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Contribution from the Institut für Anorganische Chemie, Universität Bern, CH-3000 Bern 9, Switzerland,
and the Institut für Reaktortechnik, ETH, CH-5303 Würenlingen, Switzerland

Neutron Diffraction Study of Prussian Blue, $Fe_4[Fe(CN)_6]_3\cdot xH_2O$. Location of Water Molecules and Long-Range Magnetic Order

F. HERREN,[1a] P. FISCHER,[1b] A. LUDI,*[1a] and W. HÄLG[1b]

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Prussian Blue, $Fe_4[Fe(CN)_6]_3\cdot xH_2O$ (x = 14–16), has been studied by powder neutron diffraction in four different states of hydration: dehydrated, $x(H,D)_2O$ with a vanishing scattering contribution of hydrogen, xD_2O, and xH_2O. Structural calculations using diffraction profile analysis reveal two structurally distinguishable kinds of water molecules. Six molecules of water are coordinated to Fe(III) at empty nitrogen sites; approximately eight additional water molecules are present either as isolated molecules at the center of the unit cell octants or as water molecules connected by hydrogen bonds to the coordinated ones. The corresponding O–D–O distance amounts to 2.87 Å. The disordered overall structure is described as a superposition of various ordered substructures. Magnetic contributions to the neutron intensities below the Curie temperature of 5.6 K reveal ferromagnetism. The magnetic part of the intensities corresponds to $S = {}^5/_2$ of high-spin Fe(III).

Introduction

The crystal structure of Prussian Blue and analogous polynuclear cyanides $M^A m[M^B(CN)_6]_n\cdot xH_2O$ consists of a three-dimensional cubic M^A–NC–M^B framework where a certain number of M^B sites are vacant. The number of these empty M^B (and cyanide as well) sites depends on the stoichiometry of the particular compound, i.e., on the valences of the two metal ions M^A and M^B.[2,3] Since the space group symmetry usually corresponds to $Fm3m$, a random distribution of the $M^B(CN)_6$ vacancies was assumed. Water molecules at empty nitrogen positions complete the pseudooctahedral coordination sphere of M^A. For Prussian Blue, the average composition of the Fe(III) coordination unit is $FeN_{4.5}O_{1.5}$.[2] In addition, the unit cell contains eight uncoordinated water molecules which are assumed to be linked by hydrogen bonds to the coordinated water. In an attempt to partially remove the inherent structural disorder, a slightly modified model was proposed containing two kinds of unit cells.[4]

Since our X-ray study could not present precise information concerning the network of hydrogen bonds in Prussian Blue, we decided to carry out a neutron diffraction experiment using as much structural information as possible from the X-ray data. Owing to the small crystal size, on the order of 0.15 mm and less, we obviously had to use the powder technique. Because of the strong incoherent scattering of the protons, we used mainly deuterated samples. Our strategy consisted of a stepwise solution of the structure of dehydrated, 33% deuterated, fully deuterated, and protonated samples and a consecutive application of difference Fourier calculations. Owing to the different sign of the scattering lengths of D (0.667×10^{-12} cm) and H (-0.374×10^{-12} cm), 33% deuteration results in a vanishing contribution to the diffraction intensities of H and D together ("zero-matrix"). Moreover, at low temperatures the magnetic part of the scattered intensities reveals the magnetic structure of Prussian Blue.

