

Takashi Makino and Jin Mizuguchi*

Department of Applied Physics, Graduate School of Engineering, Yokohama National University, Tokiwadai 79-5, Hodogaya-ku, Yokohama 240-850, Japan

Correspondence e-mail: mizu-j@ynu.ac.jp

Key indicators

Single-crystal X-ray study
T = 93 K
Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
H-atom completeness 96%
Disorder in solvent or counterion
R factor = 0.054
wR factor = 0.149
Data-to-parameter ratio = 11.8

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

Diaquabis(3,5-di-*tert*-butyl-2-hydroxybenzoato- κO^1)-zinc(II) dimethylacetamide trisolvate

In the title compound, $[\text{Zn}(\text{C}_{15}\text{H}_{21}\text{O}_3)_2(\text{H}_2\text{O})_2] \cdot 3\text{C}_4\text{H}_9\text{NO}$, there are two independent Zn^{II} complexes each having mirror symmetry. To each Zn atom, two 3,5-di-*tert*-butyl-2-hydroxybenzoate ligands serve as monodentate ligands, and two water molecules are additionally coordinated to form a tetrahedral geometry.

Received 19 August 2005
Accepted 14 September 2005
Online 8 October 2005

Comment

3,5-Di-*tert*-butylsalicylate zinc complex (SZC) is a powerful charge-control agent used widely for toners in electro-photography (Suganami *et al.*, 2002). However, there is one critical issue in SZC in regard to the reproducibility of the performance when embedded in toners using polymer vehicles and solvents. We assumed that the poor reproducibility might arise from the structural changes of the metal complex or molecular rearrangement during the toner preparation. In this connection, we initiated a series of investigations on the structure of SZC crystals grown from various solvents. A variety of structures have been obtained, depending on the solvents used, which include weakly polar solvents, such as ethanol (Mizuguchi, 2003), and polar ones, such as dimethylsulfoxide (DMSO) (Makino & Mizuguchi, 2005a) and acetonitrile (Mizuguchi & Makino, 2005). The main difference is in the ligand configuration; 3,5-bis(1,1-dimethylethyl)-2-hydroxybenzoate anions (TBS^-) are coordinated to Zn atoms as monodentate or bidentate ligands. The present paper deals with the structure of a four-coordinate complex, $[\text{Zn}(\text{TBS})_2(\text{H}_2\text{O})_2] \cdot 3\text{DMA}$, (I), which was obtained from a dimethylacetamide (DMA) solution. The paper which follows this publication (Makino & Mizuguchi, 2005b) will describe the structure of a five-coordinate complex, $[\text{Zn}(\text{TBS})_2(\text{H}_2\text{O})_3] \cdot 3\text{DMA}$, which was obtained from a DMA solution with water (10% in volume).

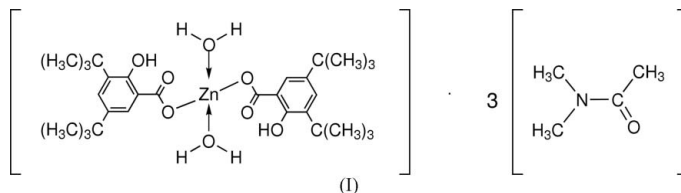


Fig. 1 shows an *ORTEP* plot (Burnett & Johnson, 1996) of the Zn complexes in (I). There are two independent half-complexes (A and B) in the asymmetric unit, and the Zn and aqua O atoms lie on a mirror plane. There are also two molecules and two half-molecules of DMA in the asymmetric unit (Fig. 2), the half-molecules being completed also by mirror symmetry. Two TBS^- ligands are coordinated to each Zn atom

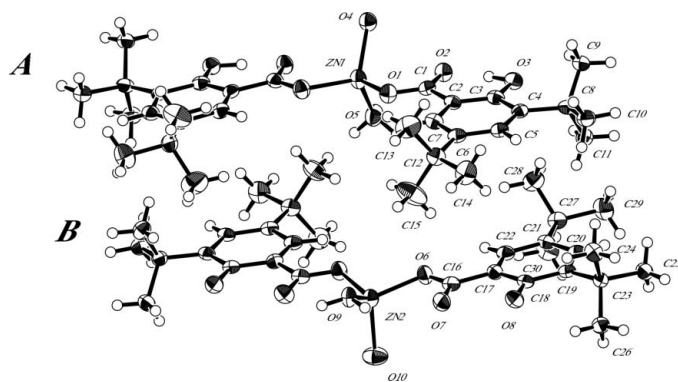


Figure 1

A view of the Zn complexes in (I), showing 50% probability displacement ellipsoids. The unlabeled atoms are related to the labeled ones by the symmetry code $(-x, y, z)$. The H atoms bonded to atoms O4, O8 and O10 were not included in the refinement.

