



## Prussian blue and Turnbull's blue: History & Chemistry

Parnajyoti Karmakar

Government General Degree College, Kalna-I, Medgachi, Purba Bardhaman 713405, West Bengal, India

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### Abstract

Prussian blue and Turnbull's blue are two known compounds to undergraduate chemistry students. These two pigments are frequently synthesized in chemistry laboratories during the qualitative tests for the detection of nitrogen as a special element in organic compounds and spot tests in the classical analytical chemistry of iron. However, these compounds have a rich history and exciting chemistry that any chemistry student should be aware of. The objective of this article is to familiarize chemistry students to the interesting history and chemistry of Prussian blue and Turnbull's blue.

**Keywords:** Prussian blue, Turnbull's blue, pigment, qualitative test, Iron

### 1. Introduction

Prussian blue, also known as ferric ferrocyanide or iron(III) hexacyanoferrate(II), is a dark blue chemical that was discovered in Berlin in the beginning of the eighteenth century. Starting in Berlin in 1706, alchemist and theologian Johann Conrad Dippel and colour manufacturer Johann Jacob von Diesbach invented this new synthetic blue pigment [1]. Since 1701, Berlin has been the capital of the newly created Kingdom of Prussia. However, Dippel's initial attempts were focused on converting base metals into gold. But when that was unsuccessful, he focused his attention on the similar type overly optimistic aim of discovering a universal ailment. In this regard, Dippel's "animal oil," which was created by distilling animal blood with added potash, was thought to be the solution to this problem. A color-maker by the name of Diesbach had joined Dippel in his lab in the year 1706. Diesbach was working on making Florentine Lake, a crimson pigment based on shells of the cochineal beetle, one afternoon. He borrowed some potash from Dippel because he had run out of his own. He was not aware that this batch of potash had been contaminated by the iron in the blood used to produce Dippel's animal oil. The result was unexpected; instead of the red Diesbach had anticipated, when he looked into it the next morning, he saw a rich blue pigment. Additional

testing revealed the new pigment to be "color-fast," or stable, which is a vital characteristic for usage in artwork. Moreover, the new pigment was given the name of the country where it was discovered, and it was applied to colour the Prussian army's uniform coats [2]. Whereas Turnbull's blue was prepared in England and named from the name of the supposed discoverer.

There are two distinct stoichiometric groups of Prussian blue complexes that simply comprise iron(II) and iron(III). The first group consists of complexes with alkali ions, such as  $KFe^{III}[Fe^{II}(CN)_6] \cdot xH_2O$ , and the second group consists of complexes without alkali ions, such as  $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot xH_2O$ . In the equation  $xH_2O$ ,  $x$  can change, but it generally falls between 10 and 16 in the second stoichiometry and less than 10 in the first. Insoluble Prussian blues are complexes that lack alkali ions in contrast to the former soluble Prussian blues, which contain alkali ions. However, historically, the term "soluble" has only been used to describe the propensity of the substance to form colloidal solutions rather than whether it is totally soluble. Additionally, Prussian blue is extremely insoluble in both forms, with a solubility product of  $ca. 1 \times 10^{-41}$  [3].

The origin of this blue colour, as well as the structure and bonding in Prussian Blue, have been the subject of several study and speculations. Particularly, Prussian Blue and Turnbull's Blue were intended to be two distinct substances, iron(III) hexacyanoferrate(II) and iron(II) hexacyanoferrate (III). However, studies conducted in the 1960s utilizing x-ray diffraction and Mössbauer spectroscopy revealed that Prussian blue and Turnbull's blue were made of the identical substances. The same mixed-valence compound as Prussian Blue is created by a very rapid electron transfer between the iron(II) and hexacyanoferrate(III) ions i.e. Turnbull's blue [4-5].

The purpose of this article is to acquaint students to the fascinating chemistry, structure and colour of Prussian blue and Turnbull's blue, two significant pigments.

