zn	98.5 (2)
O12—Zn—O11	59.96 (9)	C1—O1—Zn	82.7 (2)
N21—Zn—O11	96.67 (11)		

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

Cg3 denotes the centroid of ring P3 (C2—C7) and Cg4 denotes the centroid of ring P4 (C12—C17).

D—H...A	D—H	H...A	D...A	D—H...A
O3—H3...O1	0.92 (2)	1.75 (3)	2.577 (4)	148 (4)
O13—H13...O11	0.90 (2)	1.81 (3)	2.588 (4)	144 (4)
C6—H6...O1 ⁱⁱ	0.93	2.53	3.403 (5)	157
C7—H7...O12 ⁱⁱ	0.93	2.58	3.383 (5)	144
C17—H17...O2 ⁱⁱⁱ	0.93	2.49	3.342 (5)	152
C26—H26...O12 ^{iv}	0.93	2.55	3.351 (6)	144
C5—H5...Cg4 ^v	0.93	2.93	3.749 (4)	148
C15—H15...Cg3 ^{vi}	0.93	2.82	3.626 (6)	146

Symmetry codes: (ii) 1 + x, y, z; (iii) x - 1, y, z; (iv) 1 - x, 2 - y, 2 - z; (v) x - 1, 1/2 - y, 1/2 + z; (vi) 1 - x, 1/2 + y, 1/2 - z.

Data collection

Enraf-Nonius CAD-4
diffractometer
ω/2θ scans
Absorption correction: empirical
via multi-scan (SADABS;
Sheldrick, 1996; Blessing,
1995)
T_{min} = 0.854, T_{max} = 0.889
7380 measured reflections
3783 independent reflections

2350 reflections with I > 2σ(I)
R_{int} = 0.056
θ_{max} = 25.0°
h = -9 → 9
k = 0 → 19
l = -20 → 20
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F²
R(F) = 0.038
wR(F²) = 0.106
S = 0.99
3783 reflections
305 parameters

H atoms treated by a mixture of
independent and constrained
refinement
w = 1/[σ²(F_o²) + (0.0415P)²]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} = 0.001
Δρ_{max} = 0.35 e Å⁻³
Δρ_{min} = -0.27 e Å⁻³

Hydroxy H atoms were located in a difference map and refined freely. All other H atoms were treated as riding, with C—H distances of 0.93 Å. A common displacement parameter was refined for all H atoms.

Data collection: CAD-4 EXPRESS (Enraf-Nonius, 1994); cell refinement: CAD-4 EXPRESS; data reduction: XCAD4 (Harms & Wocadlo, 1995); program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: CAMERON (Watkin *et al.*, 1996); software used to prepare material for publication: WinGX (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1065). Services for accessing these data are described at the back of the journal.

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