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Prussian Blue—A Perpetual Challenge to Inorganic Chemists *

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Summary

Single-crystal X-ray studies of Prussian Blue, $Fe_4[Fe(CN)_6]_3 . 15\ H_2O$ show that the structure contains three different coordinations units: $[Fe(II)C_6]$ and two distinguishable $[Fe(III)N_{6-x}(H_2O)_x]$ octahedra. The overall structure can be approximately described as cubic face-centred. The correct unit cell, however is cubic primitive.

1. Introduction

For more than 250 years the iron cyanide called Prussian Blue or Berlin Blue has attracted the scientific curiosity of inorganic and physical chemists. This attraction and fascination is certainly due to the intense blue colour of this compound which was precipitated by combining the two virtually colourless solutions of Fe^{3+}_{aq} and $Fe(CN)^{4-}_6$. Equally blue products can be obtained when the oxidation states are interchanged, i.e. by mixing solutions of Fe^{2+}_{aq} and $Fe(CN)^{3-}_6$. Accordingly a confusing multitude of names appeared in the chemical literature: soluble and insoluble Prussian Blue, Turnbull's Blue, Williamson's Violet, Parisian Blue [1]. The rather recent application of Mössbauer spectroscopy [2] and ESCA [3] finally showed all these blue iron cyanides to be identical as far as the combination of oxidation states is concerned. Low-spin iron(II) is coordinated by six carbon atoms whereas the nitrogen ends of the cyano groups form

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the coordination octahedron of high-spin iron(III), the basic structural element thus being Fe(II)–C–N–Fe(III).

Despite the numerous investigations carried out with Prussian Blue its crystal structure and even its stoichiometry remained partially unresolved for a long time. Reliable analytical characterizations were impeded by the fact that Prussian Blue could only be prepared as a powder with an extremely small particle size showing a very broad range of hydration. Various ions present in the mother liquor, in particular potassium, are easily adsorbed leading thus to erroneous results for the bulk composition [4].

The foundation of all the structural work was laid down forty years ago by Keggin and Miles [5] by showing that the X-ray powder patterns of Prussian Blue correspond to a cubic face-centred cell with a lattice constant of about 10 Å. This first structural hypothesis postulated a tight three-dimensional cubic network of Fe–C–N–Fe units. Electroneutrality of the crystal was maintained by the assumption of uncoordinated metal ions randomly distributed in interstitial sites. Due to the lack of suitable crystalline samples this structural hypothesis was not tested by measurements of the density nor by appropriate crystallographic calculations.

The structure model derived by Keggin and Miles has been applied to the entire class of cubic polynuclear cyanides [6]. Our studies of transition metal cyanides lead to a modification of the Keggin-Miles structure. The modified structure does not contain interstitial transition metal ions and provides defined lattice positions for the water molecules in agreement with the analytically determined degree of hydration [7].

2. Recent Development. Crystal Growth and Crystal Structure Analysis

Prussian Blue can be dissolved in concentrated hydrochloric acid and reprecipitated by dilution with water [8]. A systematic variation of this procedure finally yielded single crystals suitable for X-ray work [9]. In a typical experiment 90 m moles of $FeCl_3$ and 67 m moles of $H_4Fe(CN)_6$ were dissolved in 1500 ml 10M HCl. Slow diffusion of water vapour into this solution produced crystals with edges up to 0.12 mm within about 10 weeks. Chemical analyses of several samples agree with the formula $Fe_4[Fe(CN)_6]_3 \cdot 15H_2O$ with small amounts (1 to 2%) of K^+ and Cl^- as impurities. The crystal data are as follows [9]:

$Fe_4[Fe(CN)_6]_3 \cdot 15H_2O$ cubic, $a = 10.166(2)$ Å
$d_{exp} = 1.75$ to 1.81 gcm^{-3} (5 samples)
$d_{cal} = 1.78$ gcm^{-3} for one formula unit per cell

Careful measurements of the intensities for four crystals revealed the occurrence of weak reflections not obeying the extinction rule for face-centred symmetry (Table 1). The dominating reflections with either even or odd indices do not vary in their intensities from crystal to crystal. The additional «primitive» reflections, however, show considerable variations from one crystal to the other. We may therefore consider the face-centred structure only as a first approximation to the overall structure.