### 2. Synthesis

The precipitation reaction provides the basis for the direct and indirect techniques that are now exploited to synthesize Prussian blue pigments.

In one step, soluble or insoluble Prussian blue is prepared using this direct method. Here, a solution of iron(III) salt, such as  $\text{FeCl}_3$ , with a solution of ferrocyanide salt, such as  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , or a solution of iron(II) salt, such as  $\text{FeCl}_2$ , with a solution of ferricyanide salt, such as  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , is combined to precipitate the extremely insoluble product.

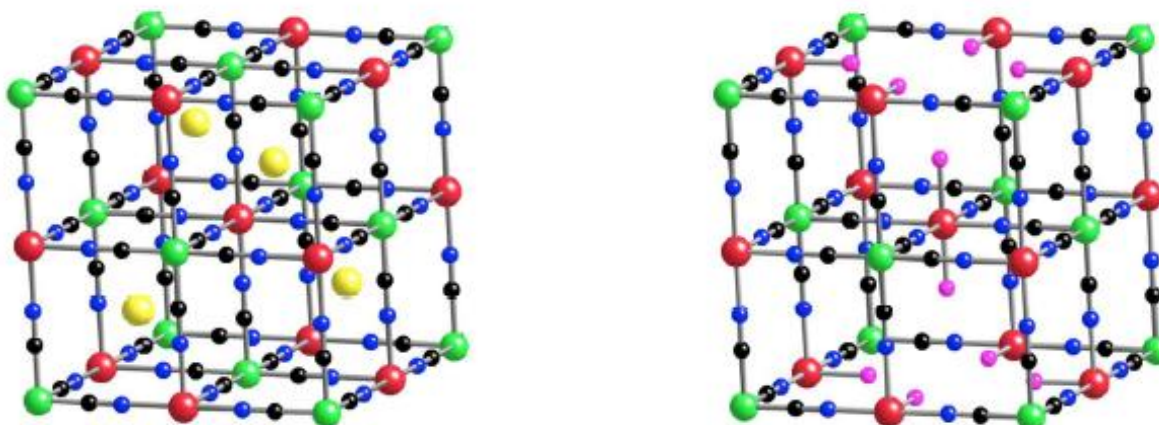
The second indirect method, which produces Berlin white,  $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ , by first combining an iron(II) salt, such as  $\text{FeCl}_2$ , with a ferrocyanide salt, such as  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , results in a white precipitate that is entirely iron(II)-containing. This method is the one that is most commonly used in the pigment industry. The final, soluble or insoluble Prussian blue is created by oxidising Berlin white, typically with  $\text{H}_2\text{O}_2$ .

A one-to-one molar ratio yields soluble Prussian blue, but utilising an excess of iron salt leads in the

precipitation of insoluble Prussian blue in either method [1, 3].

### 3. Structure

Two formulations of prussian blue have been portrayed: the "soluble" form,  $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ ; and the "insoluble" form,  $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$ . For the soluble form, Keggin and Miles proposed a face-centered cubic lattice structure with the  $\text{K}^+$  counter-ion in an interstitial site, and the high-spin ferric and low-spin ferrocyanide sites octahedrally surrounded by  $-\text{NC}$  and  $-\text{CN}$  units, respectively [6]. Although the insoluble Prussian blue structure presented by Ludi et al. in a single crystal study is also a (primitive) cubic lattice, one-fourth of the  $\text{Fe}^{\text{II}}(\text{CN})_6$  subunits are vacant, and such vacant nitrogen sites are now occupied by water molecules coordinated to  $\text{Fe}(\text{III})$  sites, along with up to eight additional water molecules that are interstitial [7]. The interstitial spaces are typically occupied by zeolitic water molecules and/or charge-balancing cations; the hydrogen bond network may aid in stabilising the structure.



