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Polymorphism of Potassium Ferrocyanide Trihydrate as Studied by Solid-State Multinuclear NMR Spectroscopy and X-ray Diffraction

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The polymorphism of bulk powder samples of potassium ferrocyanide trihydrate ($K_4Fe(CN)_6 \cdot 3H_2O$, KFCT) has been studied using ^{1}H, ^{13}C, and ^{15}N NMR spectroscopy in combination with X-ray diffraction. At room temperature, KFCT typically crystallizes in a monoclinic *C*2/*c* form, which converts irreversibly to a monoclinic *Cc* form upon cooling below −25 °C. The structure of both of these forms has been determined using single-crystal X-ray diffraction. A less common metastable tetragonal $I4_1/a$ form is also known to exist at room-temperature. This tetragonal form also converts to the monoclinic *Cc* form upon cooling, although this phase transition is irreversible and occurs at −60 °C. Initial room-temperature ^{15}N MAS NMR spectra and powder X-ray diffraction patterns of ground powder samples of KFCT prepared using a variety of crystallization methods suggested that only the *C*2/*c* form was obtained from a bulk crystallization. The ^{13}C MAS NMR spectra consisted of six peaks with equal integrated areas, a result that is inconsistent with the ^{15}N NMR spectra and known crystal structures. When the samples were not ground, the relative areas of the ^{13}C NMR peaks were altered, indicating that the bulk samples in fact consisted of the two known forms of KFCT. Using the known temperature dependence of these two polymorphs, the ^{13}C peaks corresponding to each of the *C*2/*c* and $I4_1/a$ forms were assigned. The ^{13}C NMR spectra and powder X-ray diffraction results demonstrate that upon grinding, a near 50−50 mixture of the two forms is always produced, rather than a new form entirely. The insensitivity of the ^{15}N NMR spectra to the polymorphism of KFCT is surprising, and likely arises from a fortuitous overlap of the ^{15}N NMR peaks of the two forms.

Introduction

The cyanide ligand is one of the most versatile ligands in inorganic chemistry, capable of forming monomeric and polymeric complexes with the majority of elements in the periodic table.[1,2] Our research group has long been interested in metal cyano chemistry, particularly in using multinuclear solid-state NMR spectroscopy to characterize such complexes.[3−9] Although numerous other solid-state NMR studies of cyano complexes have appeared in the literature,[10−30] no studies have focused on the simple salts of the group-8 metals. The cyano chemistry of this group, particularly the ferrocyanide ion, $[Fe(CN)_6]^{4-}$, dates back over 300 years to the accidental discovery of Prussian Blue,[1,31] a coordination compound that only relatively recently was determined to have the formula $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot xH_2O$ ($x = 14-16$).[32] Currently, there is great interest in the ferrocyanide anion as a building block in supramolecular magnetic materials.[35−38]

In the solid state, the most commonly studied diamagnetic ferrocyanide compound is its hydrated potassium salt, $K_4Fe(CN)_6 \cdot 3H_2O$ (herein referred to as KFCT).[39−60] At −25 °C, KFCT undergoes an interesting second-order phase transition from a paraelectric to a ferroelectric phase.[48,49] The ferroelectric transition is believed to be initiated by changes in the dynamics of the water molecules, which

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undergo rapid reorientations about more than one axis at room temperature[41,57,59] and become ordered when cooled below the Curie temperature.[41] The change in the water dynamics is accompanied by a phase change from monoclinic $C2/c$ ($a = 9.379$ Å, $b = 16.844$ Å, $c = 9.392$ Å, $\beta = 90.07°$)[39−41,45] above the transition temperature to monoclinic Cc ($a = 9.353$ Å, $b = 16.755$ Å, $c = 9.359$ Å, $\beta = 90.08°$) at low temperature.[44,45]

Studies of ferroelectricity in KFCT have been complicated by its tendency to form crystals that are twinned and as a result, some "single-crystal" experiments have been performed on what were actually twinned crystals.[41,45,48,49,55,59] In practice, a bulk crystallization of KFCT at room temperature can produce a mixture containing the common monoclinic $C2/c$ form, a less common tetragonal form ($I4_1/a$, $a = 9.410$ Å, $c = 33.67$ Å)[37,41] whose structure has yet to be refined, and three forms that are composed of different types of twinned crystals.[44] The tetragonal form is metastable and upon cooling below -60 °C the individual crystals convert to the aforementioned monoclinic Cc form. When warmed back to room temperature, the same crystals convert to a twinned $C2/c$ monoclinic form whose twin domains are related by a 90° rotation about the monoclinic *b*-axis.[44,52,60]

In a bulk crystallization, the relative amounts of the forms can be manipulated by altering the crystallization rate, temperature, and solution composition.[42] Rapid crystallizations tend to produce more of the pure forms, while twinning becomes more prevalent with long crystallization times.[44] A greater yield of the monoclinic modification is obtained at room temperature and with the addition of potassium chromate, while the tetragonal modification is preferred at elevated temperatures and crystallizations from a KOH solution.[42]

The majority of the structural studies of KFCT have been performed on single-crystals, and the complex crystallization behavior of bulk powder samples of KFCT is not fully understood. Although solid-state ^{1}H and ^{2}H NMR spectroscopy has been used to study the dynamics of the water molecules in KFCT,[45,57−59] solid-state NMR has yet to be used to study the solid ferrocyanide anion directly. Thus, we have used ^{13}C and ^{15}N magic-angle spinning, MAS, NMR spectroscopy, in combination with single-crystal and powder X-ray diffraction, to gain an understanding of the suprisingly complex polymorphism of KFCT.

Experimental Section

Sample Preparation. For the room-temperature ^{13}C MAS and stationary sample NMR experiments, a sample of 17% ^{13}C,^{15}N-labeled (i.e., 1 in 6 CN ligands) potassium ferrocyanide trihydrate, KFCT, was prepared by combining a 1:5 mixture of K^{13}C^{15}N (99% ^{13}C and 98% ^{15}N, CIL) and KCN (Aldrich) dissolved in distilled water with an aqueous solution of iron(II) chloride tetrahydrate (Alfa Aesar). A 4-fold excess of potassium cyanide over the stoichiometric amount was necessary to yield a pure final product. Immediately upon mixing the above solutions, the formation of a brown-red precipitate was observed. The mixture was allowed to stand for 24 to 48 h until the precipitate had dissolved and a yellow solution was obtained (typically 48 h). KFCT was precipitated by adding methanol and isolated by vacuum filtration. Subsequently,

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the solid was dissolved in a small amount of distilled water in a 20 mL beaker. This beaker was placed inside a 100 mL beaker filled partially with 95% ethanol, and the larger beaker was then sealed with parafilm. Pale yellow crystals of KFCT were obtained after allowing ethanol vapor to diffuse into the aqueous KFCT solution for 24−48 h at room temperature. The yield was 95% based on the iron(II) chloride tetrahydrate.

For the variable-temperature ^{13}C NMR experiments, a 50% ^{13}C−^{15}N-labeled sample was prepared in the same manner as described above using a 1:1 ratio of $K^{13}C^{15}N$ to KCN. A 98% ^{15}N-labeled sample, used for the ^{15}N stationary sample experiment, was prepared in the same manner described above by replacing the $K^{13}C^{15}N$, KCN mixture with $KC^{15}N$ (98% ^{15}N, CIL). For all compounds, purity was checked via FT-IR spectroscopy and solution ^{13}C or ^{15}N NMR spectroscopy in D_2O (99%, CIL) using a Varian Inova 400 spectrometer. The ^{13}C chemical shift of 177.28 ppm (relative to TMS) was in agreement with past studies.[61,62] The ^{15}N shift was 296.78 ppm relative to $NH_3(l)$ at 298 K and $^1J(^{15}N,^{13}C)_{iso}$ was 7.2 Hz.

Crystallization Methods. The relative amounts of the five crystal types of KFCT that are obtained from a bulk crystallization are influenced by the crystallization rate, temperature, and by the addition of potassium chromate, K_2CrO_4, or potassium hydroxide, KOH.[42,44,63] Crystallization of KFCT was attempted under combinations of three crystallization rates, two temperatures, and three solution compositions for a total of 18 crystallization conditions. All crystallizations were performed with approximately 125 mg of KFCT.

