

Tetrakis(2,2'-bipyridine- κ^2N,N')-tetrakis(μ -salicylato- $\kappa^3O,O':O''$)-quadro-tetrazinc(II) decahydrate

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The title compound, $[Zn_4(C_7H_4O_3)_4(C_{10}H_8N_2)_4] \cdot 10H_2O$, crystallizes as a centrosymmetric tetranuclear cyclic complex containing four Zn^{II} atoms bridged by four carboxylate groups from salicylate ligands, with a *syn-anti* configuration. Each Zn^{II} atom has a distorted trigonal-bipyramidal coordination geometry, formed by two N atoms of a 2,2'-bipyridine ligand and three O atoms from two salicylate ligands. The complex is stabilized by intramolecular π - π interactions between pairs of bipyridine rings and a 16-membered gear-wheel-shaped cyclic framework. The hydrogen-bonding network is formed *via* the water molecules.

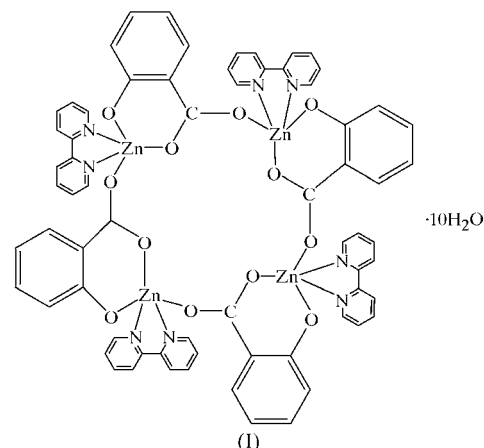
Comment

Zinc is an important and beneficial element for human growth. It is well known that the Zn^{II} atom can inhibit replication of rhinoviruses (Korant *et al.*, 1974), and Zn^{II} complexes have antibacterial and antiviral activities; for example, the complex of zinc acetate with erythromycin is used for acne therapy (Feucht *et al.*, 1980). A large number of Zn^{II} complexes have been investigated (Yaghi *et al.*, 1997; Karanović *et al.*, 2002; Gronlund *et al.*, 1995). One of the best ways to understand such effective antimicrobial species is to gain knowledge about the structure and coordination geometry of these complexes.

Our interest in the coordination chemistry of salicylic acid stems from the fact that the carboxylate group plays an important role in interaction with biologically important metal ions. Salicylic acid, one of the metabolites of aspirin, has been used in dermatology as a fungicidal treatment (Diehl, 1996) and inhibits oxidative stress (Sagone & Husney, 1987). In recent years, ligands with carboxylate groups have been employed in the design of novel complex frameworks, and many zinc compounds of this kind have been prepared. We report here the structure of the title compound, (I), which is a ternary zinc complex of salicylic acid and 2,2'-bipyridine.

In (I), there are two independent zinc centers, namely Zn1 and Zn2, and a tetranuclear unit is formed in which these

atoms are related by a center of symmetry (Fig. 1). Each Zn^{II} atom is bonded to two N atoms from a 2,2'-bipyridine moiety,



one phenolate O atom and two carboxylate O atoms from two salicylate ligands. The two independent Zn^{II} atoms show similar coordination geometry, *i.e.* distorted trigonal-bipyramidal. Atoms Zn1, N1, O2 and O6ⁱ [symmetry code: (i) $-x, 2 - y, -z$] occupy the equatorial plane, and atoms O1 and N2 are in the axial positions, with an O1–Zn1–N2 bond angle of 171.73 (7)°. Around Zn2, atoms N4, O3 and O4 form the trigonal plane, and atoms O5 and N3 occupy the axial positions, with an O5–Zn2–N3 angle of 168.69 (7)°. Atoms Zn1 and Zn2 deviate from the trigonal planes by 0.017 (3) (toward O1) and 0.111 (3) Å (toward N5), respectively.

