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(Acetato-*O*,*O*′)(acetato-*O*)(2,9-dimethyl-1,10-phenanthroline-*N*,*N*′)zinc(II)

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Abstract

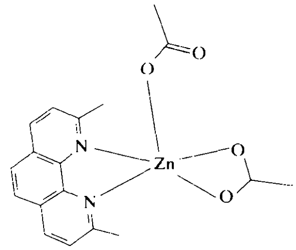
In diacetato-*O*,*O*′;*O*-(2,9-dimethyl-1,10-phenanthroline-*N*,*N*′)zinc(II), $[Zn(C_2H_3O_2)_2(C_{14}H_{12}N_2)]$, the zinc cation has a pentacoordinated environment consisting of the two N atoms of 2,9-dimethyl-1,10-phenanthroline, one O atom from a monodentate acetate group and two O atoms from a bidentate acetate group.

Comment

The study of zinc(II) complexes with *N*- and *O*-donor ligands is of current interest due to their potential use as models for zinc-containing active sites in enzymes (Creighton, 1984).

The carboxylate group, present in many of these active sites, has been found to behave as a monodentate, bidentate or bridging ligand, and many zinc acetate complexes with phenanthroline or bipyridine have been found to display these different modes of coordination (Chen, Tong & Mak, 1994; Chen, Xu *et al.*, 1994).

In this paper, we present the structure of the novel complex $[Zn(MeCO_2)_2(dmph)]$ (dmph is dimethylphenanthroline), (I), the first report of a complex in which the anion displays two different modes of coordination to the same metal centre. The Zn^{2+} ion is coordinated by two N atoms from dmph (N1 and N2), two O atoms from a bidentate acetate ion (O1*B* and O2*B*) and one O atom from the remaining acetate ion, which is monodentate; the second O atom of the monodentate acetate ion, though not formally bonded to zinc, is at a distance of 2.768 (4) Å, slightly shorter than the sum of the corresponding van der Waals radii.



(I)

The array around the cation can be described as a distorted square pyramid, the planar base being determined by atoms N1, N2, O1*B* and O2*B* [maximum deviation from the mean plane: 0.011 (4) Å for O1*B*], with the Zn^{2+} ion 0.870 (1) Å from this plane towards the apical site. The latter is occupied by the O1*A* atom from the monodentate acetate group, the bond to zinc [Zn—O1*A* 1.919 (3) Å] being tilted by 13.7 (1)° from the base normal (Fig. 1).

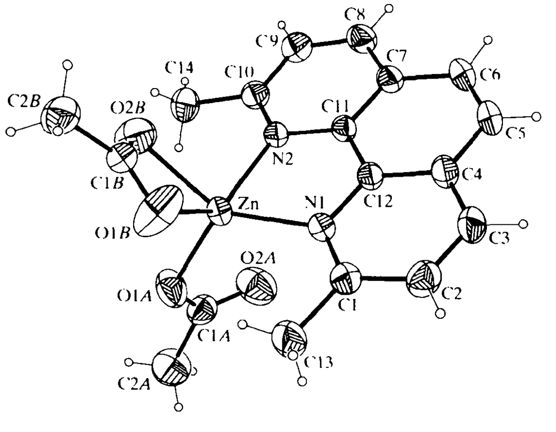


Fig. 1. The molecular diagram of (I) showing the numbering of atoms. Displacement ellipsoids are drawn at the 30% probability level.

A search in the Cambridge Structural Database (CSD; Allen & Kennard, 1993) showed that this is the first compound containing a Zn^{2+} ion complexed to acetate

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where the latter displays simultaneously these two different types of coordination to the same metallic unit in a pentacoordinated environment. The search also confirmed that the N_2O_3 pentacoordinated geometry with a bidentate carboxylate group is not very common in the chemistry of Zn^{II}. However, it can be found in biological systems, *e.g.* in the active site of Zn^{II} carboxypeptidase A (Hardman & Lipscomb, 1984), where the protein binds through two N atoms from His-69 and His-196, and the two carboxylate O atoms from Glu-72. The third O atom is provided by a water molecule. The ligand behaviour of the bidentate acetate group in the present structure [Zn—O1*B* 2.304 (4) and Zn—O2*B* 2.101 (3) Å] is similar to that of the γ-carboxylate group in the protein (Zn—O 2.30 and 2.19 Å), acting in both cases in an unsymmetrical chelate mode.

The Zn—O distances in bidentate carboxylates vary over a wide range, and values as different as 1.932 and 2.460 Å (Kremer-Aach *et al.*, 1997) have been reported where the ligand shows the greatest asymmetry in its bonding to the metal. On the other hand, although rather uncommon, the symmetrical mode of coordination has also been reported (Ishioka *et al.*, 1997). In the case of the monodentate acetate, the Zn—O distance is in the lower quartile of reported values for this type of bonding, which according to a CSD search are in the range 1.84–2.33 Å for 187 cases found. When this structure is compared with dinuclear $[Zn_2(MeCO_2)_3(bpy)_2]$ (Chen, Tong & Mak, 1994), the only other reported zinc acetate complex with a similar cation environment, it is found that the overall mean Zn—O distance is larger [2.108 (3) *versus* 2.039 (4) Å], probably due to the effect of the bidentate acetate which is not present in the latter. However, the bond valence sum (Brown & Altermatt, 1985) around zinc is maintained because of the shortening of the Zn—N distances [2.089 (3) *versus* 2.133 (5) Å].