For rapid crystallization, KFCT was dissolved in 10 mL of distilled water and precipitated by the addition of 50 mL of 95% ethanol. For the high-temperature crystallization, both the KFCT solution and ethanol were heated to 55 °C before precipitation of KFCT. For a medium rate crystallization, slow-cooling was employed. For the room-temperature crystallization, the KFCT was dissolved in about 0.8 mL of distilled water at 55 °C, and the solution was allowed to cool to room temperature in a water bath over a period of about 4 h. Attempts at a high-temperature slow-cooling crystallization were made by cooling a KFCT solution from 80 to 55 °C. Such crystallizations produced a supersaturated solution, and no crystals were obtained. Last, a slow crystallization was attempted using slow-evaporation of a saturated solution of KFCT. Because of the high solubility of KFCT in water, the small quantities of KFCT used (because of the necessity to isotopically label the samples), and the inability of KFCT to readily dissolve in other solvents, the slow-evaporation method was not ideal and produced crystals of poor quality and small size. Thus, as a slow crystallization method, a two solvent crystallization was employed in which ethanol vapor was allowed to slowly diffuse into an aqueous solution of KFCT. At room temperature, this was achieved by dissolving KFCT in 5 mL of water within a 20 mL beaker, placing this beaker within a 100 mL beaker filled with 20 mL of ethanol and covering the larger beaker. The crystallization was allowed to proceed for 1 week. For the high-temperature crystallization, about 150 mg of KFCT was dissolved in 2 mL of water within a 4 mL vial. This vial was placed inside a 20 mL vial filled with 10 mL of ethanol and subsequently covered with aluminum foil. Both vials were then placed within a pressure bomb and placed in an oven set to 55 °C for 1 week.

The above crystallizations were repeated in which the solvent was either a 0.5 M KOH solution or 20% w/v K_2CrO_4 solution. When the latter solution was utilized, K_2CrO_4 tended to crystallize along with KFCT and proved to be a poor crystallization method. In summary, a total of five crystallization conditions were thus utilized: those obtained with ethanol precipitation at room temperature, ethanol precipitation at 55 °C, slow-cooling from 55 °C to room temperature, ethanol diffusion at room temperature, and ethanol diffusion at 55 °C. These were performed with KFCT dissolved in distilled water and also in a 0.5 M KOH solution for a total of ten samples.

Solid-State NMR Spectroscopy: Methodology. The solids obtained from the above crystallization methods were placed directly into NMR rotors that were lightly tapped against a countertop to pack the crystallites inside the rotor. This is in contrast to the usual protocol whereby the sample is thoroughly ground using a mortar and pestle and then packed tightly into the NMR rotor using a packing tool. As a result of not grinding the KFCT crystals, several attempts were usually required to achieve stable sample spinning at the magic angle. After each unsuccessful attempt at spinning, the rotor was removed from the probe, additional sample was added, then tamped down, and the rotor was placed back in the probe. This was repeated until stable sample spinning was achieved.

For each sample, an initial ^{13}C and ^{15}N NMR spectrum was acquired at room temperature. Subsequently, the rotor was removed from the probe and placed into a Schlenk tube. The tube was then filled with nitrogen gas and, to alter the relative amounts of the tetragonal and monoclinic polymorphs in the sample, was cooled to −98 °C in a methanol/$N_2(l)$ bath for a minimum of 3 h. The sample was warmed to room temperature over a period of several hours before the acquisition of the subsequent ^{13}C NMR spectrum. Initial results demonstrated that the ^{15}N NMR spectra were not sensitive to the crystallization conditions and only ^{13}C NMR spectra were obtained from this point on. If changes were observed in the ^{13}C NMR spectrum in comparison to the initial spectrum, the sample was cooled again and a new ^{13}C NMR spectrum was acquired. This process was repeated until no further changes were observed in the ^{13}C NMR spectra.

After the cooling and warming cycles were complete, the rotors were unpacked, the KFCT sample was ground using a mortar and pestle, and then packed tightly into the NMR rotor in the usual method of preparing a sample for solid-state NMR spectroscopy. A spectrum of the ground sample was acquired and subsequently the rotor was cooled in the methanol/$N_2(l)$ bath for a minimum of 3 h, and new ^{13}C NMR spectra were acquired. As a result of this methodology, a minimum of four ^{13}C NMR spectra were acquired for each KFCT sample.

Solid-State NMR Spectroscopy: Experimental Details. For the MAS experiments, samples were packed into 7.0 mm o.d. or 4.0 mm

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o.d. zirconium oxide rotors and ^{1}H, ^{13}C, and ^{15}N experiments were performed at an applied magnetic field strength of 11.75 T on a Bruker Avance 500 spectrometer ($\nu_L(^1H) = 500.3$ MHz, $\nu_L(^{13}C) = 125.8$ MHz, $\nu_L(^{15}N) = 50.7$ MHz) using a Bruker double-resonance MAS probe. The ^{13}C NMR spectra were referenced with respect to TMS, $\delta_{iso}(^{13}C) = 0.0$ ppm, by setting the high-frequency resonance of adamantane to 38.56 ppm. Nitrogen-15 NMR spectra were referenced with respect to liquid ammonia at 298 K, $\delta_{iso}(^{15}N) = 0.0$ ppm, by setting the ammonium resonance of ammonium nitrate to 23.80 ppm. All MAS experiments were performed using a simple Bloch-decay pulse sequence. For spectra acquired at or above room temperature, ^{1}H decoupling did not improve the ^{13}C or ^{15}N NMR spectra and thus was not utilized. Likely, ^{1}H decoupling was unnecessary because the water molecules in KFCT are known to be undergoing more than one type of rapid motion at room temperature,[45,57−59] and the motion averages the ^{13}C−^{1}H dipolar coupling. At least one of these types of motions begins to slow as the temperature is cooled, and thus continuous-wave ^{1}H decoupling was necessary to maximize the resolution of ^{13}C and ^{15}N NMR spectra acquired below room temperature. Multiple spinning rates, ranging from 3.0 to 8.0 kHz, were used to isolate the isotropic ^{13}C and ^{15}N resonances. Spinning faster then 4.0 kHz with the 7.0 mm o.d. rotors or 8.0 kHz with the 4.0 mm o.d. rotors resulted in dehydration of the KFCT sample. For the variable-temperature experiments, temperatures were calibrated using the ^{207}Pb NMR peak of lead nitrate.[64] All ^{13}C MAS experiments were performed using a ^{13}C pulse width of 2.0 μs, ~40° flip angle, while ^{15}N MAS experiments utilized a ^{15}N pulse width of 2.0 μs, ~36° tip angle. These reduced pulse widths correspond to $\pi/2$ ^{13}C and ^{15}N pulse widths of 5.0 and 5.5 μs, respectively, and were required because of the exceedingly long ^{13}C and ^{15}N spin−lattice relaxation times that we estimated from recycle delay optimizations to be on the order of several minutes. Regardless, ^{13}C NMR experiments still required recycle delays of 4 min (KFCT) and 8 min (anhydrous KFC). For room temperature spectra, between 16−304 scans were recorded and between 4−16 scans were acquired for the variable-temperature experiments. The ^{1}H NMR spectra required between 4−16 scans, which were collected using a 2.5 μs $\pi/2$ pulse and a 10 s pulse delay.

Stationary sample ^{13}C and ^{15}N NMR experiments were performed as described above except a Hahn-echo pulse sequence[65] was used. Continuous-wave ^{1}H decoupling was applied after the initial excitation pulse and remained until acquisition of the FID was complete. The ^{13}C NMR spectrum was a result of the summation of 1056 transients, while 140 transients were acquired for the ^{15}N NMR spectrum. An additional ^{13}C NMR spectrum was acquired at an applied magnetic field strength of 7.05 T on a Bruker Avance 300 ($\nu_L(^{13}C) = 75.5$ MHz) in the same manner as the experiments performed on the Bruker 500, but a total of 400 transients were acquired.

Parameters describing the anisotropic chemical shift tensor were determined from simulations of the MAS and stationary sample spectra using the program WSOLIDS, an analytical simulation program developed in our laboratory.[66] Since the ^{13}C and ^{15}N chemical shift tensors are axially symmetric, the tensor is described by the span, Ω, which is the difference between the perpendicular, $\delta_\perp$, and parallel, $\delta_\parallel$, components of the chemical shift tensor and the isotropic chemical shift, $\delta_{iso} = (2\delta_\perp + \delta_\parallel)/3$.

