Crystal Structure of a-Salicylic-Acid-Derivative Al-complex Used as a Charge-Control Agent and Its Electrical Properties

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Abstract

The title compound (E-88: Orient Chemical Industries) is an Al-complex which includes salicylic acid derivatives as ligands and is widely used as a charge-control agent (CCA) for full color toners. However, E-88 possesses a relatively low decomposition point around 130-180 ℃. For this reason, an attempt has been made in the present investigation to improve the thermal stability by exploring a new polymorph that possesses a higher thermal stability. Recrystallization has therefore been made from solution in various solvents, among which dimethylsulfoxide yielded a hexa-nuclear Al-complex (molecular weight: 3310) that exhibits a decomposition temperature of 270 ℃. Furthermore, this phase is found to exhibit an excellent CCA performance. In addition, the temperature dependence of the electrical conductivity has also been made in connection with our previously proposed charge-control mechanism of CCAs.

Introduction

The title compound (E-88: Orient Chemical Industries, LTD) is an Al-complex used as a charge-control agent (CCA) of the negative type that creates a desired charge level and polarity. An appealing feature of E-88 is that it can be used for full color toners (yellow, magenta, and cyan), since it is colorless. Further advantage is that E-88 includes only an environmentally friendly Al metal. Fig. 1 shows the structure of E-88 proposed by Orient Chemical and registered as CAS No. 41699-28-9 (Al/TBS = 1/3). E-88 composed of three 3,5-t-butyl-salicylic-acid molecules (TBS: Fig. 2) as ligands. However, E-88 possesses a relatively low decomposition point around 130-180 °C. Obviously, a higher temperature stability is necessary for E-88, because pulverized toners are manufactured by kneading CCA, at 130-180 °C, with various toner components such as polymer resin, pigments, wax, etc. For this reason, an attempt has been primarily made in the present investigation to improve the thermal stability by exploring a new polymorph that possesses a higher thermal stability. Recrystallization has therefore been made from solution in various solvents such as alcohols, ketones, ethers and organic solvents used for organic solvents (dimethylsulfoxide (DMSO), dimethylacetoamide (DMA), dimethylformaldehyde (DMF), N-methyl pyrrolidone (NMP), dioxane etc.). Among these, DMSO is found to yield a hexa-nuclear Al-complex (molecular weight: 3310) that exhibits a decomposition temperature of 270 °C.

In parallel, we have also carried out some electrical measurements of E-88 as a function of temperature in connection with the charge-control mechanism of CCAs as described below. A number of investigation have been carried out on the toner charging and the charge-control mechanism on the basis of the effective electric field [1,2], the work function [3], mass transfer [4] and charge transfer [5]. However, no clear-cut, consistent explanation is yet available at the moment. In view of the present situation, we have proposed a novel model that assumes an appreciable temperature increase at the "toner/carrier" interface due to the tribo-electrification [6]. Because of the present local heating, the electrical conductivity of CCA (which resides on the surface of both toner and carrier) is remarkably increased to give a conductive channel, through which the carrier-flow occurs effectively to charge up the toner. These two assumptions have experimentally been verified. Especially, the local heating up to around 100 °C has been confirmed by using a pigment-marker which changes its color from black to red [7]. Around this temperature, the electrical conductivity of CCA increases appreciably by 1-3 orders of magnitude as compared with that of room temperature. Because of this, an attempt has also been made to measure the dependence of the electrical conductivity of E-88 in order to support our charge-control mechanism.

