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Crystal Structure and Mössbauer Measurements of Monoclinic Sodium Hexacyanoferrate(III) Dihydrate

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The crystal structure of monoclinic sodium hexacyanoferrate(III) dihydrate has been solved from single-crystal data. $Na_3Fe(CN)_6 \cdot 2H_2O$ crystallizes in the space group $C2/m$ with $a = 13.551(8)$, $b = 7.482(4)$, $c = 6.515(4)$ Å, $\beta = 106.12(5)°$, and two formula units in the cell. The structure was refined to an R value of 0.035 based on 857 observed reflections. The structure consists of layers formed by distorted sodium coordination octahedra, which are joined together by common edges or faces. These layers are connected together by regular $Fe(CN)_6$ octahedra. Mössbauer spectra of ^{57}Fe in $Na_3Fe(CN)_6 \cdot 2H_2O$ have been measured in the temperature range 0.04–300 K, utilizing a dilution refrigerator for cooling. A magnetic transition was observed at 0.31 K, and above this temperature a quadrupole doublet was obtained with $e^2qQ/2 = 0.669(2)$ mm/sec (at 300 K). Well below the magnetic transition temperature two six-line patterns were observed with effective magnetic fields 26.3 and 23.4 T.

Introduction

Various physical experiments with a substance generally called sodium hexacyanoferrate(III) have been performed. For instance, there are several results of Mössbauer measurements with powdered sodium hexacyanoferrate(III) samples (*1–5*). However, the crystal structure of the material is not known and there even seems to exist uncertainty about the chemical composition. The chemical formula is generally assumed to be $Na_3Fe(CN)_6 \cdot H_2O$ (*1–5*), although recent thermal decomposition studies (*6, 7*) reveal a formula $Na_3Fe(CN)_6 \cdot 2H_2O$.

In this work, the chemical composition of sodium hexacyanoferrate(III) single crystals, grown from aqueous solution, is reported. Moreover, the crystal structure including atomic positions and coordination geometry has been calculated from X-ray diffraction data. We have also performed Mössbauer measurements using powdered hexacyanoferrate(III) samples and compared the results with previous investigations. From measurements at ultra low temperatures the magnetic transition temperature has been determined.

Experimental

Preparation of the Crystals

Aqueous sodium hexacyanoferrate(III) solution was prepared by a slightly modified version of the synthesis described by Garg and Goel (*2*). Large red-brown crystals of the dihydrate suitable for X-ray analysis were grown by keeping the solution at 40°C.

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X-Ray Data Collection

The relevant crystal data for the compound are listed in Table I. The lattice constants were determined at 295 K by a least-squares refinement of the angular settings for 24 reflections in the same 2θ range measured with a Syntex $P2_1$ automatic diffractometer using graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å).

The intensity data were measured on the same diffractometer using the θ–2θ scan technique and a constant scan rate of 1° min^{-1}. A total of 1025 reflections were measured in the range $5 \leq 2\theta \leq 60°$; of those, 857 with $I_{\text{net}} > 3\sigma\,(I_{\text{net}})$ were considered as "observed" and used in the subsequent calculations. The net intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was also applied on the basis of the ϕ-scan data with eight different 2θ values. The largest measured reduction in intensity was from 1.000 to 0.802.

Structure Determination and Refinement

With two formula units in a cell and the space group $C2/m$, the positions of iron atoms are fixed; the remaining non-hydrogen atoms were found on subsequent Fourier synthesis. A least-squares block-diagonal refinement with isotropic temperature factors gave an R value of 0.079; the introduction of anisotropic thermal parameters resulted, after five cycles of refinement, in the final R value of 0.035. The scattering factors used were those given by Cromer and Mann for neutral atoms (*8*). All calculations as well as the drawings were performed using the XRAY 76 programs on a UNIVAC 1108 computer (*9*).