Powder X-ray Diffraction. Five KFCT samples were prepared for the powder X-ray diffraction experiments: precipitated from a water solution at room temperature and 55 °C, precipitated from a 0.5 M KOH solution at room temperature and 55 °C, and a crystalline sample that was ground in a mortar. In addition, diffraction data were also acquired for the anhydrous KFC sample that was prepared. The diffraction experiments were performed at room temperature on an Inel powder diffractometer using Cu Kα radiation.

Table 1. Crystallographic Data for the Potassium Ferrocyanide Compounds Included in This Study

compound	KFCT	KFCT	KFC
chemical formula	$C_6N_6FeH_6O_3K_4$	$C_6N_6FeH_6O_3K_4$	$C_6N_6FeK_4$
formula weight	422.42	422.42	368.37
T/°C	22	−80	22
crystal system	monoclinic	monoclinic	orthorhombic
space group (No.)	$C2/c$ (No. 15)	Cc (No. 9)	$Cmcm$ (No. 63)
a/Å	9.3790(10)	9.3528(13)	4.18
b/Å	16.8444(18)	16.755(2)	14.01
c/Å	9.3919(10)	9.3591(13)	21.04
β/deg.	90.0691(18)	90.076(2)	90
V/Å^3	1483.8(3)	1466.7(4)	
Z	4	4	
D_{calcd}/g cm^{-3}	1.891	1.913	
λ/Å	0.71073	0.71073	
μ/cm^{-1}	2.151	2.176	
R_1 $[F_o^2 \geq 2\sigma(F_o^2)]^a$	0.0308	0.0275	
wR_2 $[F_o^2 \geq -3\sigma(F_o^2)]^b$	0.0811	0.0722	

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Single-Crystal X-ray Crystallography. A small amount of a commercial sample of KFCT (20 mg, 0.047 mmol) was placed in a 2-dram vial and dissolved in 2.5 mL of distilled water. Ethanol, 95%, was allowed to slowly evaporate into the solution until small crystals were visible (5 days). Diffraction data were collected at 22 and −80 °C on a Bruker PLATFORM/SMART 1000 CCD diffractometer using graphite-monochromated Mo Kα radiation utilizing ω scans (0.3°, 20 s exposures). A multiscan (SADABS) absorption correction was applied to the data before refinement. The structures were solved with direct methods using Sheldrick's SHELXS-86[67] and least-squares refinement on F^2 was performed with Sheldrick's SHELXL-93.[68] Hydrogen atom positions were derived from heavy-atom coordinates and included during the refinement. The −80 °C structure was found to be a racemic twin, which was accommodated during the refinement using the SHELXL-93 TWIN instruction,[68] yielding a Flack parameter[69−71] of 0.44(2). At room temperature one of the water molecules (O2) was found to be disordered and was refined using an occupancy factor of 0.5. Crystallographic parameters for both structures are summarized in Table 1, select bond lengths and angles in Table 2, atom numbering in Figure 1, and unit cells in Supporting Information, Figure S1.

A crystal of anhydrous KFC was isolated from the high-temperature slow-diffusion crystallization of an aqueous solution of KFCT as described in Crystallization Methods portion of this section. The anhydrous KFC crystals formed needles that could easily be separated from the KFCT crystals that formed blocks. Unit cell parameters for anhydrous KFC were obtained at room temperature in the same manner as described for KFCT and are presented in Table 1. The crystal of anhydrous KFC was not of suitable quality for complete refinement, and such a crystal could not be obtained after several attempts.

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Table 2. Select Bond Lengths (Å) and Angles (deg) for KFCT above and below the Curie Temperature

KFCT at 22 °C							
Fe−C1	1.916(2)	C1−N1	1.162(3)	N1−K2	2.846(2)	N1−O2	2.977(5)
Fe−C2	1.917(2)	C2−N2	1.159(3)	N2−K1	2.835(2)	N2−O1	3.229(4)
Fe−C3	1.921(4)	C3−N3	1.156(5)	N3−K1	3.011(3)	N3−O1	3.170(3)
Fe−C4	1.942(4)	C4−N4	1.100(4)	N4−K2	3.0588(6)	N4−O2	2.901(5)
C1−Fe−C4	90.09(7)	C2−Fe−C4	89.95(7)	C3−Fe−C4	180		
KFCT at −80 °C							
Fe−C1	1.922(4)	C1−N1	1.167(6)	N1−K3	2.859(5)	N1−O3	3.036(4)
Fe−C2	1.926(4)	C2−N2	1.144(6)	N2−K4	2.838(5)	N2−O1	3.267(4)
Fe−C3	1.944(3)	C3−N3	1.098(4)	N3−K4	3.047(6)	N3−O3	2.895(4)
Fe−C4	1.914(4)	C4−N4	1.166(6)	N4−K1	2.832(5)	N4−O2	3.061(5)
Fe−C5	1.909(4)	C5−N5	1.180(6)	N5−K2	2.804(5)	N5−O2	3.176(5)
Fe−C6	1.914(3)	C6−N6	1.164(4)	N6−K4	3.014(3)	N6−O1	3.056(6)
C1−Fe−C3	88.5(2)	C2−Fe−C3	89.4(2)	C4−Fe−C3	91.7(2)		
C5−Fe−C3	90.4(2)	C6−Fe−C3	178.2(2)				

Results and Discussion

Single-Crystal X-ray Diffraction. Although a full refinement of the monoclinic *C*2/*c* KFCT structure has been reported in the literature using both X-ray[45] and neutron diffraction,[41] the most recent study is nearly 40 years old and considering the advancement of crystallography methods and equipment over the past few decades, we have reinvestigated the structure at room temperature. In addition, for the first time we have refined the structure of KFCT at low-temperature (vide infra). The major features of our room temperature structure (see Figure 1A, Table 1, Table 2, Supporting Information, Figure S1A) are in agreement with the structures reported earlier, although improvements in the precision of the atomic positions, bond lengths, and bond angles have been obtained. The ferrocyanide anions, which are slightly distorted octahedra, are in close proximity to two layers of potassium cations, the whole of which is separated by a layer of water molecules. There are two nonequivalent water molecules in the structure, one of which (O2) is disordered about N4 via the 2-fold rotation axis of the crystal. The neutron diffraction study demonstrated that both crystallographically nonequivalent water molecules are disordered.[41] The inability of X-ray diffraction to determine the disorder in the O1-containing water molecule lies in the fact that the oxygen atom is displaced by a small distance; it is the positions of the hydrogen atoms that are disordered.[41] The small oxygen displacement is accounted for in our X-ray structure by the rather large thermal parameter on O1.

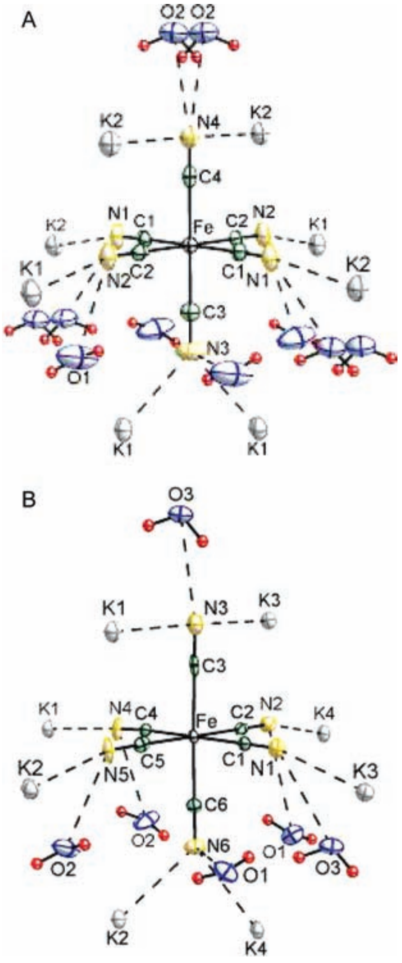

Figure 1. Perspective plot of KFCT at (A) 22 °C and (B) −80 °C. Included are the water molecules and potassium ions nearest to each nitrogen atom. The O2-containing water molecules at 22 °C are disordered, and heavy atoms are drawn with 50% probability ellipsoids.

Below the transition temperature, a complete refinement of the structure has not previously been performed, although the space group has been reported to be *Cc*.[44,45] The authors noted that little difference was expected in the positions of the heavy atoms at low temperature, regardless of the phase change and the loss of a symmetry center within the crystal.

