

The role of cations in thermal stability of azo-Fe complexes used as charge-control agents from the standpoint of the crystal structure

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Abstract

Azo-Fe complexes and their sodium salts are well-known charge-control agents (CCAs) used widely in electrophotography. Aside from the CCA performance, a high thermal stability is also required because pulverized toners are prepared by kneading CCA with various toner components at about 130–180 °C. Therefore, thermal stability has been investigated in azo-Fe complexes from the standpoint of the crystal structure. X-ray analysis revealed that the ammonium cations bridge neighboring azo-Fe complex anions through intermolecular $\text{NH}^+\cdots\text{O}^-$ hydrogen bonds. On the other hand, the Na cations are also found to connect different azo-Fe complex anions through the formation of Na complexes. These facts lead us to conclude that the high thermal stability of azo-Fe complexes is attributed to the intermolecular bonds formed by ammonium or sodium cations.

Introduction

Azo-metal complexes are well-known classical pigments as characterized by the azo group ($-\text{N}=\text{N}-$). Nowadays, azo-metal complexes have attracted much attention as materials for charge-control agents (CCAs) used in electrophotography. However, there are still two major issues on CCAs. The first one is as to why these compounds work as charge-control agents and the other issue concerns their high thermal stability although these are inherently salts.

We have previously tackled the first issue by the novel model that assumes an appreciable temperature increase at the “toner/carrier” interface due to the tribo-electrification [1]. 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.

On the other hand, little is known about mechanism of the high thermal stability of azo-metal complexes such as Fe, Cr and Al, although these are being used in practice as powerful CCAs. For this reason, an attempt has been made in the present investigation to clarify the origin of the thermal stability from the standpoint of the crystal structure. We focused on two representative azo-Fe complexes as shown in Figs. 1(a) and 1(b). The former is an ammonium salt from Hodogaya Chemical registered as T-77, while the latter is its sodium salt designated as T-77Na in the present paper.

This paper deals with the crystal structure as well as thermal properties of T-77 and T-77Na.

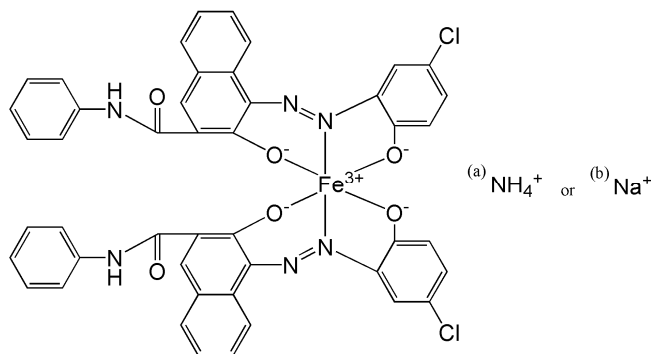


Figure 1. Molecular structure of the azo-Fe complex: (a) ammonium salt (T-77) and (b) its sodium salt (T-77Na)

Experiment

Materials and crystal growth

Single crystals of T-77 were grown by recrystallization from acetone or methanol solution [2,3]. After 48 h, a number of black crystals were obtained in the form of blocks from both solutions.

On the other hand, single crystals of T-77Na were grown by recrystallization from acetone or acetonitrile solution [4,5]. After 48 h, a number of black crystals were obtained in the form of blocks in both solutions.

Collection of reflection data and X-ray structure analysis

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

Measurements

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were made in air on acetone-solvated crystals of T-77 and T-77Na at a heating rate of 10 K/min, using a Rigaku Thermo Plus TG-8120.

Infrared (IR) spectra were measured with a JASCO MET-2000 on acetone solvated crystals of T-77Na before and after heat treatment at 250 °C for 20 min.