Experimental Section

Materials. The sample of Prussian Blue used in this work was prepared as sample II of ref 2. Dehydration was achieved by evacuating Prussian Blue to 5×10^{-4} mmHg at 80 °C for 70 h. Determination of the weight loss and rehydration experiments showed that this procedure removed 90% of the water. To produce a deuterated sample, we evacuated 11.5 g of Prussian Blue to 4×10^{-3} mmHg for a period of 6 days while slowly raising the temperature to 70 °C. Ten milliliters of D_2O was added, and the resulting suspension was kept at 20 °C for 2 h and at 50 °C for 1 h. This procedure was twice repeated, leading to a product deuterated to 96.8% as determined by mass spectroscopy. "Zero-matrix" Prussian Blue has been prepared by suspending the normal protonated sample in 33% D_2O for 2 days at room temperature. Mass spectroscopy showed a 32.6% deuteration corresponding to an effective scattering length for hydrogen of -0.035×10^{-12} cm. Generally the degree of hydration cannot be precisely fixed[2] but corresponds to 14–15 molecules of water per formula unit. The calculations of this work were all made by using the ideal stoichiometry $Fe_4[Fe(CN)_6]_3\cdot 14H_2O$.

Magnetic Measurements. The susceptibility of $Fe_4[Fe(CN)_6]_3\cdot xD_2O$ was measured in the temperature range 1.5–300 K on a moving-sample magnetometer[5] of the Institut für Festkörperphysik, ETH, Zürich. For the determination of the Curie temperature, the neutron intensity of the 111 reflection (cf. Results and Discussion: Magnetic Properties) of deuterated Prussian Blue was measured as a function of temperature from 1.9 to 8.0 K.

Collection of Neutron Intensities. The polycrystalline Prussian Blue samples were sealed in cylindrical aluminum or vanadium containers of 1- or 1.6-cm diameter. For low-temperature studies, a He-bath cryostat was used. Diffraction patterns were recorded at 293 K by means of two-axis spectrometers at Würenlingen. Wavelengths of 2.35 Å (graphite monochromator) and 1.19 Å (Ge monochromator) were used. Powder diagrams were measured in the 2θ range 7–121° in steps of 0.15°. The background was determined graphically.[6]

Data Reduction and Structural Calculations. Whereas the X-ray structure analysis showed the correct space group of Prussian Blue to be cubic primitive,[2] the neutron patterns could be indexed in terms of the corresponding cubic face-centered cell, except a very weak 210 line (deuterated). Owing to the limitations of the data set, all of the following calculations are based upon the face-centered structure. Data reduction, including an absorption correction according to the measured transmission, was carried out by using programs developed at the Institut für Reaktortechnik, Würenlingen. The following scattering lengths (b in 10^{-12} cm) were taken from ref 7: H, −0.374; D, 0.667; C, 0.665; N, 0.94; O, 0.58; Fe, 0.95. The value for b for hydrogen was adjusted to the experimentally measured D/H ratio of each sample. Magnetic form factors were taken from ref 8. The least-squares refinement was made by using Rietveld's profile analysis program providing the agreement indices R, R_n, R_m, and R_{wp}.[6] For the purpose of comparison with residuals of X-ray structure determinations the value of R may be used. For subsequent structural calculations the XRAY 72 system of programs was used. The calculations were carried out on a CDC 6400/6500, ETH, Zürich, or on IBM 375 and 3033 instruments at the University of Bern.

Dehydrated Prussian Blue. The water-free sample is cubic face centered with a slightly contracted cell compared to the hydrated compound. The refinement using the positional and occupational parameters from the X-ray work[2] produced extremely large temperature factors for all the atoms. The distortion of the $Fe(CN)_6$ octahedra by placing C and N on the position 96k proved to be a better model according to Hamilton's criterion.[9] This distortion is equivalent

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Table I. Positional and Thermal Parameters and Occupancies *p* (Number of Atoms per Cell) for Dehydrated Prussian Blue, $Fe_4[Fe(CN)_6]_3$

atom	position	*p*	*x*	*y*	*z*	*B*, Å²
Fe(III)	4a	4	0	0	0	7.8 (2)
Fe(II)	4b	3	0.5	0.5	0.5	
C	96k	18	0.3087 (6)	0.007 (4)	0.007	2.4 (3)
N	96k	18	0.1979 (5)	0.0336 (8)	0.0336	