TABLE I

CRYSTAL DATA OF $Na_3Fe(CN)_6 \cdot 2H_2O$

Crystal system	monoclinic
Space group	$C2/m$
a (Å)	13.551(8)
b (Å)	7.482(4)
c (Å)	6.515(4)
β (°)	106.12(5)
V (Å^3)	634.6
Formula weight	316.8
Z	2
D (calc.) (g/cm^3)	1.658
D (meas.) (g/cm^3)	1.66
Crystal size (mm^3)	0.4 × 0.4 × 0.2
μ (cm^{-1})	12.83
No. of collected reflections	1025
No. of refined reflections	857

Mössbauer Measurements

Mössbauer absorption spectra of powdered $Na_3Fe(CN)_6 \cdot 2H_2O$ were measured in the temperature range 0.04–300 K. At room temperature, spectra of several samples were measured using standard Mössbauer equipment. Below room temperature, an absorber made of commercial powder (K & K Laboratories, Inc., Cleveland, Ohio) with the same crystal structure was used. It was placed in the mixing chamber of a dilution refrigerator especially designed for Mössbauer measurements (*10*).

The absorber (40 mg/cm^2) was packed in a plastic holder. Small holes in its top ensured good thermal conductivity between the powder and liquid He. The source $^{57}Co:Cu$ was located above the mixing chamber. Its temperature during dilution was about 4 K. A sinusoidal velocity of the source was produced with an electromagnetic transducer at room temperature. The velocity scale was calibrated with an enriched-iron absorber at room temperature below the cryostat.

Temperatures were measured with carbon and germanium resistors which were calibrated against a CMN magnetic thermometer. The absolute temperature readings were accurate within 5% above 100 mK. During measurements at low temperatures the stability was about 1 mK. The γ rays were detected with a Kr(CO_2)-propor-

TABLE II

ATOMIC COORDINATES AND ANISOTROPIC TEMPERATURE COEFFICIENTS[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	0	0	0	1.41(1)	1.45(1)	1.54(1)	0	.15(1)	0
Na1	0.7533(1)	0.5000	0.5048(1)	2.49(2)	3.07(2)	2.85(2)	0	.49(2)	0
Na2	0	0.5000	0.5000	2.44(4)	6.59(6)	4.25(4)	0	.54(3)	0
C1	0.5702(6)	0.3215(12)	0.2057(13)	2.44(4)	2.41(4)	2.58(4)	0.01(3)	.20(3)	−0.00(3)
C2	0.3864(1)	0.5000	0.1276(2)	2.45(6)	4.05(7)	2.39(5)	0	.40(4)	0
N1	0.1147(1)	0.2762(1)	0.3351(1)	4.18(4)	3.18(4)	3.64(4)	−0.68(4)	.09(3)	−0.74(4)
N2	0.3193(1)	0.5000	0.2029(2)	3.29(6)	9.77(12)	3.69(6)	0	1.61(5)	0
O	0.8438(1)	0.5000	0.2253(2)	3.89(7)	23.12(23)	2.96(6)	0	.33(5)	0

[a] Estimated standard deviations in parentheses. The temperature coefficients have been multiplied by 100.

tional counter. Pulses were collected into a MCA operating in the time mode.

Results

The Crystal Structure

Atomic positional and thermal parameters, along with their standard deviations, are given in Table II.[1] Tables III and IV summarize the interatomic distances and angles. A listing of observed and calculated structure-factor amplitudes is available from the authors upon request.

The octahedral arrangement of cyanide ligands around the iron is regular, the Fe–C distances all being equal. The Fe–C bond lengths of 1.943 Å and C–N bond lengths of 1.152 and 1.146 Å are comparable to those found in other solid hexacyanoferrate (III) complexes (Table V). The $Fe(CN)_6$ octahedra are connected by sodium atoms which are octahedrally coordinated by cyanide nitrogens and water oxygens. Figure 1 displays a packing diagram showing the coordination around iron and sodium atoms.

The NaL_6 octahedra are strongly distorted (cf. Table IV). Both crystallographically different Na atoms have four N atoms in the equatorial plane with Na–N distances of 2.806 and 2.702 Å for Na1 and Na2, respectively. The octahedron is completed in the case of Na2 with two oxygens at the *trans* positions; this results in a more regular arrangement than in the case of Na1 which coordinates a water oxygen and fifth nitrogen atom.

