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Organometallic cyanotype: formation of Prussian blue by a photochemical decomposition of the arene iron complex

Dmitry S. Perekalin,* Dmitry S. Shved and Yulia V. Nelyubina

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: dsp@ineos.ac.ru

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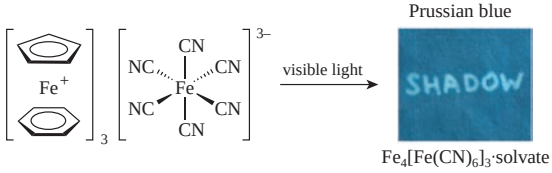
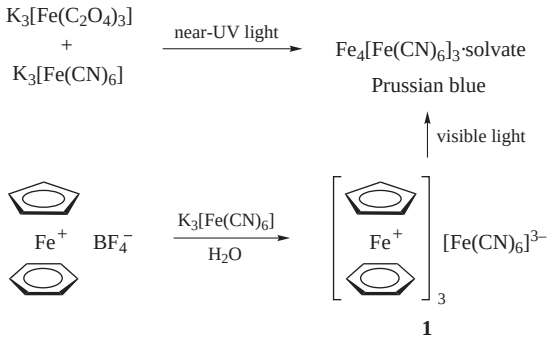
Complex salt $[(C_5H_5)Fe(C_6H_6)]_3[Fe(CN)_6]$ was synthesized and studied by X-ray diffraction. This salt was transformed into Prussian blue pigment upon the irradiation by visible light, which makes this reaction applicable to a photocopying (cyanotype) process.



The cyanotype is among the oldest known photography processes.[1] For the first half of the 20th century, it served as a main method for the production of copies of technical documents (so-called 'blueprints'), whereas nowadays it is mostly used by artists and chemistry teachers.[2] The cyanotype process is based on formation of Prussian blue pigment from $K_3[Fe(CN)_6]$ and Fe^{II} ions, which are formed *via* the photochemical decomposition of Fe^{III} oxalate or citrate (Scheme 1).[3,4] Herein, we report on the alternative cyanotype process, which is based on the photochemical decomposition of organometallic iron complex $[(C_5H_5)Fe(C_6H_6)]^+$.



Scheme 1 Classic cyanotype (top) and organometallic approach (bottom).

Sandwich complexes $[(C_5H_5)Fe(arene)]^+$ can be easily obtained *via* a reaction of ferrocene with arenes in the presence of $AlCl_3$.[5–7] They are stable both in air and water, but undergo decomposition under visible light irradiation to give Fe^{2+} cations, ferrocene and arene.[8] The type of arene and counter-anion can be varied, which allows one to vary the properties of these complexes, including solubility, absorption spectra, and the rate of photochemical decomposition. Thus, the complexes $[(C_5H_5)Fe(arene)]^+$ are widely studied as initiators for the controlled polymerization of epoxides.[9]

In the present work, we chose the simplest benzene complex $[(C_5H_5)Fe(C_6H_6)]BF_4$.† Its reaction with $K_3[Fe(CN)_6]$ in water led to the precipitation of complex $[(C_5H_5)Fe(C_6H_6)]_3[Fe(CN)_6]$ **1** and KBF_4 salt, which possess comparably moderate solubility (see Scheme 1). Complex **1** was extracted from this mixture by methanol and crystallized as bright yellow needles in 71% yield. The NMR spectra of **1** contained the characteristic upfield shift of signals of the cyclopentadienyl and benzene ligands (for 0.23 and 0.47 ppm, respectively) as compared to the starting complex $[(C_5H_5)Fe(C_6H_6)]BF_4$, due to the presence of paramagnetic counter-ion $[Fe(CN)_6]^{3-}$. The crystal structure of solvate **1**·$6H_2O$ was determined by the single crystal X-ray diffraction (Figure 1).‡ Note that complex **1** can form solvates containing a various number of incorporated water molecules: the sample chosen