Table II. Structural Parameters and Occupancies for 33% Deuterated Prussian Blue, $Fe_4[Fe(CN)_6]_3 \cdot 14(H,D)_2O$

atom	position	p^a	*x*	*y*	*z*	*B*, Å²
Fe(III)	4a	4	0	0	0	1.2 (1)
Fe(II)	4b	3	0.5	0.5	0.5	
C	24e	18	0.3132 (6)	0	0	3.42 (9)
N	24e	18	0.2002^b	0	0	
O1	24e	6	0.193 (2)	0	0	
O2	8c	3.8 (2)	0.25	0.25	0.25	7.3 (7)
O3	32f	4.2^b	0.324 (2)	0.324	0.324	

[a] See heading of Table I. [b] Constrained parameter; cf. text.

to a deviation of the Fe–C–N–Fe arrangement from linearity, the Fe–C–N angle being 164°. Results of this calculation are given in Table I; the corresponding *R* and R_{wp} values are 0.048 and 0.098, respectively.

"Zero-Matrix" Prussian Blue. Trial positions for the oxygen atoms were obtained from a difference map of $F_o(33\%\ D) - F_c(Fe,C,N)$ where the parameters to calculate F_c were taken from the X-ray results. Owing to the small number of observed reflections (26), the resulting map is rather flat. Nevertheless, two distinct peaks appear at (0.2, 0, 0; 24 e) and at about ($^1/_4$, $^1/_4$, $^1/_4$; 8c). Evidently the former maximum is assigned to an oxygen atom of a coordinated water molecule (O1) and the latter one to an oxygen of an uncoordinated water molecule (O2). Refinement with constrained parameters for Fe, C, and N and a subsequent difference map of $F_o(33\%\ D) - F_o(Fe,C,N,O1)$ revealed two positions for the uncoordinated water, O2 at ($^1/_4$, $^1/_4$, $^1/_4$; 8c) and O3 at (0.34, 0.34, 0.34; 32f). Independent refinement of the C, N, and O1 parameters always produced strong correlation effects and hence divergence of the least-squares procedure. Refinement with a fixed C–N distance of 1.14 Å converged to $R = 0.052$ and $R_{wp} = 0.073$ (Table II). The occupancies of O2 and O3 were constrained to a total of eight uncoordinated water molecules per cell in accordance with analytical data.[2]

$Fe_4[Fe(CN)_6]_3 \cdot 14D_2O$. In a first attempt to locate the D atoms, a difference map of $F_o(D) - F_c(Fe,C,N,O1,O2,O3)$ was calculated. The only well-resolved peak to be attributed to D was observed at (0.26, 0.07, 0.07; 96k) corresponding to an O–D distance of about 1 Å. In the vicinity of O2 and O3 only a blurred maximum was detected. Considering the many possible orientations of these uncoordinated water molecules and taking into account the limitations of the powder method, we treated these molecules as pseudoatoms $\{D_2O\}$ with an average scattering length $b(D_2O) = b(O) + 2b(D)$. Obviously large temperature factors are to be expected. The refinement gave $R = 0.083$ and $R_{wp} = 0.134$. These calculations were also performed with a fixed C–N distance of 1.14 Å and population parameters of $\{D_2O\}2$ and $\{D_2O\}3$ corresponding to eight uncoordinated water molecules per cell. A final difference map calculated with the parameters given in Table III was essentially structureless. The neutron diffraction pattern of the deuterated sample is shown in Figure 1 as a representative example. The refinement of the 1.2 K data gave only an insignificant reduction of the temperature factors, indicating substantial structural disorder.

