

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

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Key indicators

Single-crystal X-ray study
 $T = 93\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.010\text{ \AA}$
H-atom completeness 90%
Disorder in main residue
 R factor = 0.095
 wR factor = 0.273
Data-to-parameter ratio = 13.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $[\text{Zn}(\text{C}_{15}\text{H}_{21}\text{O}_3)_2(\text{H}_2\text{O})_3] \cdot 3\text{C}_4\text{H}_9\text{NO}$, the Zn^{II} complex has mirror symmetry. Two 3,5-di-*tert*-butyl-2-hydroxybenzoate ligands serve as monodentate ligands, and three water molecules are additionally coordinated to the Zn atom, forming a trigonal-bipyramidal geometry.

Comment

The 3,5-di-*tert*-butylsalicylate-zinc complex (SZC) is a powerful charge-control agent used widely for toners in electrophotography (Suganami *et al.*, 2002). The background of the present study has been set out in our previous paper (Makino & Mizuguchi, 2005), which reports that the compound in the crystal grown from a DMA solution was $[\text{Zn}(\text{TBS})_2(\text{H}_2\text{O})_2] \cdot 3\text{DMA}$ (TBS[−] is the 3,5-di-*tert*-butyl-2-hydroxybenzoate anion and DMA is dimethylacetamide). A minute amount of water included in commercial DMA was found to be responsible for the accommodation of water molecules in the structure. This suggests that SZC is quite sensitive to water and thus can include it as a ligand. This prompted us to study the influence of water on the coordination number of the Zn complex. An attempt was made in the present investigation to grow crystals in a water-containing DMA solution (10% in volume). In fact, the title compound, $[\text{Zn}(\text{TBS})_2(\text{H}_2\text{O})_3] \cdot 3\text{DMA}$, (I), was obtained.

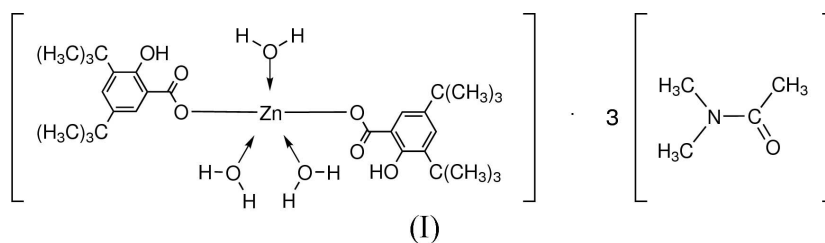


Fig. 1 shows the *ORTEP* plot (Burnett & Johnson, 1996) of (I). There is a mirror plane passing through the atoms Zn1, O8 and all the atoms of the two TBS ligands except for the *tert*-butyl groups. There are three half-molecules of DMA in the asymmetric unit; two of the DMA molecules lie on the mirror plane and the other is disordered across the mirror. Two TBS[−] anions are coordinated to the Zn atom as monodentate ligands. In addition, three water molecules are bonded to the Zn atom, forming a trigonal-bipyramidal geometry. The Zn—O(TBS) and Zn—O(water) bond distances are 2.025 (4)–2.131 (4) and 1.984 (4)–2.053 (5) Å, respectively (Table 1).

Although the hydroxyl H atoms of the TBS[−] ligands were not found in difference density maps, the O—H...O intramolecular hydrogen bonds are assumed to exist as judged

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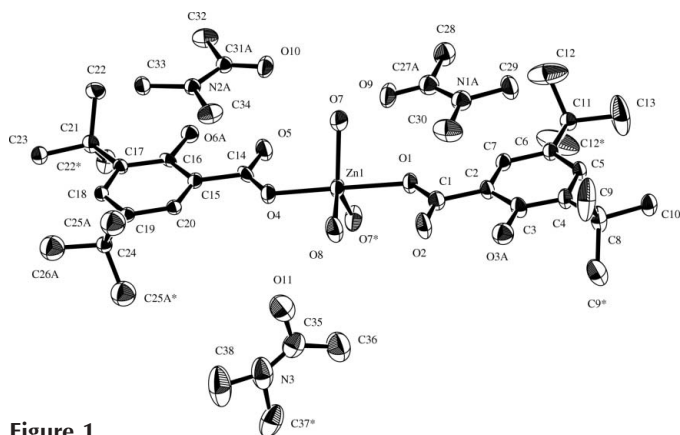