† A solution of $K_3[Fe(CN)_6]$ (49 mg, 0,15 mmol) in water (3 ml) was added to a solution of $[(C_5H_5)Fe(C_6H_6)]BF_4$ (129 mg, 0,45 mmol) in deionized water (3 ml) in the dark. The light yellow precipitate formed; the solution was pale yellow indicating that some amount of iron complex remained dissolved. The precipitate was isolated by centrifugation and dried *in vacuo*. It was then extracted with methanol (3 × 5 ml), the combined extracts were concentrated to 5 ml and the product was crystallized by diffusion of Et_2O vapors. The yield was 94 mg (71%). The compound is air stable, but light sensitive. It is readily soluble in methanol, moderately soluble in water, insoluble in acetone and Et_2O. The crystals for the single crystal X-ray diffraction were obtained by cooling saturated aqueous solution in the fridge (4 °C). ^{1}H NMR (Bruker Avance 400, 400 MHz, CD_3OD) δ: 4.77 (s, 5H, C_5H_5), 5.87 (s, 6H, C_6H_6). FTIR (Hitachi IRPrestige 21, KBr pellet, ν/cm^{-1}): 2110 (CN), 3080 (apparently CH, *cf.* ref. 20), 3400 (H_2O). Found (%): C, 52.96; H, 4.97, N 9.47. Calc. for $[(C_5H_5)Fe(C_6H_6)]_3[Fe(CN)_6]\cdot 4H_2O$ (%): C, 53.16; H, 4.69; N, 9.54. The solvate water molecules were also present in the crystal structure according to the X-ray diffraction data.

‡ *Crystal data for* **1**·$6H_2O$. $C_{39}H_{45}Fe_4N_6O_6$ (M = 917.21), orthorhombic, space group *Cmcm*, at 120 K: a = 11.5296(13), b = 14.4602(13) and c = = 23.980(2) Å, V = 3997.9(7) Å^3, Z = 4 (Z' = 1/4), d_{calc} = 1.524 g cm^{-3}, μ(MoKα) = 14.76 cm^{-1}, F(000) = 1892. Intensities of 34102 reflections were measured on a Bruker APEX2 CCD diffractometer [λ(MoKα) = = 0.71072 Å, ω-scans, 2θ < 54°], and 2344 independent reflections (R_{int} = 0.0445) were used in the further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique on F^2 in the anisotropic-isotropic approximation. Positions of hydrogen atoms were geometrically calculated, and they were refined in the isotropic approximation using the riding model. The refinement converged to wR_2 = 0.1998 and GOF = 1.298 for all the independent reflections [R_1 = 0.0609 was calculated against F for 1745 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.[21]

CCDC 1829493 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

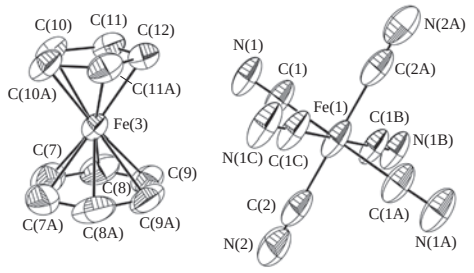


Figure 1 Molecular structure of complex **1**·6H_2O showing thermal ellipsoids at the 50% probability level (disordered cations, solvate H_2O molecules and hydrogen atoms are omitted). Selected interatomic distances (Å): Fe(1)−C(1) 1.944(5), Fe(1)−C(2) 1.952(12), Fe(3)−C(7) 2.058(5), Fe(3)−C(8) 2.069(5), Fe(3)−C(9) 2.074(4), Fe(3)−C(10) 2.043(4), Fe(3)−C(11) 2.048(4), Fe(3)−C(12) 2.033(6).

for X-ray diffraction experiment was **1**·6H_2O, while according to the elemental analysis data, the composition was **1**·4H_2O. The geometry of $[(C_5H_5)Fe(C_6H_6)]^+$ and $[Fe(CN)_6]^{3-}$ ions was generally similar to that observed in the known compounds $[(C_5H_5)Fe(C_6H_6)]PF_6$ and $(NH_4)(NEt_4)_2[Fe(CN)_6]·3H_2O$.[10,11] Noteworthy, the anions $[Fe(CN)_6]^{3-}$ in **1**·6H_2O formed intermolecular contacts with water molecules rather than with the cations $[(C_5H_5)Fe(C_6H_6)]^+$.