as monodentate ligands. In addition, unexpectedly, two water molecules are bonded to the Zn atom, forming a four-coordinate complex. The Zn–O_{TBS} and Zn–O_{water} bond distances are 1.947 (3)–1.950 (3) Å and 1.961 (5)–1.986 (5) Å, respectively (Table 1). There are O–H···O intramolecular hydrogen bonds in the TBS[−] ligands (O3–H3O···O2) and also intermolecular hydrogen bonds between the OH group of the water molecule and the O atom of the solvent DMA molecule: O5–H5O···O12 and O9–H9O···O13 (Table 2). The other short O···O distances suggest additional hydrogen bonds, although the H atoms under consideration could not be located in difference density maps [O8···O7 = 2.501 (4) Å; O4···O13($x, y + 1, z$) = 2.703 (4) Å; O10···O11($x, 1 - y, z - \frac{1}{2}$) = 2.611 (7) Å; O10···O14 = 2.585 (8) Å]. Fig. 3 shows a packing diagram. There are two kinds of stacking columns along the *b* axis, composed of complexes A and B separately. Between these columns, there is another column comprising alternating DMA molecules. The O atoms of these DMA molecules are hydrogen bonded to water molecules of the Zn complex.

The present four-coordinate complex has the same coordination number as the DMSO-solvated complex composed of two TBS[−] and containing two DMSO molecules (Makino & Mizuguchi, 2005*a*). In both complexes, TBS[−] behaves in a monodentate fashion. However, in the former complex, two DMSO molecules serve as the ligands. Instead, two water molecules are the ligands in (I), while the DMA solvent molecules remain uncoordinated. In general, commercial DMA contains less than 0.1% water, and thus these water molecules presumably coordinated to the Zn atom in the recrystallization. This suggests that SZC is quite susceptible to water and thus accommodates it as a ligand. Therefore, the charge-control ability of SZC is assumed to change in various ways, depending not only on the type of solvent but also on the extent of hydration.

Experimental

Zn(TBS)₂, obtained from Orient Chemical Industries Ltd. DMA, was first degassed under Ar for 30 min. Zn(TBS)₂ (0.5 g) was dissolved in

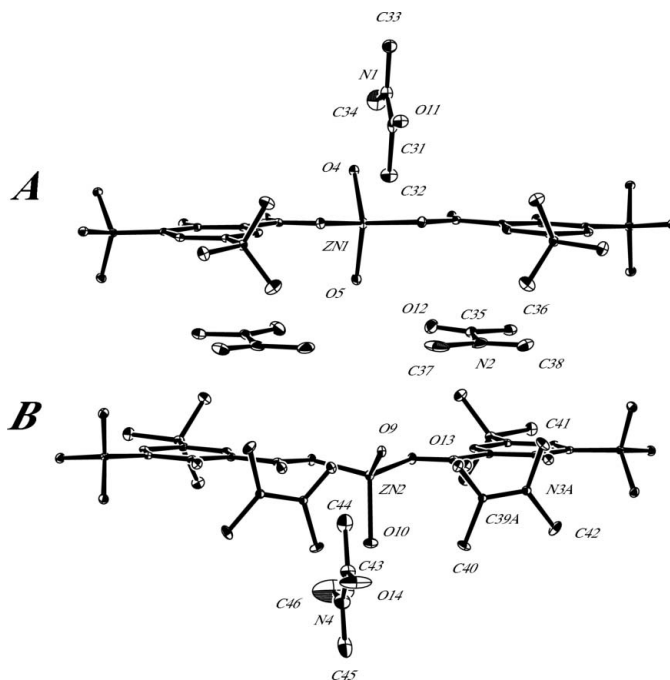


Figure 2

A view of the molecular conformation of (I), focusing on the DMA molecules, with 20% probability displacement ellipsoids. H atoms and the minor atom sites (C39*B* and N3*B*) of the disordered DMA molecule have been omitted for clarity.

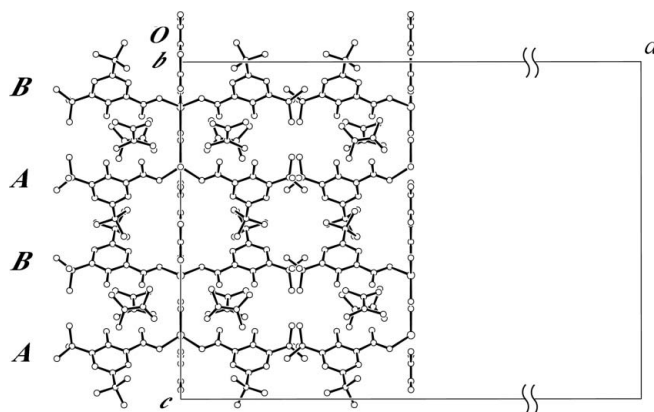


Figure 3

Packing diagram viewed down the *b* axis ($-\frac{1}{4} < x < \frac{1}{2}$). There are mirror planes perpendicular to the *a* axis.

