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# The Crystal Structure of Prussian Blue: Fe$_4$[Fe(CN)$_6$]$_3$·xH$_2$O

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Single crystals of Prussian Blue, Fe$_4$[Fe(CN)$_6$]$_3$·xH$_2$O ($x$ = 14–16), have been grown by very slow diffusion of water vapor into a solution of Fe$^{3+}$ and Fe(CN)$_6^{4-}$ in concentrated hydrochloric acid. The crystal structure of this compound has been investigated by x-ray diffraction studies of several single crystals from three different preparations. According to the density $d_{\text{exptl}}$ = 1.75–1.81 g cm$^{-3}$, one unit of Fe$_4$[Fe(CN)6]$_3$·xH$_2$O is contained in the cubic primitive elementary cell with $a$ = 10.166 Å, $d_{\text{calcd}}$ = 1.78 g cm$^{-3}$ for $x$ = 15. The observation of non-face-centered reflections indicates a deviation from the well-known model for cubic polynuclear transition-metal cyanides in the space group $Fm3m$ ($O_h^5$). The Fe(CN)$_6$ positions are only partly occupied. Partial ordering of the corresponding vacancies, possibly related to the conditions for growing the crystals, causes the deviation from $Fm3m$ symmetry. The least-squares refinement in the space group $O_h^1$-$Pm3m$ for three different crystals gave $R$ factors of 0.032, 0.042, and 0.046, respectively. The corresponding average distances are Fe(II)–C = 1.92 Å, C–N = 1.13 Å, and Fe(III)–N = 2.03 Å.

## Introduction

The blue pigment called Prussian Blue can be considered as the first synthetic coordination compound.[2] Owing to its intense color, a property which is completely absent in the two constituent mononuclear complexes, Fe$_{\text{aq}}^{3+}$ and Fe(CN)$_6^{4-}$, it also found some analytical applications, e.g., spot tests in the classical analytical chemistry of iron and qualitative tests for nitrogen in organic compounds. Many investigations and speculations were concerned with the interpretation of the origin of this blue color and with the structure and bonding in Prussian Blue.[3] Very often Prussian Blue served as a test substance when new experimental techniques were developed[4,5] and when new theoretical concepts emerged. In particular, it represents the prototype of the mixed valence compounds,[6] a class of compounds which has attracted widespread interest during the last few years.

Depending on the specific conditions of the preparation, a wide variety of different names has been used for this polynuclear cyanide.[7] In particular, Prussian Blue and Turnbull's Blue were assumed to be two distinct compounds, namely iron(III) hexacyanoferrate(II) and iron(II) hexacyanoferrate(III), respectively. The results of various physical techniques, however, unambiguously demonstrated that the final product is always an iron(III) hexacyanoferrate(II) regardless of the combination of the starting complexes.[8] A further distinction was usually made between "soluble" and "insoluble" Prussian Blue. In this context the term "soluble" does not refer to a true solubility but only to the tendency of certain Prussian Blue samples to form colloidal solutions. This distinction has been related to the presence or absence of potassium, the formula KFeFe(CN)$_6$ representing the "soluble" and the formula Fe$_4$[Fe(CN)$_6$]$_3$ representing the "insoluble" form.[7,8]

Although numerous investigations were carried out with Prussian Blue, the details of its crystal structure and even the analytical composition were for a long time only partly resolved. The chemical literature (see ref 7–10 and references cited therein) reports the two formulas KFeFe(CN)$_6$ and/or

$Fe_4[Fe(CN)_6]_3$. Usually these two stoichiometries were assumed to be correct without subjecting the samples to a complete and careful chemical analysis. As a consequence, structural descriptions were given and elaborate and sophisticated physical experiments were performed with samples whose exact composition had not been reliably determined.[10,11] The lack of precise analytical data is easily understood by considering the fact that Prussian Blue was available only as a very fine precipitate. Accordingly, significant amounts of adsorbed ions, in particular potassium, led to erroneous analytical results for the bulk composition. Misleading analytical data can also arise from surface adsorption or zeolitic bonding of organic solvents used in washing the precipitates. These difficulties are not unique for Prussian Blue but are typical for the entire class of polynuclear transition-metal cyanides.[8]

The first structural hypothesis by Keggin and Miles[12] was derived from x-ray powder patterns and postulated the occurrence of interstitial metal ions within the cubic face-centered unit cell in order to achieve electroneutrality. According to this model, the unit cell contains $^4/_3$ formula units of $Fe_4[Fe(CN)_6]_3$, i.e., 4 ferrocyanide octahedra (Fe in "C hole"), 4 iron(III) coordinated by the nitrogen end of the cyanide ("N hole"), and $^4/_3$ ferric ions randomly distributed in an eightfold interstitial position.[12] This postulated content of the unit cell was not conclusively tested by measurements of the density, mainly owing to the extremely small particle size and the analytical uncertainties mentioned above.

In the course of our studies of the structural chemistry of polynuclear cyanides, we derived a general structural model with space group symmetry $Fm3m$ for cubic cyanides of various stoichiometries. This modified version of the Keggin–Miles structure does not contain any uncoordinated interstitial transition-metal ions and provides sufficient crystallographic positions for the water molecules according to the analytically determined degree of hydration.[13] A series of single-crystal x-ray studies confirmed this modified structural description.[14] This work prompted us to intensify our efforts to grow single crystals of Prussian Blue, the prototype of the polynuclear cyanides, and to solve its crystal structure. A first preliminary study showed that the structure of Prussian Blue can be satisfactorily described in terms of the modified model. This investigation, however, also presented evidence for deviations from a face-centered unit cell.[15] A complete x-ray investigation was undertaken in order to obtain a clearer picture of the crystal structure of this well-known compound.