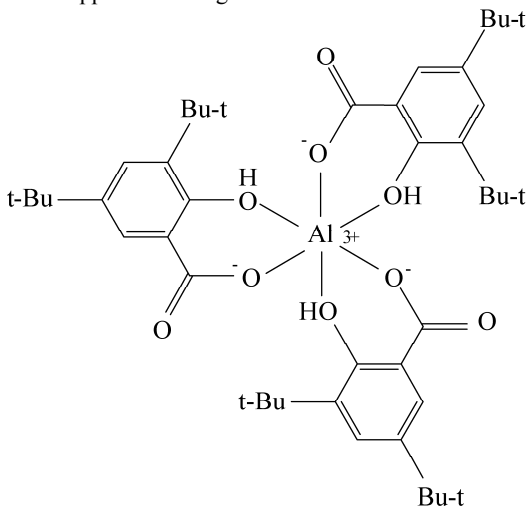

Figure 1. *Previously proposed structure of E-88 (CAS No. 41699-28-9)*

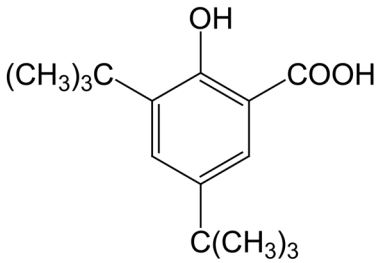

Figure 2. *Molecular structure of the 3,5-t-butyl-salicylic acid (TBS)*

Experiment

Crystal growth of E-88

E-88 was obtained from Orient Chemical Industries Ltd. We explored a stable polymorph through recrystallization from a variety of solvents, alcohols, ketones, ethers, and solvents used for organic pigments (DMF, DMSO, NMP, etc.). As a result, colorless single crystals were only isolated from solution in dimethylsulfoxide (DMSO) in the form of blocks (size: 0.20×0.10×0.08 mm^3).

X-ray structure analysis

Reflection data were collected on an R-AXIS RAPID-F diffractmeter from Rigaku using Cu$K\alpha$ as the radiation source (λ = 1.5418 Å) at 93 K. The structure was solved by direct methods (SHELXS97 [8]) and refinement was carried out by the full-matrix least-squares method of F^2 (SHELXL97 [9]).

Sample preparation for electrical measurements

A thin layer of DMSO-solvated E-88 was directly prepared by spin coating onto an interdigital electrode made of ITO (Indium-Tin-Oxide) as shown in Fig. 3.

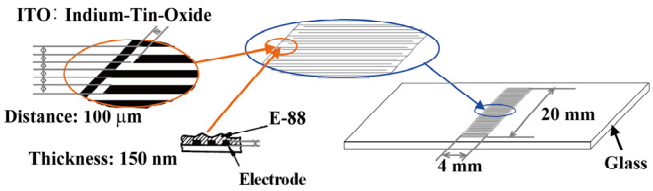

Figure 3. *Interdigital electrode made of ITO. Both the width of the electrode and the spacing between the electrodes are 100 μm*

Measurements

The temperature dependence of the electrical conductivity was measured in the temperature range between room temperature and 200 °C by means of a 6514 Keithley electrometer with a heating rate of 3 K/min.

Thermogravimetric analysis (TGA) was made in air on the polymorph of E-88 recrystallized from solution in DMSO, using a Rigaku Thermo Plus TG-8120 at a heating rate of 10 K/min.

Tribo-electrification measurements were made on toners composed of styrene acryl resin (100 parts), carbon black (6 parts), wax (2 parts) and the polymorph of E-88 recrystallized from solution in DMSO (1 part) in accordance with the standard procedure specified by Imaging Society of Japan, using the blow-off equipment (TB-200: Toshiba Chemical).

Results and discussion

Crystallographic parameters and molecular conformation

Table 1 details the crystallographic parameter for DMSO-solvated crystal of E-88.

Fig. 4 shows the conformation of the hexa-nuclear Al-complex and eight bulk DMSO molecules (*i.e.* free solvents). The environment around each Al-center is exactly the same. That is, the Al-complex includes equally six O atoms as ligands, of which four O atoms are from TBS, one O atom from DMSO, and another O atom from hydroxyl ion.

