Crystal structure of an azo Fe-complex used as a charge control agent and its electrical properties

Yohei Sato, Kazuya Uta, and Jin Mizuguchi; Graduate School of Engineering, Yokohama National University; 79-5 Tokiwadai, Hodogaya-ku, 240-8501 Yokohama, Japan

Abstract

The title compound (azo Fe-complex) is a well-known charge-control agent (CCA) used widely in electrophotography. Structure analysis as well as electrical measurements has been carried out in the present study in order to support our charge control mechanism that is based upon local heating and charge transfer through conductive channels at the "toner/carrier" contact. Methanol or acetone-solvated single crystals were isolated from solution in methanol or acetone, respectively. The former is found to crystallize in space group of P-1 while $P2_1/n$ in the latter crystal. The electrical conductivity of these crystals increases exponentially with temperature and the value around 100 ˚C is two-three orders of magnitude higher than that of room temperature.

1. Introduction

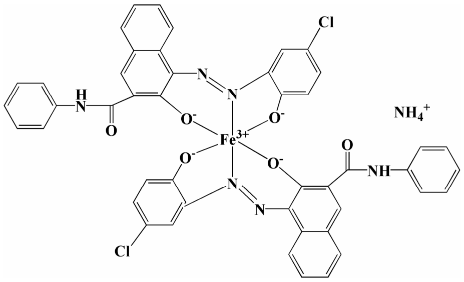

Fig. 1 *Molecular structure of the azo Fe-complex.*

The title compound (azo Fe-complex) is a charge-control agent (CCA) of the negative type used in electrophotography that creates a desired charge level and polarity. A number of investigation have been carried out on the charge-control mechanism on the basis of the work function [1], mass transfer [2] and charge transfer [3]. However, no clear-cut, consistent explanation has been established yet at the moment. In view of the present situation, we have recently proposed a novel model that assumes an appreciable temperature increase at the "toner/carrier" interface due to the tribo-electrification. 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 [4]. 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. Around this temperature, the electrical conductivity of CCA increases appreciably by two-three orders of magnitude as compared with that of room temperature.

In the present investigation, an attempt has been made to clarify the crystal structure of the azo Fe-complex shown in Fig. 1 and also to study its temperature dependence of the electrical conductivity in order to clarify the charge-control mechanism.

2. Experiment

2.1 Preparation of the sample and its crystal growth

The azo Fe-complex (T77 from Hodogaya Chem.: CAS No. 104815) was synthesized according to the method previously reported [5] and purified three times by recrystallization from methanol.

Single crystals were grown by recrystallization from methanol or acetone in solution. After 48 h, a number of black crystals were obtained in the form of platelets from a methanol solution (size: 0.20×0.20×0.10 mm^3) and in the form of blocks from an acetone solution (size: 0.10×0.10×0.04 mm^3). Both crystals were found to include one solvent molecule according to the thermogravimetric analysis.

2.2 Collection of reflection date and X-ray structure analysis

Reflection data were collected on a R-AXIS RAPID diffractometer from Rigaku using MoKα radiation (λ = 0.71075 Å) at 93 K, since the single crystals are found to include solvent molecules. The structures both crystals were solved by direct method (SIR2004 [6]) and refinement was carried out by the full-matrix least-squares method on F^2 (SHELXL97 [7]).

2.3 Preparation of samples for the electrical measurements

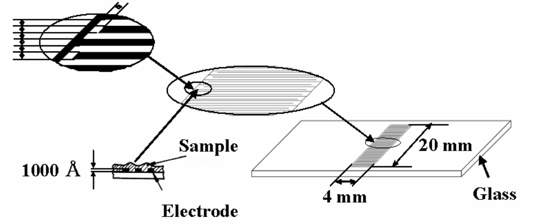

Fig. 2 *Interdigital electrodes made of Indium-Tin-Oxide.*

Measurements of the electrical conductivity in the form of powders are generally not very much reproducible and reliable due to the packing density of the powder as well as the electroding problems. Therefore, thin layers of methanol or acetone-solvated crystals were directly prepared on ITO (Indium-Tin-Oxide) interdigital electrodes by spin coating (Fig. 2).