Indeed, at −80 °C we observed only minor changes to the positions of the ferrocyanide anion atoms and potassium ions in comparison to the room-temperature structure; the major difference being that all six carbon and nitrogen atoms within the same ferrocyanide anion are crystallographically nonequivalent at −80 °C (see Figure 1B, Table 1, Table 2, Supporting Information, Figure S1B). Furthermore there are three nonequivalent water molecules with no positional disorder; the water molecule containing O3 resides in one of the two positions that was occupied by O2 at room temperature. The ^{1}H and ^{2}H NMR spectra acquired at −80 °C indicate that while the translational motion has ceased and the positions of the oxygen atoms are thus fixed, the water molecules are still undergoing flips about the water molecule's C_2-axis such that the hydrogen atom positions remain disordered.[45,57,58]

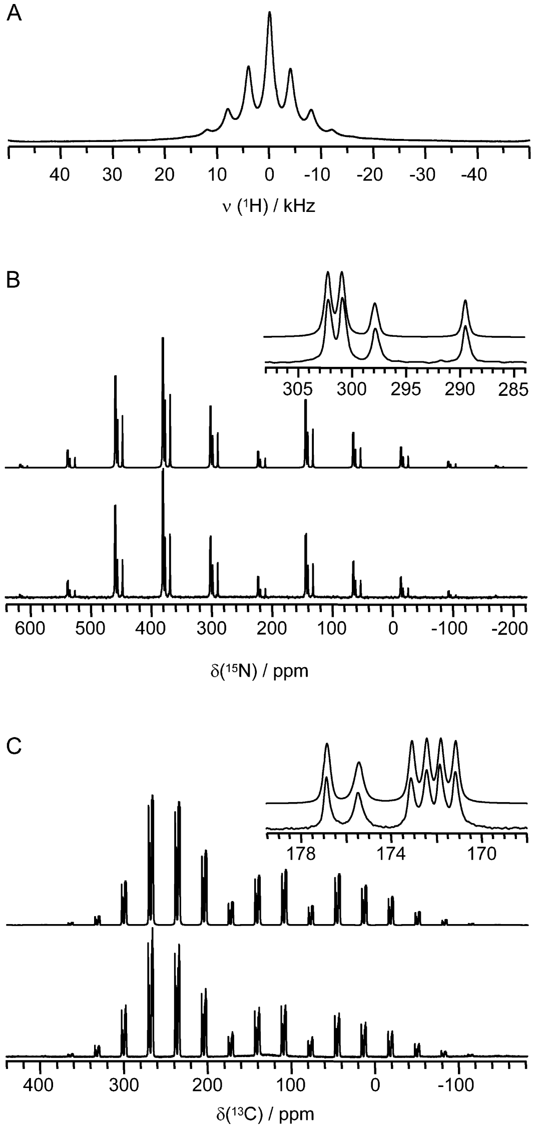

Figure 2. (A) ^{1}H, (B) ^{15}N, and (C) ^{13}C MAS NMR spectra of a ground sample of KFCT acquired with $\nu_{\text{rot}} = 4.0$ kHz. For the ^{13}C and ^{15}N spectra, the lower traces represent the experimental NMR spectra, while the upper traces represent simulated NMR spectra. Simulation parameters are presented in Table 3. The insets in (B) and (C) are expansions of the isotropic regions of each spectrum.

The unit cell parameters determined for anhydrous KFC indicate that the room-temperature structure of KFCT changes dramatically upon dehydration, changing from monoclinic *C*2/*c* to orthorhombic *Cmcm*. The ^{13}C and ^{15}N NMR spectra presented in the following section are also sensitive to the structure change upon dehydration.

Solid-State ^{1}H, ^{13}C, and ^{15}N NMR Spectroscopy of a Ground Sample of KFCT. The initial sample of KFCT studied by multinuclear solid-state NMR spectroscopy was prepared by crystallizing KFCT at room temperature by ethanol diffusion into a solution of KFCT in distilled water. Using the standard protocol for preparing solid-state NMR samples, the KFCT crystals were ground thoroughly using a mortar and pestle and packed tightly into an NMR rotor. The ^{1}H, ^{13}C, and ^{15}N NMR spectra subsequently obtained are presented in Figure 2.

Table 3. Carbon-13 and Nitrogen-15 NMR Parameters for a Ground Sample of Potassium Ferrocyanide Trihydrate (KFCT) and Anhydrous Potassium Ferrocyanide (KFC) at Room Temperature[a]

		δ_{iso} of site/ppm					
compound	nucleus	**1**	**2**	**3**	**4**	**5**	**6**
KFCT[b]	^{13}C	176.9	175.4	173.0	172.3	171.7	171.0
KFC[c]	^{13}C	181.0	177.8	176.7	170.5	169.7	165.8
KFCT[d]	^{15}N	302.2	302.2	300.9	300.9	297.8	289.5
KFC[e]	^{15}N	304.4	304.1	303.2	297.7	297.4	291.9

[a] Skew of the CS tensor is assumed to be +1.0 and the uncertainty in δ_{iso} is ± 0.1 ppm in all cases. [b] Span of the CS tensor is 360(5) ppm for all sites as derived from stationary sample spectra (see Supporting Information, Figure 2). The $R_{\text{eff}}(^{15}\text{N},^{13}\text{C})$ was determined to be −1850(50) Hz. [c] Span of the CS tensor is 365(10) ppm for all sites as derived from an analysis of the spinning sideband manifold. [d] Span of the CS tensor is 530(10) ppm for all sites as derived from stationary sample spectra (see Supporting Information, Figure 2). [e] Span of the CS tensor is 530(10) ppm for all sites as derived from an analysis of the spinning sideband manifold.

The ^{1}H NMR spectrum has a very small spinning sideband manifold, which indicates that the water molecules are undergoing several types of motion. If no motion was present, the ^{1}H spectrum would take the shape of the classic "Pake" doublet[72] because of the ^{1}H−^{1}H homonuclear dipolar coupling (splitting ≈ 46 kHz) that is slightly distorted by the ^{1}H chemical shift anisotropy, CSA.[73,74] Clearly, the water dynamics essentially average these two interactions, giving rise to the spectrum presented in Figure 2.

As expected, the CN ligands give rise to a large CSA that dominates the ^{13}C and ^{15}N NMR spectra and results in numerous spinning sidebands under MAS. Parameters describing the CSA have been determined from simulations of the MAS spectra presented in Figure 2 and stationary sample spectra presented in Supporting Information, Figure S2; simulation parameters are given in Table 3.

An expansion of the isotropic regions of the ^{13}C and ^{15}N MAS NMR spectra are presented as insets to Figure 2. Note that the isotropic region has the same appearance if the spinning sidebands are summed into the isotropic region. Based upon the monoclinic crystal structure at room temperature, in which there are four crystallographically and magnetically nonequivalent cyanide ligands, it was expected that the ^{13}C and ^{15}N MAS NMR spectra would have four unique isotropic sites. The isotropic region of the ^{15}N NMR spectrum (inset of Figure 2B) is consistent with the crystal structure having four peaks with relative areas of 2:2:1:1; the two high-frequency ^{15}N NMR peaks result from the four equatorial sites. The ^{13}C spectrum, on the other hand, has six distinct isotropic peaks, each having nearly the same relative area (inset of Figure 2C), suggesting that all six carbon atoms in the ferrocyanide anion are nonequivalent. Such a spectrum is not consistent with the monoclinic *C*2/*c* form discussed above, nor with the known tetragonal form. Rather, the ^{13}C spectrum suggests the presence of a new room-temperature form of KFCT.