Table 1: Distribution of Intensities of Prussian Blue

Crystal	Number of Observed Reflections	
	a)	b)
1	60	105
2	133	13
3	73	–
4	47	1

a) h,k,l all even or all odd (face-centred)
b) h,k,l with mixed parity (primitive)

Since the unit cell contains one formula unit of $Fe_4[Fe(CN)_6]_3 \cdot 15H_2O$ the positions of Fe(III) and Fe(II) do not have the same occupancies. The positions of Fe(II), C, and N are occupied to only 75% by these atoms, the empty nitrogen sites being filled by water molecules. Due to the face-centred symmetry of this model the corresponding vacant lattice sites are assumed to be distributed completely at random (Fig. 1). Consequently only the average composition $[FeN_{4.5}(H_2O)_{1.5}]$ can be given for the coordination unit of Fe(III). Fe(II) on the other hand sits in a regular $[FeC_6]$ octahedron. Crystallographic calculations show that the face-centred model gives a good general description of the structure of Prussian Blue [10]. Finer details, however, are only obtained if a proper primitive unit cell is chosen.

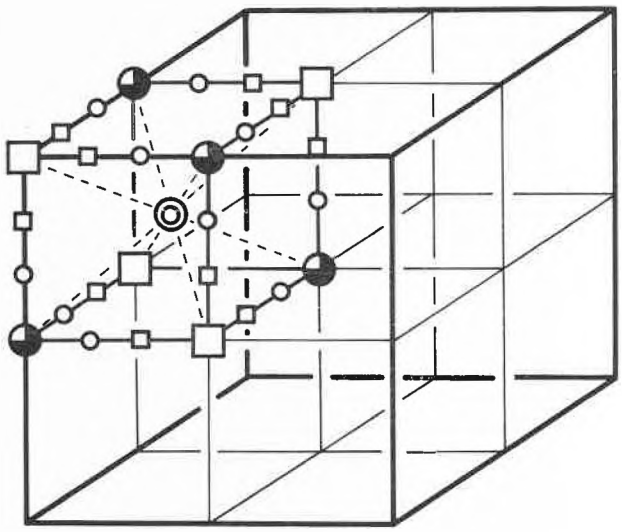

Fig. 1: The Unit Cell of Prussian Blue, Face-Centred Approximation
□: Fe(III); ◕: 0,75 Fe(II); ○: 0,75 C;
□: 0,75 N + 0,25 O; ◎: Zeolitic Water

When the structure is described in terms of the appropriate primitive space group O_h^1-Pm3m the atoms of each kind are distributed in several structurally inequivalent positions [11]. This is particularly important for Fe(II), C, N where various distributions are possible. These arrangements are described by two new parameters which also define the composition of the two non-equivalent $[Fe(III)N_x(H_2O)_{6-x}]$ octahedra [10]. The values of these parameters have to be determined in the course of the crystallographic calculations. It can be shown that variations of these parameters do not affect the face-centred intensities but only the primitive ones. For crystal 1, the one with the highest number of primitive reflections, complete crystallographic calculations have been carried out. The best results ($R = 6.3\,\%$) were obtained for a completely ordered structure: The three Fe(II) fully occupy the threefold position, the coordination polyhedra of Fe(III) are represented by 3 $[FeN_4(H_2O)_2]$ and 1 $[FeN_6]$ (Fig. 2). An additional eight zeolitic water molecules are located at interstitial sites. The following interatomic distances have been determined: Fe–C: 1.93(3) Å, Fe–N: 2.00(2) Å, Fe–O: 2.14(3) Å, C–N: 1.15(3) Å [10]. The primitive structure certainly represents a significant improvement compared to the face-centred overall approximation, but it would be premature to say that this ordered structure is the correct general structure of Prussian Blue. Our results so far represent the best structural description of crystal 1. Slightly different compositions of the two coordination units of Fe(III) will result from solution of the structure of other crystals.

