Crystal Structure of Solvated Zinc Complexes Based on Salicylic Acid Derivatives

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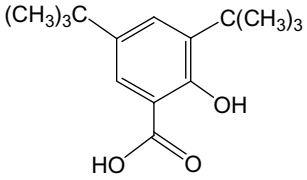
Abstract

A zinc complex based on salicylic acid derivatives (E-84 from Orient Chem.) is a powerful charge-control agent for toners used in electrophotography. However, its charge-control ability is known to greatly depend on the process of toner preparations. It is therefore probable that the structure of E-84 can be modified during the process, or the molecules might rearrange themselves in a different way, leading to different characteristics. For this reason, structure analysis of E-84 has been carried out on single crystals recrystallized from solution in dimethylacetoamide (DMA), or dimethylsufoxide (DMSO) in the presence or absence of water. As a result, a variety of complexes have been isolated. 3,5-di-*tert*-butyl-salicylic acid (TBS) is found to coordinate to the Zn atom as a monodentate ligand in all complexes: four-coordinate E-84/$(DMSO)_2$, five-coordinate E-84/$(H_2O)_3$ and. four-coordinate E-84/$(H_2O)_2$. The present results lead us to conclude that various Zn complexes form easily in the process of toner preparations, depending on solvents, polymers etc. This may result in scattered characteristics of the charge-control ability.

Introduction

Metal complexes based on salicylic acid derivatives play an important role in the electrophotographic process to control the toner charge. However, it has been pointed out that the charge-control ability depends greatly on the process of toner preparation. We assumed that the structural changes of the metal complexes or rearrangement of the molecules might occur during the toner preparation process. For this reason, we have previously started our investigation on the structure analysis of 3,5-di-*tert*-butyl-salicylric acid (TBS: Fig.1(a)) as well as its zinc complex called "E-84" (Fig.1(b)) recrystallized from solution in ethanol and acetonitrile. In TBS, two kinds of hydrogen-bonded dimers (A-A and B-B pairs) are formed in the crystal (Fig.2).[1] In E-84, two TBS molecules are coordinated as bidentate ligands to the central Zn atom. In addition, two ethanol molecules are also coordinated to form a six-coordinate complex (E-84/$(ethanol)_2$: Fig.3).[2] On the other hand, acetonitrile-solvated E-84 (Fig.4) forms a trinuclear complex composed of one six-coordinate Zn complex and two four-coordinate Zn ones. TBSs are coordinated to Zn atoms as bidentate, but each O-atom (*i.e.* ligand) of TBS is bonded to a different Zn-atom.[3]

(a)



(b)

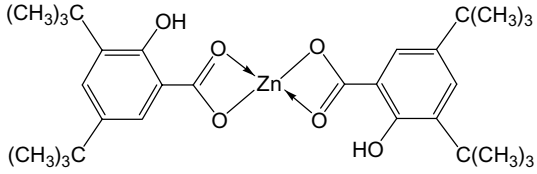


Figure 1. Molecular conformation of TBS and E-84: (a) TBS and (b) E-84.

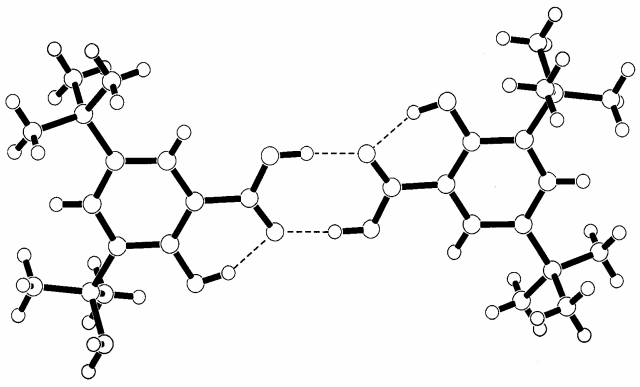


Figure 2. Hydrogen-bonded dimer of A-A pair.

In the present investigation, our further attempt was made to analyze the structure of E-84 complexes recrystallized from solution using polar solvents such as dimethylsulfoxide (DMSO) and dimethylacetoamide (DMA) in the presence or absence of water.

This paper deals with DMSO-solvated or hydrated complexes of E-84 and discusses the coordination number and ligand species coordinated to the central Zn atom.