To shed some light on the unexpected ^{13}C NMR results, a series of experiments were performed. First, solution NMR

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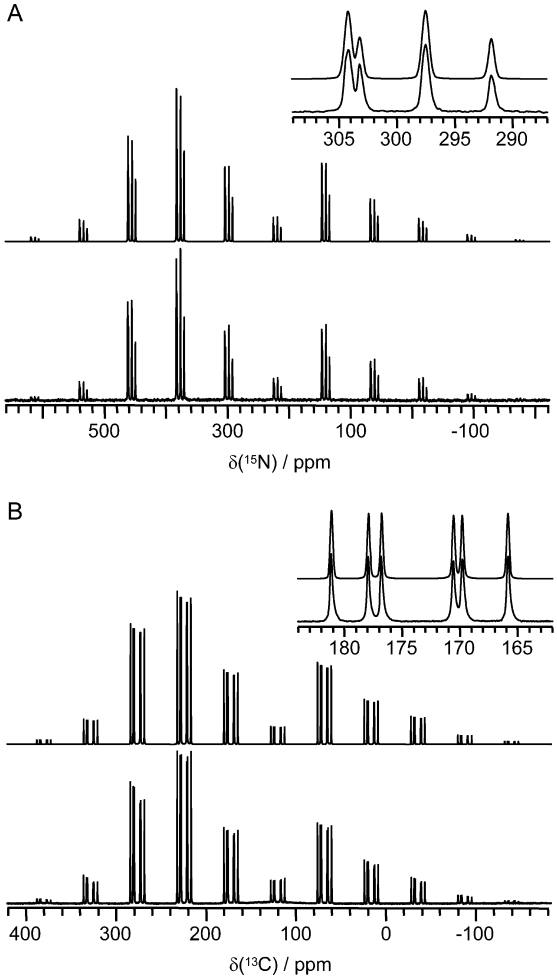

Figure 3. Experimental (lower traces) and simulated (upper traces) (A) ^{15}N and (B) ^{13}C MAS NMR spectra of anhydrous KFC acquired with ν_{rot} = 4.0 kHz. (Insets) Expansions of the isotropic region of each spectrum. Simulation parameters are presented in Table 3.

and IR spectroscopy have been used to verify that no impurities were present. Additional solid-state NMR experiments, performed on additional samples of KFCT containing different amounts of isotropic ^{13}C−^{15}N labeling, demonstrated that no spin−spin coupling interactions can account for the additional peaks in the ^{13}C NMR spectrum. The additional peaks in the ^{13}C NMR spectrum must then occur from some solid-state effect, namely polymorphism or a different hydrate of KFCT. For the latter case, no hydrates greater than the trihydrate have been reported in the literature; a monohydrate form has been suggested,[43,75] and a stable anhydrous form is known but has not been previously characterized.[76,77] Thermal Gravimetric Analysis, TGA, indicates that the KFCT sample studied indeed consists of three water molecules per ferrocyanide anion; there are no other stable hydrates of KFC and complete dehydration is achieved when heated over 85 °C. The ^{13}C and ^{15}N NMR spectra of anhydrous KFC are shown in Figure 3. While there are no significant changes to the CSA parameters (see Table 3), the isotropic regions of the ^{13}C and ^{15}N NMR spectra of anhydrous KFC differ from those of KFCT. Comparison of the isotropic ^{13}C chemical shifts between KFCT and anhydrous KFC (see Table 3) clearly demonstrates that the anhydrous form of KFC is not responsible for any of the six peaks observed in the ^{13}C MAS NMR spectrum of ground KFCT (see Figure 2).

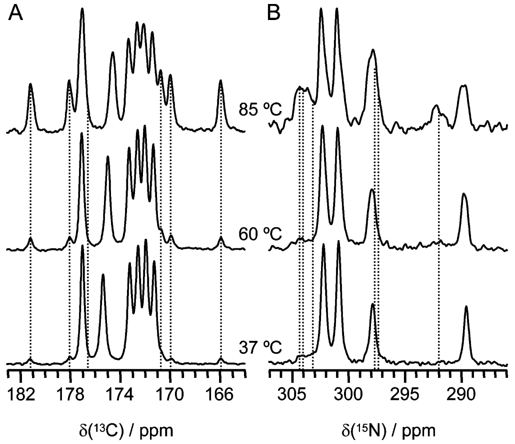

Figure 4. Isotropic regions of (A) ^{13}C and (B) ^{15}N MAS NMR spectra of KFCT acquired at elevated temperatures. For each spectrum, the spinning sidebands have been summed into the isotropic region, and the peaks corresponding to anhydrous KFC have been marked with dotted lines.

Last, to ensure that additional hydrates of KFC are not responsible for the additional ^{13}C peaks in Figure 2, variable-temperature ^{13}C and ^{15}N experiments were performed up to 85 °C and are presented in Figure 4. At 37 °C, additional peaks at around 181, 178, 170, and 166 ppm begin to appear in the ^{13}C NMR spectrum, although no additional peaks are evident in the ^{15}N NMR spectrum at this temperature. At 60 °C, these additional peaks in the ^{13}C NMR spectrum grow in intensity and some broadening of the two low-frequency ^{15}N peaks occurs. At 85 °C, the intensities of the additional peaks are significant in both the ^{13}C and ^{15}N NMR spectra. The chemical shifts of these peaks correspond exactly to those found in the anhydrous KFC sample, and the absence of any other peaks demonstrates that no intermediate hydrates of KFC are formed upon heating.

Solid-State ^{13}C and ^{15}N NMR Spectroscopy of Unground Samples of KFCT. On the basis of the discussion presented in the previous section, the additional peaks in the room-temperature ^{13}C NMR spectrum of KFCT (see Figure 2) must be due to polymorphism. To determine if polymorphism can account for the additional peaks in the ^{13}C NMR room-temperature spectrum, we crystallized KFCT under ten crystallization conditions as described in the Experimental Section. These samples, however, were not subject to grinding before acquisition of the ^{13}C and ^{15}N NMR spectra. Regardless of the crystallization method utilized, the relative intensities and chemical shifts of the four isotropic peaks in the ^{15}N MAS NMR spectra obtained are the same as the ^{15}N NMR spectrum of the ground sample (see Figure 2). The isotropic region of the ^{13}C NMR spectra are shown in Figure 5, with the crystallization rate of the samples increasing from left to right. These spectra are sensitive to the crystallization method used, specifically the relative intensities of the four

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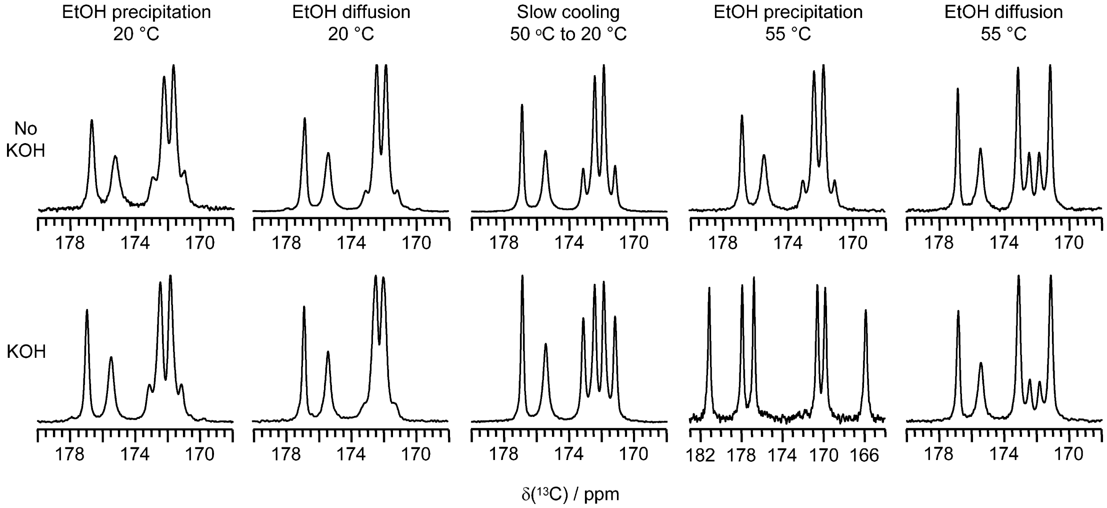

Figure 5. Isotropic region of the ^{13}C MAS NMR spectra of a variety of KFCT samples, with each KFCT sample crystallized under the conditions described in the text. The samples in the top row were crystallized from distilled water while the samples in the bottom row were crystallized from a 0.5 M KOH solution. For each spectrum, the spinning sidebands have been summed into the isotropic region.

low-frequency peaks varied depending on how the crystals were formed. In all cases, however, the relative areas of the two high-frequency peaks compared to the sum of the four low-frequency peaks are 1:1:4, and the chemical shifts of the six peaks do not differ between the samples. For the remainder of this paper, the relative areas of the four low-frequency peaks will be expressed so the total area of the four peaks is normalized to four.