The steric limitations imposed by the planar shape of the dmph ligands strongly influence the packing: these flat molecules lie parallel to (100) in four layers per cell in which the cations are embedded, and the two different acetate groups extend perpendicular to them along the '*a*' crystallographic axis, ending up with their free ends in the vicinity of the neighbouring upper/lower layers, thus helping the intra- and inter-layer stability through some rather weak C—H···O interactions [shortest: H9*B*···O2*A*($2-x$, $-y$, $1-z$) 2.46 (4) Å].

Experimental

The title compound was obtained by mixing a water solution of zinc acetate and a methanolic solution of 2,9-dimethyl-1,10-phenanthroline in stoichiometric quantities. After several weeks of slow evaporation, a crop of colorless crystals suitable for X-ray diffraction was obtained.

Crystal data

$[Zn(C_2H_3O_2)_2(C_{14}H_{12}N_2)]$
$M_r = 391.71$
Monoclinic
$C2/c$
$a = 14.618\ (3)$ Å
$b = 9.323\ (2)$ Å
$c = 25.766\ (5)$ Å
$\beta = 99.31\ (3)^\circ$
$V = 3465.2\ (12)$ Å^3
$Z = 8$
$D_x = 1.502$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5$–12.5°
$\mu = 1.442$ mm^{-1}
$T = 293\ (2)$ K
Needle
0.32 × 0.10 × 0.08 mm
Colourless

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Molecular Structure Corporation, 1988)
$T_{min} = 0.65$, $T_{max} = 0.90$
4315 measured reflections
3980 independent reflections

2375 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 27.49^\circ$
$h = -18 \rightarrow 18$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 33$
2 standard reflections every 98 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.121$
$S = 1.015$
3980 reflections
299 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 1.640P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.01$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Zn—O1*A*	1.919 (3)	C1*A*—O2*A*	1.240 (5)
Zn—N1	2.076 (2)	C1*A*—O1*A*	1.240 (4)
Zn—O2*B*	2.101 (3)	C1*B*—O2*B*	1.199 (4)
Zn—N2	2.102 (3)	C1*B*—O1*B*	1.201 (4)
Zn—O1*B*	2.304 (4)		
O2*A*—C1*A*—O1*A*	122.0 (4)	O2*B*—C1*B*—O1*B*	119.7 (4)

Non-H atoms were refined anisotropically on F^2. H atoms defined by the stereochemistry were located at their calculated positions, riding on their host atoms; the terminal methyl groups were found in the difference Fourier synthesis and refined with restrained C—H and H···H distances.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *MSC/AFC Diffractometer Control Software*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *PARST* (Nardelli, 1983) and CSD (Allen & Kennard, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1237). Services for accessing these data are described at the back of the journal.

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Diisopropylammonium oxalatotriphenylstannate

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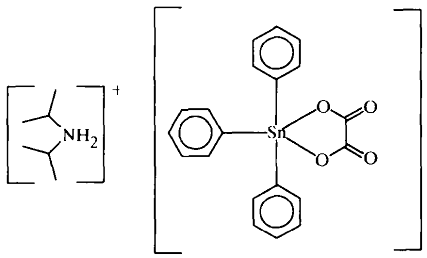
Abstract

The coordination polyhedron of the five-coordinate Sn atom in the title compound, diisopropylammonium (oxalato-O^1,O^2)triphenylstannate, $[NH_2(C_3H_7)_2][Sn(C_6H_5)_3(C_2O_4)]$, is a *cis*-$C_3SnO_2$ trigonal bipyramid [$Sn—O_{eq}$ = 2.115 (1) and $Sn—O_{ax}$ = 2.260 (1) Å] that is approximately 50% displaced towards the square pyramid along the Berry pseudo-rotation pathway. Two cations and two anions participate in a hydrogen-bonded cluster [N···O 2.808 (3)–3.044 (3) Å]

Comment

With few exceptions, five-coordinate triorganotin compounds adopt a trigonal-bipyramidal configuration at the Sn atom, and examples of the *trans*-C_3SnXY form vastly outnumber those of the *cis*-C_3SnXY form. The latter arrangement can be effected by the use of a bidentate monoanionic group; the use of a bidentate dianionic group introduces the additional influence of a counterion, whose effect on the structure of the onium triorganostannate may be difficult to predict *a priori*. The oxalato group chelates to the triphenyltin cation in the dicyclohexylammonium derivative (Ng & Kumar Das, 1995), but it merely links adjacent triphenyltin girdles in a linear chain in the trimethylsulfonium salt (Ng *et al.*, 1994). On the other hand, the ligand exhibits both binding abilities in the 1/1 complex of tetramethylammonium oxalatotriphenylstannate with bis(triphenyltin) oxalate (Ng & Kumar Das, 1993).



(I)

The geometry of the Sn atom in the title compound, (I), is a *cis*-trigonal bipyramid and bond dimensions involving the Sn atom are similar to those found in the bis(dicyclohexylammonium) salt, which crystallizes in a triclinic as well as in a monoclinic modification (Ng & Kumar Das, 1995). The geometry is displaced by 55% along the tbp–sq (trigonal bipyramid–square pyramid) Berry pseudo-rotation coordinate (Spek, 1990), which exceeds the average value of 30% found for the two independent ion pairs in the triclinic bis(dicyclohexylammonium) salt. The hydrogen-bonding interactions [N···O = 2.808 (3) and 2.864 (3) Å] are similar to those found in bis(diisopropylammonium) bis(mercaptoacetatotriphenylstannate) [2.753 (5) and 2.886 (5) Å], whose Sn atom is *O,S*-chelated by the anionic group (Ng *et al.*, 1996).

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