**Fig. 1.** The unit cell structure of Prussian blue: **a** soluble  $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ , **b** insoluble  $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$ . Iron(II) ions are depicted as green, iron(III) ions as red, potassium ions are depicted as yellow, carbon is depicted as black, nitrogen is depicted as blue, and aqueous oxygen is depicted as pink. The potassium ion sites in the left figure are only  $\frac{1}{4}$  occupied. With permission from the Royal Society of Chemistry (F. Grandjean, L. Samain and G. J. Long, 2016), the unit-cell crystal structure of both soluble and insoluble Prussian blue is reproduced here.

### 4. Origin of colour

Prussian blues, including both soluble  $\text{KFe}_2(\text{CN})_6$  and insoluble  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ , exhibit a vivid deep blue colour when light-coloured aqueous  $\text{Fe}^{\text{II}}$  and  $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$  (or  $\text{Fe}^{\text{III}}$  and  $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ ) are combined. Its striking blue colour is the result of an intervalence charge transfer from an iron(II) ion to an iron(III) ion. A wavelength of about 700 nm centres the corresponding strong metal to

metal charge transfer absorption band. Because of this powerful absorption, prussian blue was widely employed as a colour in oil paintings and other cultural goods [1].

### 5. Magnetism

As it can be prepared at room temperature from chemically stable and well-characterized building blocks, the metal centres are linked covalently into a 3D network, and a variety of metals with different

spin states and oxidation states can be substituted into the structure, Prussian Blue structures are particularly alluring. Additionally, the bridging cyanide ligands can greatly promote magnetic exchange couplings between paramagnetic centres. These properties allow for extensive control over the type and intensity of local magnetic exchange interactions.

Prussian Blue was established to be a ferromagnet with  $T_c = 5.6\text{K}$ . Due to the diamagnetic nature of the low-spin spin  $d^6$   $\text{Fe}^{\text{II}}$  centres, which occupy the strong ligand-field locations, the magnetic ordering temperature is quite low. As a result, the through-bond distance between two paramagnetic high-spin  $d^5$   $\text{Fe}^{\text{III}}$  is  $10.28\text{\AA}$  in  $\text{Fe}^{\text{III}}\text{-NC-Fe}^{\text{II}}\text{-CN-Fe}^{\text{III}}$  entities, and the exchange coupling that results is quite weak. Ferromagnetism between the high-spin  $\text{Fe}^{3+}$  ions is caused by the mingling of the ground state and low-lying inter-valence  $\text{Fe}^{\text{II}}\text{-Fe}^{\text{III}}$  excited state [8].

### 6. Uses

From the middle of the eighteenth century to the beginning of the twentieth century, painters employed Prussian blue as a pigment in oil paintings and watercolours. Blue jeans, blueprints, and cyanotype photography have all used prussian blue. It is also used in typewriter ribbons and carbon paper although they are obviously no longer in use. To find iron in tissue or cell samples, prussian blue is often employed in histology, histopathology, and clinical pathology.

In the 1960s, Prussian blue was discovered to be a versatile substance for resolving complex problems. It all started with the discovery of its potential utility as a thallium and radioactive cesium-137 poison antidote, an application that is still widely used today. Insoluble Prussian blue, when taken orally, can increase the excretion of radioactive cesium and thallium ions into the stool during the enterohepatic cycle, inhibiting reabsorption and lowering the body's radioactive load.

It is also widely studied because of its electrochromism, low-temperature magnetism, semiconductor behaviour, and zeolitic nature.

### 7. Conclusion

A chemistry student should be knowledgeable about the intriguing past of Prussian blue and its analogues as well as their characteristics and potential applications. Additionally, the accidental discovery of Prussian blue demonstrates how minor errors made during laboratory work can result in significant, unanticipated discoveries. So pupils, don't be afraid of making mistakes because this too may be an opportunity. Prussian blue has many applications, and more research into this

substance is required as some of these uses are still being discovered but have the potential to significantly enhance existing products and procedures in a wide range of human pursuits.

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