In the four samples prepared at room temperature (by ethanol precipitation and ethanol diffusion, first and second column of Figure 5), the two outer ^{13}C NMR peaks of the low-frequency “quartet” are low in intensity relative to the two inner peaks. In the samples prepared by ethanol precipitation, the relative integrated areas of the four peaks is approximately 0.4:1.6:1.6:0.4. A slight decrease in the relative intensities of the outer peaks relative to those of the inner peaks is observed for the crystals prepared by ethanol diffusion. Regardless, for both crystallization methods at room temperature the inclusion of KOH has little effect on the ^{13}C NMR spectrum obtained.

When slow-cooling to room temperature was utilized (middle column of Figure 5), the relative intensities of the outer two peaks were found to increase in comparison to the KFCT samples prepared at 20 °C. The increase observed is only slight for the sample prepared from a water solution, but is significant for the KOH sample. For the latter sample, the intensities of the four peaks are nearly equal, and the relative integrated areas are 0.9:1.1:1.1:0.9.

From the four samples prepared at 55 °C, three distinct ^{13}C NMR spectra were obtained. First, the spectrum obtained for the sample prepared by ethanol precipitation from a water solution (Figure 5, top row, second column from the right) appears to be the same as the spectrum obtained for the four samples that were prepared at room temperature. When the sample was precipitated from a KOH solution (Figure 5, bottom row, second column from the right), anhydrous KFC was formed (compare this spectrum to that of Figure 3). When ethanol diffusion was utilized, there is no major difference in the composition of the KFCT sample obtained whether or not KOH was used. For these samples, the intensities of the outer peaks of the low-frequency quartet are much larger than those of the inner peaks, with the relative areas of the peaks being 1.4:0.6:0.6:1.4.

In general, the ^{13}C NMR spectra presented in Figure 5 demonstrates that the crystallization rate and solution composition have little influence on the KFCT sample obtained at room temperature, but these factors become important at elevated temperatures. The changes to the sample composition are reflected by variations in the relative intensities of the low-frequency quartet of the ^{13}C NMR spectra. The reason why the intensities of the ^{13}C NMR peaks are altered depending on the crystallization temperature can be inferred from what is known from the various crystallography studies that have been performed on KFCT. As described earlier, the most common form of KFCT is a monoclinic form, although a tetragonal form has been reported. From a bulk crystallization, a pure form of KFCT is never obtained but the relative amounts of the various forms can be manipulated by altering the crystallization conditions.[42,44] At elevated temperatures, the tetragonal form is preferred, whereas at room temperature the monoclinic *C*2/*c* form is preferred.[42] Taken with the ^{13}C NMR spectra presented in Figure 5, we believe that the spectra obtained are a convolution of two individual ^{13}C NMR spectra, one resulting from the monoclinic form and another from the tetragonal form. Each individual spectrum consists of four peaks with the relative integrated areas of 1:1:2:2, and the chemical shifts of the two high-frequency peaks are the same for both polymorphs. The only difference are the chemical shifts of the two low-frequency peaks; the monoclinic form, which is dominant at room temperature, giving rise to the inner peaks in the low-frequency quartet, and the tetragonal form, which is dominant at elevated temperatures, giving rise to the outer peaks of the low-frequency quartet. The different ^{13}C NMR spectra obtained therefore result from different relative amounts of each polymorph.

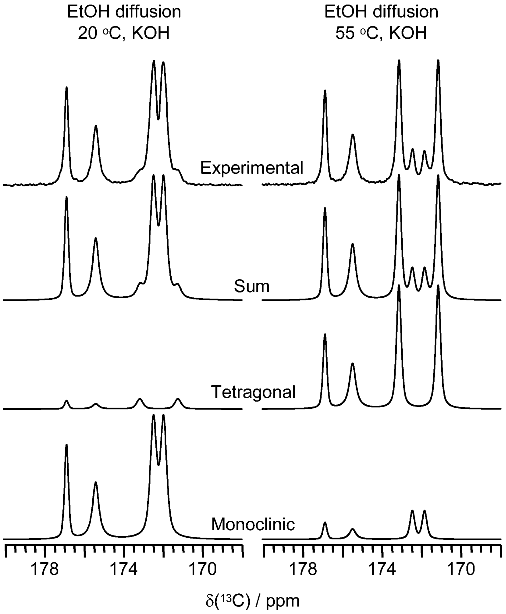

Figure 6. Deconvolutions of the isotropic region of the ^{13}C MAS NMR spectra of a KFCT sample obtained from ethanol diffusion into a 0.5 M KOH solution of KFCT at room temperature (left column), and a sample obtained in the same manner at 55 °C (right column). The monoclinic (*C*2/*c*) form comprises 90% of the former sample and 20% of the latter sample.

To demonstrate how the experimental ^{13}C MAS NMR spectra can be composed of two polymorphs, theoretical spectra have been constructed for each polymorph using the chemical shifts of the peaks presented in Table 2, fitting the theoretical linewidths to the experimental linewidths, and then adjusting the intensities to ensure that the relative areas of the four peaks were exactly equal to 1:1:2:2. Note that the chemical shifts of the two high-frequency peaks are the same for both polymorphs. The spectra were then summed using different weighted amounts of each polymorph. In Figure 6, the individual theoretical spectra are presented and summed to simulate the ^{13}C NMR spectra obtained for the two crystallization conditions that produced the greatest relative amount of each polymorph; ethanol diffusion at room temperature for the monoclinic *C*2/*c* polymorph (upper left spectrum of Figure 6) and ethanol diffusion at 55 °C for the tetragonal polymorph (upper right spectrum of Figure 6). Simulations of the experimental spectra were obtained by adding the spectra arising from different weighted amounts of each polymorph. Using this procedure, we have found that the room-temperature sample spectrum is composed of about 90% of the monoclinic polymorph, while this polymorph comprises only about 20% of the high-temperature sample.

As mentioned earlier, the same ^{15}N NMR spectrum is obtained regardless of the crystallization condition, and it appears as though ^{15}N NMR is insensitive to the polymorphism. Given that ^{13}C has a smaller chemical shift range than ^{15}N, it was expected that the ^{15}N NMR spectra would actually be more sensitive to the polymorphism than the ^{13}C NMR spectra. It appears that the ^{15}N peaks of the two different polymorphs fortuitously overlap such that the same overall ^{15}N NMR spectrum is obtained regardless of the relative amounts of each polymorph.

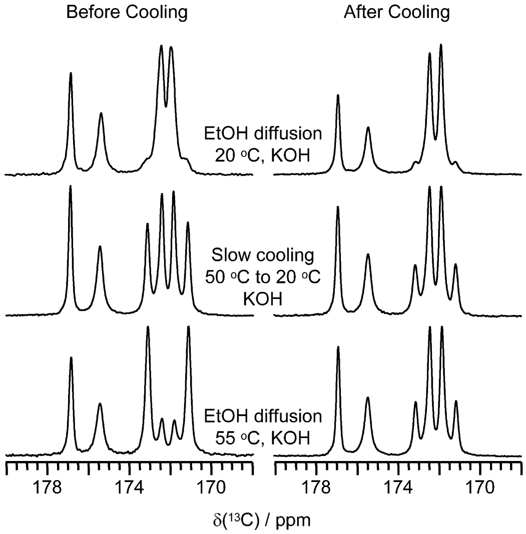

Figure 7. Isotropic region of room-temperature ^{13}C MAS NMR spectra of three different samples of KFCT acquired at room temperature before and after cooling down to −98 °C. For each spectrum, the spinning sidebands have been summed into the isotropic region.