The Zn1–O1(phenolate) bond distance in the axial direction is longer than the Zn2–O4(phenolate) bond in the

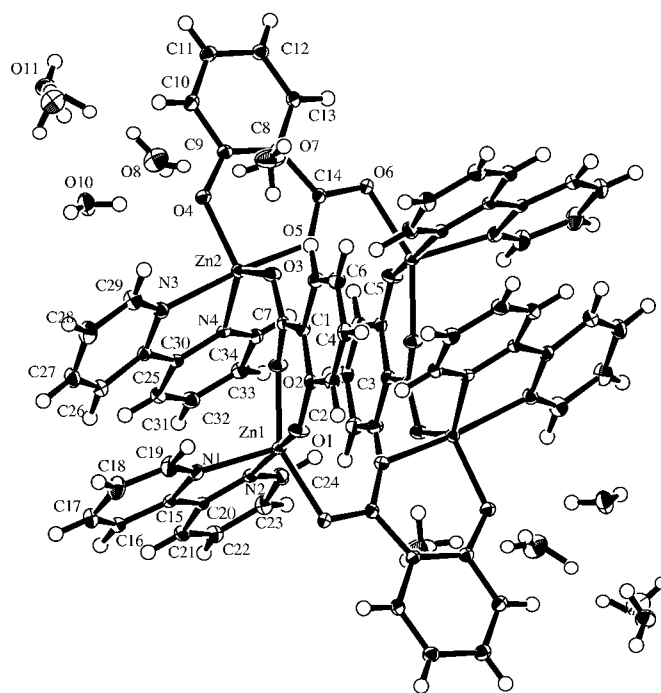


Figure 1

An ORTEP-3 (Farrugia, 1997) drawing of (I), with the atomic numbering scheme. Displacement ellipsoids for non-H atoms are shown at the 50% probability level.

equatorial plane (Table 1). This difference may be due to the Jahn–Teller effect of the d^{10} metal atom. Similarly, the Zn2–O5(carboxylate) bond in the axial direction is longer than the Zn1–O2(carboxylate) bond in the equatorial plane. In its role as bridging atom, atom O3 is connected to atom Zn2 more tightly than atom O6ⁱ is to Zn1, where both atom O3 and atom O6ⁱ are in the trigonal plane. This difference may be due to the bipyridine molecules being twisted to different degrees. In the bipyridine group in which atoms N1 and N2 are bonded to atom Zn1, the two pyridine rings are nearly coplanar, with a dihedral angle of only 3.6 (3)°. In the bipyridine group with atoms N3 and N4 bonded to atom Zn2, the two ring planes intersect at an angle of 13.38 (6)° with respect to one another.

The carboxylate group in each salicylate ligand bridges neighboring Zn^{II} atoms to form a tetrameric cyclic complex containing four Zn atoms, four 2,2'-bipyridine molecules and four salicylate ligands in a *syn-anti* configuration (Clegg & Little, 1988). Four repeating Zn–O–C–O units construct a 16-membered gear-wheel-shaped cyclic framework, which stabilizes the complex molecule. The structure is further stabilized by intramolecular π – π interactions between bi-

pyridine ligands, with contact distances ranging from 3.336 (5) (C15···C26) to 3.592 (5) Å (C21···C31). Intermolecular π – π interactions between the salicylate ligands of adjacent complexes are also present, with a mean distance of 3.564 (2) Å.

A linear array of three metal ions bridged by carboxylate ligands in *syn-anti* or *syn-syn* configurations was mentioned by Clegg & Little (1988). They reported the crystal structures of complexes of the general formula $[MZn_2(\text{crot})_6(\text{base})_2]$ ($M = \text{Zn, Mn, Co, Ni}$ and Cd), which contained two monodentate monoatomic crotonate (crot) bridges. Moreover, a trinuclear linear array of Zn^{II} atoms was also described, with formula $[\text{Zn}_3(\text{CH}_3\text{COO})_6(\text{py})_2]$ or $[\text{Zn}_3(\text{CH}_3\text{COO})_6(\text{bppz})_2]$ [bppz is 2,5-bis(2-pyridyl)pyrazine; Singh *et al.*, 1997; Neels & Stoeckli-Evans, 1999]. However, to our knowledge, (I) is the first reported complex in which four Zn^{II} atoms are circularly arrayed with aromatic ligand species.

The average Zn–O(carboxylate) bond distance of (I) was compared with the similar circular wheel-shaped zinc(II) complexes of formula $[\text{Zn}_2(\text{RCOO})_4L_2]$, in which two Zn^{II} atoms are connected by benzoate ligands in a *syn-syn* configuration (Zeleňák *et al.*, 2004). The value of 2.031 (3) Å in (I) is slightly shorter than the average value of 2.048 (8) Å, where RCOO^- is benzoate and L is [1-(3,4-dimethoxyphenyl)methyl]-6,7-dimethoxyisoquinoline, 2.038 and 2.041 Å, where RCOO^- is acetate and L is pyridine, and 2.034, 2.039 and 2.042 Å, where RCOO^- is indomethacin and L is 1-methylpyrrolidinone, pyridine or dimethylacetamide, all cited by Zeleňák *et al.* (2004).

