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Diacetonitrileheptakis[μ-3,5-bis(1,1-dimethylethyl)-2-hydroxybenzoato-κ^2O,O']trizinc(II)

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Key indicators

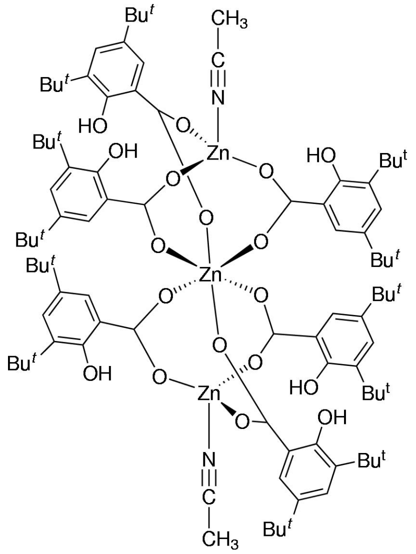
Single-crystal X-ray study
T = 93 K
Mean σ(C–C) = 0.011 Å
Disorder in main residue
R factor = 0.064
wR factor = 0.164
Data-to-parameter ratio = 18.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[Zn_3(C_{15}H_{21}O_3)_6(C_2H_3N)_2]$, has a center of symmetry and contains one six-coordinate Zn atom located at the center of the molecule and two four-coordinate Zn atoms at the periphery. Each 3,5-bis(1,1-dimethylethyl)-2-hydroxybenzoate anion serves as a bridging ligand between the central and peripheral Zn atoms. An acetonitrile molecule is coordinated to each peripheral Zn atom.

Comment

1:2 Zn complexes or zinc salts of 3,5-bis(1,1-dimethylethyl)-2-hydroxybenzoate (SZC) are powerful charge-control agents used widely for toners in electrophotography (Suganami *et al.*, 2002). However, it has often been pointed out that the charge-control ability depends greatly on the process of toner preparation. Thus, we assumed that structural changes of the metal complex or molecular rearrangement might occur during the toner preparation process. For this reason, we have carried out the structure analysis of SZC on single crystals grown from mild solvents such as ethanol, as well as from polar ones such as dimethyl sulfoxide (DMSO) and acetonitrile.



(I)

The single crystals grown from ethanol are found to contain a deformed octahedral complex, in which two 3,5-bis(1,1-dimethylethyl)-2-hydroxybenzoate anions (TBS$^-$) are coordinated to the Zn atom as bidentate ligands, while two ethanol O atoms are bonded to the Zn atom in a *cis* fashion (Mizuguchi, 2003). On the other hand, the single crystals grown from a DMSO solution contain a deformed tetrahedral Zn complex consisting of two TBS$^-$ and two DMSO molecules. However,

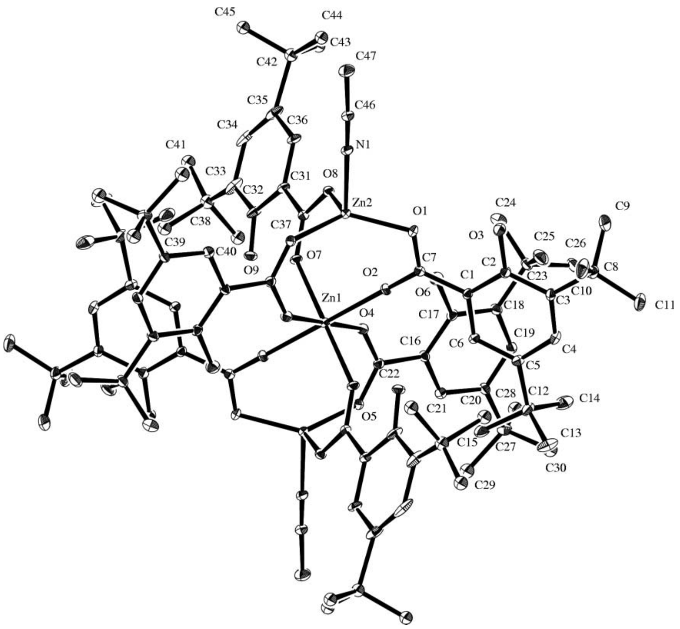


Figure 1

A view of the molecular structure of (I), showing 10% probability displacement ellipsoids. The unlabeled atoms are related to labeled atoms by $(1 - x, -y, 1 - z)$. The site occupancy of atoms O9 and C38–C45 is 62%, while that for atoms C28–C30 is 75%. H atoms and minor sites have been omitted for clarity.

TBS^- functions here as a monodentate ligand (Makino & Mizuguchi, 2005). In both ethanol and DMSO-solvated SZCs, the basic structure of SZC {*i.e.* $[Zn(TBS)_2]$} is still retained. Conversely, when SZC was recrystallized from acetonitrile, a completely different complex, *viz.* the title compound, (I), was formed. The present paper deals with the structure of (I).

Fig.1 shows an *ORTEPIII* (Burnett & Johnson, 1996) plot of (I), which has an inversion center at the Zn1 atom. The present complex contains one six-coordinate Zn complex located at the center of the molecule and two four-coordinate Zn complexes above and below the central six-coordinate complex. The skeleton of SZC is no longer recognized in the present complex. It is remarkable that all TBS^- ions act as bidentate ligands, and bridge between Zn1 and Zn2 (or $Zn2^i$) atoms [symmetry code: (i) $1 - x, -y, 1 - z$]. The acetonitrile molecule is coordinated to atom Zn2. The geometry of one of the carboxylate bridges, Zn1—O2—C7—O1—Zn2, is asymmetric and quite different from those of the other two; the Zn1—O2—C7 and Zn2—O1—C7 bond angles are 169.5 (5) and 105.0 (3)°, respectively, whereas the Zn—O—C bond angles in the other bridges are 124.9 (4)–142.2 (4)° (Table 1).