Figure 1
A view of the molecular structure of (I), showing 30% displacement ellipsoids. All H atoms as well as the minor groups of the disordered *tert*-butyl groups and DMA molecules have been omitted for clarity.

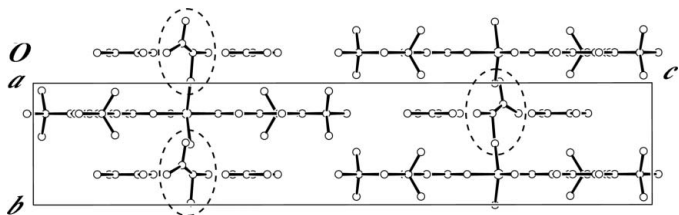


Figure 2
Packing, viewed down the *a* axis. There are mirror planes perpendicular to the *b* axis and the dotted circles surround the DMA molecules which are disordered across the mirror plane.

from the short atomic contacts: O2···O3A (occupancy 67%) = 2.45 (1) Å; O1···O3B (33%) = 2.44 (2) Å; O5···O6A (90%) = 2.46 (1) Å; O4···O6B (10%) = 2.41 (5) Å. Between water ligands and DMA molecules, there exist also O—H···O intermolecular hydrogen bonds in view of the short atomic contacts: O7···O9 = 2.754 (5) Å; O7···O10 = 2.675 (5) Å; O8···O11 = 2.740 (15) Å; O8···O11(*x*, $\frac{1}{2} - y$, *z*) = 2.740 (15) Å; O9···O7 = 2.754 (5) Å; O9···O7(*x*, $-\frac{1}{2} - y$, *z*) = 2.754 (5) Å; O10···O7 = 2.675 (5) Å; O10···O7(*x*, $-\frac{1}{2} - y$, *z*) = 2.675 (5) Å; O11···O8 = 2.740 (15) Å. Fig. 2 shows the packing viewed down the *a* axis. There are two kinds of stacking columns along the *a* axis, each of which is composed of the Zn complexes alone or DMA. Among three subcolumns of DMA molecules, the column of rather horizontally arranged DMAs (denoted by a dotted circle) is sandwiched between two columns of vertically arranged DMA molecules. Furthermore, the five-coordinate complex and two uncircled DMA molecules lie on the same plane.

Compared with the four-coordinate complex, [Zn(TBS)₂(H₂O)₂], obtained from a DMA solution (Makino & Mizuguchi, 2005), the coordination number of the Zn complex in (I) increased to five (the number of the aqua ligands increased to three) due to the addition of 10% water into the DMA solution. This result indicates that the Zn(TBS)₂ complex has a tendency to accommodate water molecules as a ligand. In other words, SZC is of highly hygroscopic nature. These facts lead us to conclude that the charge-control ability of SZC is considered to change in

various ways, depending on the choice of solvents as well as on the extent of hydration.

Experimental

Zn(TBS)₂ was obtained from Orient Chemical Industries Ltd. Zn(TBS)₂ (0.5 g) was dissolved in a DMA solution (5 ml) in the presence of 10% water by volume at about 373 K. Single crystals of (I) were grown by gradual cooling of this solution.