## Experimental Section

**Crystal Growth.** Prussian Blue can be easily dissolved in concentrated HCl and reprecipitated by dilution with water. The x-ray powder pattern of the resulting sample shows very sharp lines but also has a few extra lines which cannot be indexed in terms of the cubic face-centered unit cell.[16] By allowing only a very slow diffusion of water vapor into the HCl solution of Prussian Blue it became possible to grow single crystals suitable for x-ray work. The crystals used in this work were grown by the three following procedures (all the chemicals were of the highest quality available from Fluka or Merck; deionized water was used).

**Sample I.** $FeCl_2 \cdot 4H_2O$ (7.5 mmol) and 2.5 mmol of $K_4Fe(CN)_6 \cdot 3H_2O$ were separately dissolved in water and added to the appropriate amount of hydrochloric acid to give 500 mL of solution containing 10 mol of HCl/L. The beaker with this solution was placed in a desiccator containing approximately 500 mL of water. The stopcock of the desiccator was left open for the diffusion of air into the solution to slowly oxidize the ferrous ions. After 8 weeks dark cube-like crystals with edges up to 0.15 mm could be collected.

**Sample II.** $FeCl_3 \cdot 6H_2O$ (4.8 mmol) and 3.6 mmol of $H_4Fe(CN)_6$, prepared by ion exchange of a $K_4Fe(CN)_6$ solution over a Dowex 50 column, were mixed as above to give 200 mL of solution containing 10 mol of HCl/L. A beaker with this mixture was placed in a nitrogen-filled desiccator containing approximately 500 mL of water.

Table I. Analytical Data for Prussian Blue[a]

| | Sample I | | Sample II | | Sample III | | Fe$_4$[Fe-(CN)$_6$]$_3$·15H$_2$O | |
|---|---|---|---|---|---|---|---|---|
| | A | B | A | B | A | B | A | B |
| Fe | 33.4 | 6.9 | 33.2 | 6.7 | 33.1 | 6.6 | 34.6 | 7 |
| C | 18.1 | 17.3 | 17.9 | 16.8 | 18.3 | 16.8 | 19.1 | 18 |
| N | 21.3 | 17.4 | 21.1 | 17.0 | 20.8 | 16.5 | 22.3 | 18 |
| H$_2$O | 22.8 | 14.5 | 24.7 | 15.4 | 25.9 | 15.9 | 23.9 | 15 |
| K | 1.47 | 0.43 | 0.63 | 0.18 | <0.01 | 0.00 | | |
| Cl | 2.60 | 0.84 | 2.35 | 0.75 | 2.59 | 0.81 | | |
| Total | 99.7 | | 99.9 | | 100.7 | | 100.0 | |

[a] $A$ = percent by weight, $B$ = number of atoms per elementary cell as determined from density and lattice constant.

Some white $H_4Fe(CN)_6$ originally precipitated redissolved after a few days. After 3 weeks, crystals with edges up to 0.07 mm had formed.

**Sample III.** Because sample II was still contaminated with potassium (cf. Table I) owing to incomplete ion exchange, the same procedure was repeated. An ion exchange column with the tenfold capacity required for the actual amount of $K_4Fe(CN)_6$ was used. The absence of $K^+$ in the eluate was verified by atomic absorption spectroscopy. HCl (1500 mL, 10 M) contained 133 mmol of $FeCl_3$ and 100 mmol of $H_4Fe(CN)_6$. After 10 weeks the solid Prussian Blue was collected. The largest crystals had edges of about 0.12 m.

In each preparation the solid product was collected by filtration, washed with 2 M HCl, 0.1 M HCl, and finally a continuous stream of water until no detectable turbidity was formed upon addition of $AgNO_3$. The main portion of the air-dried products consisted of irregulary shaped particles, but a few single crystals with six well-developed faces could always be found, usually on the walls of the beaker used for preparation. The color of the completely opaque crystals was violet by reflected light in air and reddish-purple when the product was immersed in water.

**Analytical Data and Composition. Metals.** The solid samples were treated with boiling concentrated $H_2SO_4$ and the iron sulfate formed was dissolved by adding a minimum of concentrated HCl. K was determined by flame photometry and Fe by complexometric titration[17] after boiling with an excess of $H_2O_2$. C, N, H, and Cl analyses were carried out by the Microanalytical Laboratory of the ETH, Zürich. $H_2O$ was calculated from H and checked by thermogravimetric analysis and by use of a moisture analyzer.

The results of the chemical analyses clearly demonstrate that all of our samples have a composition close to the ideal formula $Fe_4[Fe(CN)_6]_3 \cdot 15H_2O$; i.e., they correspond to the stoichiometry of "insoluble Prussian Blue". The use of concentrated HCl as solvent for growing the crystals invariably leads to a contamination by chloride. Compensation for its negative charge is assumed to be achieved by $H^+$ (as $H_3O^+$)[18] and/or a corresponding small excess of $Fe^{3+}$. Prussian Blue exhibits a very strong tendency to incorporate small amounts of potassium into its lattice. The percentage of potassium, however, was not higher than 2% when the solid product was prepared from $FeCl_3$ and $K_4Fe(CN)_6$ in a ratio corresponding to the stoichiometry of "soluble Prussian Blue", $KFeFe(CN)_6$. The uptake of potassium was also observed when small quantities of Prussian Blue from sample III were kept in contact with KCl solutions of various concentrations for a period of 8 weeks. Even treatment with saturated KCl produced a sample containing only 2.8% $K^+$, i.e., a composition still far from the stoichiometry of "soluble Prussian Blue".

The degree of hydration depends greatly on temperature and humidity. At room temperature and with a relative humidity of about 45%, one formula unit of Prussian Blue contains 14 to 15 molecules of water. Pumping the samples to $10^{-2}$ mm Hg at 70 °C or heating to 150 °C removes approximately 90% of the water. Re-exposure of the solid to ambient conditions of pressure, temperature, and humidity reversibly restores the original degree of hydration.

**Densities** were determined by flotation in the mixture of bromobenzene and bromoform. The density of sample III was also measured pycnometrically. The two methods gave perfect agreement.