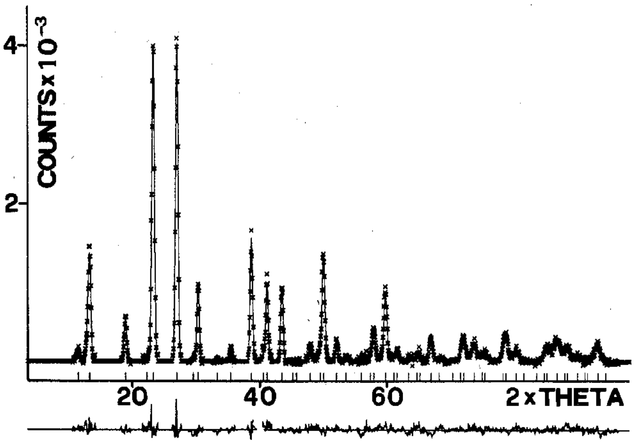

Figure 1. Observed (×), calculated (line), and difference profiles for the powder neutron diffraction pattern (λ = 1.19 Å) of deuterated Prussian Blue, $Fe_4[Fe(CN)_6]_3 \cdot 14D_2O$.

$Fe_4[Fe(CN)_6]_3 \cdot 14H_2O$. Owing to the high background and hence rather poor counting statistics, no attempt was made to independently refine the structural parameters of the fully protonated sample. With fixed parameters (Table III) the following results were obtained: $R = 0.184$, $R_{wp} = 0.232$.

Results and Discussion

Description of the Structure. The X-ray study of several single crystals presented clear evidence for deviations from the cubic face-centered symmetry of Prussian Blue owing to a variable degree of ordering of the vacant Fe(II) sites.[2] The distribution of the light atoms C, N, O, and H, on the other hand, deviates much less from the face-centered symmetry. Whereas Fe contributes heavily to the X-ray intensities, neutron diffraction is dominated by these light atoms (Table IV). Only spurious and very weak lines with indices of mixed parity were observed in the neutron diffraction patterns, best visible in the powder pattern of the dehydrated sample. The results of the neutron data are therefore discussed in terms of space group *Fm*3*m*. The interatomic distances of the three

Table III. Structural Parameters and Occupancies for $Fe_4[Fe(CN)_6]_3 \cdot 14D_2O^a$

atom	position	p^b	*x*	*y*	*z*	*B*, Å²
Fe(III)	4a	4	0	0	0	0.67 (7) 0.8 (1)
Fe(II)	4b	3	0.5	0.5	0.5	0.67^c 0.8^c
C	24e	18	0.3111 (9) 0.3104 (7)	0	0	2.80 (6) 3.5 (1)
N	24e	18	0.1981^c 0.1974^c	0	0	2.80^c 3.5^c
O1	24e	6	0.193 (3) 0.207 (3)	0	0	2.80^c 3.5^c
D	96k	12	0.253 (4) 0.242 (3)	0.063 (1) 0.068 (2)	0.063 0.068	5.6 (5) 8.8 (8)
$\{D_2O\}2$	8c	4.5 (3) 5.9 (2)	0.25	0.25	0.25	20 (1) 26.0 (8)
$\{D_2O\}3$	32f	3.5^c 2.1^c	0.322 (3) 0.341 (4)	0.322 0.341	0.322 0.341	20^c 26^c

[a] Upper line is 1.19-Å data; lower line is 2.35-Å data. [b] See heading of Table I. [c] Constrained parameter; cf. text.

Table IV. Relative Contribution (%) to $|F|$ ($2\theta = 0°$) for $Fe_4[Fe(CN)_6]_3 \cdot 14H_2O$ (H) and $Fe_4[Fe(CN)_6]_3 \cdot 14D_2O$ (D) from X-Ray and Neutron Diffraction Methods

		Fe	C	N	O	H, D
X-ray		33	19	23	20	5
neutron	H	13	22	31	15	19
	D	11	19	27	13	30

Table V. Interatomic Distances (Å) and Angles (Deg) from Neutron Diffraction Data of Prussian Blue

	dehydrated[a]	zero matrix[a]	deuterated[b]
a	10.13	10.11	10.155 (4)
Fe(II)–C	1.94	1.89	1.92 (1)
Fe(III)–N	2.06	2.02	2.01 (1)
C–N	1.13	1.14	1.148[c]
Fe(III)–O1		1.95	1.96 (3)
O1–D			1.10 (3)
O1–$\{D_2O\}2$			3.64 (1)
O1–$\{D_2O\}3$		2.84	2.87 (3)
D–O1–D′			112 (3)
O1–D–$\{D_2O\}3$			169 (3)
R (%)	4.81	5.20	8.28
R_{wp} (%)	9.79	7.27	13.71

[a] Owing to the uncertainty of the neutron wavelength and hence of the refined lattice constant from profile analysis, no standard deviation has been estimated. [b] The distances have been calculated by using the lattice constant determined from a KCl-calibrated X-ray powder pattern (1.19-Å data). [c] C–N distance was kept fixed during refinement (cf. text).