Table 1: Crystallographic parameter for the polymorph of E-88 recrystallized from solution in DMSO

Formula	$C_{157}H_{252}O_{41}S_{11}Al_6$
Molecular weight	**3310.24**
Crystal system	**monoclinic**
Space group	***Cc***
Z	**4**
a **(Å)**	**19.3525(4)**
b **(Å)**	**35.4460(4)**
c **(Å)**	**27.9608(7)**
β **(°)**	**110.1240(7)**
Density (g/cm³)	**1.224**

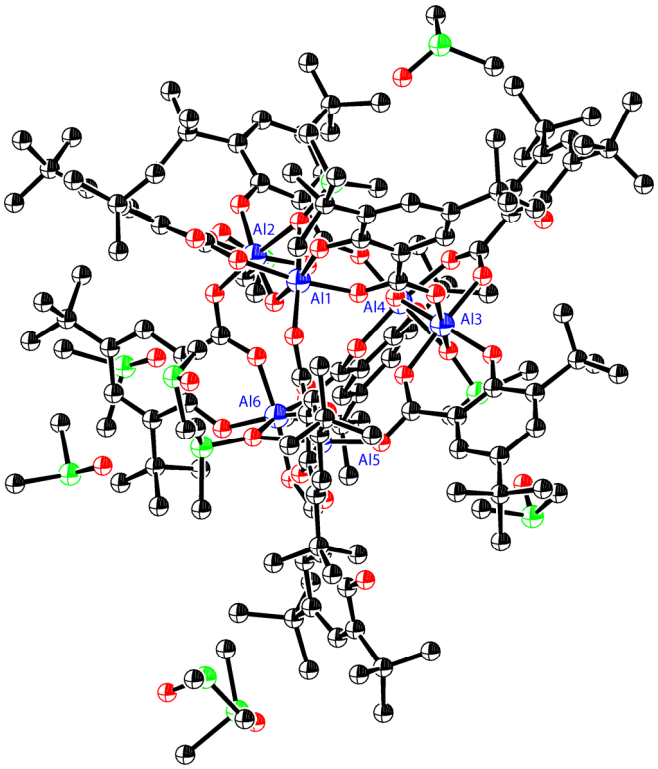

Figure 4. *ORTEP plot of the polymorph of E-88 recrystallized from solution in DMSO*