**Spectral Characterization.** Infrared spectra (400–4000 cm$^{-1}$) and electronic spectra (5500–35000 cm$^{-1}$) of samples I, II, and III were found to be in good agreement with published data.[3,19]

**Crystal Data.** Very thin crystals of Prussian Blue were optically isotropic under the polarizing microscope. Precession and Weissenberg

**Table II.** X-Ray Data Collection for Prussian Blue

| Crystal no. | Size, μm | Instrument | $2\theta_{max}$, deg | No. of observations[a] $h + k, k + l = 2n$ | Others |
|---|---|---|---|---|---|
| I | 116 × 72 × 116 | Picker FACS-I | 50 | 71 (60) | 155 (103) |
| | | Syntex P1̄ | 50 | | |
| II.1 | 59 × 68 × 68 | Picker FACS-I | 80 | 204 (133) | 22 (6) |
| II.2 | 57 × 55 × 57 | Picker FACS-I | 110 | 227 (73) | Not measd |
| III | 48 × 105 × 105 | Syntex P2₁ | 45 | 56 (47) | 34 (1) |

[a] Number of observations with $I > 3\sigma(I)$ in parentheses.

photographs showed the crystals to belong to the cubic system. The strong dominating reflections with either only even or only odd indices indicate a face-centered lattice. Additional weak reflections with indices of mixed parity were observed, their number and intensities varying from crystal to crystal (cf. next section). The lattice constant $a$ was determined from NaCl-calibrated Weissenberg photographs using the following data: $\lambda(Fe K\alpha_1)$ 1.935 97 Å; $\lambda(Fe K\alpha_2)$ 1.939 91 Å; $\lambda(Fe K\beta)$ 1.756 53 Å; $a_0(NaCl)$ 5.640 05 Å (21 °C).[20] Crystal data for Prussian Blue, $Fe_4[Fe(CN)_6]_3 \cdot 15H_2O$: $a = 10.166$ (3) Å, $d_{calcd} = 1.78$ g cm$^{-3}$ for $Z = 1$, $d_{exptl} = 1.81$ g cm$^{-3}$ (sample I), 1.78 g cm$^{-3}$ (sample II), and 1.75 g cm$^{-3}$ (sample III). No reflections contradicting this unit cell were observed, even after very long exposure time.

**Collection of X-Ray Intensities.** The intensities were collected using three different four-circle diffractometers with monochromatized Mo K$\alpha$ radiation (Table II). The crystals were mounted with a cubic axis approximately parallel to the spindle axis. The orientation and the instrumental lattice constants of the crystals were determined by automatically centering 12 to 15 reflections. The peak half-width under the measuring conditions had a typical $2\theta$ value of 0.2°. The intensities were measured with $\theta$–$2\theta$ scans over $2\theta$ intervals of 1.8 or 2°. Scan rates were 0.5°/min for the strong and 0.125°/min for the weak reflections with the Picker FACS-I. Variable scan rates of the same order of magnitude were used with the Syntex instruments. The background was measured by stationary counting at both ends of the scan interval. No significant change of the intensities of the standard reflections (600, 060, 006) could be observed. Reflections were classified as observed if their intensity $I$ was greater than $3\sigma(I)$ ($\sigma(I)$ = standard deviation as determined from counting statistics and from the intensity variation of the standard reflection). The rather small number of observed reflections for crystal II.2 is due to the fact that in this case a quartz monochromator was used producing a less intense incident x-ray beam than the graphite monochromator used in the other cases. Therefore, more reflections were classified as unobserved. A careful inspection of the intensities showed the Laue class $m3m(O_h)$ to be appropriate.

**Data Reduction and Structural Calculations.** A modified and extended version of the x-ray system of Stewart et al.[21] was used for the reduction and the preliminary refinement of the x-ray data. Absorption and Lorentz and polarization corrections were applied to each data set. The two data sets of crystal I were merged after scaling. Tabulated scattering factors[20] were used to calculate the structure factors with an anomalous dispersion correction[20] provided for Fe. In the final refinement the function $\sum w(|F_o| - |F_c|)^2$ was minimized.[22] Fortran subroutines were included to set the proper relations between the atomic parameters and the derivatives according to the symmetry and the additional constraints used during the refinement. The weights $w$ were initially chosen as $\sigma^{-2}(F_o)$ but were set to unity for the final refinement for reasons mentioned below. The agreement indices used were $R = \sum ||F_o| - |F_c||/\sum |F_o|$ and $R' = (\sum (|F_o| - |F_c|)^2/\sum F_o^2)^{1/2}$. The calculations were carried out at the computation centers in Zürich (CDC 6400/6500), Lausanne (CDC CYBER 70) and Austin (CDC 6400/6600). The scaling of structure amplitudes for the purpose of comparison was accomplished by the least-squares method[23] on a Data General Nova 820 computer. The program, written in Basic, also calculated the agreement indices $r = \sum |F_i - F_I|/\sum {}^1/_2(F_i + F_I)$ and $r_w = (\sum w_i(F_i - F_I)^2/\sum {}^1/_4 w_i(F_i + F_I)^2)^{1/2}$ with $F_I$, $F_i$ = structure amplitudes of crystal no. I and i, respectively; $w_i = 1/(\sigma^2(F_i) + \sigma^2(F_I))$.