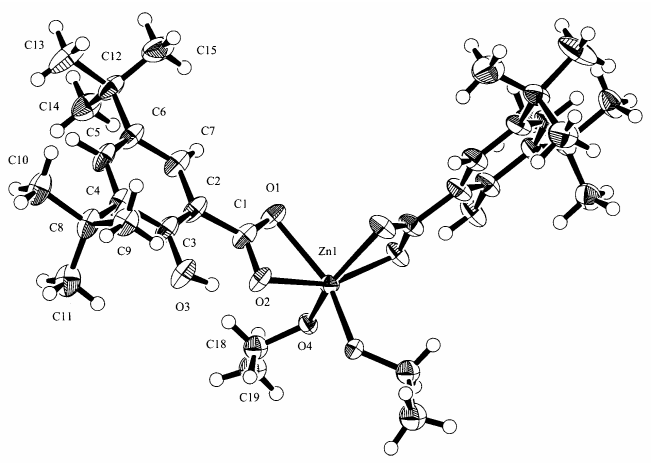


Figure 3. ORTEP plot of E-84/(ethanol)$_2$: six-coordinated complex.

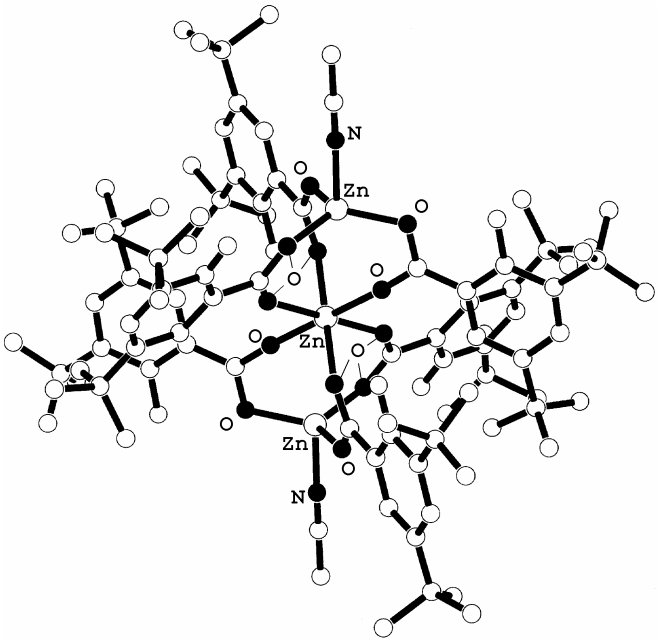


Figure 4. A perspective view of acetonitrile-solvated E-84: trinuclear complex.

Crystal Growth and Structure Analysis

E-84 was purchased from Orient Chemical Industries, Ltd. The product was used without further purification. Single crystals of E-84 were obtained by recrystallization from solution in dimethylsulfoxide (DMSO) and dimethyl-acetoamide (DMA) in the presence or absence of water. DMSO-solvated crystal as well as two kinds of hydrated crystals was isolated.

Table 1. Crystallographic Parameters for Solvated Crystals.

Solvated crystal	DMSO	DMA/H_2O (α)	DMA/H_2O (β)
Formula	E-84/$(DMSO)_2$	[E-84/$(H_2O)_3$]$(DMA)_3$	[E-84/$(H_2O)_2$]$(DMA)_3$
Molecular weight	720.30	879.45	861.43
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P\,2_1/a$	$P\,2_1/m$	$Cmc2_1$
Molecular symmetry	C_1	C_s	C_s
Z	4	2	8
a (Å)	16.688(4)	9.719(1)	32.673(4)
b (Å)	12.946(3)	6.9405(8)	11.739(2)
c (Å)	19.178(4)	35.456(4)	23.932(3)
β (º)	111.97(2)	94.63(1)	-
V (Å^3)	3842(4)	2383(1)	9179(4)
D_{calc} (g/cm^3)	1.245	1.247	1.225
R	0.0600	0.1284	0.0505

Reflection data were collected by means of a R-AXIS RAPID-F diffractometer from Rigaku, using Cu$K\alpha$. All measurements were carried out at 93 K in order to suppress the solvent evaporation. The programs to solve the structure were SHELXS-86 for DMSO-solvated crystal, SIR92 for hydrated crystal (α) and SHELXS-97 for hydrated crystal (β).