The connection of sodium octahedra into layers is depicted in Fig. 2. Na1 octahedra share edges with each other and form columns in the direction of the y axis. These columns are connected together by Na2 octahedra through a shared face and thus a layer is formed parallel to (001). The

TABLE III

ENVIRONMENT OF Fe WITH BOND LENGTHS (Å) AND ANGLES (°)

Fe–C1	(×4)	1.943(1)	C1–Fe–C1	86.79(3)
Fe–C2	(×2)	1.943(1)	C1–Fe–C2	89.97(3)
Fe–N1	(×4)	3.093(1)	N1–Fe–N1	83.84(2)
Fe–N2	(×2)	3.089(2)	N1–Fe–N2	89.98(2)
C1–N1		1.152(1)	Fe–C1–N1	176.03(7)
C2–N2		1.146(2)	Fe–C2–N2	180.0(2)

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[1] A table of observed and calculated structure factors has been deposited as NAPS Document No. 03655. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance (in U.S. funds only) for each NAPS Accession Number. Institutions and organizations may use purchase orders when ordering; however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are \$5.00. Microfiche are \$3.00. Outside of the U.S. and Canada, postage is \$3.00 for a photocopy or \$1.50 for a fiche.

TABLE IV

ENVIRONMENT OF Na WITH BOND LENGTHS (Å) AND ANGLES (°)

Na1–N1	(×2)	2.806(1)	Na2–N1	(×4)	2.702(1)
Na1–N1	(×2)	2.461(1)	Na2–O	(×2)	2.362(1)
Na1–N2		2.375(2)			
Na1–O		2.461(2)			
O–Na1–N2		174.90(4)	N1–Na2–N1	(×2)	180.0
N1–Na1–N1	(×2)	175.42(3)	O–Na2–O		180.0
O–Na1–N1′		97.19(3)	O–Na2–N1		78.92(3)
O–Na1–N1		82.01(3)	N1–Na2–N1		76.59(3)
N1–Na1–N1		94.89(3)			

layers are connected together in the direction of the z axis by $Fe(CN)_6$ octahedra through common nitrogen atoms.

Mössbauer Data

The results of Mössbauer measurements using powdered $Na_3Fe(CN)_6 \cdot 2H_2O$ absorbers are shown in Figs. 3–5. Above the magnetic ordering temperature a pure quadrupole splitting was seen (Figs. 3, 4). Mössbauer parameters from least-squares fitting of experimental data for the quadrupole spectra at various temperatures are shown in Table VI. The isomer shift *IS* changes as a function of temperature due to the temperature dependence of the second-order Doppler shift. It should be noted that the source is also cooled during the low-temperature measurements. At low temperatures the spectrum becomes asymmetric, but the area of the absorption lines still remains almost equal. This can be explained by electronic relaxation effects.

Well below the magnetic ordering temperature two partly resolved six-line patterns with an intensity ratio of approximately 2 : 1 are observed. A spectrum measured at 0.040 K is shown in Fig. 5b. It is fitted with two separate Hamiltonians having an axially symmetric electric field gradient. For the two patterns the isomer shift, the linewidth, and the angle θ between the magnetic field B_{eff} and the electric field gradient were constrained to be equal. The fitted Mössbauer parameters are shown in Table VII.

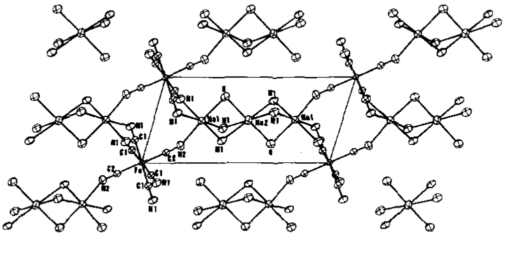

FIG. 1. A perspective view of the structure along the *b* axis.

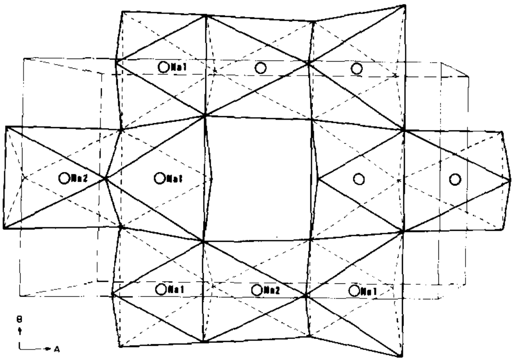

FIG. 2. A layer of sodium coordination octahedra in the structure of $Na_3Fe(CN)_6 \cdot 2H_2O$. The Fe atoms at (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, 0) are not depicted.