**Structural Model and Refinement. Comparison of the Structure Amplitudes.** The structure amplitudes $F_o$ of the observed reflections of all crystals were brought to the same basis by scaling the data sets no. II.1, II.2, and III to data set no. I. The $F_o$ values of the allowed reflections for $Fm3m$ symmetry are presented in Table III (reflections

**Table III.** Comparison of the Four Sets of Structure Amplitudes Corresponding to the Face-Centered Unit Cell of Prussian Blue[a]

| | $10F_o$ | | | |
|---|---|---|---|---|
| hkl | I | II.1 | II.2 | III |
| 111 | 513 (3) | 502 (1) | 455 (8) | 684 (7) |
| 200 | 3016 (6) | 3069 (3) | 3066 (8) | 3311 (9) |
| 220 | 2325 (5) | 2309 (2) | 2267 (9) | 2357 (6) |
| 222 | 621 (3) | 625 (1) | 615 (14) | 609 (8) |
| 311 | 286 (2) | 273 (1) | 202 (33) | 410 (6) |
| 333 | 159 (6) | 126 (2) | | 226 (17) |
| 400 | 4023 (8) | 4038 (3) | 4015 (11) | 4114 (11) |
| 420 | 1845 (2) | 1892 (4) | 1884 (10) | 1988 (4) |
| 422 | 1257 (2) | 1212 (4) | 1201 (12) | 1224 (4) |
| 440 | 2548 (5) | 2548 (2) | 2511 (12) | 2556 (7) |
| 442 | 1240 (2) | 1248 (1) | 1238 (14) | 1258 (4) |
| 444 | 1624 (5) | 1612 (5) | 1604 (15) | 1550 (7) |
| 511 | 490 (1) | 481 (1) | 449 (20) | 626 (4) |
| 531 | 346 (2) | 339 (1) | 356 (26) | 442 (4) |
| 533 | 226 (3) | 204 (5) | | 252 (10) |
| 551 | 239 (3) | 236 (5) | 274 (43) | 308 (9) |
| 553 | 301 (3) | 289 (5) | | 365 (5) |
| 600 | 2509 (5) | 2574 (3) | 2597 (13) | 2659 (7) |
| 620 | 1840 (2) | 1835 (5) | 1856 (13) | 1806 (3) |
| 622 | 924 (2) | 920 (4) | 922 (17) | 999 (4) |
| 640 | 1723 (2) | 1741 (5) | 1733 (15) | 1684 (3) |
| 642 | 1276 (2) | 1262 (1) | 1239 (17) | 1254 (3) |
| 644 | 1257 (3) | 1254 (5) | 1248 (19) | 1227 (5) |
| 660 | 1533 (3) | 1545 (5) | 1548 (17) | 1489 (5) |
| 662 | 1050 (3) | 1029 (5) | 990 (21) | 1004 (5) |
| 664 | 1135 (3) | 1131 (5) | 1084 (21) | 1053 (5) |
| 666 | 989 (6) | 975 (6) | 950 (23) | 900 (11) |
| $r$ | | 0.013 | 0.025 | 0.059 |
| $r_w$ | | 0.015 | 0.024 | 0.057 |

[a] Estimated standard deviations are given in parentheses in this and the next table.

**Table IV.** Comparison of Structure Amplitudes of Reflections with Mixed Indices

| | $10F_o$ | |
|---|---|---|
| hkl | I | II.1 |
| 210 | 361 (1) | 43 (3) |
| 300 | 387 (2) | 59 (2) |
| 410 | 367 (1) | 59 (2) |
| 520 | 288 (2) | 70 (5) |
| 610 | 353 (1) | 53 (9) |
| 641 | 246 (2) | 51 (8) |

with $h$, $k$, $l > 6$ are omitted for brevity). As a test for the correspondence of the various sets of structure amplitudes $r$ and $r_w$ factors were calculated (cf. Experimental Section). Table III shows that the intensities of the face-centered reflections are quite similar for all four crystals. The agreement among the potassium-containing crystals (I, II.1, II.2) is better than between these and the potassium-free crystal (III). Only for the comparison of the crystals I and II.1 were there sufficient observed reflections with mixed parity, which are systematically absent for $Fm3m$ symmetry (subsequently referred to as "primitive" reflections). The results are presented in Table IV using the same scale factor as in Table III.

From Table IV it is obvious that there is a significant discrepancy between the intensities of the "primitive" reflections of the two crystals. The same effect was observed with estimated intensities from powder x-ray and Weissenberg films of various samples. A model for the

Table V. Atom Distribution in the Unit Cell of Prussian Blue and Average Coordination of the Iron in the Space Groups $Fm3m$ and $Pm3m$

| Atom | $Fm3m$ | | | $Pm3m$ | | |
|---|---|---|---|---|---|---|
| | Pos | Occ | Coord | Pos | Occ | Coord |
| 4 Fe(III) | 4a | 1 | $FeN_{4.5}$-$O_{1.5}$ | 1a | 1 | $FeN_{6-2p}O_{2p}$ |
| | | | | 3c | 1 | $FeN_{4+(2/3)p}$-$O_{2-(2/3)p}$ |
| 3 Fe(II) | 4b | $^3/_4$ | $FeC_6$ | 1b | $p$ | $FeC_6$ |
| | | | | 3d | $1-(p/3)$ | $FeC_6$ |
| 18 C, 18 N | 24e | $^3/_4$ | | 6e | $1-(p/3)$ | |
| | | | | 6f | $p$ | |
| | | | | 12h | $1-(p/3)$ | |
| 6 O | 24e | $^1/_4$ | | 6e | $p/3$ | |
| | | | | 6f | $1-p$ | |
| | | | | 12h | $p/3$ | |
| 8 O | 8c | 1 (zeo-litic) | | 8g | 1 | |

structure of Prussian Blue therefore has to be capable of reproducing the large intensity variations of the "primitive" reflections. This requirement strongly reduces the degrees of freedom any model may have to explain the deviation of Prussian Blue from cubic face-centered symmetry.

**Cubic Face-Centered Approximation.** A reasonable starting point for solving the structure is the modified version[13] of the Keggin–Miles model referred to in the Introduction. Analytical data, density, and lattice constants unambiguously show that the unit cell of Prussian Blue contains one formula unit of the ideal composition $Fe_4[Fe(CN)_6]_3 \cdot 15H_2O$ (cf. Table I). Since the smallest number of equivalent positions in space group $Fm3m$ is four,[20] the unit cell has to include positions with fractional occupancies. The distribution of the atoms among the special positions of the unit cell according to the model is shown in the left half of Table V. O at position 24e occupies the empty N sites and thus completes the coordination sphere of Fe(III). O in excess of 14, $K^+$, and $Cl^-$ were neglected.

