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

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Abstract

The title compound is an azo-Cr complex (S-34Na) used as a charge-control agent in electrophotography. A high thermal stability of S-34Na has been investigated from the standpoint of the crystal structure. X-ray analysis revealed that S-34Na is a dinuclear complex of octahedral Cr^{III} *and* Na^{I} *units and forms a one-dimensional polymer running along the c axis, contributing to a significant thermal stability of S-34Na. On the other hand, the electrical conductivity of S-34Na at about 100 ℃ is found to be higher than that of room temperature by three orders of magnitude. This supports our charge-control mechanism that assumes an appreciable temperature increase at the "toner/carrier" interface due to tribo-electrification.*

Introduction

The title compound is an azo-Cr complex (Fig. 1: sodium salt of S-34 from Orient Chemical Industries, Ltd.) used as a charge-control agent (CCA) of the negative type in electrophotography that creates a desired charge level and polarity [1].

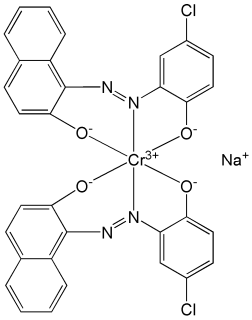

Figure 1. *Molecular structure of the sodium salt of an azo-Cr complex: S-34Na*

Pulverized toners are usually prepared by kneading CCA with various toner components such as polymers at about 130-180 °C. For this reason, a high thermal stability is prerequisite for CCAs. While azo-metal complexes such as Fe, Cr and Al are being used in practice as powerful CCAs, little is known about their high thermal stability above 200 °C although these are inherently salts. This motivated us to investigate the thermal stability of an azo-Fe complex, typically T-77 from Hodogaya Chemical Co., Ltd. (Fig. 2(a)) on the basis of the crystal structure.

To our surprise, the ammonium cation (NH_4^+) is found to bridge azo-Fe anion complexes through NH···O intermolecular hydrogen bonds between the NH group of the ammonium cation and the carbonyl or phenoxy O atom of the anion complex, as shown schematically in Fig. 3(a) [2,3]. The present hydrogen-bond network is found to appreciably increase the thermal stability. Then, we tackled the sodium salt of T-77 (Fig. 2(b): Na^+ instead of NH_4^+) (abbreviated to T-77Na). T-77Na is known to be equally stable, although a sodium cation is incapable of forming hydrogen bonds. X-ray structure analysis revealed that the Na dimer bridges azo-Fe anion complexes through formation of a five-coordinate Na cation with again the carbonyl O atoms of the anion complex (Fig. 3(b)) [4,5]. This contributes to the thermal stability of T-77Na.

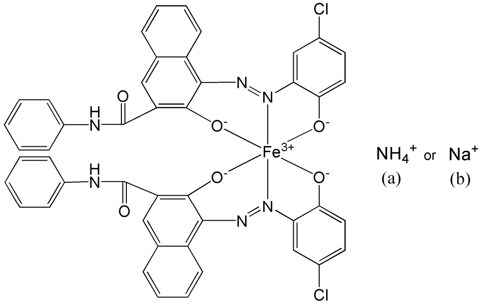

Figure 2. *Molecular structure of the azo-Fe complex: (a) ammonium salt (T-77) and (b) sodium salt (T-77Na)*

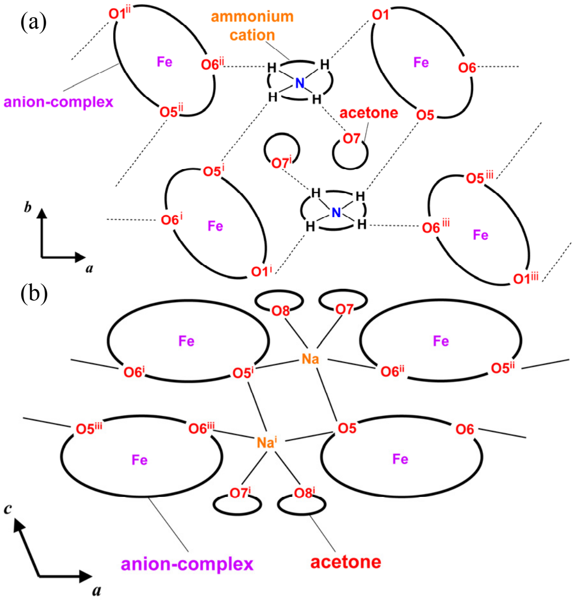

Figure 3. *Schematic illustration of the crystal structure: (a) acetone-solvated T-77 and (b) acetone-solvated T-77Na*

In T-77 and T-77Na, the carbonyl O atoms play the key role for bridging azo-Fe anion complexes. Then, an important question arises as to what happens, if there is no carbonyl O atom in azo-metal complexes such as S-34Na (Fig. 1). This subject has been addressed in the present investigation from the standpoint of the crystal structure. In parallel, the temperature dependence of the electrical conductivity has also been investigated in order to verify our charge-control mechanism of CCA [6]. Our proposed model assumes an appreciable temperature increase at the “toner/carrier” interface due to the tribo-electrification. Because of the present local heating above 100 °C, 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.