Discussion

The chemical composition of our sodium hexacyanoferrate(III) sample is Na₃Fe

TABLE V

INTERATOMIC DISTANCES IN $Fe(CN)_6$ OCTAHEDRA OF SOME FERRICYANIDES

Compound	Fe–C (Å)	C–N (Å)	Ref.
$Co_3[Fe(CN)_6]_2$	1.886	1.153	(*14*)
$K_3Fe(CN)_6$	1.927–1.952	1.131–1.167	(*15*)
$K_3Fe(CN)_6$ (monoclinic)	1.929–1.945	1.147–1.152	(*16*)
$K_3Fe(CN)_6$ (orthorhombic)	1.936	1.142–1.155	(*16*)
$H_3Fe(CN)_6$	1.913	1.141	(*17*)
$LaFe(CN)_6 \cdot 5H_2O$	1.931	1.155	(*18*)
$Cs_2LiFe(CN)_6$	1.926	1.148	(*19*)
$Cs_2NaFe(CN)_6$	1.917–1.939	1.133–1.155	(*20*)
$Cs_2KFe(CN)_6$	1.921–1.930	1.146–1.159	(*20*)
$Na_3Fe(CN)_6 \cdot 2H_2O$	1.943	1.146–1.152	This work

TABLE VI

MÖSSBAUER PARAMETERS[a] OF THE QUADRUPOLE SPECTRA SHOWN IN FIGS. 3 AND 4

T (K)	*IS* (mm/sec)	*QS* (mm/sec)	Γ_1 (mm/sec)	Γ_2 (mm/sec)	I_2/I_1
293	−0.361(1)	0.669(2)	0.248(1)	0.245(1)	1.034(2)
4.2	−0.392(5)	0.997(8)	0.509(19)	0.549(21)	0.934(28)
0.34	−0.417(6)	1.010(9)	0.621(20)	0.779(29)	0.826(21)

[a] *IS* is the isomer shift relative to $^{57}Co:Cu$ and *QS* is the quadrupole splitting. Γ_1, Γ_2 and I_1, I_2 are the linewidths and amplitudes of the two Lorentzian lines, respectively.

$(CN)_6 \cdot 2H_2O$, in agreement with Refs. (*5*, *6*) but not with Refs. (*1*–*4*). There is also some disagreement between the results of previous Mössbauer experiments. In Ref. (*2*) the quadrupole splitting at room temperature was 0.38 ± 0.03 mm/sec while Epstein (*1*) gives 0.60 mm/sec Raj and Danon (*3*) show spectra with a splitting comparable to our measurements ($e^2qQ/2 = 0.669 \pm 0.002$ mm/sec). A pure two-line quadrupole spectrum is also compatible with the crystal structure. The splitting is quite large although the environment of the iron atom is rather symmetric.

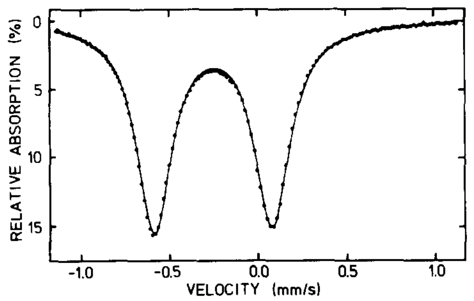

FIG. 3. A ^{57}Fe Mössbauer spectrum of $Na_3Fe(CN)_6 \cdot 2H_2O$ with a thickness of 60 mg/cm² at 293 K. The source is $^{57}Co:Rh$.

