

# A New Approach toward Cyanotype Photography Using Tris-(oxalato)ferrate(III): An Integrated Experiment

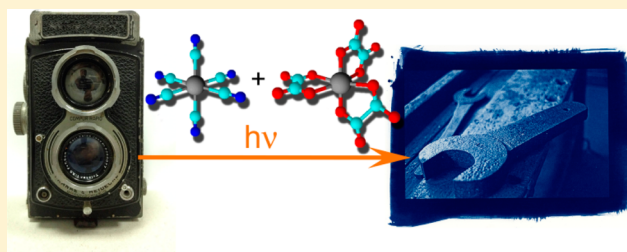
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## S Supporting Information

**ABSTRACT:** This work presents an approach that integrates the preparation of a coordination compound, potassium tris-(oxalato)ferrate(III), with its photochemical behavior and provides a possible application, the printing of a photograph using the cyanotype technique. Through this experiment, students can be taught several concepts that occur in a coordination chemistry course, including the thermodynamic aspects of forming a compound, its photochemistry, the detection of its photoproducts, and the observation of the formation of a new compound and the resulting intervalence band, which generates the blue print.

**KEYWORDS:** Upper-Division Undergraduate, Inorganic Chemistry, Interdisciplinary/Multidisciplinary, Hands-On Learning/Manipulatives, Photochemistry



## INTRODUCTION

Iron(II,III) hexacyanoferrate(II,III), commonly known as Prussian blue, is a coordination compound that is often used as an example in the instruction of several topics during coordination chemistry courses. This compound can be introduced during a historic overview that discusses its discovery in the 16th century and its influence on the arts.<sup>1</sup> Later, when the intervalence absorption spectrum is presented, Prussian blue can be used as an example while discussing this concept with the students. In our approach to coordination chemistry, we prefer to demonstrate some applications of the prepared compounds, and an experiment demonstrating the photochemical processes of coordination compounds that can be used for this purpose.

The tris-(oxalato)ferrate(III) ion is useful for several undergraduate experiments<sup>2,3</sup> and is especially interesting when demonstrating photochemical processes. This complex is a well-known chemical actinometer; therefore, its photochemical reactions and quantum yield are well understood and established. Before determining its photochemical processes, students can prepare this compound and measure its absorption spectrum. Through this approach, this complex can be utilized during an integrated course because students can perform the synthetic procedures, discuss the reaction yields and complex formation, obtain absorption spectra, and discuss the electronic transitions involved in the light absorption process. Finally, the photochemical reactions involving this compound can be discussed.

The photochemical reaction of tris-(oxalato)ferrate(III) releases  $\text{Fe}^{2+}$  ions to the medium, which can be conveniently employed during the formation of Prussian blue. This process is utilized in the production of a cyanotype, which is one of the oldest photographic processes. Briefly, this technique involves coating a paper with a mixture of potassium ferricyanide and a

ferric salt, such as tris-(oxalato)ferrate(III). When the paper is exposed to light, the ferric salt is reduced to a ferrous salt, which precipitates Prussian blue when using ferricyanate, providing permanent images in an elegant assortment of blue hues. When used during photography, the cyanotype requires a negative that is the same size as the final print. The resulting image is highly stable but can be degraded by alkaline solutions, which hydrolyze Prussian blue.<sup>4</sup> Previous reports propose that using old photography techniques will increase interest in the hard sciences<sup>5,6</sup> while explaining the cyanotype process<sup>7,8</sup> or to introduce the concept of the *human element* at chemistry education.<sup>9</sup>

We report an integrated experiment for chemistry students in their third-year to be conducted in two or three laboratory sessions of 2 h each. The students begin by preparing and characterizing potassium tris-(oxalato)ferrate(III) before investigating its photochemical behavior and applying it to a photographic process, which involves the formation of Prussian blue.

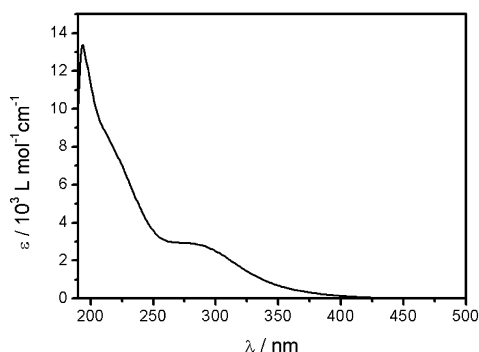
## EXPERIMENTAL OVERVIEW

### Preparation of the $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ Sensitizer

The  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$  complex can be easily prepared and purified by students within a 2 h laboratory session when using a procedure described in the literature.<sup>10,11</sup> Briefly, potassium oxalate monohydrate (12.2 g; 66 mmol) is dissolved under vigorous stirring in 10–20 mL of water at 55 °C. Subsequently,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (6.0 g; 22 mmol) in 5 mL of water is poured into the solution, and the mixture is stirred for 30 min at 45 °C. Green crystals are obtained after the mixture reaches room