Experiment

Materials and crystal growth

S-34Na was obtained from Orient Chemical Industries, Ltd. Single crystals were grown by recrystallization from an acetone solution. After 48 h, a number of black crystals were obtained in the form of blocks (size: $0.29\times0.10\times0.09$ mm^3).

X-ray structure analysis

Reflection data were collected on an R-AXIS RAPID-F diffractometer from Rigaku using Mo$K\alpha$ radiation (λ=0.71075 Å) at 93 K, since the single crystals are found to include solvent molecules. The structure was solved by direct methods (SIR2004 [7]) and refinement was carried out by the full-matrix least-squares method on F^2 (SHELXL97 [8]).

Sample preparation for electrical measurement

A thin layer of acetone-solvated S-34Na was directly prepared by spin coating onto an interdigital electrode made of ITO (Indium-Tin-Oxide) as shown in Fig. 4.

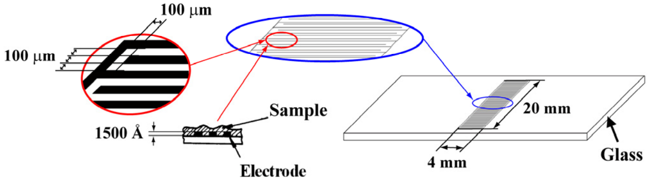

Figure 4. Interdigital electrodes made of Indium-Tin-Oxide

Measurements

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

Thermogravimetric analysis (TGA) was made in air, in the temperature range between room temperature and 480 °C, on recrystallized powders of S-34Na from an acetone solution using a Rigaku Thermo Plus TG-8120 with a heating rate of 10 K/min.

Infrared (IR) spectra were measured with a JASCO MET-2000 on the sample as recrystallized from an acetone solution, as well as the one with heat treatment at 240 °C for 5 min to remove included acetone molecules.

Result and discussion

Crystallographic parameters and molecular conformation

Table 1 details the crystallographic parameters for the acetone-solvated azo-Cr complex (S-34Na/acetone) [9]. This compound includes two acetone molecules: S-34Na/2CH_3COCH_3. S-34Na is a dinuclear complex of octahedral Cr^{III} and Na^{I} units and is found to form a one-dimensional polymer running along the *c* axis.

Table 1: Crystallographic parameters for S-34Na/acetone

	S-34Na/acetone
Formula	$C_{32}H_{18}Cl_2CrNaN_4O_4$ /2CH_3COCH_3
Crystal system	orthorhombic
Space group	*Pnna*
Molecular weight	784.55
Z	4
a (Å)	18.5082(17)
b (Å)	26.199(3)
c (Å)	7.1726(6)
Density (g/cm^3)	1.498

Fig. 5 shows the ORTEP plot of the monomeric unit of S-34Na/acetone. The unit is composed of an octahedral Cr^{III} unit and an octahedral Na^{I} one. The anion complex exists in the *cis* form, just as in the ordinary azo-Fe complexes previously reported [2-5]. Each Cr^{III} atom is chelated by the N and two O atoms from two [(5-chloro-2-oxidophenyl)diazenyl]-2-naphtholate ligands. On the other hand, the Na^{I} cation coordinates to a phenoxy O atom from the two ligands of each octahedral Cr^{III} unit, a naphthoxy O atom from the two ligands of each neighboring Cr^{III} unit and two acetone molecules. The octahedral Cr^{III} unit and the octahedral Na^{I} one are repeated alternately to form a one-dimensional polymer along *c* through the four O ligands in common (Figs. 6 and 7). The polymer formation contributes to a significant stabilization of S-34Na whose property is prerequisite for the CCA application in electrophotography.

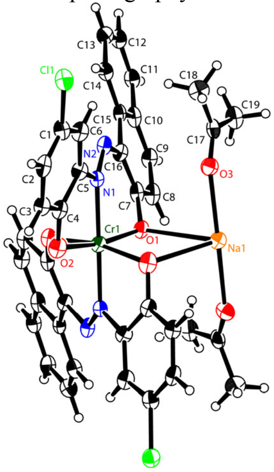

Figure 5. ORTEP plot of S-34Na/acetone

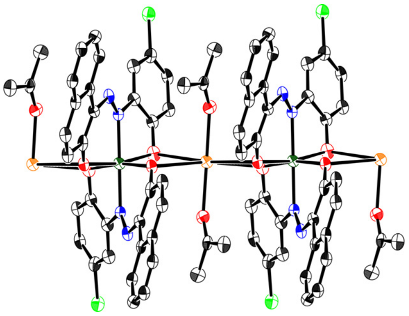

Figure 6. Polymeric structure of S-34Na/acetone

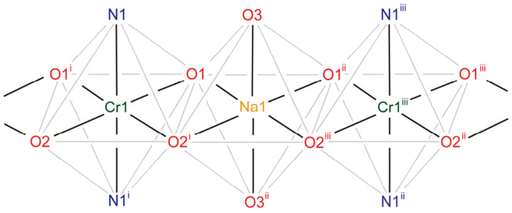

Figure 7. Schematic illustration of the dinuclear complex of octahedral Cr^{III} and Na^{I} units and this forms a one-dimensional polymer running along the c axis

TGA measurements in air

Fig. 8 shows the TGA curve for S-34Na/acetone. The onset of the weight-loss occurs around 187 °C, showing a weight-loss of 13.89 %. This corresponds to two acetone molecules. Finally, the decomposition takes place around 333 °C, which is extremely high for ordinary metal complexes. The present high thermal stability is obviously due to the polymer formation of S-34Na.