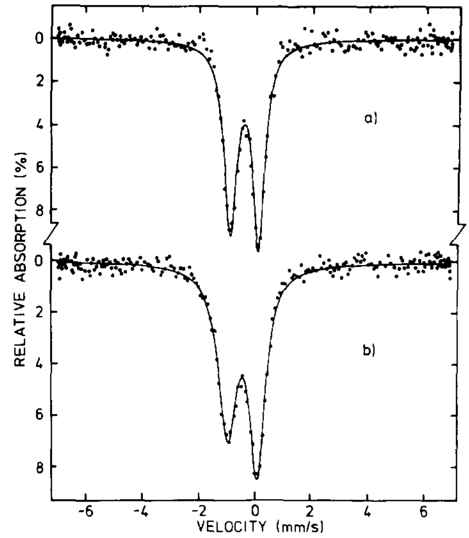

FIG. 4. Mössbauer spectra of $Na_3Fe(CN)_6 \cdot 2H_2O$ (40 mg/cm²) at: (a) $T = 4.2$ K, and (b) $T = 0.34$ K. The source is $^{57}Co:Cu$ at approximately 4 K.

The quadrupole splitting of the Mössbauer spectra of hexacyanoferrates(III) has been discussed in several papers (*11*). It is expected to increase below room temperature. Dominiques and Danon report a value 0.958 mm/sec for $Na_3Fe(CN)_6 \cdot H_2O$ at liquid nitrogen temperature (*5*). This is in agreement with our results (Table VI). Since generally the quadrupole splittings of hexacyanoferrates are sensitive to the amount of crystalline water in the lattice, we are tempted to suggest that the sodium hexacyanoferrate(III) of Refs. (*1*, *3*, *5*) are of the same chemical composition as ours.

Our sample showed a magnetic transition at $T_{crit} = 0.31$ K. This is quite expected, if compared with the anhydrous $K_3Fe(CN)_6$ with a transition temperature of 0.13 K. Orthorhombic $K_3Fe(CN)_6$ is known from

TABLE VII

RESULTS FROM LEAST-SQUARES FITTING OF SPECTRUM b IN FIG. 5[a]

	A	B
IS (mm/sec)*	−0.388(4)	−0.388(4)
QS (mm/sec)	0.816(26)	0.773(31)
B_{eff} (T)	26.3(2)	23.4(3)
θ (°)*	18(2)	18(2)
Γ (mm/sec)*	0.343(10)	0.343(10)
I_{rel}	1.000	0.526(30)

[a] The two resolved patterns are marked A and B. The dashed parameters are constrained to be equal.

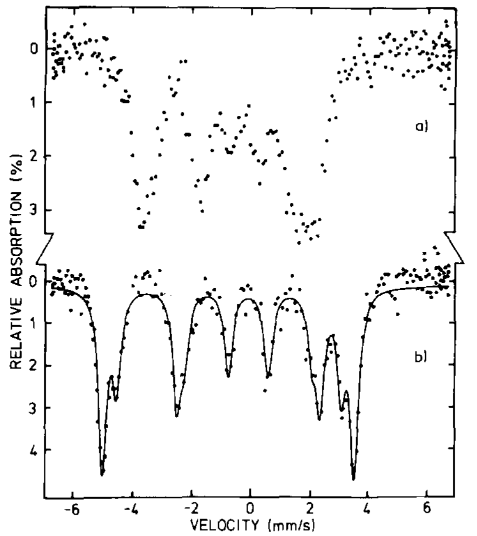

FIG. 5. Mössbauer spectra of $Na_3Fe(CN)_6 \cdot 2H_2O$ (40 mg/cm^2) at: (a) $T = 0.28$ K, and (b) $T = 0.040$ K. The source is $^{57}Co:Cu$ at approximately 4 K.

polarimetric Mössbauer measurements to be antiferromagnetic. The spin structure has also been determined (*12*). Since no other measurements of the magnetic properties of $Na_3Fe(CN)_6 \cdot 2H_2O$ are known, the spin structure in the ordered state cannot be resolved yet. In an investigation of $K_3Fe(CN)_6$ (*13*), the monoclinic sample showed two six-line patterns below the magnetic transition temperature somewhat similar to the spectrum in Fig. 5b. At low temperatures the Mössbauer spectra can be affected by a modification of crystal structure or polytype structure which is known to exist in several hexacyanoferrates.

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