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temperature; they are washed with 3 mL of cold water. The compound is then recrystallized by dissolving the solid in a minimal volume of water at 65 °C and slowly cooling the solution to room temperature. The students achieved yields of 5.4–6.5 g (50–60%). The compound can be characterized by its absorption spectrum in  $\text{H}_2\text{SO}_4$  (0.1 mol  $\text{L}^{-1}$ ) solution ( $\epsilon_{193\text{ nm}} = 1.3 \times 10^4\text{ L mol}^{-1}\text{ cm}^{-1}$ ;  $\epsilon_{280\text{ nm}} = 2.9 \times 10^3\text{ L mol}^{-1}\text{ cm}^{-1}$ ), Figure 1.



**Figure 1.** Absorption spectrum of the prepared compound  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$  in  $\text{H}_2\text{SO}_4$  (0.1 mol  $\text{L}^{-1}$ ) solution.  $[\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}] = 1.28 \times 10^{-4}\text{ mol L}^{-1}$ .

### Sensitized Paper

**Caution!:** This procedure should proceed under reduced light.

A mixture of 5 mL of a 0.3 mol  $\text{L}^{-1}$   $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$  in an acidic solution (0.1 mol  $\text{L}^{-1}$   $\text{H}_2\text{SO}_4$ ) and 5 mL of 0.3 mol  $\text{L}^{-1}$  potassium ferricyanide solution is painted onto watercolor paper, which is left to dry in the dark. Any unused solutions can be stored separately in brown bottles away from light but will not last long after mixing.

### Photographic Printing

A negative image can be previously prepared by the students or instructors, by using a photographic computer program, such as GIMP, and printed onto a transparency sheet. The negative image is placed onto the sensitized paper and topped with a glass sheet to avoid any changes in position; this apparatus is fixed with clamps and exposed to sunlight for several minutes. The exposure time depends on the weather conditions of the day and must be determined on the day that the experiment is carried out. Alternatively, a studio illuminator can be used to substitute the sunlight. Good results are also achieved by this method. However, longer exposition time is necessary in this case. After exposure to sunlight, the photograph is washed with excess water to remove any remaining sensitizer and immersed in a  $\text{H}_2\text{O}_2$  solution (0.3%). Afterward, the photograph is washed with water to remove any  $\text{H}_2\text{O}_2$ .

### Complementary Experiment

An assay tube containing a few milliliters of the  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  acid solution is exposed to a light source for a few seconds. A few drops of 2,2'-bipyridine ethanolic solution should be added, and the changes should be observed.

A suggestion for student's laboratory procedure for photographic printing and complementary experiment is available as Supporting Information.

### HAZARDS

The use of  $\text{H}_2\text{SO}_4$  should be contained to a fume hood when preparing 0.1 mol  $\text{L}^{-1}$  solution. Concentrated  $\text{H}_2\text{SO}_4$  causes

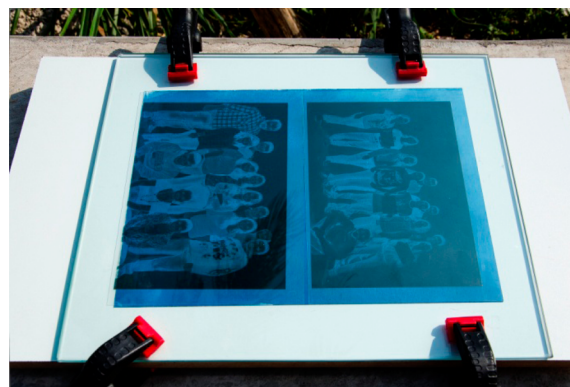
severe skin burns and eye damage. Wear protective gloves, protective clothing, eye and face protection.  $\text{H}_2\text{O}_2$  (30% solution) causes serious eye damage. Wear protective gloves, protective clothing, eye and face protection.

Avoid the exposure of  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  solution to light in order to prevent any undesired photochemical reaction.

## RESULTS AND DISCUSSION

The first part of this experiment involves the synthesis and characterization of a  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  complex. The procedure is simple for a third year student, but some aspects of the reaction are still interesting. The coordination of oxalate to an  $\text{Fe}(\text{III})$  ion is thermodynamically favorable because oxalate is a bidentate ligand, and the chelate effect occurs. The equilibrium constant can be used during this discussion. The chelate effect means that  $K_{\text{formation}} \gg 1$  because the dissociation of the ligand is unlikely; dissociation is disfavored because both chemical bonds must be broken during this process, which is statistically unfavorable. Other thermodynamic aspects, such as the entropy associated with the changes in the degree of freedom because the ligand is coordinated by one or two sites, can also be used for this discussion. The compound can be characterized by its absorption spectrum and the nature of its electronic transitions can also be discussed.