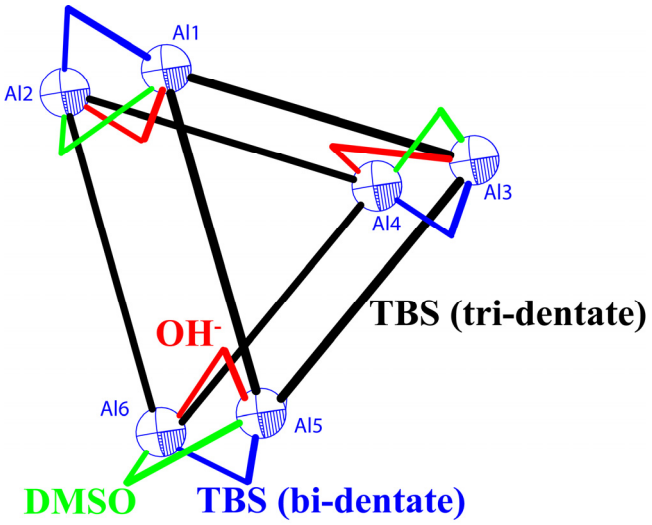

Figure 5. *A schematic illustration of the hexa-nuclear complex*

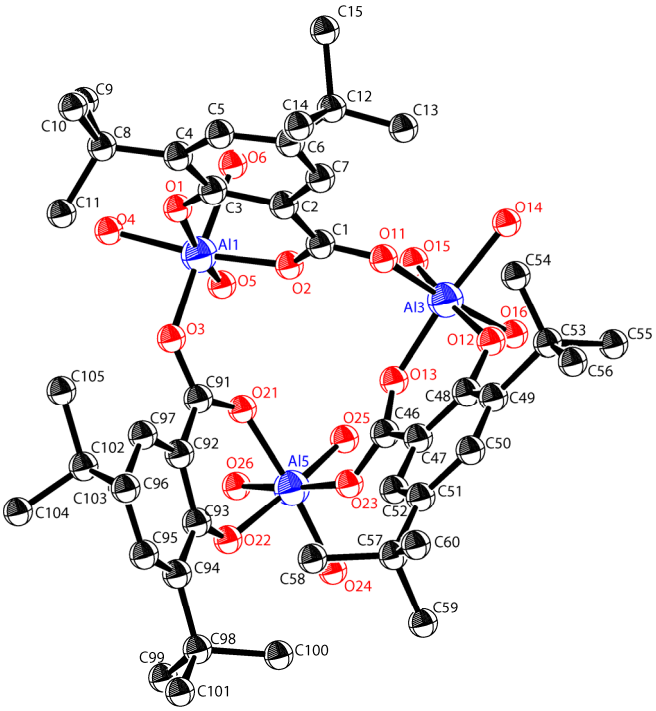

Figure 6. *The triangle composed of three Al atoms and three TBS molecules*

The asymmetric unit is composed of six Al atoms, nine TBS molecules, eleven DMSOs, and three hydroxyl ions. Among nine TBSs, six TBS molecules serve as the tri-dentate ligands, two of which are the O atoms of the carboxyl group and the third one is that of the hydroxyl group (see Fig. 2). The remaining three TBSs work as the bi-dentate ligands: two O atoms of the carboxyl group.

The hexa-nuclear Al-complex is pictured as composed of two triangles as shown in Fig. 5, in which all apices are occupied by six Al-atoms. The first triangle comprises Al1, Al3, and Al5, and two Al atoms are bridged by one tri-dentate TBS as shown in Fig. 6, for example, between Al1 and Al3, and between Al3 and Al5. This is also the case in the second triangle consisting of Al2, Al4, and Al6. It is also remarkable to note that the two triangles {(Al1, Al3. Al5) and (Al2, Al4. Al6)} are connected through each apices of the triangles (for example, Al1 and Al2) by one bi-dentate TBS, one DMSO, and one hydroxyl ion (see Fig. 5). Likewise, Al3 and Al4, as well as Al5 and Al6 are bridged by TBS, DMSO and OH^-. This constitutes a dimeric structure of two triangles. It is to be noted that the TBS and the hydroxyl ion are expected to play the major role among the above three bridging molecules for dimerization. This gives a ratio of Al/TBS=1/1.5.

As described above, the hexa-nuclear Al-complex is found to constitute a three-dimensional network which ensures a high thermal stability.

TGA measurement under air

Fig. 7 shows the TGA curve for the hexa-nuclear complex, and that for commercial E-88.

In the hexa-nuclear complex, the first weight-loss of about 15.74 % occurs in the temperature range between 30 and 170 °C. This corresponds approximately to six free DMSO molecules. This indicates the absence of bulk DMSO (*i.e.* free solvents) and the temperature range between 170 and 270 °C indicates a remain of the stable hexa-nuclear complex composed of six Al atoms, nine TBS molecules, three DMSO molecules and three hydroxyl ions. After that, the hexa-nuclear complex starts to decompose at about 270 °C.

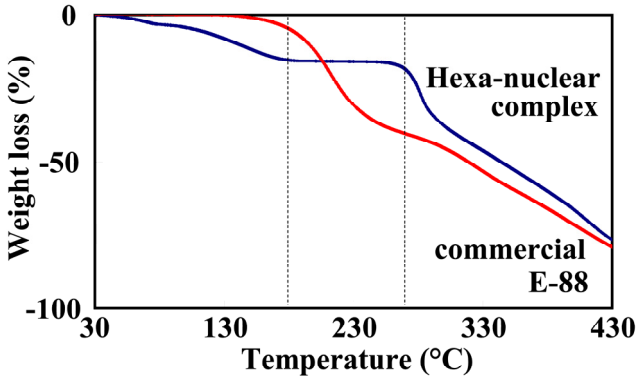

Figure 7. *The TGA curve for the hexa-nuclear complex, and that for commercial E-88*

On the other hands, commercial E-88 is stable up to 150 °C, followed by the onset of the weight-loss. This indicates that the hexa-nuclear complex shows a higher thermal stability than commercial E-88 by about 100 °C.

Tribo-electrification of toner which includes hexa-nuclear complex

Fig. 8 shows the charging characteristics of toners which include the hexa-nuclear complex in the absence of bulk DMSO molecules (*i.e.* free solvents) and that which includes commercial E-88 as a function of time. (The bulk DMSO-free state was obtained, for example, by heating above 200 °C for a while.)