Result and discussion

Crystallographic parameters and molecular conformation of T-77

Table 1: Crystallographic parameters for T-77 [2,3]

	T-77/methanol	T-77/acetone
Formula	$(\text{NH}_4)[\text{Fe}(\text{C}_{23}\text{H}_{14}\text{ClN}_3\text{O}_3)_2](\text{CH}_3\text{O})$	$(\text{NH}_4)[\text{Fe}(\text{C}_{23}\text{H}_{14}\text{ClN}_3\text{O}_3)_2](\text{C}_3\text{H}_6\text{O})$
Crystal system	triclinic	monoclinic
Space group	$P-1$	$P2_1/n$
Molecular Weight	937.58	963.62
Z	2	4
a (Å)	10.1107(4)	11.3199(14)
b (Å)	14.1645(6)	13.7962(17)
c (Å)	15.3877(7)	27.757(4)
α (°)	103.2240(11)	90.0000
β (°)	102.8270(12)	93.747(3)
γ (°)	94.0860(12)	90.0000
Density (g/cm ³)	1.501	1.480

Table 1 details the crystallographic parameters for methanol or acetone-solvated azo-Fe complexes. Both compounds include one solvent molecule: T-77/CH₃OH and T-77/CH₃COCH₃. It is interesting that the space group is different, depending on the solvent used: $P-1$ and $P2_1/n$.

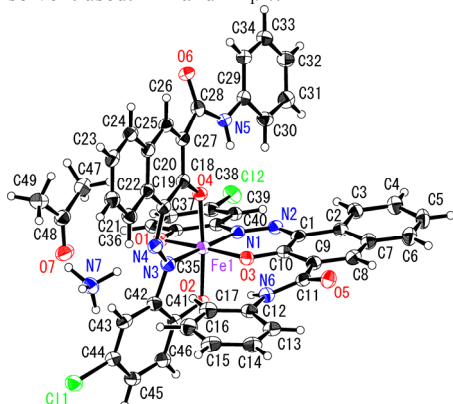


Figure 2. ORTEP plot of T-77/acetone

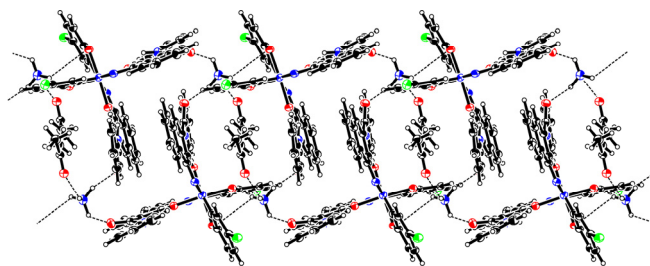


Figure 3. Packing arrangement of T-77/acetone

Fig. 2 shows the ORTEP plot of acetone-solvated T-77 (*i.e.* T-77/acetone). The azo-Fe 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.

Fig. 3 shows the molecular arrangement of T-77/acetone. The ammonium cation shares its H-atoms with the phenoxo

oxygen atom (O1) or the two carbonyl oxygen atoms (O5ⁱ and O6ⁱⁱ) (symmetry code: (i) $-1+x, y, z$; (ii) $-x, 1-y, 1-z$) of the three different anion complexes through $\text{NH}\cdots\text{O}$ hydrogen bonds and also with oxygen atom of the acetone molecule, again $\text{NH}\cdots\text{O}$ hydrogen bond. These hydrogen bonds constitute a sheet-like network along the *a* axis. This is schematically illustrated in Fig. 4(a). At this point, it should be stressed that the ammonium cation serves as a “bridging mediator” for the hydrogen-bond network.

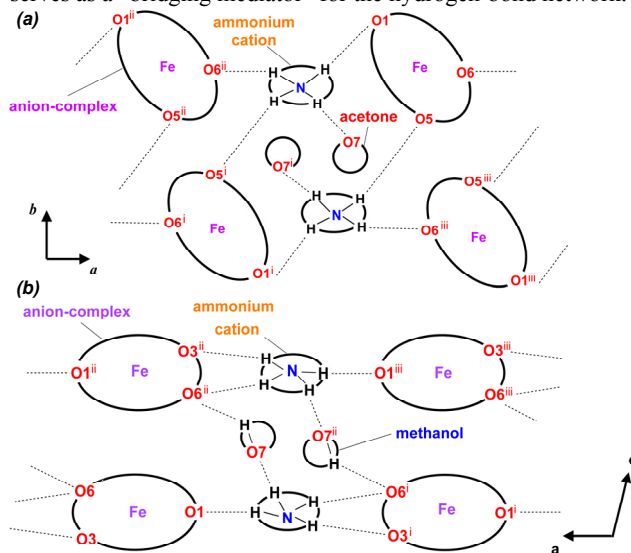


Figure 4. Schematic illustration of the crystal structure: (a) T-77/acetone and (b) T-77/methanol