The only positional parameters to be varied are the $x$ coordinates of the atoms at position 24e. Starting values of 0.31 for C and 0.20 for N were chosen.[15] The parameters of O at position 24e were not refined because the correlation with the parameters of N led to divergence. The refinement was carried out in the usual way, i.e., using only observed reflections and assigning $\sigma^{-2}(F_o)$ as the weight to each reflection. $R$ values around 10% indicated an acceptable fit, but some of the thermal parameters had unreasonable values. The corresponding average bond distances are Fe–C = 2.00 (4) Å, Fe–N = 1.98 (4) Å, and C–N = 1.10 (5) Å (cf. Discussion).

**Cubic Primitive Model.** The proper space group for Prussian Blue according to the $m3m$ Laue symmetry is either $P432$, $P\bar{4}3m$, or $Pm3m$. All occupied special positions are equivalent in these primitive space groups except the position of the uncoordinated $H_2O$ which splits into two independent positions in $P\bar{4}3m$. Since no evidence for this possibility could be found, the space group with the highest symmetry, $Pm3m$, was chosen. As a consequence of the transition from $Fm3m$ to $Pm3m$ certain positions are no longer related by symmetry (cf. Figure 1). The relations between the special positions of interest are shown in Table V. With three Fe(II) at positions 1b and 3d the occupancies of these sites have to be treated as variables. The occupancy $p$ of position 1b was chosen as an independent parameter to be refined. The occupancy of position 3d is then determined by stoichiometry. The occupancies of the C and N positions 6e, 6f, and 12h can easily be derived from Figure 1 by considering the chemical evidence of always having fully C-coordinated $Fe^{II}(CN)_6$ groups. The O of the coordinated $H_2O$ fills the empty N sites, thus completing the coordination sphere of Fe(III). Table V summarizes the resulting occupancy parameters for all the positions and shows the average Fe coordination. The initial $Fm3m$ model is a special case with $p = {}^3/_4$. Another special value is $p = 0$ when all occupancies become integers, yielding a completely ordered structure. A change of $p$ causes a redistribution of atoms between positions which are equivalent in the space group $Fm3m$. The average Fe(III) coordination can vary from $FeN_4O_2$ to $FeN_6$ corresponding to an average composition of $FeN_{4.5}O_{1.5}$ (cf. Table V). Therefore at least two, possibly more, different coordination units occur with the right distribution to form the given fractional average coordination. A recent Mössbauer study produced
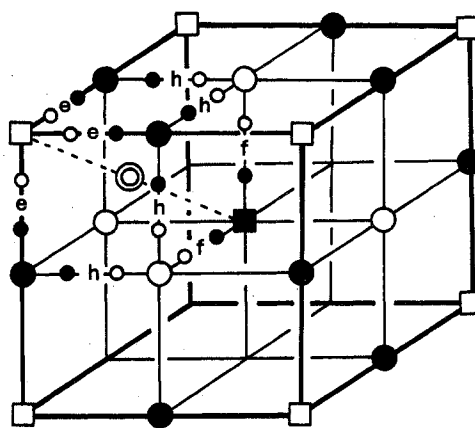
some evidence for the occurrence of different Fe(III) sites in Prussian Blue.[24]

The phases of most of the face-centered structure factors are determined by this model, regardless of the initial values of the parameters. The phases of the "primitive" structure factors, however, depend on the choice of the starting parameters, in particular of $p$. By letting $p$ pass through the special value $^3/_4$, most "primitive" structure factors reverse their sign. As a consequence there are generally two solutions to the least-squares refinement for a given set of structure amplitudes of which the more probable one should give better agreement indices and/or more reasonable parameters.

**Refinement of the Structure.** The information about the deviation of the structure from face-centered symmetry, such as the value of $p$, is primarily contained in the structure amplitudes of the weak "primitive" reflections. By the usual procedure of classifying very small intensities as unobserved and assigning small least-squares weights to all weak reflections much of this information is submerged by the dominant "face-centered" reflections resulting in a poorly defined $p$ value and high correlations between certain parameters. For that reason, unit weights were used, and reflections with intensities less than $3\sigma(I)$ were included in the least-squares refinement.

The final positional and thermal parameters from the refinement in $Fm3m$ were used as starting parameters. Crystal I was refined with a starting $p$ of 0 and 1, respectively, until convergence was obtained (maximum shift to error ratio 0.1). The refinement of the positional and thermal parameters of the following atoms was coupled by constraints: C(6f) and C(6e), N(6f) and N(6e), O(6e), O(12h), and O(6f). The much higher $R$ value of 17%, very short C–N distances of 1.00 and 1.06 Å, and the occurrence of nonpositive definite temperature parameter tensors obtained with $p > {}^3/_4$ leave no doubt that the correct phases of the primitive reflections of crystal I are obtained for $p < {}^3/_4$. Attempts to include the analytically determined amount of Cl at empty Fe(II) positions failed because of high correlations. The final parameters are listed in Table VI and the corresponding $R$ factors in Table VII. The data[25] of crystals II.1 and III are so close to face-centered symmetry that the $Fm3m$ symmetry relations between all positional and thermal parameters had to be used to avoid excessive correlations. Because of the small amount of data from crystal III, convergence of the refinement could only be obtained by setting constraints between the corresponding parameters of N and O occupying the same crystallographic positions. The difference between the $x$ parameters and the ratios of the $U_{11}$ and the $U_{22}$ parameters were held constant. The constraining relations were derived from the final parameters of crystal I where the distinction between the N and O parameters is much better. For both crystals the refinement converged for $p > {}^3/_4$ as well as $p < {}^3/_4$ (maximum shift to error ratio 0.2). The equal quality of the fit in both cases does not allow a clear decision about the correct phases of the "primitive" reflections. The only significant difference in the values of the positional and thermal parameters is the value of $x$ of the oxygen on position 8g $(x, x, x)$ which is either slightly above or below $^1/_4$ as the phases are reversed. By comparison with the final parameters



Figure 1. The unit cell of Prussian Blue in space group $Pm3m$. The atom types and crystallographic positions are partially indicated by the following symbols: (□) Fe(III), 1a (origin); (○) Fe(III), 3c; (▢) Fe(II), 1b; (●) Fe(II), 3d; (◎) O, 8g; (●) C, 6e, 6f, 12h; (○) N or O, 6e, 6f, 12h (cf. Table V).