Effects of Cooling on the ^{13}C NMR Spectra of the Crystalline Samples. To further verify that the crystallized sample contains a mixture of the monoclinic and tetragonal polymorphs, after the initial ^{13}C NMR spectra were acquired (see Figure 5), the samples were cooled to −98 °C, warmed to room temperature, and then new ^{13}C NMR spectra were acquired. According to literature reports, the tetragonal polymorph converts irreversibly to the monoclinic *Cc* polymorph upon cooling below about −60 °C.[44,60,76,78] Warming the *Cc* polymorph above the Curie temperature of −25 °C leads to the *C*2/*c* structure. If the outer peaks in the ^{13}C NMR spectra belong to the tetragonal polymorph, then after a cooling/warming cycle the intensities of these peaks in the room-temperature ^{13}C MAS NMR spectrum should decrease relative to the inner peaks that we have assigned to the monoclinic *C*2/*c* polymorph. In general, this is exactly what was observed in all cases, and the results for three crystal samples are shown in Figure 7. These samples represent the crystallization condition with the least amount of the tetragonal polymorph (top row: ethanol diffusion at room temperature, KOH solution), the condition that produced a roughly equal amount of each polymorph (middle row: slow-cooling from 55 °C to room temperature, KOH solution), and the condition that produced the greatest amount of the tetragonal polymorph (bottom row: ethanol diffusion, 55 °C, KOH solution). On the left-hand column of Figure 7, the original ^{13}C NMR spectra are shown and on the right-hand column, the room-temperature ^{13}C NMR spectra acquired after a cooling/warming cycle are presented. For the first sample, there is no appreciable change to the ^{13}C NMR spectrum after cooling, consistent with the initial sample containing primarily the monoclinic polymorph. For the second sample, which has about an even amount of each polymorph, there is a considerable decrease in the intensities of the outer peaks after cooling, although a significant amount

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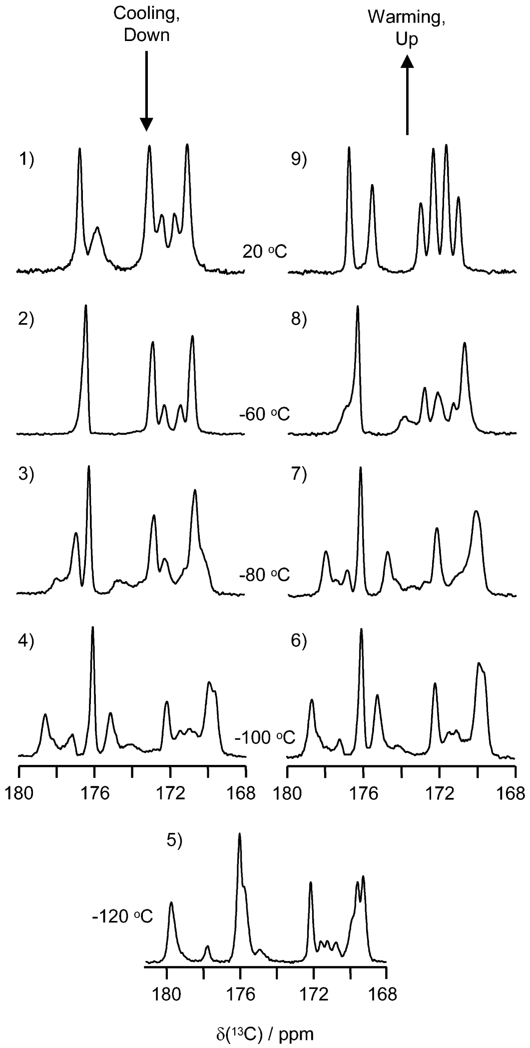

Figure 8. Isotropic region of the ^{13}C MAS NMR spectra of KFCT upon cooling to −120 °C (left column, down) and subsequently warming back to 20 °C (right column, up). The numbers indicate the order in which the spectra were acquired. For each spectrum, the spinning sidebands have been summed into the isotropic region. The sample of KFCT was obtained from a crystallization in which ethanol slowly diffused into a water solution of KFCT at 55 °C.

of the tetragonal polymorph still remains. From a deconvolution of the spectrum obtained after cooling, the tetragonal polymorph still comprises about 25% of the sample. Last, for the high-temperature sample, again a decrease in the intensities of the outer peaks relative to those of the inner peaks was observed; the resulting ^{13}C NMR spectrum obtained is the same for this sample as the previous sample.

To further examine the effects of cooling we performed a series of low-temperature experiments on a freshly crystallized high-temperature sample. C-13 NMR spectra were obtained every 20 °C when cooling the sample from 20 to −120 °C, which is the lowest stable temperature that can safely be achieved with the NMR probe utilized, and upon warming back to room temperature. The spectra obtained are shown in Figure 8. As the temperature decreases, five of the six peaks move to lower frequency, while the peak that has a shift of 175.4 ppm at room temperature moves to higher frequency. This carbon site is also the most sensitive to the changes in temperature. At −60 °C, we expected to observe a change to the monoclinic *Cc* form, whereas in reality the only major change is that there are now five ^{13}C peaks, as the temperature-sensitive peak described above has merged with its neighboring peak. At −80 °C, this peak is to the high-frequency of its neighboring peak, with a shift of 176.9 ppm. At this temperature, several new peaks appear in the ^{13}C NMR spectrum, having chemical shifts of approximately 178, 175, and 170 ppm.

Upon further cooling, the intensities of the ^{13}C peaks arising from the initial KFCT sample continue to decrease while the new peaks continue to increase and at −120 °C, there are six main peaks in the ^{13}C NMR spectrum, with shifts of 179.6, 175.9, 175.7, 172.1, 169.5, and 169.2 ppm. Likely these peaks are due to the *Cc* monoclinic structure that we presented earlier where the six cyanide ligands are nonequivalent and thus should give rise to six ^{13}C NMR peaks. Such a transition from the tetragonal structure to the low-temperature monoclinic structure has been reported in the literature and is irreversible.[44,60,76,78]

Upon warming, the ^{13}C NMR spectra, with the exception of the spectra at −100 °C, differ from those obtained on cooling. Of particular interest are the spectra obtained at −60 °C. During cooling, there are six peaks belonging to the *C*2/*c* and tetragonal forms of KFCT. During warming, the ^{13}C NMR spectra clearly indicate that an additional phase of KFCT is present. Not until 0 °C (spectrum not shown) are the peaks arising from this additional phase absent from the ^{13}C NMR spectrum. The phase transition observed upon warming is that of the *Cc* structure to the *C*2/*c* structure; this transition has been documented to occur at −25 °C.[44,46,48,49,63,76−80]

At room temperature, the ^{13}C NMR spectrum obtained after the cooling and heating cycle differs significantly from the initial spectrum obtained. As shown earlier, the relative amount of the two polymorphs has changed in such a way that more of the monoclinic *C*2/*c* polymorph is present, although some tetragonal polymorph does remain. The fact that some of the tetragonal form remains after cooling has not been previously reported in the literature. In all previous studies the tetragonal polymorph was apparently removed upon cooling. Such studies, however, have focused on a single-crystal only, whereas we are studying a bulk sample that contains different polymorphs, crystallites of which range in size from powders to crystals of several millimeters. One possibility is that a minority of the bulk sample is composed of powders for which the phase-change from monoclinic to tetragonal does not occur. We have examined the effects of grinding to gain further insight into this possibility.

Effects of Grinding on the ^{13}C NMR Spectra of the Crystalline Samples. After cooling, the samples were unpacked, ground using a mortar and pestle, and repacked tightly into the NMR rotors. For all but the precipitated samples, the ^{13}C NMR spectra of the ground samples are essentially the same as presented in Figure 2. Specifically

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the isotropic regions of the spectra contain six ^{13}C peaks of roughly equal integrated intensity. For the precipitated samples, grinding did result in an increase in the intensity of the outer peaks of the isotropic region, but the integrated areas of the four peaks were about 0.7:1.3:1.3:0.7.

Although there have been a few instances in which grinding samples has been shown to influence the solid-state NMR spectrum obtained,[81−85] such reports are rare. The phase transitions arise from heating that arises from the friction between mortar, pestle, and sample,[84] from the mechanical stress that is placed on the sample,[81,82] or from both simultaneously.[83] For KFCT, no solid−solid phase transitions above room temperature have been reported in the literature, nor is there any evidence of such a transition from the ^{13}C NMR spectra obtained above room temperature (see Figure 4). Thus the changes to KFCT from grinding must arise solely from the stress placed upon the sample. But what changes are induced in KFCT by grinding? First, recall that we concluded earlier that there are no stable forms of KFC other than the trihydrate and anhydrous forms. Therefore any loss of water because of heating that is caused by grinding results in small amounts of anhydrous KFC. Indeed in some ^{13}C NMR spectra of ground samples of KFCT, peaks arising from the anhydrous form are present in small amounts. The presence of anhydrous KFC is so slight that TGA of ground samples is consistent with the trihydrate form. Therefore, there are two likely possibilities: the grinding is producing an even distribution of the two polymorphs, or, as mentioned earlier, the grinding is resulting in a polymorph, yet to be reported in the literature, in which none of the cyanide ligands are related by symmetry. Although having an even amount of each polymorph seems unlikely, crystallizations of poly(L-alanine) have been shown to result in a near equal amount of a beta-pleated sheet and α-helix conformations.[81] For KFCT, there is no obvious thermodynamic reason why either of the two polymorphs would be favored and it is possible that a ground sample contains an equal amount of each polymorph. However, on the basis of the ^{13}C NMR results alone, the existence of an as yet uncharacterized polymorph can not be ruled out. We have utilized powder X-ray diffraction to shed further light on this situation.