On the other hand, in methanol-solvated T-77 (*i.e.* T-77/methanol), the situation is slightly different but a similar hydrogen-bond network is also observed [3]. In T-77/methanol, the ammonium cation bridges two different anion complexes, and forms the polymer-like hydrogen-bond network running along the *a* axis. Fig. 4(b) illustrates this situation schematically.

In summary, the ammonium cation plays a crucial role in bridging anion complexes in both T-77/acetone and T-77/methanol, resulting in a high thermal stability.

Crystallographic parameters and molecular conformation of T-77Na

Table 2: Crystallographic parameters for T-77Na [4,5]

	T-77Na/acetone	T-77Na/acetonitrile
Formula	$[\text{FeNa}(\text{C}_{23}\text{H}_{14}\text{ClN}_3\text{O}_3)_2](\text{C}_3\text{H}_6\text{O}_2)$	$[\text{Fe}_2\text{Na}_2(\text{C}_{23}\text{H}_{14}\text{ClN}_3\text{O}_3)_4](\text{C}_2\text{H}_3\text{N})_2(\text{H}_2\text{O})_4]2\text{H}_2\text{O}$
Crystal system	triclinic	triclinic
Space group	$P-1$	$P-1$
Molecular Weight	1026.64	2011.21
Z	2	1
a (Å)	13.8165(4)	11.4416(5)
b (Å)	13.8623(4)	14.1161(7)
c (Å)	14.1524(5)	15.0105(7)
α (°)	98.8179(10)	72.396(1)
β (°)	105.3882(12)	76.2850(9)
γ (°)	109.0641(8)	83.015(1)
Density (g/cm ³)	1.431	1.481

Table 2 details the crystallographic parameters for acetone or acetonitrile-solvated azo-Fe complexes. Both compounds include solvent molecules: T-77Na/2CH₃COCH₃ and T-77Na/CH₃CN·3(H₂O)

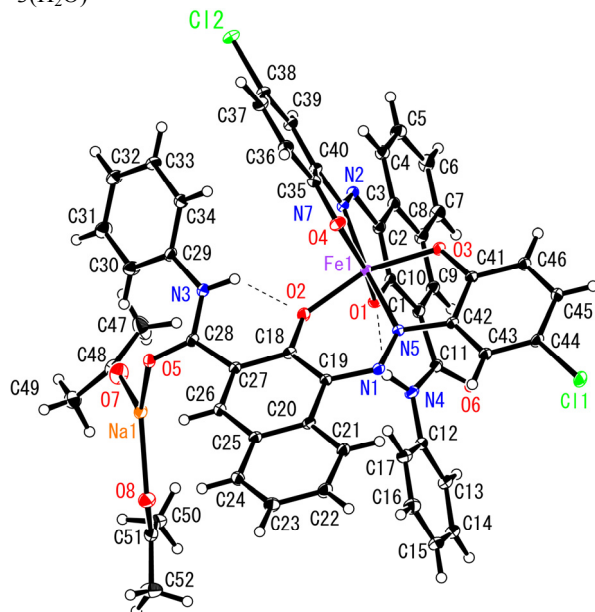


Figure 5. ORTEP plot of T-77/acetone

Fig. 5 shows the ORTEP plot of acetone-solvated T-77Na (*i.e.* T-77Na/acetone). Here again, there is no inversion symmetry in the anion complex, just as in the case of T-77/acetone.

