Bis{(μ-acetato)[μ-bis(salicylidene)-1,3-propanediaminato]zinc(II)}zinc(II)[1]

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In the title linear trinuclear compound, [Zn{Zn(CH$_3$COO)-(C$_{17}$H$_{16}$N$_2$O$_2$)}$_2$], the central Zn^{2+} ion, which is located on an inversion centre, has a distorted octahedral coordination involving four bridging O atoms from two N,N'-bis(salicylidene)-1,3-propanediaminate ligands in the equatorial plane and one O atom from each bridging acetate group in the axial positions. The coordination around the terminal Zn^{2+} ion is irregular square pyramidal, with two O and two N atoms of the ligand in the basal plane and one O atom from an acetate group in the apical position. The acetate bridges linking the central and terminal Zn^{2+} ions are mutually *trans*. The Zn···Zn distance is 3.0520 (8) Å. The relationship of this structure to that of [Zn{Cu(CH$_3$COO)(C$_{17}$H$_{16}$N$_2$O$_2$)}$_2$] is discussed.

Comment

Structural studies and the magnetic properties of trinuclear complexes prepared with the deprotonated N,N'-bis(salicylidene)-1,3-propanediamine (SALPD^{2-}, C$_{17}$H$_{16}$N$_2$O$_2$$^{2-}$) ligand have been the subject of considerable interest in our laboratory. In these complexes, acetate or nitrite anions constitute the μ-bridging between the three metal ions, which are also doubly oxygen bridged, so that the metal ions used in the synthesis (M is Zn^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+} or Co^{2+}) are all triply bridged (Ülkü *et al.*, 1999; Atakol, Arici, Ercan & Ülkü, 1999; Atakol, Arici, Tahir *et al.*, 1999; Atakol, Tatar *et al.*, 1999; Tahir *et al.*, 1998; Ülkü, Ercan *et al.*, 1997; Ülkü, Tahir *et al.*, 1997, and references therein). Since there are three metal ions in these linear complexes, various combinations of metallic ions are possible in the central and terminal locations, so that homonuclear as well as heteronuclear compounds can be synthesized. When the synthesis involves a paramagnetic ion, then the magnetic properties of the compound become interesting, due to the superexchange interaction between the diamagnetic ions of the bridges. The ligand stereochemistry

around the metal ions and the structure of the O-atom bridges influence these magnetic exchange interactions, and therefore the structural parameters are important.

The synthesis of similar trinuclear complexes of the general formulae [MCu$_2$(SALPD)$_2$(CH$_3$COO)$_2$] (M is Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} or Zn^{2+}) and [MNi$_2$(SALPD)$_2$(CH$_3$COO)$_2$] (M is Mg^{2+}, Mn^{2+}, Co^{2+} or Ni^{2+}) were reported by Fukuhara *et al.* (1990). Only the structure of [ZnCu$_2$(SALPD)$_2$(CH$_3$COO)$_2$] in this group of compounds has been determined by X-ray diffraction to date (Fukuhara *et al.*, 1990). Gerli *et al.* (1991) reported trinuclear structures formulated as [M$_3${(SALPN)-(CH$_3$COO)[(CH$_3$)$_2$NCHO]}$_2$] [M is Co^{2+} or Fe^{2+}; SALPN is N,N'-bis(salicylidene)-2,2-dimethylpropylenediamine]. We report here a new member of the linear homometallic trinuclear compound family, the title compound, (I), in which the central as well as the terminal metal ion locations are occupied by Zn atoms.
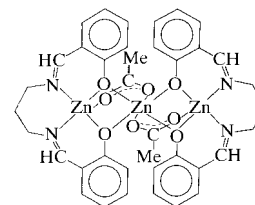
(I)

Among the trinuclear complexes cited above, (I) resembles [Zn{Cu(CH$_3$COO)(C$_{17}$H$_{16}$N$_2$O$_2$)}$_2$], (II) (Fukuhara *et al.*, 1990), more than any other trinuclear complex, and the two molecules are almost identical. In both molecules, the central Zn^{2+} ion, located on an inversion centre, has as its nearest neighbours four bridging O atoms from two SALPD^{2-} ligands (O1, O2, O1^i and O2^i) and two O atoms from two bridging acetate groups [O3 and O3^i; symmetry code: (i) −x, −y, −z].
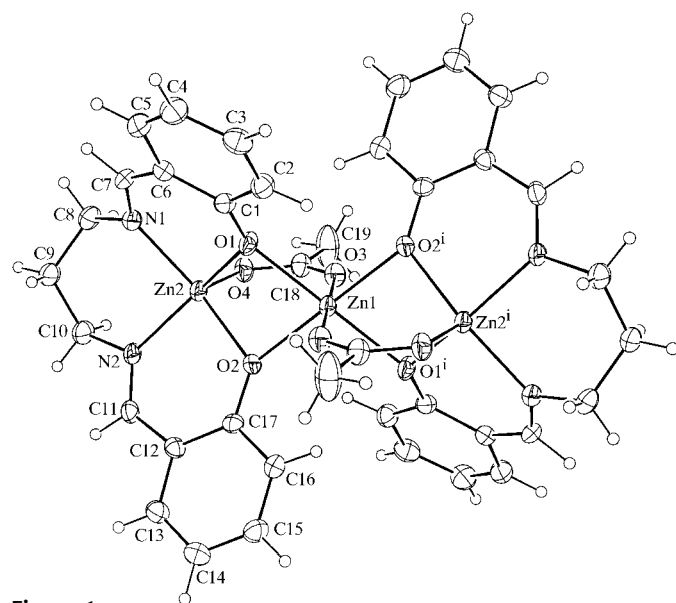

Figure 1
The molecular structure (*ORTEP*-3; Farrugia, 1997) of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small circles of arbitrary radii [symmetry code: (i) −x, −y, −z].

metal-organic compounds

This environment constitutes an irregular octahedral geometry around the Zn ion. The Zn—O bond lengths around the central Zn ion in both complexes have values equal within experimental error.