Results of Structure Analysis

1. Crystallographic Parameters

Table 1 details the crystallographic parameters for three different kinds of solvated-crystals of E-84: DMSO-solvated crystal and two kinds of hydrated crystals which are referred to as DMA/H_2O (α) and (β).

2. DMSO-Solvated Crystal: E-84/$(DMSO)_2$

DMSO-solvated E-84 crystal has been obtained from DMSO solution in the presence or absence of water. Irrespective of the presence or absence of water, the single crystals isolated includes two DMSO molecules: E-84/$(DMSO)_2$.

Figure 4 shows the ORTEP plot of E-84/$(DMSO)_2$. The basic structure of E-84 shown in Fig.1(b) is still retained. In this respect, the present conformation is similar to that of E-84/$(ethanol)_2$[2]. However, TBS is coordinated to the Zn atom as bidentate in E-84/$(ethanol)_2$ while as monodentate in E-84/$(DMSO)_2$. In addition, the molecular symmetry is characterized by C_1 symmetry, not C_2 as in the case of E-84/$(ethanol)_1$. Table 2 lists the distance between the Zn atom and O atoms of TBS as well as of DMSO molecule.

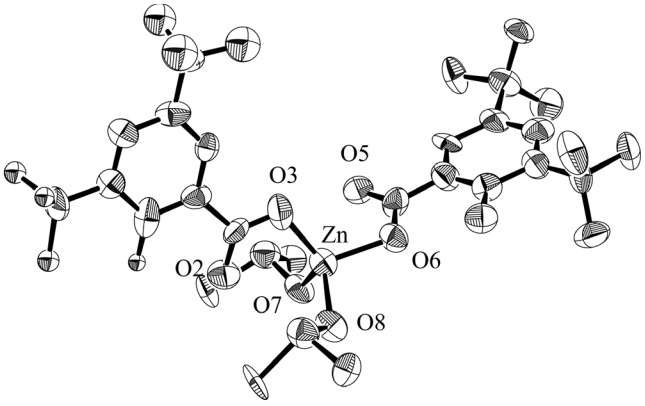


Figure 4. ORTEP plot of E-84/$(DMSO)_2$: four-coordinate complex.

Table 2. Distance between the Zn-atom and O-atoms of ligands in E-84/(DMSO),

Atoms	Bond length (Å)	Ligand
Zn/O3	1.959(7)	TBS
Zn/O6	1.981(8)	TBS
Zn/O7	1.980(7)	DMSO
Zn/O8	1.995(8)	DMSO

3. DMA/H_2O (α): [E-84/$(H_2O)_3$](DMA)$_3$

The present crystal was grown from a DMA solution in the presence of water and includes three water molecules as ligands, forming a five-coordinate complex: E-84/$(H_2O)_3$. In addition, three DMA molecules are also included in the lattice, but not coordinated to the Zn atom, as quite contrary to the recrystallization from solution in ethanol, acetonitrile and DMSO. Figure 5 shows the ORTEP plot of E-84/$(H_2O)_3$. The molecular symmetry is C_s as characterized by a mirror plane as shown. Here again, TBS behaves as a monodentate ligand as in the case of $Zn(TBS)_2(DMSO)_2$.

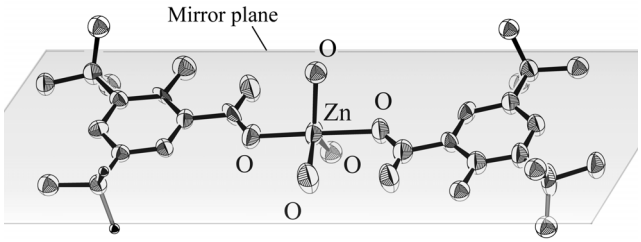


Figure 5. ORTEP plot of E-84/$(H_2O)_3$: five-coordinate complex.

4. DMA/H_2O (β): [E-84/$(H_2O)_2$](DMA)$_3$

The present crystal was grown from a DMA solution in the absence of water. However, the crystal includes two water molecules as ligands, giving rise to a four-coordinate complex: E-84/$(H_2O)_2$ (Fig. 6). As in DMA/H_2O (α), three DMA are also included in the crystal lattice, but not coordinated to the Zn atom. Since a trace of water is present in DMA, it is likely that these water molecules could have been coordinated to the Zn atom. The molecular symmetry is C_s as characterized by a mirror plane as shown. TBS is again coordinated to the Zn atom as monodentate as found in DMA/H_2O (α).