**Table VI.** Results of the Least-Squares Refinement of Prussian Blue in the Space Group $Pm3m^a$

| Atom | Pos | Occupancy | $x$ | $U$ or $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{i \neq j}$ |
|---|---|---|---|---|---|---|---|
| Fe(III) | 1a | 1 | | 12 (1) | | | |
| | | 1 | | 24 (1) | | | |
| | | 1 | | 28 (2) | | | |
| Fe(III) | 3c | 1 | | 41 (2) | 23 (1) | $U_{22}$ | 0 |
| | | 1 | | 24 | | | |
| | | 1 | | 28 | | | |
| Fe(II) | 1b | 0.267 (15) | | 20 (5) | | | |
| | | 0.665 (17) | | 18 (1) | | | |
| | | 0.824 (25) | | 32 (2) | | | |
| Fe(II) | 3d | 0.911 | | 13 (1) | 23 (1) | $U_{22}$ | 0 |
| | | 0.778 | | 18 | | | |
| | | 0.725 | | 32 | | | |
| C | 6e, 6f | 0.911, 0.267 | 0.3108 (13) | 24 (7) | 21 (4) | $U_{22}$ | 0 |
| | | 0.778, 0.665 | 0.3125 (6) | 18 (2) | 28 (2) | $U_{22}$ | 0 |
| | | 0.725, 0.824 | 0.3087 (21) | 48 (16) | 29 (7) | $U_{22}$ | 0 |
| C | 12h | 0.911 | 0.1887 (10) | 28 (6) | 20 (5) | 41 (6) | 0 |
| | | 0.778 | 0.1875 | 18 | 28 | $U_{22}$ | 0 |
| | | 0.725 | 0.1913 | 48 | 29 | $U_{22}$ | 0 |
| N | 6e, 6f | 0.911, 0.267 | 0.2005 (11) | 11 (6) | 44 (5) | $U_{22}$ | 0 |
| | | 0.778, 0.665 | 0.1994 (13) | 18 (3) | 81 (8) | $U_{22}$ | 0 |
| | | 0.725, 0.824 | 0.1979 (14) | 14 (6) | 64 (6) | $U_{22}$ | 0 |
| N | 12h | 0.911 | 0.2995 (9) | 23 (5) | 31 (5) | 121 (10) | 0 |
| | | 0.778 | 0.3006 | 18 | 81 | $U_{22}$ | 0 |
| | | 0.725 | 0.3021 | 14 | 64 | $U_{22}$ | 0 |
| O | 6e, 6f | 0.089, 0.733 | 0.2100 (25) | 79 (19) | 171 (18) | $U_{22}$ | 0 |
| | | 0.222, 0.335 | 0.2138 (42) | 87 (32) | 45 (13) | $U_{22}$ | 0 |
| | | 0.275, 0.176 | 0.2074 | 61 | 206 | $U_{22}$ | 0 |
| O | 12h | 0.089 | 0.2900 | 79 | 171 | $U_{22}$ | 0 |
| | | 0.222 | 0.2862 | 87 | 45 | $U_{22}$ | 0 |
| | | 0.275 | 0.2926 | 61 | 206 | $U_{22}$ | 0 |
| O | 8g | 1 | 0.2608 (12) | 159 (7) | $U_{11}$ | $U_{11}$ | 49 (1) |
| | | 1 | 0.2517 (15) | 177 (8) | $U_{11}$ | $U_{11}$ | 7 (14) |
| | | 1 | 0.2577 (38) | 228 (25) | $U_{11}$ | $U_{11}$ | 71 (40) |

$^a$ The results for the crystals I, II.1, and III are indicated in this order. The esd's given in parentheses are only approximate values of the actual standard deviations since the refinement was done with unit weight. The error of constrained parameters is only listed with the parameter appearing first. Thermal parameters (in $A^2$) are multiplied by $10^3$. The anisotropic temperature factor expression is $\exp[-2\pi^2 a^{*2} \cdot (U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2U_{i \neq j}(hk + hl + kl))]$.

**Table VII.** Interatomic Distances (A) and Agreement Indices$^a$

| | | | | | Obsd only | | All refl | |
|---|---|---|---|---|---|---|---|---|
| Crystal | Fe–C | Fe–N | C–N | Fe–O | $R$ | $R'$ | $R$ | $R'$ |
| I (6e,f) | 1.924 (13) | 2.038 (11) | 1.122 (17) | 2.134 (25) | 0.042 | 0.037 | 0.050 | 0.040 |
| (12h) | 1.918 (10) | 2.039 (9) | 1.126 (14) | | | | | |
| II.1 | 1.906 (6) | 2.027 (13) | 1.150 (15) | 2.173 (43) | 0.032 | 0.034 | 0.049 | 0.041 |
| III | 1.945 (21) | 2.012 (14) | 1.127 (26) | 2.108 | 0.046 | 0.052 | 0.073 | 0.061 |
| Mean values$^b$ | 1.923 (8) | 2.029 (6) | 1.131 (6) | 2.138 (19) | | | | |

$^a$ See footnote of previous table concerning the errors. $^b$ Standard deviations of the mean calculated by $(\Sigma_i{}^n(x_i - \bar{x})^2/n(n-1))^{1/2}$.