Irradiation of aqueous solution of complex **1** by visible light (incandescent lamp, 60W) provided a considerable amount of Prussian blue in 10 min. However, the product was difficult to isolate since it formed a colloid solution. In contrast, irradiation of **1** in methanol quickly gave the well-formed precipitate of Prussian blue, which was isolated in 85–90% yield.§ Because of the known tendency of Prussian blue to form non-stoichiometric solvates,[12] the elemental analysis of the product varied for different experiments (*e.g.*, one of the samples corresponded well to the formula $Fe_4[Fe(CN)_6]_3·7H_2O·5MeOH$). Nevertheless, the identity of the product was confirmed by the characteristic strong and broad absorption band at 2066 cm^{-1} in the IR spectrum, which was assigned to the vibration of CN ligand in Fe–CN–Fe moiety.

We conducted qualitative cyanotype tests using complex **1** in comparison with the classic ferrioxalate system[2] (Figure 2).¶ The paper samples were soaked in the solution of complex **1** or $K_3[Fe(C_2O_4)_3]/K_3[Fe(CN)_6]$; the concentration of $K_3[Fe(C_2O_4)_3]$ and $K_3[Fe(CN)_6]$ salts corresponded to the concentrations of $[(C_5H_5)Fe(C_6H_6)]^+$ and $[Fe(CN)_6]^{3-}$ ions in the solution of complex **1**. The paper samples were dried, placed under a glass with a non-transparent sign 'shadow', and then irradiated by 60 W incandescent lamp for 10 min. The images produced by photodecomposition of complex **1** had a notably more intensive color as compared with those produced by the ferrioxalate system. The difference became even more pronounced for the paper samples irradiated through the color filters ZS-7 and KS-10, which blocked the most of light with wavelengths 420–500 and 300–600 nm, respectively.[13] In this case, the images produced by decomposition of complex **1** remained visible, while the images produced by ferrioxalate system were almost completely faded. This observation correlates with the well-known fact that the classical cyanotype procedure requires near-UV light with wavelength range of about 300–400 nm.[1,14] On the contrary, photodecomposition of the $[(C_5H_5)Fe(arene)]^+$ complexes is effective under the visible light (*e.g.*, quantum efficiency of photodecomposition was about 0.6 at 458 nm irradiation and 0.15 at 683 nm).[15]

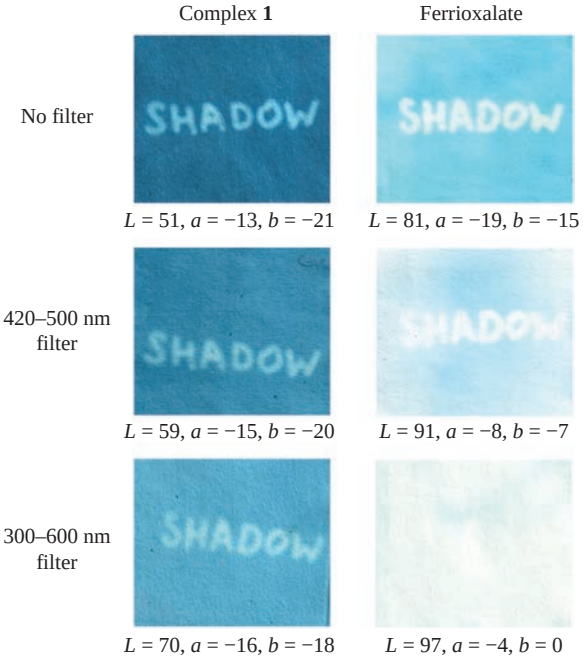


Figure 2 Cyanotype results for complex **1** and the classic ferrioxalate system $K_3[Fe(C_2O_4)_3]/K_3[Fe(CN)_6]$.