Powder X-ray Diffraction Results. To characterize the various KFC forms, we have performed powder X-ray diffraction experiments on several samples. Since we are limited to powder forms of KFCT, only samples of KFCT that have been produced by precipitation or grinding can be compared to the theoretical diffraction pattern generated from the monoclinic polymorph. In addition, the anhydrous form has been studied. The diffraction patterns are presented in Figure 9. In comparison to the theoretical pattern, the pattern for the precipitated sample contains few peaks whose positions match those of the theoretical pattern. Even though the particles for the precipitated sample are small, likely the lack of grinding has resulted in some form of preferential alignment of the crystals and the poor distribution of crystallite orientations results in the lack of peaks in the diffraction pattern. Upon grinding, there is a considerable increase in the number of peaks appearing in the diffraction pattern. While the diffraction pattern matches the theoretical pattern well, there are some additional peaks that do not appear in the theoretical pattern. The most intense of these peaks appear at 2θ angles of approximately 25°, 30°, 31.5°, and 32.5°; however, these peaks can be found in the experimental diffraction pattern of the anhydrous sample. This is consistent with the NMR data that indicated that some of the anhydrous sample is produced upon grinding the KFCT sample.

Since all peaks in the diffraction pattern of the ground sample of KFCT can be matched to peaks in the theoretical pattern of the monoclinic polymorph and the experimental pattern of anhydrous KFC, there is no evidence of a new polymorph upon grinding. By corollary, there is also no evidence from the X-ray diffraction study that any of the tetragonal polymorph is present. However, we know from the ^{13}C and ^{15}N NMR spectra and the similarity of the unit cell parameters that the structure of the two polymorphs are so similar that it is possible that a powder X-ray diffraction pattern is not able to distinguish between the monoclinic and tetragonal forms.

Conclusions

Potassium ferrocyanide trihydrate has been studied by ^{13}C and ^{15}N solid-state NMR spectroscopy and X-ray diffraction. The ^{15}N NMR spectra have four peaks with relative integrated areas of 2:2:1:1; a result that appears to be fortuitously consistent with the crystal structure at room temperature. The ^{13}C NMR spectra, however, consist of six peaks, two high-frequency and four low-frequency peaks with similar chemical shifts. The relative intensities of the four low-frequency peaks change depending on the crystallization conditions, by cooling and by grinding. Of the crystallization conditions studied, the temperature at which the crystals are formed has the greatest effect on the high-resolution ^{13}C NMR spectra. At room temperature, the intensities of the inner peaks in the low-frequency set are much greater than the intensities of the outer peaks; at elevated temperatures the relative intensities of the four peaks are reversed.

The disagreement between the ^{13}C NMR results and the crystal structure has been shown to arise from polymorphism between the monoclinic *C*2/*c* structure and a previously reported tetragonal structure. From crystallizations at room temperature, the monoclinic form is favored, giving rise to a ^{13}C NMR spectrum in which the inner peaks of the low-frequency set of peaks are the most intense whereas at elevated temperatures, the tetragonal form is favored and the outer peaks are the most intense in the ^{13}C NMR spectrum. Cooling to −98 °C converts most of the tetragonal form to

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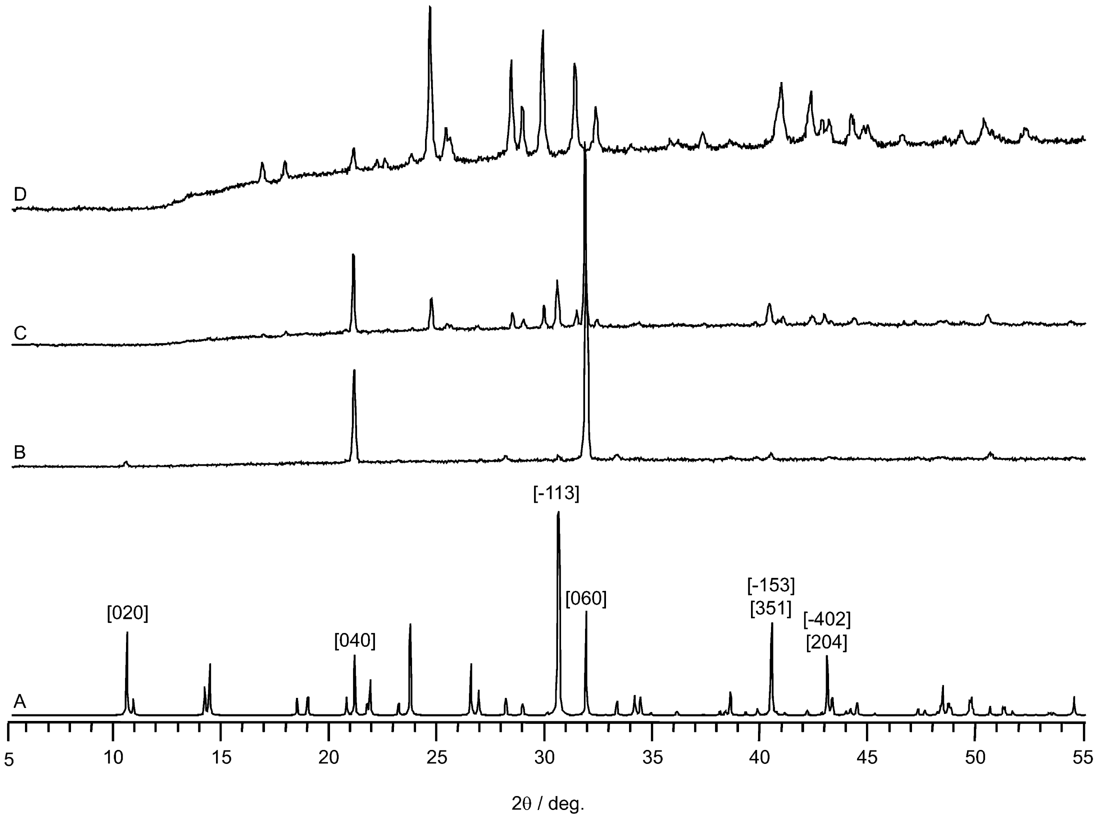

Figure 9. (A) Theoretical powder X-ray diffraction pattern of the room-temperature monoclinic (*C*2/*c*) form of KFCT as generated from the single-crystal X-ray diffraction data. Experimental powder X-ray diffraction patterns of (B) a sample of KFCT prepared by precipitating KFCT from a water solution at room temperature with ethanol, (C) a powder sample of KFCT prepared by grinding a crystalline sample of KFCT, and (D) a powder sample of anhydrous KFC.

the monoclinic form and after warming to room temperature, the intensities of the outer ^{13}C NMR peaks are reduced relative to those of the inner peaks. Low-temperature ^{13}C NMR experiments demonstrate that this conversion begins below −60 °C; however, this phase change is to a well-known low-temperature *Cc* phase of KFCT in which six cyanide ligands are crystallographically nonequivalent. Upon warming back to room temperature, the phase change occurs around −40 °C and the sample consists mostly of the *C*2/*c* form.

The relative intensities of peaks in the ^{13}C NMR spectra of KFCT are also sensitive to grinding. After grinding using a mortar and pestle, the relative integrated areas of the six peaks are approximately equal. Variable temperature ^{13}C NMR experiments performed on a ground sample of KFCT have demonstrated that additional peaks are present upon heating and such peaks arise from the formation of anhydrous KFC; no hydrates of KFC aside from the trihydrate are formed. In addition, powder X-ray diffraction experiments do not suggest the formation of an unknown polymorph of KFCT upon grinding but rather that grinding results in a near equal amount of the monoclinic and tetragonal polymorphs.

In summary, the results presented here illustrate the extreme sensitivity of high-resolution solid-state ^{13}C NMR spectroscopy to subtle changes in crystal structure. From this study and previous research,[86,87] it is clear that solid-state NMR is ideally suited to study polymorphism in bulk samples.

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Supporting Information Available: X-ray crystallographic files in CIF format and crystal packing diagrams for KFCT at 22 and −80 °C. Carbon-13 and ^{15}N stationary sample NMR spectra of KFCT. This material is available free of charge via the Internet at http://pubs.acs.org.

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