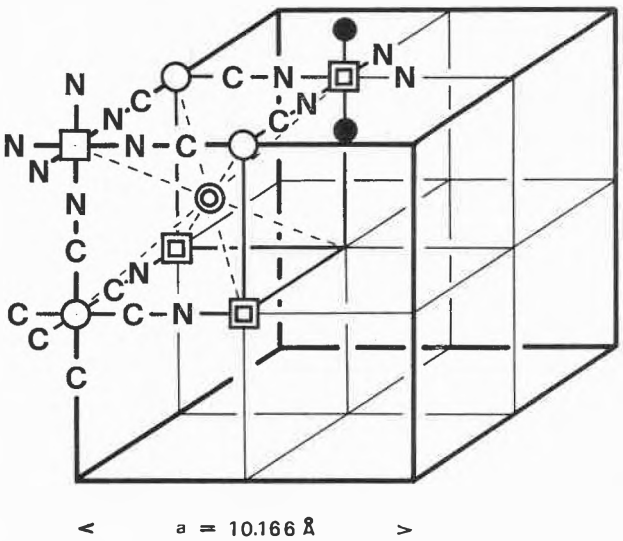

Fig. 2: The Primitive Unit Cell of Prussian Blue
□, ⊡ : Fe(III); ○: Fe(II);
●: Coordinated Water; ◎ : Zeolitic Water

3. Unresolved Problems; Outlook to Future Studies

Whereas the general features of the crystal structure of Prussian Blue could be elucidated from single crystal X-ray studies there are still some questions which have to be answered. It has not yet been possible to locate precisely the water molecules and to get a clear picture of the hydrogen bonding between zeolitic and coordinated water. Also, more crystallographic data should provide better information concerning the two different coordination octahedra of Fe(III). X-ray investigations clearly have to be combined with other experimental techniques in order to solve these problems. Preliminary Mössbauer studies and neutron diffraction experiments are in good agreement with our X-ray results [12]. Moreover these investigations gave new insights into the electronic properties of Prussian Blue demonstrating its ferromagnetic behaviour at temperatures below 5.5 K [12, 13]. The most imminent challenge, however, is faced by the preparative inorganic chemist. Single crystals without contamination have to be grown and the crystal growth has to be improved hopefully to produce crystals in the order of 1 mm. Neutron scattering, Mössbauer spectroscopy, optical studies, and the investigation of semiconducting properties could then be carried out with single crystals. The combined results of these techniques should eventually lead to a deeper understanding of the various properties of our old compound. Prussian Blue is not only an interesting compound on its own. This coordination polymer represents the prototype of mixed valence compounds which have attracted widespread interest during the last years owing to their often remarkable optical, electrical and magnetic properties.

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References

1 Gmelins Handbuch der Anorganischen Chemie, Eisen B, 1932, p. 670.
2 *E. Fluck, W. Kerler* and *W. Neuwirth:* Angew. Chem. *75* (1963) 461.
3 *G. K. Wertheim* and *A. Rosencwaig:* J. Chem. Physics *54* (1971) 3235.
4 *R. E. Wilde, S. N. Ghosh* and *B. J. Marshall:* Inorg. Chem. *9* (1970) 2512.
5 *J. F. Keggin* and *F. D. Miles:* Nature *137* (1936) 577.
6 *B. M. Chadwick* and *A. G. Sharpe:* Advances Inorg. Chem. Radiochem. *8* (1966) 83.
7 *A. Ludi* and *H. U. Güdel:* Structure & Bonding *14* (1973) 1.
8 *H. B. Weiser, W. O. Milligan* and *J. B. Bates:* J. Physic. Chem. *46* (1942) 99.
9 *H. J. Buser:* Ph. D. thesis, Universität Bern, 1975; *H. J. Buser, A. Ludi, W. Petter* and *D. Schwarzenbach:* J. Chem. Soc. Chem. Commun. *1972*, 1299.
10 *H. J. Buser, P. Fischer, A. Ludi, W. Petter* and *D. Schwarzenbach:* to be published in J. Amer. Chem. Soc.
11 «International Tables for X-Ray Crystallography», Vol. 1, Kynoch Press, Birmingham 1952.
12 *H. J. Buser, A. Ludi, P. Fischer, T. Studach* and *B. W. Dale:* Z. phys. Chem. (NF) *92* (1974) 354.
13 *A. Ito, M. Suenaga* and *K. Ono:* J. Chem. Physics *48* (1968) 3597.