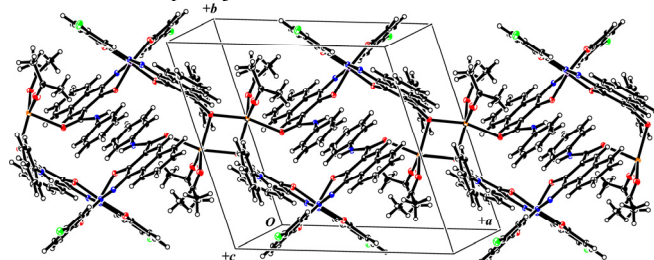


Figure 6. Packing arrangement of T-77Na/acetone

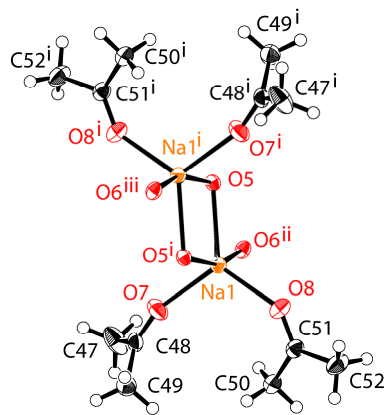


Figure 7. The sodium cation dimer with four acetone molecules. [Symmetry code: (i) $-x, 1-y, 1-z$; (ii) $1-x, 1-y, 1-z$; (iii) $-1+x, y, z$]

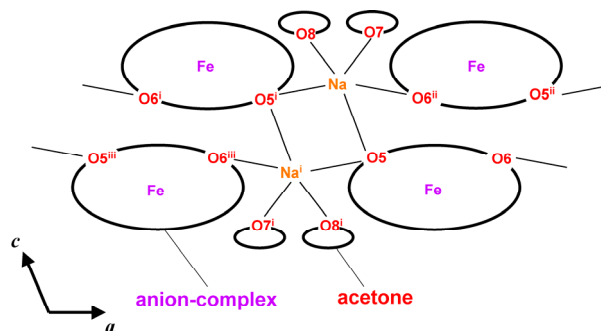


Figure 8. Schematic illustration of the crystal structure of T-77Na/acetone

Fig. 6 shows the molecular arrangement of T-77Na/acetone. The sodium cation is found to form a dimer with another sodium one (Fig. 7), where each sodium cation is coordinated by five ligands: three carbonyl oxygen of the three different anion complexes (O5 O5ⁱ and O6ⁱⁱ) (symmetry code: (i) $-x, 1-y, -z$; (ii) $1-x, 1-y, 1-z$) and two acetone molecules (O7 and O8). It is interesting to note that each sodium cation unites three different anion complexes through the carbonyl oxygen atoms: O5 O5ⁱ and O6ⁱⁱ. This indicate that anion complexes form a two-dimensional network parallel to the *a* axis. Fig. 8 shows the schematic illustration of the crystal structure of T-77Na/acetone.

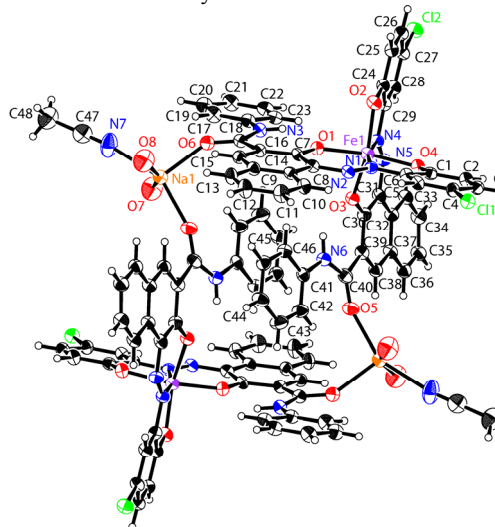


Figure 9. ORTEP plot of the anion-complex dimer in T-77Na/acetonitrile

On the other hand, in acetonitrile-solvated T-77Na (*i.e.* T-77Na/acetonitrile), the situation of the sodium coordination is quite different. The sodium cation bridges two different anion complexes to form an anion-complex dimer as shown in Fig. 9 [5]. This dimerization contributes to the stabilization of T-77Na/acetonitrile.

