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Key indicators

Single-crystal X-ray study
 $T = 93\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.018\text{ \AA}$
Disorder in main residue
 R factor = 0.058
 wR factor = 0.170
Data-to-parameter ratio = 15.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bis[3,5-di-*tert*-butyl-2-hydroxybenzoato- κO]-
bis(dimethyl sulfoxide- κO)zinc(II)

The title compound, $[\text{Zn}(\text{C}_{15}\text{H}_{21}\text{O}_3)_2(\text{C}_2\text{H}_6\text{OS})_2]$, is a powerful charge-control agent used widely for toners in electrophotography. This Zn^{II} complex has no molecular symmetry and possesses a deformed tetrahedral coordination geometry. Two 3,5-di-*tert*-butyl-2-hydroxybenzoate ligands serve as monodentate ligands, while two dimethyl sulfoxide molecules are coordinated to the Zn atom.

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Comment

The title compound, (I), is a 1:2 complex of the zinc salt, *i.e.* the 3,5-di-*tert*-butylsalicylate zinc complex, SZC, solvated with two molecules of dimethyl sulfoxide (DMSO). SZC is a powerful charge-control agent 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 DMSO. A single crystal grown from ethanol was found to form 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). The present paper deals with the structure of a single crystal grown from DMSO.

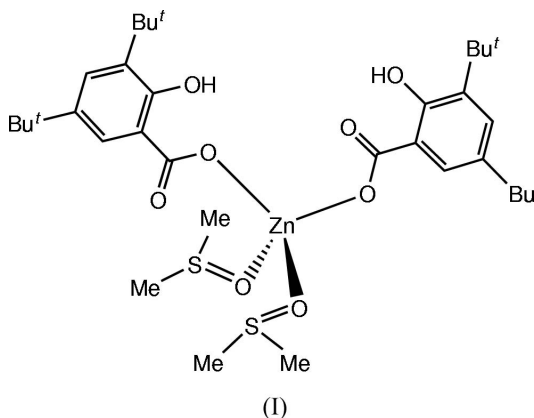


Fig. 1 shows the *ORTEP* plot of compound (I), which has C_1 symmetry, as characterized by a deformed tetrahedral structure. Two TBS^- anions serve as monodentate ligands, forming an inner salt complex, while two DMSO molecules are coordinated to the Zn atom.

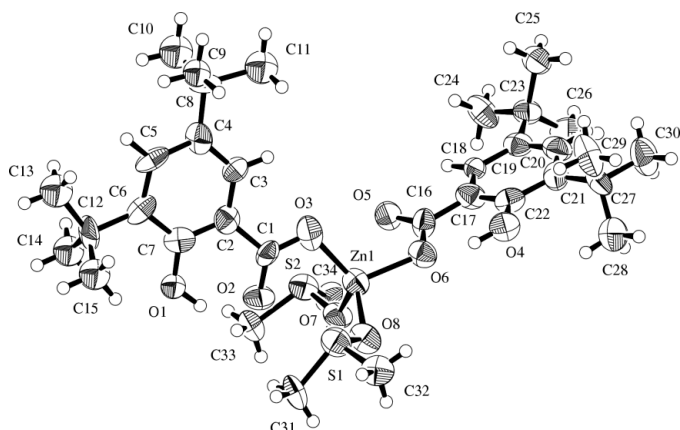


Figure 1
A view of the molecular structure of (I), showing 50% displacement ellipsoids. The site occupancy of atoms O1/C9/C10/C11/C13/C14/C15 is 65%. The minor sites have been omitted for clarity.

