Single-crystal Study of Prussian Blue: $Fe_4[Fe(CN)_6]_2$, $14H_2O$

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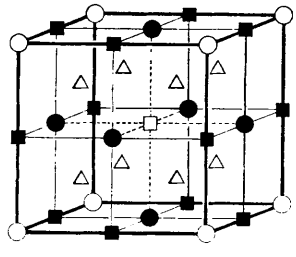
Summary A single-crystal *X*-ray structure analysis of Prussian Blue, $Fe_4[Fe(CN)_6]_3,14H_2O$, reveals that the space group symmetry of the approximate structure is O_h^5-*Fm*3*m* with occupancy factors of 0·75 for Fe^{II}, C, and N; the more detailed investigation demonstrates deviations from the cubic face-centred symmetry.

PRUSSIAN BLUE is considered to be the oldest synthetic co-ordination compound. Until now no single-crystals could be grown, mainly due to the low solubility of this compound.[1,2] The complete crystal structure has therefore not yet been solved, but a structural model with space group symmetry *Fm*3*m* was deduced from powder data.[3]

Prussian Blue has been prepared by diffusion of aerial oxygen and water vapour into a solution of $FeCl_2$ and $K_4Fe(CN)_6$ in 10M HCl.[4] The cubelike crystals of composition $Fe_4[Fe(CN)_6]_3,14H_2O$ were contaminated by 1—2% K^+ and Cl^-.

Crystal data: $Fe_4[Fe(CN)_6]_3,14H_2O$; $M = 1112$; cubic, $a = 10{\cdot}179(8)$ Å; $V = 1055$ Å^3; $D_m = 1{\cdot}81$ g/cm^3; $D_c = 1{\cdot}75$ g/cm^3 for $Z = 1$, space group of average structure *Pm*3*m* (see below).



	*Pm*3*m*	*Fm*3*m*			*Pm*3*m*	*Fm*3*m*	
○	1*a*	4*a*	Fe^{III}	——	6*e*		C,N
●	3*c*			------	6*f*	24*e*	O
□	1*b*	4*b*	Fe^{II}	——	12*h*		C,N
■	3*d*			△	8*g*	8*c*	O

Intensity data, to a limit of $\sin\theta/\lambda = 0{\cdot}6$, were collected using Mo-K_α radiation. The intensity data were also corrected for absorption.

All strong reflections belong to a cubic face-centred cell, space group O_h^5-*Fm*3*m*. In addition, much weaker reflections with no space group extinctions are observed.

Initially, only the 60 face-centred reflections corresponding to *Fm*3*m* were used (Figure).[2] The resulting distances were Fe^{II}–C 2·05(3), Fe^{III}–N 1·98(3), and C–N 1·04(4) Å, *R* 0·055, *RW* (weighted *R* factor) 0·070. This, however, furnishes only a crude picture of the structure. It must be emphasized that in the structure of Prussian Blue not all of the atomic positions are uniformly and completely occupied. For *Fm*3*m* the vacancies are assumed to occur at random corresponding to a population factor of 0·75 for Fe^{II}, C, and N.

The primitive cell which has to be considered by the inclusion of all reflections is described by O_h^1-*Pm*3*m*. The first calculation was based on $4Fe^{III}$ (1*a* and 3*c*), $3Fe^{II}$ (3*d*), 18C, and 18N (6*e* and 12*h*). The corresponding difference Fourier map showed peaks at 8*g* ($x \approx 0{\cdot}26$), 6*f* ($x \approx 0{\cdot}21$), and 1*b*. 6*f* and 8*g* were occupied with O, 1*b* with a variable fraction of Cl; the non-stoicheiometry of Prussian Blue was thus taken into account to some extent. This model was refined anisotropically to $R = 0{\cdot}063$ and $RW = 0{\cdot}064$ (165 observed reflections). The structure consists of three different co-ordination units: $3Fe^{II}C_6$, $1Fe^{III}N_6$, $3Fe^{III}N_4O_2$. The final interatomic distances are: Fe^{II}–C 1·93(4), Fe^{III}–N 2·00(3), Fe^{III}–O 2·16(3), C–N 1·15(4) Å. These distances are in agreement with similar, known, bond lengths.[1,5]

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