Crystal Structure and Chromic Properties of an Iron(II) Complex Salt of a N-Salicylideneaniline Derivative

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The crystal structure of an iron(II) complex salt, [Fe(phen)₃](SASO₃⁻); (phen = phenanthroline; SASO₃⁻ = 3-[(2-hydroxyphenyl)methylidene]amino]benzene-1-sulfonate), was determined by single crystal X-ray structural analysis. It was revealed: monoclinic, C2/c, a = 26.951(3), b = 10.8492(8), c = 21.899(3)Å, β = 125.390(19)°, Z = 4, V = 5220.1(14)Å³, R₁ = 0.0493[I > 2σ(I)]. Although, 3-[(2-hydroxyphenyl)methylidene]amino]benzene-1-sulfonic acid (SASO₃H) was known as a photochromic compound, title compound did not exhibit photochromism due to the non-photochromic molecular conformation of the SASO₃⁻ anions in the crystal.

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N-Salicylideneaniline (SA) is a classical organic chromic compound. SA crystals exhibit photochromism from yellow to red upon UV irradiation. A reversible color change is caused by photo-induced molecular isomerization via the 
\textit{keto} \textit{cis-keto} form. The photochromic activity is known to depend on the molecular conformation. Only twisted molecules with a dihedral angle of between two aromatic rings more than 30° exhibit photochromism in contrast to non-photochromic planar molecules with a dihedral angle of less than 30° (SA planarity rule). Moreover, SA crystals also exhibit thermochromism from yellow to colorless due to a tautomeric equilibrium shift from the keto to enol form as the temperature is lowered. Therefore, SA and its derivatives are tautomeric equilibrium shift from the \textit{keto} to \textit{enol} form. The photochromic activity is known to depend on the molecular conformation. Only twisted molecules with a dihedral angle of between two aromatic rings more than 30° exhibit photochromism in contrast to non-photochromic planar molecules with a dihedral angle of less than 30° (SA planarity rule). Moreover, SA crystals also exhibit thermochromism from yellow to colorless due to a tautomeric equilibrium shift from the keto to enol form as the temperature is lowered. Therefore, SA and its derivatives are tautomeric equilibrium shift from the \textit{keto} to \textit{enol} form.

In this study, we synthesized a complex salt including SA derivative anions and metal complex cations. The complex salt crystal was supposed to exhibit photochromism and thermochromism with color tones modified by the optical properties of the metal complex, such as a ligand-to-metal charge-transfer (MLCT) transition state. Indeed, 3-[(2-hydroxyphenyl)methylidene]amino]benzene-1-sulfonic acid (SASO₃H) was synthesized to form a complex salt with a tris-phenanthroline iron(II) complex having a strong MLCT absorption band.

The title compound, [Fe(phen)₃](SASO₃⁻); (I), was synthesized and obtained as violet-colored crystals (The synthesis procedure was given in the Supporting Information).

Single-crystal X-ray diffraction data were collected at 293 K by Xta-Lab mini (RIGAKU) with Mo-Kα radiation. Data-collection scaling and absorption corrections were performed by the CrysAlisPro program (Rigaku Oxford Diffraction, 2015). Crystal data and refinement detail are given in Table 1. An initial structure was determined using a dual space method with SHEXL-2014/4, and refined by full-matrix least-squares on F² with SHEXL-2018/3.15 All hydrogen atoms were generated by geometrical calculations and treated using a riding model with Uiso(H) = 1.2 × Ueq(C) or 1.5 × Ueq(O).

Complex I crystallizes in the monoclinic space group of C2/c. The crystal structure contains two non-coordinated SASO₃⁻ anions and one [Fe(phen)]²⁺ cation (Fig. 2). The central iron(II) ion is located on the two-fold axis. The coordination geometry of the iron(II) ion is a square planar coordination of nitrogen atoms of the phenanthroline ligands. The iron(II) ion is located on the two-fold axis.

![Chemical structure of complex 1](image)

Fig. 1 Chemical structures of complex 1.

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Table 1 Crystal data and refinement detail of 1

| Parameter | Value |
|-----------|-------|
| Chemical formula: C₃₆H₂₄N₆Fe, 2(C₁₃H₁₀NO₄S) | |
| Formula weight | 1149.02 |
| Temperature | 293.15 K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | C2/c |
| a = 26.951(3) Å | |
| b = 10.8492(8) Å | β = 125.390(19)° |
| c = 21.899(3) Å | |
| V = 5220.1(14) Å³ | Z = 4 |
| Z' = 0.5 | |
| Density | 1.462 g·cm⁻³ |
| F(0 0 0) | 2376 |
| Crystal size: 0.2 × 0.1 × 0.1 mm³ | |
| Reflections collected/unique | R[1σ(int)] = 6441 [0.0258] |
| θ range for data collection: 2.629 to 28.281° | |
| Completeness (theta) = 99.4% | |
| Data/Restraints/Parameters | 6441/0/367 |
| Goodness-of-fit on F² | 1.063 |
| R indices | |
In a related study, the isostructural crystals [Cu(phen)3]2+ and [Ni(phen)3]2+ cations are stacked alternatively along the [Fe(phen)3]2+ cation. Thus, SASO3– anions and molecular conformation of the SASO3– anion in the crystal.12 Also, both crystals showed a slight thermochromic color change as the temperature was lowered. In the study, temperature-controlled fluorescence spectroscopy showed that SASO3– anions tautomerized from keto to enol form when the temperature was lowered. However, the thermochromic color changes were unclear because the intense MLCT absorption band of the phenanthroline metal complexes covered a small color change of the SASO3– anions.

In this study, we successfully synthesized and determined the crystal structure of a complex salt crystal containing SA derivative anions and tris-phenanthroline Fe(II) complex cations. Crystals of 1 did not exhibit photochromism due to the small twisted conformation of SASO3– anions. Moreover, the thermochromic color change was unclear because of the strong MLCT absorption band of the [Fe(phen)2]2+ cation. Although crystals of 1 did not exhibit either photochromism or thermochromism, a salt formation with metal complex cations is one of the promised methods to develop SA-based chromic materials through changing the chromism colors and activities.

Supporting Information

This material is available free of charge on the Web at http://www.jsac.or.jp/xraystruct/.

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