The coordination polyhedra around the inversion-related terminal ions, *i.e.* Zn in (I) and Cu in (II), are slightly distorted square pyramids whose basal plane is made up of the two bridging O atoms and two N atoms of the SALPD²⁻ ligand, while the apical positions are occupied by an O atom of the acetate group. The corresponding M—O and M—N distances within the coordination polyhedra around the terminal ions are different in these two complexes, so that the square pyramid around the Cu²⁺ ion in (II) is slightly elongated when compared with the square pyramid around the Zn²⁺ ion in (I).

These two almost identical molecules of (I) and (II) crystallize in space groups $P2_1/c$ and $P2_1/a$, respectively, and have almost the same unit-cell volume [1771.8 (4) and 1766.7 (9) Å³, respectively]. However, the unit-cell parameters of the Cu–Zn–Cu trimer, (II) [a = 16.228 (5), b = 11.971 (2), c = 9.239 (3) Å and β = 100.15 (3)°], are considerably different from the corresponding values of the Zn–Zn–Zn trimer, (I), especially with respect to a and b.

In the Zn–Zn–Zn trimer, there is one intermolecular hydrogen bond between C11—H11 and O4ⁱⁱ [H11···O4 2.53 Å, C11···O4 3.475 (7) Å and C11—H11···O4 175°; symmetry code: (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$].

Experimental

N,N'-Bis(salicylidene)-1,3-propanediamine (0.564 g, 2 mmol) was dissolved in methanol (250 ml) by heating to boiling point. A solution of Zn(CH₃COO)₂·2H₂O (0.660 g, 3 mmol) in hot methanol (100 ml) was added to the solution. The resulting mixture was set aside for 1 d and the colourless prismatic crystals of (I) which formed were filtered off and dried in air.

Crystal data

[Zn₃(C₁₇H₁₆N₂O₂)₂(C₂H₃O₂)₂]
M_r = 874.91
Monoclinic, $P2_1/c$
a = 10.4243 (14) Å
b = 20.3334 (18) Å
c = 8.3832 (11) Å
β = 85.639 (13)°
V = 1771.8 (4) Å³
Z = 2

D_x = 1.640 Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 8.64–11.39°
μ = 2.07 mm⁻¹
T = 295 K
Prism, colourless
0.20 × 0.10 × 0.05 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*MolEN*; Fair, 1990)
T_{min} = 0.798, T_{max} = 0.902
4101 measured reflections
3724 independent reflections
2514 reflections with $I > 2\sigma(I)$

R_{int} = 0.033
θ_{max} = 26.7°
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 25$
$l = -10 \rightarrow 10$
3 standard reflections
  frequency: 120 min
  intensity decay: negligible

Refinement

Refinement on F
R = 0.045
wR = 0.056
S = 1.01
2514 reflections
241 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F) + (0.02F)^2 + 0.25]$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.84 e Å⁻³
$\Delta\rho_{min}$ = −0.23 e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Zn1—Zn2	3.0520 (8)	Zn2—O4	1.975 (4)
Zn1—O1	2.098 (3)	Zn2—N1	2.060 (4)
Zn1—O2	2.113 (4)	Zn2—N2	2.071 (4)
Zn1—O3	2.124 (4)	O3—C18	1.254 (7)
Zn2—O1	2.057 (4)	O4—C18	1.256 (7)
Zn2—O2	2.034 (4)		
O1—Zn1—O2	77.5 (1)	O2—Zn2—O4	101.2 (2)
O1—Zn1—O3	86.5 (1)	O2—Zn2—N1	155.0 (2)
O2—Zn1—O3	87.6 (2)	O2—Zn2—N2	89.4 (2)
O1—Zn1—O1ⁱ	180.0	O4—Zn2—N1	102.9 (2)
O1—Zn1—O2ⁱ	102.5 (1)	O4—Zn2—N2	104.9 (2)
O1—Zn1—O3ⁱ	93.5 (2)	N1—Zn2—N2	90.9 (2)
O2—Zn1—O2ⁱ	180.0	Zn1—O1—Zn2	94.5 (1)
O2—Zn1—O3ⁱ	92.4 (2)	Zn1—O2—Zn2	94.8 (2)
O3—Zn1—O3ⁱ	180.0	Zn1—O3—C18	138.4 (4)
O1—Zn2—O2	80.3 (1)	Zn2—O4—C18	119.5 (4)
O1—Zn2—O4	103.7 (2)	O3—C18—O4	124.9 (5)
O1—Zn2—N1	87.5 (2)	O3—C18—C19	119.7 (6)
O1—Zn2—N2	150.9 (2)	O4—C18—C19	115.4 (6)

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

The H atoms on C19 were taken from a difference map, while the other H atoms were placed geometrically 0.95 Å from their parent atoms. For all H atoms, a riding model was used with U_{eq}(H) = $1.3U_{eq}$(C).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993); cell refinement: *MolEN*; data reduction: *MolEN*; program(s) used to solve structure: *MolEN*; program(s) used to refine structure: *MolEN*; molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *MolEN* and *PLATON* (Spek, 1990, 2000).

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