2.4 Measurements

The temperature dependence of the electrical conductivity was measured on the above two samples, with a 6514 Keithley electrometer, in the temperature range between room temperature and 200 °C at a heating rate of 3 K/min.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were made in air on methanol or acetone recrystallized powders of T77 at a heating rate of 10 K/min, using a Rigaku Thermo Plus TG-8120.

3. Result and discussion

3.1 Crystallographic parameters and molecular conformation

Table 1 details the crystallographic parameters for methanol or acetone-solvated azo Fe-complexes. Both compounds include one solvent molecule: T77/methanol and T77/acetone. It is interesting that the space group is different (*i.e.* molecular arrangement is different), depending on the solvent used: P-1 and $P2_1/n$.

Table 1. Crystallographic parameters for T77/methanol or T77/acetone.

	T77/methanol	T77/acetone
Formula	$C_{46}H_{32}Cl_2FeN_7O_6/CH_3OH$	$C_{46}H_{32}Cl_2FeN_7O_6/CH_3COCH_3$
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/n$
Molecular weight	937.58	963.62
Z	2	4
a (Å)	10.1107	11.3199
b (Å)	14.1654	13.7962
c (Å)	15.3877	27.757
α (°)	103.2240	90.0000
β (°)	102.8270	93.747
γ (°)	94.0860	90.0000
Density (g / cm³)	1.501	1.480

Fig. 3 shows the ORTEP plot of T77/methanol. The metallic anion-complex has no crystallographic symmetry. Pairs of the equivalent ligands lie *cis* to each other, showing that the anion complex has no inversion symmetry and that the molecular conformation is obviously different from that shown Fig. 1, although the chemical formula with inversion symmetry has been always presented in literature [8]. The correct scheme is shown in Fig. 4.

Fig. 5 shows the ORTEP plot of T77/acetone. As in the case of T77/methanol, there is no inversion symmetry in the anion complex .