Crystal data

[Zn(C₁₅H₂₁O₃)₂(H₂O)₃]·3C₄H₉NO
M_r = 879.45
 Monoclinic, *P*2₁/*m*
a = 9.7191 (14) Å
b = 6.9405 (8) Å
c = 35.456 (4) Å
 β = 94.635 (11)°
V = 2383.9 (5) Å³
Z = 2

D_x = 1.225 Mg m⁻³
 Cu K α radiation
 Cell parameters from 16824 reflections
 θ = 3.8–68.3°
 μ = 1.20 mm⁻¹
T = 93.1 K
 Platelet, colorless
 0.40 × 0.20 × 0.05 mm

Data collection

Rigaku R-Axis RAPID diffractometer
 48 frames, Δ = 15° φ scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
T_{min} = 0.680, *T_{max}* = 0.942
 21526 measured reflections

4524 independent reflections
 2687 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.063
 θ_{\max} = 68.2°
h = -10 → 10
k = -8 → 8
l = -42 → 42

Refinement

Refinement on F^2
R [$F^2 > 2\sigma(F^2)$] = 0.095
wR (F^2) = 0.273
S = 1.00
 4524 reflections
 336 parameters

H-atom parameters not refined
 $w = 1/[\sigma^2(F_o^2) + (0.1785P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.71 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.60 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Zn1—O1	2.131 (4)	O1—C1	1.269 (8)
Zn1—O4	2.025 (4)	O2—C1	1.254 (10)
Zn1—O7	1.984 (4)	O4—C14	1.282 (8)
Zn1—O8	2.053 (5)	O5—C14	1.243 (10)
O1—Zn1—O4	178.8 (2)	O7—Zn1—O7 ⁱ	124.30 (19)
O1—Zn1—O7	83.76 (12)	O7—Zn1—O8	117.00 (12)
O1—Zn1—O8	89.8 (2)	Zn1—O1—C1	130.3 (5)
O4—Zn1—O7	96.77 (12)	Zn1—O4—C14	122.4 (5)
O4—Zn1—O8	89.0 (2)		

Symmetry code: (i) *x*, $-y + \frac{1}{2}$, *z*.

Several atoms were found to be disordered over two sites. The occupancies were determined in such a way as to balance the atomic displacement parameters of each disordered pair. Two hydroxyl O atoms are disordered: O3A/O3B (occupancy: 0.67/0.33), which are bonded to C3 and C7, respectively, and O6A/O6B (occupancy: 0.90/0.10), which are bonded to C16 and C20, respectively. One of four *tert*-butyl groups is disordered: C25A/C26A and C25B/C26B. The former major group gave an occupancy of 0.70. These disordered atoms (O3A/O3B, O6A/O6B, C25A/C26A and C25B/C26B) were refined isotropically. The independent three half-molecules of DMA in the asymmetric unit show orientational disorder. For the two DMA molecules on the mirror plane, the occupation factors of N1A/C27A and N1B/C27B are 0.72 and 0.28, respectively, and those of N2A/C31A and N2B/C31B are 0.69 and 0.31, respectively. The positions of the four outer atoms (O9/C28/C29/C30 and O10/C32/C33/

C34) are shared by the two orientations, connected such as O9—C27A(—C28)—N1A(—C29)—C30 and O9—C27B(—C30)—N1B(—C28)—C29. For the third DMA molecule, only atoms N3/C36/C38 lie on the mirror plane, showing two possible orientations: O11—C35(—C36)—N3(—C37ⁱⁱ)—C38 [symmetry code: (ii) $x, \frac{3}{2} - y, z$] and O11ⁱⁱ—C35ⁱⁱ(—C36)—N3(—C37)—C38.

Six H atoms of the water molecules and two H atoms of the hydroxyl group were not found in difference density maps and were therefore omitted. The methyl H atoms of the DMA molecules were positioned geometrically, with C—H = 0.95 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. All remaining methyl H atoms were positioned geometrically and included in a riding-model approximation, with C—H = 0.98 Å and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. The highest residual density peak is located 0.93 Å from Zn1.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/

MSC, 2004); program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *CrystalStructure*.

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