We also attempted to produce cyanotypes using another organometallic photosensitive system, *viz.*, the mixture of ferrocene with CBr_4.[16] Under near-UV irradiation (λ_{max} ~ 390 nm) ferrocene was oxidized by CBr_4 to initially afford ferrocenium cation $[(C_5H_5)_2Fe]^+$ and eventually Fe^{3+} ion.[17,18] The paper samples were treated with solution of Cp_2Fe/CBr_4 mixture in CH_2Cl_2 and then with aqueous solution of $K_3[Fe(CN)_6]$ or $K_4[Fe(CN)_6]$. The samples were irradiated by incandescent lamp and then heated at 80 °C in order to promote autocatalytic reaction as well as to remove the residual ferrocene and CBr_4 by sublimation. However, cyanotype images were not formed. In particular, the samples with $K_4[Fe(CN)_6]$ remained pale (*i.e.*, no Prussian blue formed), while the samples with $K_3[Fe(CN)_6]$ became bright blue even without irradiation, presumably due to the oxidation of ferrocene. Perhaps, the quality of images may be

§ A solution of complex **1**·4H_2O (43 mg, 0.049 mmol) in methanol (5 ml) was placed in the Petri dish (diameter of 10 cm) and irradiated for 15 min with 60 W incandescent lamp placed ~20 cm above the dish. Irradiation of the solution in the test tube was notably less efficient presumably due to an inner-filter effect. The blue precipitate formed was suspended in additional methanol and collected by centrifugation. It was then successively washed with water (3 ml), methanol (3 ml), Et_2O (6 ml), and then dried *in vacuo*. The yield was 17 mg (90%, based on $Fe_4[Fe(CN)_6]_3·7H_2O·5MeOH$ formula and $[Fe(CN)_6]^{3-}$ as the limiting reagent). FTIR (Hitachi IRPrestige 21, KBr pellet, ν/cm^{-1}): 3400 (H_2O), 2066 (CN, lit.,[22] 2080). Found (%): C, 24.20; H, 2.36; N, 21.80; Fe, 35.5. Calc. for $Fe_4[Fe(CN)_6]_3·7H_2O·5MeOH$ (%): C, 24.11; H, 2.99; N, 22.01; Fe, 34.12.

¶ Complex **1**·4H_2O (50 mg, 0.058 mmol) was dissolved in methanol (5 ml). A mixture of $K_3[Fe(C_2O_4)_3]·3H_2O$ (85 mg, 0.174 mmol) and $K_3[Fe(CN)_6]$ (19 mg, 0.058) was dissolved in water (5 ml). The solutions were poured into two Petri dishes. The paper samples (4×4 cm) were soaked in the solutions for 5 min and dried at 60 °C in the dark. Then the samples were covered by a glass with a 'shadow' sign and irradiated for 10 min by 60 W incandescent lamp, which was placed ~10 cm above them. Finally, the samples were washed several times with water and dried. The estimates of the color intensity were obtained from scanned samples using color averaging function of Adobe Photoshop CS software. The colors are represented as the unitless CIELAB parameters: *L* (lightness), *a* (red-greenness), and *b* (yellow-blueness). Although these results can be considered only as qualitative, value *L* clearly shows the difference in intensity of color of the samples (see Figure 2). Ferrioxalate system was more effective if the initial solutions were acidified to pH ~ 2 by the diluted sulfuric acid, however the images still had less intensive colors than those produced by complex **1** (see Online Supplementary Materials).

improved by an adjustment of reagent concentrations as well as conditions of irradiation and heating. However, given the more complex procedure of sample preparation, this system was not further investigated.

In conclusion, we have demonstrated the utilization of organometallic complex $[(C_5H_5)Fe(C_6H_6)]^+$ as the light-sensitive component for the cyanotype process. Compared to the classic agent $K_3[Fe(C_2O_4)_3]$, the organometallic iron complex is notably more sensitive to irradiation by the visible light (400–700 nm) and therefore produces brighter images. Another advantage is the opportunity to adjust the properties of $[(C_5H_5)Fe(arene)]^+$ complexes *via* a modification of their structure. Apart from the cyanotype process, the developed photochemical synthesis of Prussian blue may also be useful for manufacturing electroactive films and sensors.[19]

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.01.024.

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