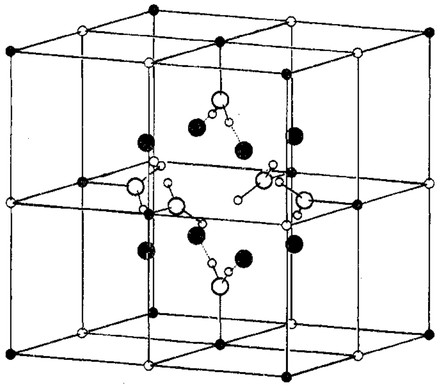

Figure 2. ORTEP plot of the unit cell of Prussian Blue (substructure B) displaying part of the hydrogen-bond network. Cyanide ions are omitted for the sake of clarity and the radii of the atoms are chosen arbitrarily (key: ●, Fe(III), ○, Fe(II); ◯, O1; ∘, D; ⬤, $\{D_2O\}3$).

Table VI. Distribution of Ordered Substructures for Prussian Blue, $Fe_4[Fe(CN)_6]_3 \cdot 14H_2O$

substructure	no. of Fe(II) atoms at 4b	probability[a]
A	4	0.316 (0.198)
B	3	0.422 (0.395)
C	2	0.211 (0.296)
D	1	0.047 (0.099)
E	0	0.004 (0.013)

[a] Values in parentheses refer to the composition $M^{II}_3[M^{III}(CN)_6]_2 \cdot 12H_2O$; occupancy of 4b = $^2/_3$ (cf. ref 3, 4, 10).

samples investigated in this work are summarized in Table V.

In a difference Fourier map calculated with $F(D) - F(H)$ as coefficients (phases of $F(H)$ and $F(D)$ according to the parameters of Table III) two kinds of peaks were observed. Two broad maxima at (0.25, 0.07, 0.07) and around the center of the octant (diameter ~3 Å) are easily assigned to the coordinated and uncoordinated water molecules, respectively. A sharp peak at (0.45, 0.05, 0.05), its intensity corresponding to two hydrogen atoms, might be attributed to the hydrogens of a water molecule filling an empty Fe(II) site.[4] However, no evidence for this assignment could be obtained from the $F_o(D) - F_c$ map. Moreover, inclusion of this additional water molecule in the profile analysis led to significantly higher R values ($R = 0.107$, $R_{wp} = 0.152$). The origin of a second sharp peak at (0.25, 0.25, 0) and of the only hole at (0.4, 0, 0) remains unclear. It must be kept in mind, however, that the structure amplitudes used in this difference Fourier calculation depend on the structural model because coinciding reflections are resolved according to the calculated intensities. We thus cannot exclude the possibility that some of these features might be artifacts.

An important result of the neutron refinement is the confirmation of two crystallographically and chemically distinct kinds of water molecules within the relatively open cubic Fe(III)–N–C–Fe(II) framework of Prussian Blue. The first kind of water molecules (O1) is part of the coordination shell of Fe(III) and fills empty nitrogen sites of the $Fe(CN)_6$ vacancies. The second kind (O2 and O3) occupies interstitial positions and represents therefore uncoordinated water. For the ideal stoichiometry $Fe_4[Fe(CN)_6]_3 \cdot 14D_2O$ the unit cell contains six coordinated and eight uncoordinated water molecules. The O–O distances are 3.64 Å for O1–O2 and 2.87 Å for O1–O3. Only the second distance can be considered as a hydrogen bond between the two kinds of water.