The second aspect of this experiment is the production of a photographic print using the cyanotype technique. The students prepare the sensitized paper and cover it with the negative, and then they use sunlight to observe the formation of the blue print, as shown in Figure 2. During this stage, the

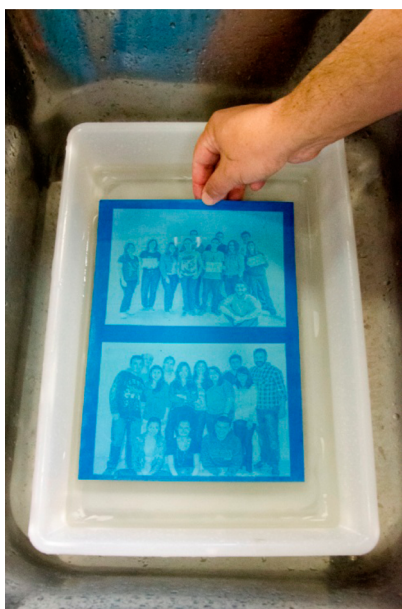


**Figure 2.** Photograph being exposed to sunlight.

students must determine the optimal exposure time needed for the sensitized paper to produce the best blue print. The experiment was carried out on sunny days in Santo Andre, and the exposure time was determined at approximately 1–4 min by the students.

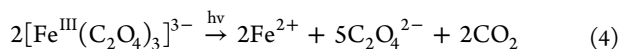
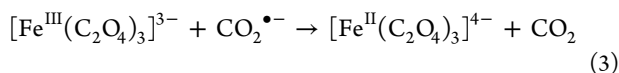
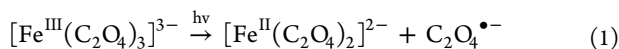
After exposure, the photograph is washed with water until the yellowish solution is no longer released, indicating that the excess sensitizer has been completely removed and the picture is clearly observed as a blue print on the watercolor paper, as shown in Figure 3. Better contrast is observed in the photograph after immersion into the  $\text{H}_2\text{O}_2$  solution, which increases the intensity of the blue color.

Discussion with the students is important to assess their knowledge of the processes that occur to obtain the blue photograph. This discussion begins with the photochemical process of the tris-(oxalato)ferrate(III). This compound is a chemical actinometer, and its photochemical reactions are very well

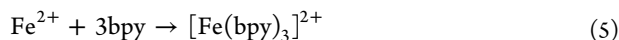


**Figure 3.** Photograph during a water wash to remove the excess sensitizer.

established after having been described by Hatchard and Parker.<sup>10</sup> The primary photochemical reaction shown in eq 1 and the subsequent thermal reactions shown in eqs 2 and 3 release 2 equiv of  $\text{Fe}^{2+}$  ions to the medium, as shown in eq 4.

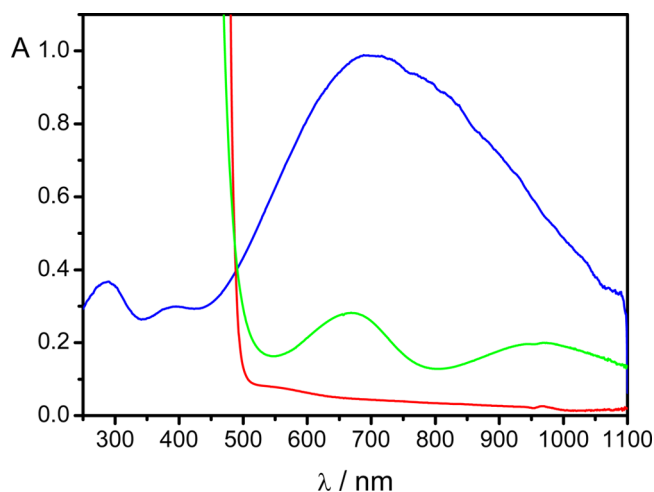


The formation of free  $\text{Fe}^{2+}$  in solution is detected after it reacts with 2,2'-bipyridine, bpy, eq 5, generating an intense red solution due to the MLCT absorption band of  $[\text{Fe}(\text{bpy})_3]^{2+}$  ( $\epsilon \sim 1.1 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) formed in the auxiliary experiment. This experiment is important because the students must explain the formation of the blue print.