The intramolecular Zn1···Zn2 [4.7249 (5) Å] and Zn1···Zn2ⁱ [4.5310 (3) Å] distances in (I) are much longer than those in the above-mentioned complexes. The longer Zn···Zn separations may be attributed to the further coordination of zinc with the phenolate O atom in each salicylate ligand. Moreover, the bridging mode of *syn-anti* configuration (Clegg & Little, 1988) is a reasonable explanation of the further separation of each two Zn atoms. Compared with a previous example (Hatch *et al.*, 2003) containing the same ligand molecule (2,2'-bipyridine), the Zn^{II} atom of this study seems to be more strongly coordinated to the N atoms, with Zn–N bond lengths ranging from 2.143 (5) to 2.185 (4) Å.

All of the water molecules participate in the formation of a characteristic hydrogen-bonding network including the O atoms of the salicylate ligands (Table 2). One of the water H atoms attached to each of atoms O7, O8 and O9 is disordered over two sites, as a result of O7–H31···O7(1–x, 2–y, –z) and O9–H37···O9(1–x, 1–y, 1–z) hydrogen bonds. The positional disorder of the water H atoms can be explained by assuming two possible configurations of the hydrogen-bonding network (Fig. 2).

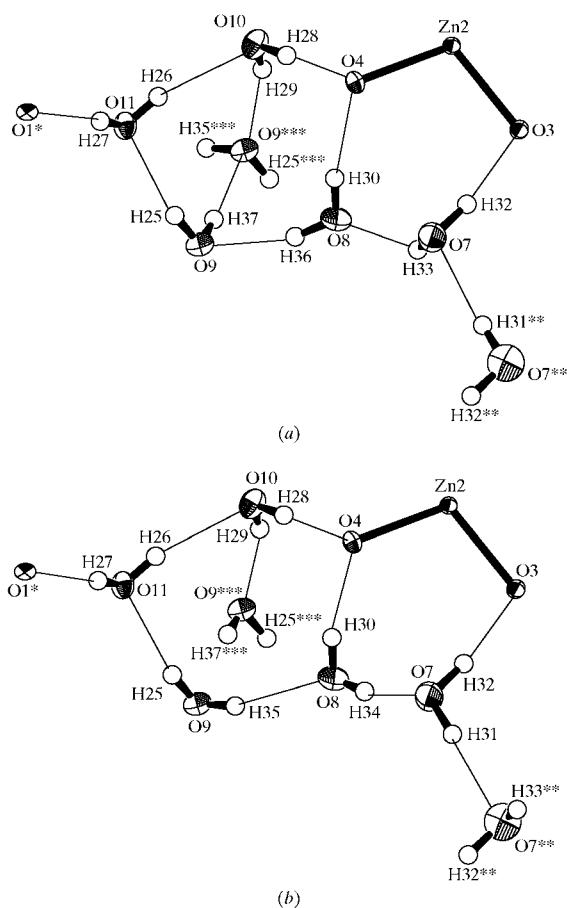


Figure 2

Two patterns, (a) and (b), of the hydrogen-bonding network formed by the water molecules. The site-occupation factors of atoms H31, H33, H34, H35, H36 and H37 are 50%. Thin lines indicate hydrogen bonds. [Symmetry codes: (*) $x, y, 1+z$; (**) $1-x, 2-y, -z$; (***) $1-x, 1-y, 1-z$.]

Experimental

Thin yellow prism-shaped crystals of (I) were obtained by slow evaporation of an aqueous methanol solution (10 ml) of a mixture of salicylic acid (5 mg), 2,2'-bipyridine and ZnCl_2 (molar ratio 1:1:1) at room temperature.