of crystal I the phase assignment for the other crystals was based on the $p$ value yielding $x > {}^1/_4$ for O(8g). The final parameters are included in Table VI. The parameters of crystal II.2 were not refined because of the low intensity level of the data. The choice of unit weights for the refinement was reflected by rather high values for the standard deviation of an observation of unit weight, which were 1.77, 1.89, and 4.02 for crystals I, II.1, and III, respectively.
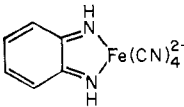
## Discussion

Whereas the simple Keggin–Miles model correctly reflects the polymeric nature of Prussian Blue, the actual structure is more complicated. The next best approximation is still using a cubic face-centered unit cell. According to the reliably determined analytical and density data, a number of positions in this unit cell are only partially occupied, the vacant sites being randomly distributed. Any nonrandom distribution necessarily leads to a cubic primitive or lower symmetry lattice. The x-ray data clearly demonstrate that in general the lattice is cubic primitive. The large intensity differences of the "primitive" reflections from various crystals can be attributed to a varying degree of ordering of the vacant sites described by the occupancy parameter $p$ of Fe(II) in the center of the unit cell. For the crystal with the strongest "primitive" re-

flections, crystal I, a $p$ value of 0.27 indicates that with a 73% probability the central $Fe^{II}(CN)_6$ group is missing. Only 9% of the $Fe^{II}(CN)_6$ groups are missing on the other positions. This is a rather high degree of ordering of the vacancies compared with the two other crystals.

The conditions under which the single crystals were prepared seem to be important for the deviation from the completely disordered structure usually observed for rapidly precipitated Prussian Blue. The slow crystallization along with the inclusion of $Cl^-$ or $H^+$ from the hydrochloric acid might be the reason for the nonstatistical distribution of the vacancies. The ordering of the vacancies can be partially destroyed by dehydrating and heating the crystals. In a qualitative experiment, a portion of sample III was exposed to a vacuum of $10^{-3}$ Torr at 70 °C for 3 days and then rehydrated by contact with the laboratory atmosphere. This sample had considerably weaker "primitive" reflections in a powder x-ray diagram than the untreated sample III, whereas the face-centered reflections did not noticeably change.

The interatomic distances (cf. Table VII) resulting from the final parameters are well in the range of the values from other structural data. The results from the different crystals do not

**Table VIII.** Comparison of Selected Bond Lengths (A)

| Compd | Fe(II)-C | C-N | Footnote |
|---|---|---|---|
| $Cs_2MgFe(CN)_6$ | 1.90 | 1.14 | a |
| (benzimidazole)Fe(CN)$_4^{2-}$ | 1.917, 1.918, 1.932, 1.942 | 1.144, 1.145, 1.148, 1.160 | b |
| $BaFe(CN)_5NO$ | 1.88, 1.92, 1.95, 1.96 | 1.09, 1.13, 1.17, 1.21 | c |
| $Na_4Fe(CN)_6\cdot10H_2O$ | 1.902, 1.906, 1.920 | 1.165, 1.174, 1.180 | d |
| $H_4Fe(CN)_6$ | 1.882, 1.884, 1.906 | 1.140, 1.153, 1.156 | e |
| $Na_2Fe(CN)_5NO\cdot2H_2O$ | 1.90, 1.91, 1.93 | 1.14, 1.15, 1.19 | f |
| Prussian Blue | 1.91, 1.92, 1.92, 1.94 | 1.12, 1.13, 1.13, 1.15 | This work |

| | Fe(III)-N | Fe(III)-OH$_2$ | |
|---|---|---|---|
| $[FeB(NCS)_2]ClO_4$<br>(B = macrocyclic ligand) | 2.01 (NCS)<br>2.23 (N, macrocyclic ligand) | | g |
| $[RbFe(EDTA)H_2O]H_2O$ | 2.317 | 2.106 | h |
| $[LiFe(EDTA)H_2O]H_2O$ | 2.325 | 2.107 | h |
| $K_5Fe_3(SO_4)_6(OH)_2\cdot nH_2O$ | | 2.138 | i |
| $FeAsO_4\cdot2H_2O$ | | 2.061, 2.125 | j |
| Prussian Blue | 2.01, 2.03, 2.04, 2.04 | 2.11, 2.13, 2.13, 2.17 | This work |

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differ significantly. For the purpose of comparison, a few selected bond lengths are presented in Table VIII. The chemical similarity of the various compounds allows a direct comparison of the Fe–C and C–N distances. The comparison of the Fe–N and Fe–O distances, however, has to be considered only as a rough guideline owing to the lack of structural data for octahedral high-spin iron(III) compounds with simple nitrogen-containing ligands.

The thermal parameters of the N indicate a larger amplitude of vibration perpendicular to the bonding direction than parallel to it, in agreement with intuition and the results of recent structure determinations of analogous compounds.[26] Disregarding the results of the crystals II.1 and III because of the high correlations, the same can be concluded for the coordinated oxygen. No important deviation from isotropic vibration can be found for C. The oxygen atoms, in particular O(8g), have rather large vibrational amplitudes. This is not unexpected, the uncoordinated $H_2O$ sitting in a "hole" which is considerably larger than its space requirement.

It may seem surprising that the positional and thermal parameters derived from the three measurements do not show a better agreement. This does not necessarily reflect a real difference, since in a disordered structure, especially when atoms of a different type occupy symmetry-related crystallographic positions, their parameters are strongly correlated and therefore not as well defined as in a completely ordered structure. The systematic error can then considerably exceed the esd of the affected parameters. This is true in particular for the parameters of the coordinated O and the N in crystal II.1 with correlation coefficients close to ±1 (−0.82 between both $U_{22}$). In crystal III N and O could not at all be refined separately. In the case of crystal I, on the other hand, the high degree of ordering resulted generally in a much better parameter separation.