There are intramolecular O—H···O hydrogen bonds (Table 2) in the TBS^- ligands. The Zn1—O distances [2.040 (4)–2.111 (5) Å] are slightly longer than the Zn2—O distances [1.924 (4)–1.971 (4) Å]. Furthermore, it is also to be noted that TBS^- functions here as a bidentate ligand, but each O atom is coordinated to a different Zn atom, *i.e.* the ligand acts as a bridge between two Zn atoms. However, in ethanol-solvated SZC, TBS^- acts as a bidentate ligand chelating to a single Zn atom (Mizuguchi, 2003), while it acts as a monodentate ligand in DMSO-solvated SZC (Makino & Mizuguchi, 2005). These results indicate that the coordinating function of SZC is quite sensitive to solvents used in the recrystallization. In other words, the charge-control ability of SZC can change as a result of structural changes, depending on the solvent used in the toner preparation process.

Experimental

SZC was obtained from Orient Chemical Industries Ltd. Single crystals of (I) were grown from an acetonitrile solution by slow solvent evaporation.

Crystal data

$[Zn_3(C_{15}H_{21}O_3)_6(C_2H_3N)_2]$
$M_r = 1774.19$
Monoclinic, $P2_1/c$
$a = 17.518$ (3) Å
$b = 16.667$ (3) Å
$c = 18.414$ (3) Å
$\beta = 113.25$ (1)°
$V = 4939.8$ (15) Å^3
$Z = 2$
$D_x = 1.193$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 29 412 reflections
$\theta = 3.0$–68.3°
$\mu = 1.35$ mm^{-1}
$T = 93.2$ K
Block, colorless
0.20 × 0.15 × 0.15 mm

Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer
ω scans
Absorption correction: multi-scan (Higashi, 1995)
$T_{min} = 0.788$, $T_{max} = 0.817$
39 583 measured reflections
8775 independent reflections
3745 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.083$
$\theta_{max} = 68.3°$
$h = -21 \rightarrow 21$
$k = -20 \rightarrow 20$
$l = -22 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.164$
$S = 1.03$
8775 reflections
471 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + \{0.05[\mathrm{Max}(F_o^2,0) + 2F_c^2]/3\}^2]$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.73$ e Å^{-3}
$\Delta\rho_{min} = -0.99$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Zn1—O2	2.080 (3)	Zn2—O5^i	1.924 (4)
Zn1—O4	2.040 (4)	Zn2—O8	1.935 (4)
Zn1—O7	2.111 (5)	Zn2—N1	2.074 (6)
Zn2—O1	1.971 (4)		
O2—Zn1—O4	85.1 (2)	O8—Zn2—N1	101.8 (2)
O2—Zn1—O7	94.4 (2)	Zn2—O1—C7	105.0 (3)
O4—Zn1—O7	85.5 (2)	Zn1—O2—C7	169.5 (5)
O1—Zn2—O5^i	125.5 (2)	Zn1—O4—C22	135.5 (4)
O1—Zn2—O8	118.3 (2)	Zn2^i—O5—C22	131.5 (4)
O1—Zn2—N1	95.9 (2)	Zn1—O7—C37	142.2 (4)
O5^i—Zn2—O8	110.4 (2)	Zn2—O8—C37	124.9 (4)
O5^i—Zn2—N1	96.5 (2)		

Symmetry code: (i) $-x + 1, -y, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O9—H9*O*···O7	0.95	1.82	2.56 (1)	132
O9'—H9'*O*···O8	0.95	1.81	2.55 (1)	133
O3—H3*O*···O1	0.95	1.79	2.52 (1)	131
O6—H6*O*···O4	0.95	1.81	2.52 (1)	130

The O9 hydroxy group shows positional disorder, and its minor component is bonded to atom C36, indicating two possible orientations of the ligand. The *tert*-butyl groups of this ligand show positional disorder, and the major sites of the *tert*-butyl groups (C38–C41 and C42–C45) and their minor ones were treated as rigid groups. The occupancy factors of atoms O9 and C38–C45 were assumed to be the same, and these 12 atoms were refined isotropically. Atoms C31–C36 in the benzene ring were not split into two sites as an approximation; this caused unreliable distances for C36—O9′ and C33—C38′. The site-occupancy factor of O9 was first estimated in such a way as to equalize the $U_{\rm iso}$ parameters for the major (O9) and minor (O9′) sites. The resulting occupancy was then applied to the C atoms in the *tert*-butyl groups, followed by further refinement, balancing, as much as possible, the $U_{\rm iso}$ values of the disordered O and C atoms, the occupancy of the major sites being 0.62 (1). There is also a rotational disorder of another *tert*-butyl group (C28–C30). Similarly, the site occupancy factor was determined in a manner to equalize the $U_{\rm iso}$ parameters for the major (C28–C30) and minor (C28′–C30′) sites, the occupancy of the major sites being 0.75 (1).

The H atoms of the hydroxy groups (O3, O6 and O9) could not be found in difference density maps. Therefore, these atoms were positioned by calculation, assuming sp^2 hybridization of the O atoms and an intramolecular O—H···O hydrogen bond in the ligand. All remaining H atoms were positioned geometrically and included in a riding-model approximation, with C–H = 0.95 Å and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). A *PLATON* (Spek, 2003) check revealed that the crystal structure contains solvent-accessible voids of 39 Å^3. We think that a solvent molecule such as H_2O may not be accommodated, since the maximum difference-density (1.7 e Å^{-3}) is located at Zn2, whereas the second highest peak is positioned at Zn1, all the rest being under 1 e Å^{-3}.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *TEXSAN*.

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