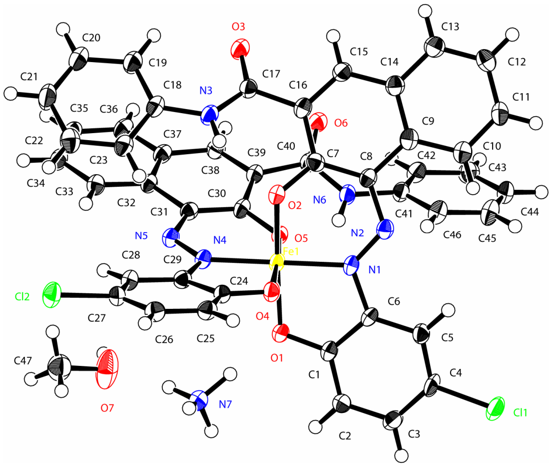

***Fig. 3** ORTEP plot of T77/methanol.*

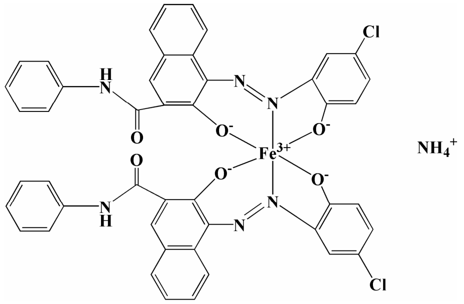

***Fig. 4** Chemical scheme of T77.*

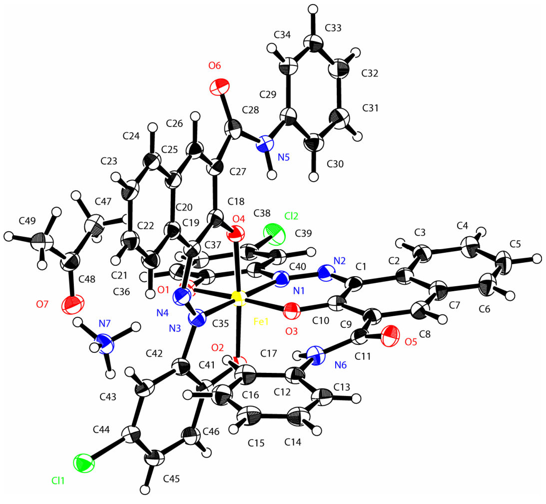

***Fig. 5** ORTEP plot of T77/acetone.*

It is remarkable to note that the molecular arrangement is strikingly different between T77/methanol and T77/acetone. In T77/methanol, the H atoms of the ammonium cation are hydrogen-bonded to O1, O3^i and O6^i of the anion complex (symmetry code: (i) -1+x, y, z) (*i.e.* bonded to two different anion complexes) as well as to O7 of methanol. Another intermolecular hydrogen-bond is between O7 and O6^{ii} (symmetry code: (ii) 1-x, 1-y, -z). Fig. 6 illustrates the packing arrangement of T77/methanol, showing that a pair of the molecules reside on an inversion center of the unit cell and that the H-bond network described above links the metal complexes in chains running along the *a* axis.

In T77/acetone, the network of H-bonds that links the metallic complexes is different from that in T77/methanol (Fig. 7). The ammonium cation shares its H-atoms with the O atoms of the three different metal anion-complexes through NH···O hydrogen bonds and also with O atom of the acetone molecule, again NH···O hydrogen bond. On the other hand, in T77/methanol, the ammonium cation shares its H-atoms with two metal anion-complexes and one solvate molecule. Interestingly the molecules are again assembled in chains that run along the *a* axis.

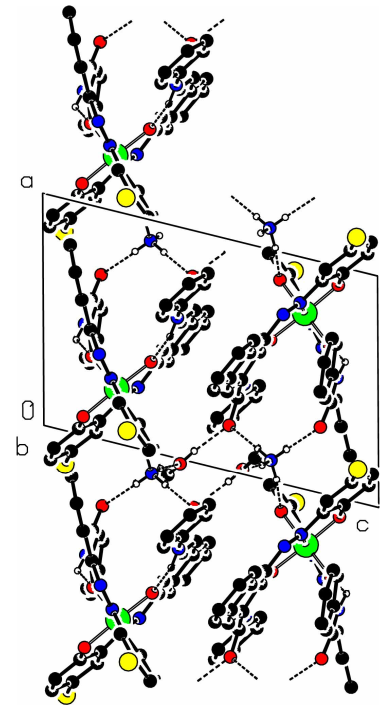

Fig. 6 *Packing arrangement of T77/methanol.*

It is important to note that it is the ammonium cation that bridges anion complexes (two in T77/methanol) and (three in T77/acetone), not the solvent molecule. Furthermore, the difference in molecular arrangement between T77/methanol and T77/acetone suggests that the temperature dependence of the electrical conductivity can behave in a different way. It is also anticipated that the solvent itself may affect the conductivity. Furthermore, the main framework of the molecular arrangement is assumed to remain mostly intact, although desorption of the solvent molecule occurs with increasing temperature.