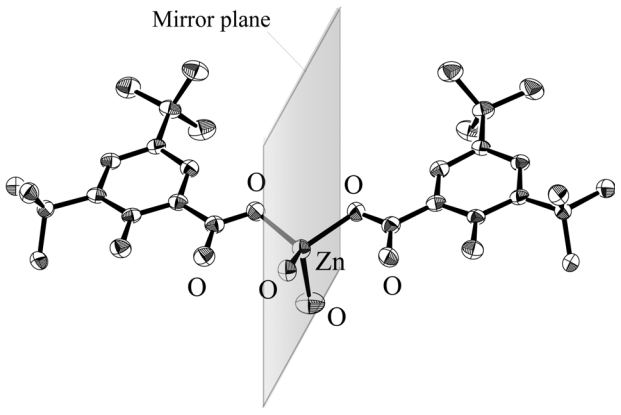


Figure 6. ORTEP plot of E-84/$(H_2O)_2$: four-coordinate complex.

Discussions

Changes in Coordination Number and Ligand Species

In our previous reports[1-3] as well as in the present investigation, we have seen that the coordination number as well as ligand species changes variously, depending on the solvent choice and recrystllization conditions. Table 3 summarizes these results.

When an E-84 single crystal is recrystallized from a mild solvent such as ethanol, initial E-84 structure shown in Fig.1(b) is basically preserved as seen in ethanol-solvated crystal (Fig. 3). TBS behaves here as bidentate in this complex. Additional coordination with two ethanol molecules makes the coordination number six. When acetonitrile is used as a solvent, a trinuclear complex of E-84 is formed that is composed of one six-coordinate Zn complex and two four-coordinate Zn ones. TBSs are coordinated to Zn atoms as bidentate, but each O-atom (*i.e.* ligand) of TBS is bonded to a different Zn-atom (Fig. 4). On the contrary, in more polar solvents such as DMSO and DMA, however, TBS coordination changes from bidentate to monodentate. The coordination number is four for DMSO and DMA/H_2O (β) and five for DMA/H_2O (α).

As described above, several structural changes occur in coordination number and ligand species, depending on choice of solvents and crystallization conditions. Then, it is obvious that the charge-control ability changes in accordance with structural changes of E-84 complexes.

Table 3. Changes in Coordination Number and Ligands

Solvated crystal	Coordination number of Zn	TBS
Ethanol[2]	6	bi-dentate
Acetonitrile[3]	4 & 6	bi-dentate
DMSO	4	mono-dentate
DMA/H_2O (α)	5	mono-dentate
DMA/H_2O (β)	4	mono-dentate

E-84 in Toners

Toner includes a variety of constituents such as binder, dyestuff, wax, charge-control agent etc. Solvents are also used to dissolve polymers. Judging from our present and previous results, it is highly probable that the basic structure of E-84 can variously be modified, depending on the solvent choice, process temperature and other conditions. This may lead to a scattered performance of the charge-control ability of E-84 in the electrophotographic process.

Conclusions

Structure analysis of E-84 has been carried out on single crystals recrystallized from solution in DMSO and DMA in the presence or absence of water. In solvated complexes isolated, coordination number as well as ligand species is found to change variously, depending on the solvent choice and recrystallization conditions. On the basis of the present and previous results, we conclude that E-84 is quite sensitive to surrounding conditions and the structural change can easily occur. This may lead to a scattered performance of the charge-control ability in toners. Therefore, it is crucial to precisely control the toner preparation process in order to achieve a high performance of the charge-control power.

References

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2. J. Mizuguchi, "*cis*-Bis(3,5-di-*tert*-butyl-2-hydroxybenzoato-κ^2O,O')bis(ethanol)zinc(II)" *Acta Cryst.*, E**59**, m955-m956 (2003).
3. J. Mizuguchi, "Crystal Structure of Charge-control Agents: 3,5-Di-tert-Butyl-2-Hydroxybenzoic Acid and Its Zinc-Complexes" Proceedings of NIP20 (2004).

Biography

Takashi Makino received his Bachelor of Engineering from Yokohama National University in 2004. He is currently in the graduate course for applied physics at the same university. His research interest includes crystal structure of charge-control agents.