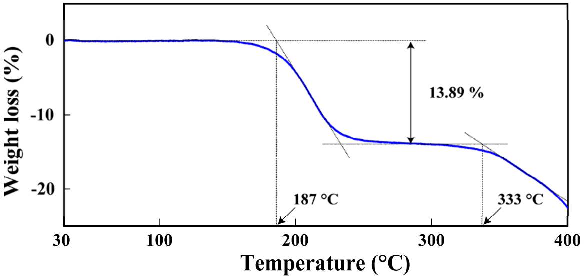

Figure 8. TGA curves for S-34Na/acetone

IR spectra

Fig. 9 shows the IR spectra of S-34Na/acetone before and after heat treatment (*i.e.* before and after desorption of acetone molecules). The noisy characteristic bands of water moisture are absent in the IR spectrum before heat treatment, whereas these are clearly observed in the IR spectrum after heat treatment. This indicates that water moisture is presumably adsorbed on the Na site as soon as the acetone molecules are desorbed from the Na atom. This is probably due to the hygroscopic properties of Na.

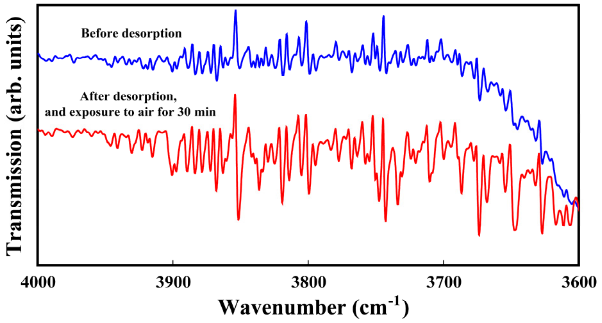

Figure 9. IR spectra of powdered S-34Na/acetone before and after heat treatment at 240 °C

Temperature dependence of the electrical conductivity

Since S-34Na 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.

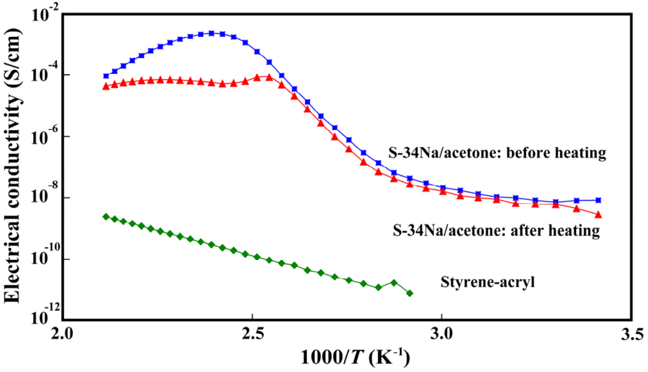

Figure 10. Temperature dependence of the electrical conductivity of S-34Na/acetone before and after heat treatment, as well as of St-Ac

Fig. 10 shows the temperature dependence of the electrical conductivity (Arrehnius plot) for S-34Na/acetone before and after heat treatment at 240 °C, as well as for styrene-acryl (St-Ac) resin which is the main constituent of toners. A good linearity is observed in St-Ac, indicating semiconductor-like behavior. On the other hand, the S-34Na/acetone sample before heat treatment exhibits a gradual increase in conductivity up to 75 °C, and then with a higher gradient up to 140 °C. After that, the conductivity decreases abruptly, due presumably to the desorption of solvated acetone molecules. Similarly, the sample with heat treatment (in the absence of solvated acetone molecules) behaves exactly in the same way up to 120 °C and then conductivity remains nearly constant. In both samples before and after heat treatment, the electrical conductivity at about 100 °C is higher than that of room temperature by three orders of magnitude. On the other hand, the electrical conductivity of St-Ac resin is much lower than that of S-34Na/acetone by three orders of magnitude. This indicates that S-34Na with or without solvent molecules serves as a conductive channel between toner and carrier while the electrical charge is expected to reside on St-Ac resin.

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

Conclusion

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

1. An acetone-solvated azo-Cr complex is found to crystallize in the space group of *Pnna*.
2. S-34Na is a dinuclear complex of octahedral Cr^{III} and Na^{I} units and forms a one-dimensional polymer running along the *c* axis. This greatly contributes to the thermal stability.
3. The electrical conductivity of S-34Na/acetone at about 100 °C is higher than that of room temperature by three orders of magnitude. The present temperature dependence supports our charge-control mechanism of the toner charging.

References

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Author Biography

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