Crystal data

[Zn₄(C₇H₄O₃)₄(C₁₀H₈N₂)₄]·10H₂O
M_r = 1610.85
 Triclinic, *P* $\bar{1}$
a = 12.633 (13) Å
b = 12.735 (14) Å
c = 13.29 (3) Å
 α = 61.60 (3)°
 β = 66.23 (4)°
 γ = 63.22 (3)°
V = 1630 (4) Å³

Z = 1
D_x = 1.641 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 13 658 reflections
 θ = 3.1–27.5°
 μ = 1.54 mm⁻¹
T = 296.1 K
 Prism, colorless
 0.30 × 0.20 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
T_{min} = 0.718, *T_{max}* = 0.857
 15 951 measured reflections

7327 independent reflections
 5512 reflections with *F*² > 2σ(*F*²)
R_{int} = 0.019
 θ_{max} = 27.5°
h = -16 → 16
k = -16 → 16
l = -17 → 17

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.024
wR(*F*²) = 0.066
S = 1.00
 7327 reflections
 462 parameters

H-atom parameters constrained
w = 1/[σ²(*F_o*²) + (0.0387*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.42 e Å⁻³
 Δρ_{min} = -0.30 e Å⁻³

Table 1
 Selected geometric parameters (Å, °).

Zn1—O1	1.996 (5)	Zn2—O3	2.023 (5)
Zn1—O2	2.008 (5)	Zn2—O4	1.969 (5)
Zn1—N1	2.105 (5)	Zn2—O5	2.040 (5)
Zn1—N2	2.154 (5)	Zn2—N3	2.181 (5)
Zn1—O6 ⁱ	2.052 (5)	Zn2—N4	2.095 (5)
O1—Zn1—O2	89.42 (7)	O3—Zn2—O4	107.50 (7)
O1—Zn1—N1	96.08 (6)	O3—Zn2—O5	96.02 (5)
O1—Zn1—N2	171.73 (7)	O3—Zn2—N3	92.81 (5)
O2—Zn1—N1	107.28 (8)	O3—Zn2—N4	133.48 (8)
O2—Zn1—N2	97.02 (7)	O4—Zn2—O5	91.26 (7)
N1—Zn1—N2	77.10 (6)	O4—Zn2—N3	92.82 (7)
O1—Zn1—O6 ⁱ	88.49 (8)	O4—Zn2—N4	118.09 (6)
O2—Zn1—O6 ⁱ	148.42 (6)	O5—Zn2—N3	168.69 (7)
N1—Zn1—O6 ⁱ	104.3 (1)	O5—Zn2—N4	91.91 (6)
N2—Zn1—O6 ⁱ	88.75 (7)	N3—Zn2—N4	76.86 (7)

Symmetry code: (i) -*x*, 2 - *y*, -*z*.

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O7—H31...O7 ⁱⁱ	0.90	1.90	2.755 (7)	158
O7—H32...O3	0.96	1.94	2.882 (4)	168
O7—H33...O8	0.91	2.06	2.771 (7)	135
O8—H30...O4	0.81	2.03	2.819 (7)	165
O8—H34...O7	0.77	2.04	2.771 (7)	157
O8—H36...O9	0.90	1.96	2.836 (7)	163
O9—H35...O8	0.91	2.00	2.836 (7)	153
O9—H37...O9 ⁱⁱⁱ	0.78	2.08	2.855 (4)	176
O9—H25...O11	0.80	1.98	2.756 (6)	163
O10—H28...O4	0.85	2.06	2.902 (7)	175
O10—H29...O9 ⁱⁱⁱ	0.71	2.30	2.977 (7)	161
O11—H26...O10	0.83	2.19	2.962 (7)	155
O11—H27...O1 ^{iv}	0.75	1.97	2.721 (3)	174

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

All H atoms, except those of water molecules, were located from difference Fourier maps, and were then placed at idealized positions and treated as riding, with C—H distances of 0.93 Å and *U_{iso}*(H) values of 1.2*U_{eq}*(C). Water H atoms bonded to atoms O10 and O11 were located from difference Fourier maps. One of the H atoms attached to each of atoms O7, O8 and O9 shows positional disorder over two sites, viz. H31/H33, H34/H36 and H35/H37, respectively, with occupation factors of 50% each. The positional parameters of the disordered H atoms were calculated on the basis of the positions of the other H atoms (H25, H30 and H32), which were located from difference Fourier maps, and by assuming two possible configurations of the hydrogen-bonding network (Fig. 2). The positional parameters of the water H atoms were fixed, with *U_{iso}*(H) values of 0.020 Å², the O—H distances and H—O—H bond angles being 0.71–0.96 Å and 92–116°. The short H32...H4 (the atom bonded to C6) contact distance of 2.1 Å suggests that the reported position of atom H32 is slightly shifted from its true position.

Data collection: *RAPID-AUTO* (Rigaku, 2003); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2004) and *CRYSTALS* (Watkin *et al.*, 1996); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999) and *DIRDIF99* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1191). Services for accessing these data are described at the back of the journal.

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