As a test for the validity of our model we calculated difference Fourier maps with the final parameters of the three crystals. The three maps, having similar characteristics, do not indicate any serious discrepancy. The residual peaks are within ±0.8 e/Å³ at the Fe sites and, except for O(6f) in I, within ±0.5 e/Å³ at the C, N, and O sites. Peaks of +0.5 e/Å³ and −0.8 e/Å³ on both sides of O(6f) in crystal I suggest that the calculated Fe(III)–O distance is slightly too short. The

absence of any large difference peak at the occupied positions supports strongly the atomic distribution of the model, including its considerable variability for the Fe(II) and C sites.

In addition there are three peaks of low magnitude (+0.3 to +0.6 e/Å³) at the positions 8g (0.36, 0.36, 0.36), 24m (0.2, 0.2, 0.3), and 24l (0.5, 0.4, 0.2). No attempts were made to assign these small peaks to any atoms not yet accounted for by the presented model. The number of atoms per unit cell being smaller than indicated by the ideal composition (cf. Table I) suggests that even more structural defects occur than postulated by the model, thus additionally complicating the situation. Neutron diffraction studies with deuterated Prussian Blue currently under way are expected to clarify some of the remaining questions.

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# Synthetic, Structural, and Magnetic Properties of the Pyrazine-Bridged Lanthanide Organometallic Complex μ-Pyrazine-bis[tris(cyclopentadienide)ytterbium(III)], (C₅H₅)₃Yb(NC₄H₄N)Yb(C₅H₅)₃

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The synthesis, characterization, and structural and magnetic properties of the title compound are reported. The reaction of $Yb(C_5H_5)_3$ with pyrazine under inert atmosphere conditions in benzene gives the dinuclear product. Slow sublimation under vacuum begins at 75 °C and gives green-brown crystals. The structure has been determined from three-dimensional x-ray diffraction data collected by counter methods. The molecular unit is located about a crystallographic inversion center. Two ytterbium atoms, each with three $\eta^5$-cyclopentadienide rings, are nearly linearly bridged by a pyrazine ring coordinated through its nitrogens. The ytterbium–nitrogen distance is 2.61 Å and the average ytterbium–carbon distance is 2.68 (1) Å. The coordination about the ytterbium is nearly $C_{3v}$ in symmetry. The crystals conform to space group $C2/c$ with $a = 14.006$ (5) Å, $b = 8.299$ (3) Å, $c = 24.637$ (9) Å, $\beta = 102.83$ (1)°, $Z = 4$, and $\rho_{calcd} = 1.94$ g/cm³. A total of 4857 reflections were collected of which 1304 independent reflections with $F^2 \geq 3\sigma(F^2)$ were used in the final refinement to give a weighted $R$ factor of 4.5%. The magnetic susceptibility of the title compound has been measured in the range 3–100 K and shows linear Curie–Weiss behavior with $C = 1.51$ (4), $\Theta = 1.3$ (6) K, and $\mu_{eff} = 3.48$ $\mu_B$. There is no evidence of any magnetic interaction between metal centers or reduction of magnetic moment due to f-orbital covalency. This lack of interaction and the consistency of the $MCp_3$ bonding parameters in both lanthanide and actinide compounds make an ionic formulation of the bonding most appropriate, in contrast to some previous suggestions for related compounds.

## Introduction

The organometallic compounds of the lanthanides and actinides have a chemistry which is distinct from both the organometallic chemistry of the d-transition elements and the usual coordination chemistry of the f-block elements. We have been interested in delineating the structural and bonding characteristics of these compounds and have recently reviewed this subject.[1] The preparation of species in which two paramagnetic metal centers are isolated in a single molecule is of particular interest because the magnetic properties of such complexes can give important information about the chemical bonding. Previous studies[2-4] of such lanthanide compounds have involved $Ln(C_5H_5)_2^+$ or $Ln(C_8H_8)^+$ moieties bridged by simple anions such as $Cl^-$, $CH_3CO_2^-$, or $CH_3^-$, but only three structural studies have appeared[5-7] and there are no low-temperature magnetic data available. In the case of the actinides, the synthesis of $[(C_5H_5)_3UC_6H_4U(C_5H_5)_3]$ has been reported,[8] but no further studies or characterizations have been forthcoming.

The strong Lewis acidity of $Ln(C_5H_5)_3$ complexes,[9] the recent use of pyrazine as an effective electron-transfer agent in transition-metal chemistry,[10] and our desire for a complex with a continuous π-bridging ligand system to complement previous studies suggested to us the possibility of a pyrazine-bridged molecule. Such a complex would place the metal atoms far enough apart to eliminate through-space magnetic interactions so that any electron exchange would have to take place through the ligand π system. Furthermore, the anticipated approximate $C_{3v}$ site symmetry at the metal center would allow structural comparison with the $(C_5H_5)_3U-X$ complexes of uranium(IV). We now report the successful synthesis and the structural and magnetic characterization of the pyrazine-bridged complex μ-pyrazine-bis[tris(cyclopentadienide)ytterbium(III)].

## Experimental Section

All reactions were carried out under an inert atmosphere of high-purity nitrogen or argon on a vacuum line. Transfer and handling of the organometallic complexes were facilitated by the use of Schlenk techniques or a Vacuum Atmospheres HE 93-A inert-atmosphere glovebox having an oxygen- and moisture-free argon atmosphere. Samples for elemental ytterbium analyses were weighed on a Cahn Model 4400 electrobalance in the glovebox. The Yb analyses were performed by carefully decomposing a weighed (approximately 50 mg) sample with water, oxidizing with $H_2O_2$ until a clear solution was obtained, and titrating with standard ~0.01 M EDTA solution at pH 5–6 using xylenol orange as indicator. The C, H, and N analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Engelskirchen, West Germany. Infrared spectra were measured with a Perkin-Elmer Model 337 spectrophotometer; an AEI-MS12 mass spectrometer was used to record mass spectral data; a Cary 14 spectrophotometer was used to measure optical spectra. Crystalline samples for x-ray diffraction were handled in a horizontal-format glovebox equipped with a binocular microscope.

**Materials.** Dried and degassed solvents were used in all syntheses and characterizations. Toluene, benzene, tetrahydrofuran (THF),