DMA (5 ml) at about 373 K. Single crystals of (I) were grown by gradual cooling of this solution.

Crystal data

[Zn(C₁₅H₂₁O₃)₂(H₂O)₂]₂·3C₄H₉NO
M_r = 861.43
 Orthorhombic, *Cmc*2₁
a = 32.673 (4) Å
b = 11.7393 (16) Å
c = 23.932 (3) Å
V = 9179 (2) Å³
Z = 8
D_x = 1.247 Mg m^{−3}

Cu Kα radiation
 Cell parameters from 25809 reflections
 θ = 3.0–68.3°
 μ = 1.22 mm^{−1}
T = 93.1 K
 Platelet, colorless
 0.40 × 0.30 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID
diffractometer
48 frames, $\Delta = 15^\circ \varphi$ scans
Absorption correction: multi-scan
(*ABSCOR*; Higashi, 1995)
 $T_{\min} = 0.689$, $T_{\max} = 0.884$
41349 measured reflections

8355 independent reflections
6593 reflections with $F^2 > 2\sigma(F^2)$
 $R_{\text{int}} = 0.051$
 $\theta_{\text{max}} = 68.3^\circ$
 $h = -39 \rightarrow 38$
 $k = -13 \rightarrow 13$
 $l = -28 \rightarrow 28$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.149$
 $S = 0.96$
8355 reflections
557 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.90 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.46 \text{ e } \text{\AA}^{-3}$
Absolute structure: (Flack, 1983),
3955 Friedel pairs
Flack parameter: 0.19 (3)

Table 1
Selected geometric parameters (\AA , $^\circ$).

Zn1—O1	1.950 (3)	O1—C1	1.279 (5)
Zn1—O4	1.977 (4)	O2—C1	1.246 (5)
Zn1—O5	1.961 (5)	O3—C3	1.346 (5)
Zn2—O6	1.947 (3)	O6—C16	1.267 (5)
Zn2—O9	1.973 (5)	O7—C16	1.250 (5)
Zn2—O10	1.986 (5)	O8—C18	1.341 (5)
O1—Zn1—O1 ⁱ	101.47 (13)	O6—Zn2—O9	117.97 (11)
O1—Zn1—O4	112.96 (11)	O6—Zn2—O10	104.46 (12)
O1—Zn1—O5	110.88 (13)	O9—Zn2—O10	109.78 (18)
O4—Zn1—O5	107.7 (2)	Zn1—O1—C1	113.9 (2)
O6—Zn2—O6 ⁱ	100.57 (12)	Zn2—O6—C16	114.1 (2)

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

Table 2
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3O \cdots O2	0.98	1.55	2.507 (4)	163
O5—H5O \cdots O12	0.96	1.79	2.717 (5)	161
O9—H9O \cdots O13	0.93	1.82	2.725 (4)	165

One of the solvent DMA molecules shows orientational disorder. The occupation factors of N3A/C39A and N3B/C39B are 60 and 40%, respectively, estimated on the basis on the atomic displacement parameters. These four atoms were refined isotropically. The positions of the four outer atoms (O13, C40, C41 and C42) are shared by the two orientations, connected as O13—C39A(—C40)—N3A(—C41)—C42 and O13—C39B(—C41)—N3B(—C40)—C42. The H atoms bonded to O3, O5 and O9 were found in difference density maps and fixed during the refinement [$U_{\text{iso}}(\text{H}) = 0.062 \text{ \AA}^2$]. However, the H atoms bonded to O4, O8 and O10 could not be located and were therefore omitted. The H atoms bound to C atoms were positioned geometrically and included in a riding-model approximation, with C—H = 0.95–0.96 \AA , 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: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *CrystalStructure* (Rigaku/MSC, 2004).

References

Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Makino, T. & Mizuguchi, J. (2005a). *Acta Cryst.* **E61**, m679–m681.
Makino, T. & Mizuguchi, J. (2005b). *Acta Cryst.* **E61**, m2223–m2225.
Mizuguchi, J. (2003). *Acta Cryst.* **E59**, m955–m956.
Mizuguchi, J. & Makino, T. (2005). *Acta Cryst.* **E61**, m953–m955.
Molecular Structure Corporation (2001). *TEXSAN*. Version 1.11. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2004). *CrystalStructure*. Version 3.6.0. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Suganami, K., Takeuchi, M. & Oguchi, T. (2002). IS&T NIP18 International Conference on Digital Printing Technologies, pp. 302–305. The Society for Imaging Science and Technology.