Since the occupancy of the $Fe(CN)_6$ sites is 0.75, the cubic face-centered symmetry clearly requires a statistical distribution of the corresponding vacancies. This inherent structural disorder, which is representative for the whole class of cubic polynuclear transition-metal cyanides,[3] is also reflected in the noninteger composition $FeN_{4.5}O_{1.5}$ of the ferric ion in Prussian Blue. X-ray and neutron diffraction obviously can provide only an average structure which is composed of several ordered substructures. The occupancies of these substructures are either 1 or 0; i.e., the positions having fractional occupancies in the average structure are either full or empty. The possible substructures of Prussian Blue can be generated by using the following simple probability arguments. We consider the octant of the unit cell (Figure 2) where position 4a contains 4 Fe(III) atoms and position 4b an average of 4 × $^3/_4$ Fe(II) atoms. The probability that in a given octant all the Fe(II) positions are occupied is equal to $0.75^4 = 0.316$. Similarly the probabilities for the other possible ordered arrangements can be calculated (Table VI). Milligan et al.[4,10] proposed a less general structural description for $M^{II}_3[Co(CN)_6]_2 \cdot 12H_2O$ based on the two structures A and C (note the shift of origin by $^1/_2$ in ref 4 and 10). Arbitrarily the weights of A and C were fixed at 0.33 and 0.67 although substructure B has the highest possibility for this stoichiometry (cf. Table VI). Correspondingly the occupancies of the two uncoordinated water molecules were not refined.

The numbers of Table VI can be illustrated by the following description. The probability for an uncoordinated water molecule in an octant to "see" structure A is 0.316; for structure B it is 0.422, etc. Therefore, 31.6% of these water molecules are unable to form hydrogen bonds. Their most probable equilibrium position is the center of the octant ($^1/_4$, $^1/_4$, $^1/_4$; 8c). The most probable substructure B (Figure 2) with one $Fe(CN)_6$ vacancy contains three coordinated water molecules. Moving the uncoordinated water molecule from 8c to 32f corresponds to an energetically more favorable situation because hydrogen bonds O1–H–O3 can now be formed. The same arguments hold for the less probable substructures C, D, and E. This description easily explains at least in a qualitative way the two different positions for the uncoordi-

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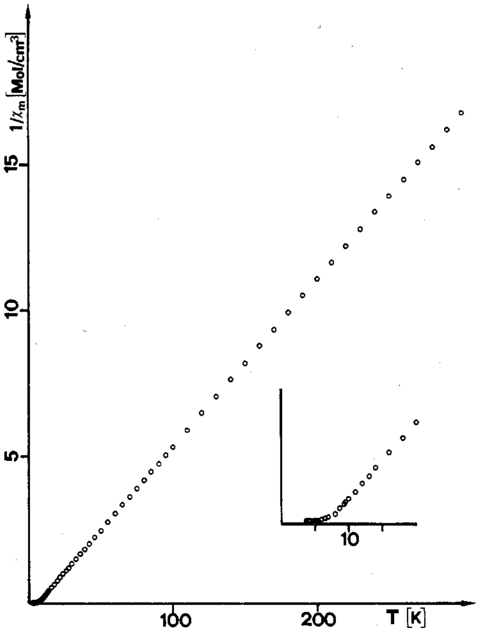

Figure 3. Reciprocal susceptibility of Prussian Blue as a function of temperature.

nated water obtained by the analysis of the neutron diffraction data of Prussian Blue.