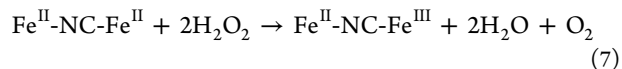
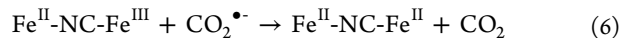
The  $\text{Fe}^{2+}$  ions released by the photochemical reaction of  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  are promptly coordinated to the nitrogen atoms available on the ligands of the  $[\text{Fe}(\text{CN})_6]^{3-}$ . This coordination process forms the Prussian blue  $(\text{Fe}^{\text{II}}\text{--NC--Fe}^{\text{III}})_n$ , responsible for the intense blue color observed in the cyanotype. The blue color is ascribed to the intervalence absorption band of this compound. The absorption spectrum of a blue region of the photograph can be measured using a spectrophotometer with a diffuse reflectance accessory, as shown in Figure 4, and compared to the spectra of  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ .

The existence of excess  $\text{CO}_2^{\bullet-}$  radicals in the medium reduces the  $\text{Fe}^{3+}$  ions in the Prussian blue to  $\text{Fe}^{2+}$ , as shown in eq 6, and the intensity of the blue color decreases because the number of  $\text{Fe}^{\text{II}}\text{--NC--Fe}^{\text{III}}$  moieties responsible for the intervalence absorption band decreases. Immersing the photograph into a  $\text{H}_2\text{O}_2$  solution is necessary to reoxidize these  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  ions,



**Figure 4.** Absorption spectrum of a blue region of the photograph measured using a diffuse reflectance technique (blue line) and the absorption spectra of  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  (green line) ( $0.3 \text{ mol L}^{-1}$ ) and  $[\text{Fe}(\text{CN})_6]^{3-}$  (red line) ( $0.3 \text{ mol L}^{-1}$ ) in  $\text{H}_2\text{SO}_4$   $0.1 \text{ mol L}^{-1}$  solution (optical path =  $1.000 \text{ cm}$ ).

as shown in eq 7. This process recovers the intervalence band and, consequently, enhances the contrast of the photograph.



Finally, a cyanotype photograph is produced for the students to keep, Figure 5.

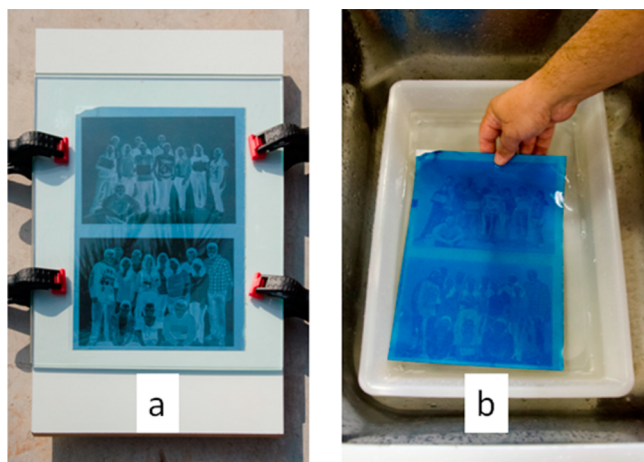


**Figure 5.** Cyanotype photograph prepared by the students.

### Overexposure

Exposing the photograph to sunlight for longer periods (approximately 10 min) produces interesting results. These photographs initially provide a surprisingly accurate reproduction of the negative. After washing with water, the same result is observed, but the photograph is correctly printed after immersion in  $\text{H}_2\text{O}_2$ , as shown in Figure 6.

Overexposure to sunlight results in an extensive photochemical reaction of  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ , which produces a large excess of the  $\text{CO}_2^{\bullet-}$  radical. Consequently, the  $\text{Fe}^{3+}$  ions of the Prussian blue are reduced, as shown in eq 5, to a great extent, and bleaching is



**Figure 6.** Overexposure of the photograph to sunlight (a) and during  $\text{H}_2\text{O}_2$  immersion (b).

observed in the areas exposed directly to sunlight. In the dark regions, no overexposure is observed, but the formation of the Prussian blue responsible for the blue print can be seen. When the photograph is immersed in  $\text{H}_2\text{O}_2$  solution, however, the  $\text{Fe}^{2+}$  is oxidized to  $\text{Fe}^{3+}$ , as shown in eq 6, and the intervalence absorption band is restored. Because a higher concentration of Prussian blue is present in the exposed region, a complete inversion of the image is observed, resulting in the desired photograph.

## CONCLUSIONS

In this experiment, the synthesis of tris-(oxalato)ferrate(III) is integrated with studies of its photochemistry and a possible application. This approach demonstrates that several concepts can be integrated during discussions in a coordination chemistry laboratory. To evaluate that students met the intended learning outcomes, a lab test was applied to a group of students that executed this experiment and to another group to which only the test of  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  was carried out. The students having the integrated experiment demonstrated a better comprehension of the  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  photochemical process as well as the subsequent thermal reactions. During laboratory section, the students having this integrated approach were able to make the correlation of the auxiliary test and the formation of Prussian blue and, thus, with its intervalence absorption band responsible for the blue print.

## ASSOCIATED CONTENT

### Supporting Information

Student laboratory procedure. This material is available via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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