3.2 TGA measurements in air

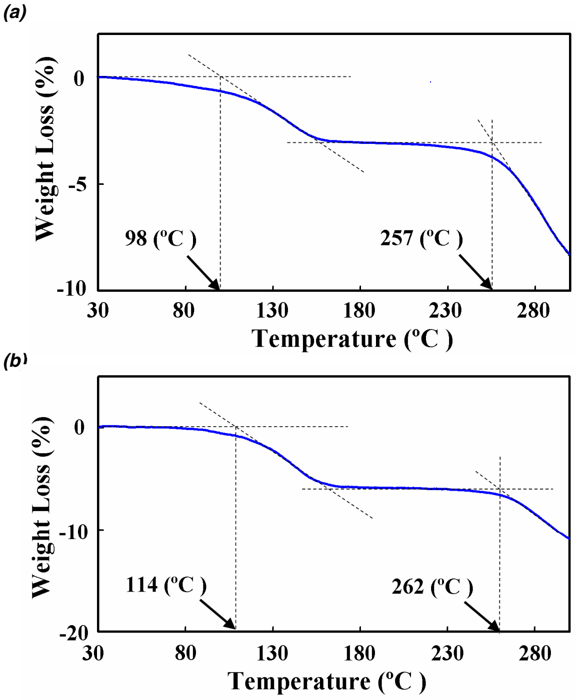

Fig. 8 *TGA curves for: (a) T77/methanol and (b) T77/acetone.*

Fig. 8(a) shows the TGA curve for T77/methanol. The onset of the weight-loss occurs around 98 °C, showing a weight-loss of 3.3 %. This corresponds to one methanol molecule. On the other hand, the onset temperature of T77/acetone is 114 °C and

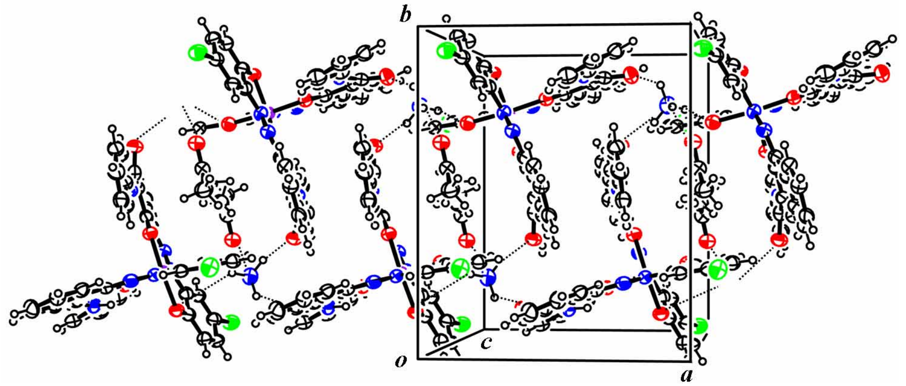

Fig. 7 *Packing arrangement of T77/acetone.*

the weight-loss amounts to 5.9 % (Fig 8(b)). The present weight-loss is due to desorption of one acetone molecule. In addition, the decomposition temperature of both metal anion-complexes is rather high because of the H-bond network: 257 °C in T77/methanol; 262 °C in T77/acetone.

It should be noted that the desorption and decomposition temperature of T77/acetone are higher than that of T77/methanol. This is closely correlated to the strength of the intermolecular forces and is mainly attributed to the fact that ammonium cation unites two different anion-complexes in T77/methanol through NH···O hydrogen bonding; whereas the cation connects three anion-complexes in T77/acetone.

3.3 Temperature dependence of the electrical conductivity

Since azo Fe-complexes are regarded as organic semiconductors, the temperature dependence of the electrical conductivity is assumed to follow the Boltzmann distribution and is given by:

$$n=n_0\exp(-\Delta E/k_BT) \tag{1}$$

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

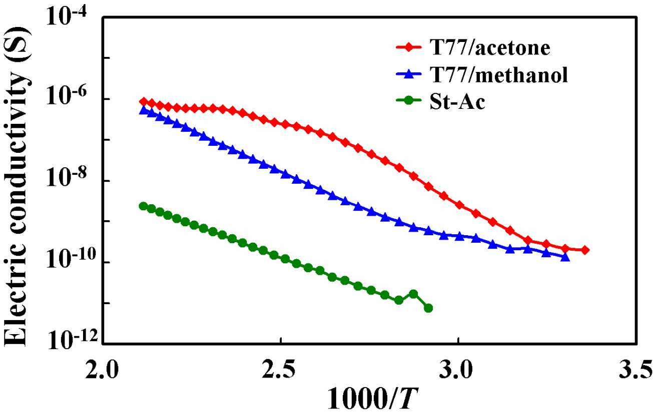

***Fig. 9** Temperature dependence of the electrical conductivity of T77/methanol, T77/acetone and St-Ac.*

Fig. 9 shows the temperature dependence of the electrical conductivity (Arrehnius plot) for T77/methanol, T77/acetone and styrene-acryl (St-Ac) resin which is the main constituent of toners. A good linearity is observed in T77/mechanol and St-Ac polymer; whereas the temperature dependence in T77/acetone is characterized by a swell in the whole temperature range. The latter is presumably related to the acetone molecules included firmly in the lattice and these remain more tenaciously in the crystal.

The electrical conductivity of T77/methanol at about 100 °C is higher by two orders of magnitude than that at room temperature, while three orders of magnitude in T77/acetone. In addition, the electrical conductivity of St-Ac resin is lower than that of T77/methanol by more than two orders of magnitude. This indicates that T77 with or without solvent molecules serves as an conductive channel between toner and carrier while the electrical charge is expected to reside on St-Ac polymer.

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

4. Conclusion

The conclusions drawn from the present investigation can be summarized as follow.

1. Two kinds of solvated azo Fe-complexes are isolated as single crystals. The space groups for T77/methanol and T77/acetone are P-1 and $P2_1/n$, respectively.
2. In both azo Fe-complexes, pairs of the equivalent ligands lie *cis* to each other, showing that the anion complex has no inversion symmetry, although the chemical formula with inversion symmetry has been always presented in literature.
3. The ammonium cation bridges two metal anion-complexes in T77/methanol through NH···O hydrogen bonding; whereas three anion-complexes are held together in T77/acetone. This situation is well reflected in the difference in decomposition temperature of both crystals.
4. The electrical conductivity of T77/methanol at about 100 °C is higher by two orders of magnitude than that at room temperature, while three orders of magnitude in T77/acetone. The present temperature dependence supports our charge-control mechanism.

References

[1] Robert J. Nash, Michael L. Grande and Richard N. Muller, "CCA Effects on the Triboelectric Charging Properties of a Two-Component Xerographic Developer", Proceedings of IS & T's NIP 17, 358-364 (2001).

[2] Atsushi Suka, Manabu Takeuchi, Keiki Suganami and Toshihiko Oguchi, "Toner Charge Generated by CCA Particles at the Interface between Toner and Carrier", J. Imag. Soc. Jpn. 45, 127-132 (2006).

[3] J. Guay, J. E. Ayala, and A. F. Diaz, "The Question of Solid-State Electron Transfer in Contact Charging between Metal and Organic Materials", Chem. Mater, 3, 1068-1073 (1991).

[4] Jin. Mizuguchi, Akio. Hitachi, Yohei. Sato and Kazuya. Uta: A study of the charge control mechanism, Proceedings of ICJ 2006 Fall Meeting, 121–124.

[5] M.Okubo et al: Jpn.P 2000-47433.

[6] Burla, M. C. , Camalli, M., Carrozzini, B., Cascarano, G. L., Giacovazzo, C., Polodori, G. & Spagna, R. (2003). J. Appl. Cryst. 36, 1103.

[7] Sheldrick, G. M. (1997). SHELXL97. University of Gottingen, Germany.

[8] For example, K. Tanaka: Triboelectric Charge Control for Toner, J. Electrostatics (Japanese Version) 19, 15-21 (1995).

Author Biography

Yohei Sato received his Bachelor of Engineering from Yokohama National University in 2007. He is currently in the graduate course for applied physics at the same university. His research interest includes a charge-control mechanism of CCA (Charge Control Agent). He is a member of the Chemical Society of Japan, ISJ and IS&T. E-mail:d07gd213@ynu.ac.jp.