Magnetic Properties. The magnetic susceptibility of Prussian Blue, which was determined for the first time by Davidson and Welo,[11] agrees with the expected magnetic properties of iron(III) hexacyanoferrate(II), namely, high-spin Fe(III) and low-spin Fe(II). Since these measurements were conducted in a limited temperature range (300, 275, and 203 K), no information about magnetic ordering could be obtained. Magnetization measurements and magnetically perturbed Mössbauer spectra indicate ferromagnetic behavior at low temperatures with a Curie temperature T_C of 5.5 ± 0.5 K.[12] Our susceptibility data determined between 1.3 and 300 K show perfect Curie–Weiss characteristics between 10 and 300 K (Figure 3). The onset of magnetic order is indicated by deviations from linearity below 10 K. The corresponding Curie constant C is 17.92 ± 0.02 cm^3 K mol^{-1}, and the Weiss constant Θ is 6.74 ± 0.07 K. The effective magnetic moment given by $\mu_{\text{eff}} = 2.828(C/4)^{1/2} = 5.98 \pm 0.02\ \mu_B$ per Fe(III) agrees well with the spin-only value of high-spin Fe(III).

The ferromagnetism of Prussian Blue originates from the $(t_{2g}{}^3)(e_g{}^2)$ configuration of the four high-spin Fe(III) ions at position 4a of space group *Fm*3*m*. The corresponding magnetic saturation moment is $m = gS\ \mu_B \simeq 5\ \mu_B$. In the ferromagnetic state the Fe(III) ions produce coherent magnetic intensity superimposed on the nuclear diffraction peaks.[13] The ordered magnetic moment was obtained from profile analysis[6] of powder patterns recorded at 4.2 and 1.2 K. Introducing an overall temperature factor and keeping all of the structural parameters fixed (Table III), we obtain the following values: μ(Fe(III)) = 3.2 (1) at 4.2 K with $R_m = 0.156$, $R_n = 0.0716$, $R_{wp} = 0.106$ for 19 reflections; μ(Fe(III)) = 4.4 (1) at 1.2 K with $R_m = 0.107$, $R_n = 0.079$, $R_{wp} = 0.106$ for 18 reflections.

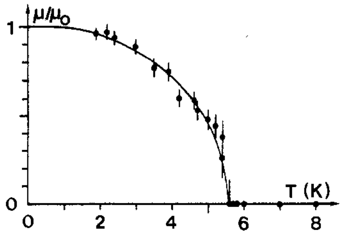

Figure 4. Temperature dependence of the reduced ordered magnetic moment of Prussian Blue determined from the magnetic part of the 111 intensity. The line represents the calculated curve for $S = {}^5/_2$.

Because of the rapid decrease of the magnetic form factor with increasing Bragg angle, the additional magnetic contribution is most clearly observable in weak nuclear reflections at low diffraction angles. Therefore the integrated intensity of the 111 reflection of deuterated Prussian Blue was measured as a function of temperature. The temperature dependence of the normalized ordered magnetic moment is in very good agreement with the theoretical curve predicted by molecular field theory for $S = {}^5/_2$[14] (Figure 4). The Curie temperature extracted from these data is $T_C = 5.6 \pm 0.1$ K, i.e., well within the range of T_C reported for nondeuterated Prussian Blue.[12] Magnetic ordering has also been observed in other polynuclear transition-metal cyanides containing two paramagnetic metal ions.[15] In the case of Prussian Blue the observed ferromagnetism involves a long-range order of the Fe(III) ions. The shortest Fe(III)–Fe(III) distances are 7.2 Å through space (diagonal of an octant face; cf. Figure 2) and 10.2 Å along the Fe(III)-NC-Fe(II)-CN-Fe(III) sequence. It is assumed that the magnetic interaction is due to a superexchange mechanism along this sequence. Obviously this mechanism is related to the mixed-valence interaction which predicts a Curie temperature on the order of the observed value.[16]

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Registry No. $Fe_4[Fe(CN)_6]_3$, 14038-43-8; $Fe_4[Fe(CN)_6]_3 \cdot 14H_2O$, 39611-22-8; $Fe_4[Fe(CN)_6]_3 \cdot 14D_2O$, 72845-22-8.

Supplementary Material Available: Listing of calculated and observed neutron intensities together with their estimated standard deviations (1 page). Ordering information is given on any current masthead page.

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