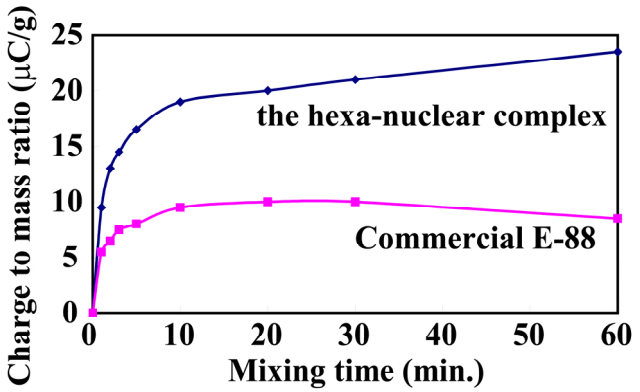

Figure 8. *The charging characteristic of toners with hexa-nuclear complex or with commercial E-88*

Toners with the hexa-nuclear complex also show a rapid charge up to the saturation and a stable charging level. The hexa-nuclear complex also exhibits an excellent CCA characteristic. This indicates that the hexa-nuclear complex can be used for the CCA which shows a higher thermal stability than that of commercial E-88.

Temperature dependence of the electrical conductivity

Since E-88 is pictured as an organic semiconductor, the electrical conductivity is expected to be governed by the Boltzmann distribution function as shown below:

$$n=n_0\exp(-\Delta E/k_BT)$$

where n, ΔE, T and k_B denote the number of carriers, the activation energy, the temperature and Boltzmann constant, respectively.

Fig. 9 shows the temperature dependence of the electrical conductivity (Arrehnius plot) for the hexa-nuclear complex and styrene-acryl (St-Ac) resin which is the main constituent of toners. A good linearity is observed in both samples, indicating the semiconductor-like behavior.

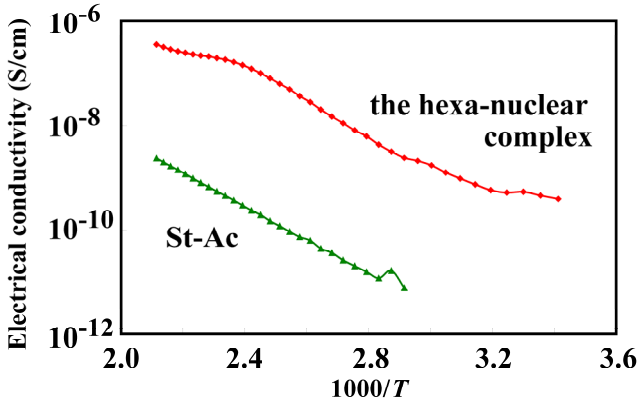

Figure 9. *Temperature dependence of the electrical conductivity for the hexa-nuclear complex*

The electrical conductivity of the hexa-nuclear complex at about 100 °C is higher than that of room temperature by 1.5 orders of magnitude. Furthermore, the electrical conductivity of St-Ac resin is lower than that of the hexa-nuclear complex by two orders of magnitude in the whole temperature range.

The above temperature dependence of the electrical conductivity of the hexa-nuclear complex supports our charge-control mechanism described in Introduction.

Conclusions

1. The framework of the hexa-nuclear complex (Al/TBS=1/1.5) is composed of two triangles whose apices are occupied by Al atoms. Each triangle is then formed by bridging two Al-atoms through one tri-dentate TBS. Furthermore, two triangles are found to form a dimer by connecting two Al-apices by one bi-dentate TBS, one DMSO, and one hydroxyl ion.
2. The hexa-nuclear complex shows a higher thermal stability than that of E-88/commercial (Al/TBS=1/3) by about 100 °C.
3. The hexa-nuclear complex also exhibits an excellent CCA characteristic. The hexa-nuclear complex can be used for the CCA which shows a higher thermal stability than that of commercial E-88.
4. The electrical conductivity of the hexa-nuclear complex at about 100 °C is higher than that at room temperature by 1.5 orders of magnitude. This supports our charge-control mechanism.

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Author Biography

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