There are intramolecular O—H...O hydrogen bonds (Table 2) in the TBS[−] ligands. The molecular planes of the two TBS[−] ligands are almost perpendicular to each other. The Zn—O distances between the central Zn atom and the O atom of TBS[−] are slightly different, at 1.962 (8) Å for Zn1—O3 and 1.984 (7) Å for Zn1—O6. The unbonded distances for Zn1...O2 and Zn1...O5 are 2.743 (7) and 2.668 (7) Å, respectively. Furthermore, it is to be noted that TBS[−] functions here as a monodentate ligand in DMSO-solvated SZC, but as a bidentate ligand in ethanol-solvated SZC (Mizuguchi, 2003). This indicates that the structure of SZC is quite sensitive to the solvent used. In other words, the charge-control ability of SZC can change due to 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 a DMSO solution. Since the crystals were found to include solvent molecules, data collection was carried out at 93 K in order to suppress solvent evaporation.

Crystal data

$[\text{Zn}(\text{C}_{15}\text{H}_{21}\text{O}_3)_2(\text{C}_2\text{H}_6\text{OS})_2]$	$D_x = 1.245 \text{ Mg m}^{-3}$
$M_r = 718.29$	Cu $K\alpha$ radiation
Monoclinic, $P2_1/a$	Cell parameters from 11 185 reflections
$a = 16.688 (4) \text{ \AA}$	$\theta = 3.0\text{--}67.9^\circ$
$b = 12.946 (3) \text{ \AA}$	$\mu = 2.27 \text{ mm}^{-1}$
$c = 19.178 (4) \text{ \AA}$	$T = 93.2 \text{ K}$
$\beta = 111.97 (2)^\circ$	Platelet, colourless
$V = 3842.4 (16) \text{ \AA}^3$	$0.10 \times 0.08 \times 0.02 \text{ mm}$
$Z = 4$	

Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer	6152 independent reflections
ω scans	944 reflections with $F^2 > 2\sigma(F^2)$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$R_{\text{int}} = 0.175$
$T_{\text{min}} = 0.743$, $T_{\text{max}} = 0.956$	$\theta_{\text{max}} = 68.2^\circ$
24 925 measured reflections	$h = -17 \rightarrow 17$
	$k = -15 \rightarrow 15$
	$l = -23 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.058$
 $wR(F^2) = 0.170$
 $S = 0.47$
 6152 reflections
 399 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + 2F_c^2/3]^2$
 $(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.62 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.40 \text{ e \AA}^{-3}$
 Extinction correction: none

Table 1

Selected geometric parameters (Å, °).

Zn1—O3	1.962 (8)	O2—C1	1.26 (1)
Zn1—O6	1.984 (7)	O3—C1	1.29 (1)
Zn1—O7	1.981 (6)	O4—C22	1.37 (1)
Zn1—O8	1.997 (6)	O5—C16	1.22 (1)
O1—C7	1.32 (1)	O6—C16	1.31 (1)
O3—Zn1—O6	109.4 (3)	O6—Zn1—O8	100.8 (3)
O3—Zn1—O7	116.5 (3)	O7—Zn1—O8	101.6 (3)
O3—Zn1—O8	113.7 (3)	Zn1—O3—C1	108.6 (7)
O6—Zn1—O7	113.7 (3)	Zn1—O6—C16	106.2 (7)

Table 2

Hydrogen-bond geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O1—H1O...O2	0.95	1.66	2.45 (1)	138
O1A—H1O'...O3	0.95	1.62	2.41 (1)	140
O4—H4O...O6	0.95	1.79	2.52 (1)	131

Atom O1, as well as atoms C9/C10/C11 and C13/C14/C15 in the *tert*-butyl groups, are disordered. On the basis of the non-disordered arrangement of the *tert*-butyl groups in one of the TBS[−] ligands, we assumed that the disorder in O1 and that in C9/C10/C11 and C13/C14/C15 occur with the same occupancy. For this reason, the site-occupancy factor of O1 was first estimated in such a way as to equalize the U_{iso} parameters for the major (O1) and minor (O1A) 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_{iso} values of the disordered O and C atoms. The occupancy of the major sites is 65%. The H atoms bonded to atoms O1 and O4 could not be found in difference density maps. Therefore, these H atoms were positioned by calculation, assuming the sp^2 hybrid structure of the O atom 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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

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: *ORTEP III* (Burnett & Johnson, 1996); software used to prepare material for publication: *TEXSAN*.

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