In summary, the sodium cation plays a decisive role in bridging anion complexes in both T-77Na/acetone and T-77Na/acetonitrile crystals, leading to a high thermal stability of these compounds.

TGA measurements in air

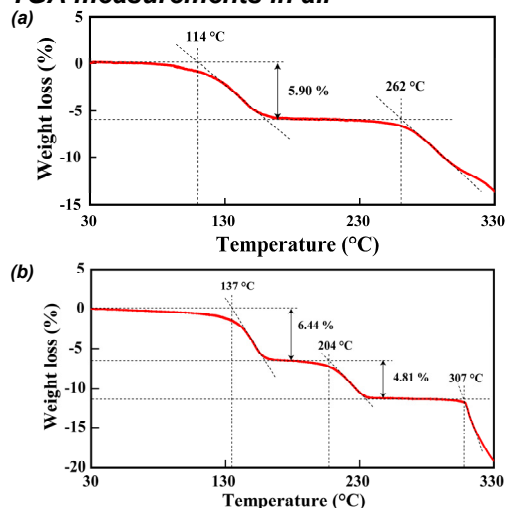


Figure 10. TGA curves for solvated crystals: (a) T-77/acetone and (b) T-77Na/acetone

Fig. 10(a) and 10(b) show the TGA curve for T-77/acetone and T-77Na/acetone, respectively. In T-77/acetone, the onset of the weight-loss occurs around 114 °C, showing a weight-loss of 5.90 %. This corresponds to one acetone molecule. Then, the decomposition takes place at about 262 °C. The present high decomposition temperature is clearly attributed to the hydrogen-bond network formed by the ammonium cation.

On the other hand, the weight-loss in T-77Na/acetone occurs in two steps at about 137 °C (weight-loss: 6.44 %) and at about 204 °C (weight-loss: 4.81 %). The total weight-loss of 11.25 % corresponds to two acetone molecules. Then, the decomposition occurs at about 307 °C. The present high decomposition point is obviously due to the coordination network caused by sodium cations.

IR spectrum measurements

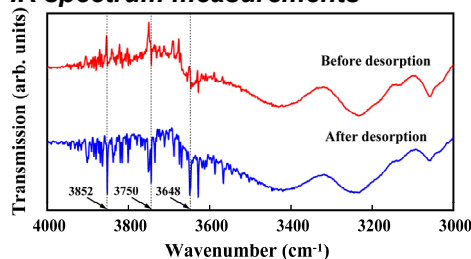


Figure 11. IR spectra of powdered T-77Na/acetone.

Fig. 11 shows the IR spectra of T-77Na/acetone before and after heat treatment (*i.e.* before and after desorption of acetone molecules). Before desorption of acetones, the noisy peaks in the region between 3400 and 3900 cm^{-1} are absent in the IR spectrum. On the other hand, the characteristic noisy bands that are typical of water moisture can be observed after acetone desorption. This suggests that water moisture is newly adsorbed on the coordination site of the Na cation where two acetone molecules were adsorbed

(see Fig. 8). In other words, the sodium cation has a tendency to accept lone pairs of the O atoms of water molecules. Water absorption may affect the tribo-electrification of toners.

Conclusions

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

1. In azo-Fe complex anions, pairs of the equivalent ligands lie *cis* to each other, showing that the anion complex has no inversion symmetry.
2. The ammonium cation in T-77 bridges two or three azo-Fe anion complexes through $\text{NH}\cdots\text{O}$ hydrogen bonds. The ammonium cation plays a crucial role in bridging anion complexes in both T-77/acetone and T-77/methanol, resulting in a high thermal stability.
3. The sodium cation in T-77Na is coordinated by five ligands: carbonyl O atoms of the anion complex plus O atoms of solvent molecules. The Na cation plays a decisive role in bridging anion complexes in both T-77Na/acetone and T-77Na/acetonitrile, leading to a high thermal stability of these compounds.
4. The decomposition temperature of T-77/acetone and T-77Na/acetone is quite high because of the sheet-like two-dimensional network formed by ammonium or sodium cations.

References

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Author Biography

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