^{14}N Nuclear Quadrupole Resonance Study of the Phase Transitions of $Ba[Fe(CN)_5NO] \cdot 3H_2O$ *

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The ^{14}N nuclear quadrupole resonance (NQR) of the cyanides in $Ba[Fe(CN)_5NO] \cdot 3H_2O$ (BNP) was observed between 77 and 293 K. Phase transitions exist at 118, 131 (both weakly first order) and 233 K (second order). Most of the cyanides were perturbed by the structural changes except for one of the trans cyanides that was only affected by the transition at 131 K. The mechanism of the phase transitions is interpreted in terms of soft modes resulting from the ion rearrangement produced by the slowing down of the water molecules upon cooling. A comparison of the NQR spectrum of BNP with that of $Na_2[Fe(CN)_5NO] \cdot 3H_2O$ showed that the substitution of Na^+ by Ba^{2+} produced only minor changes in the charge distribution of the nitroprusside ion.

Key words: Magnetic Resonance (NQR), Nitroprussides, Phase Transitions

Introduction

The discovery of a metastable electronic excited state of the nitroprusside anion in $Na_2[Fe(CN)_5NO] \cdot 3H_2O$ (SNP) by laser light irradiation [1] at 77 K stimulated an intensive search for similar photochromic phenomena in other complexes. One of the mixed cyanides that showed a similar excited state [2] was $Ba[Fe(CN)_5NO] \cdot 3H_2O$ (BNP). On the other hand, several structural and spectroscopic studies were performed [3–6] on BNP, and indications of phase transitions were observed [6]. A differential thermal anlysis (DTA) [7] starting at 77 K, showed three phase transitions at 118.1, 130.5 and 234.3 K with very small changes in enthalpy in each case. In order to obtain information about: a) the changes in the electronic distribution of the nitroprusside anion on changing the cation, and b) the events at the phase transitions, a ^{14}N NQR study of BNP was undertaken from 77 K to room temperature.

Experimental

^{14}N NQR spectra were obtained by means of a MATEC pulsed spectrometer [8, 9]. Free induction decays (FID) obtained from the cyanide lines after “90° pulses” were added and transformed with a Nicolet 1280 Data System [9]. The sample was cooled by controlled injection of liquid N_2. Sample temperature was estimated to be accurate within ± 0.5 K. The temperatur difference along the glas vial containing the sample was less than 0.3 K and the long-term stability was found to be ± 0.3 K over many hours at any temperature down to 77 K. A sample of about 25 g of BNP was prepared following [4]. The resulting orange-pink crystals were recrystallized twice from deionized water and the purity was checked by atomic absorption spectroscopy.

Results

As ^{14}N has a spin $I = 1$, usually two NQR lines are observed per each crystallographically inequivalent ^{14}N site [10]. The lines are $\nu^{\pm} = (3e^2 qQ/4h)(1 \pm \eta/3)$, where $e^2 qQ/h$ is the Nuclear Quadrupole Coupling Constant (NQCC) and η is the asymmetry parameter of electric field gradient (EFG). If $\eta = 0$, only one line $\nu^{\circ} = 3e^2 qQ/4h$ is found for this site. At room temperature we found nine lines between 2550 and 2780 kHz. These frequencies are similar to those found for the cyanides of SNP, so we assigned them to the same groups in BNP. The first structure proposed [3] (orthorhombic, space group $Pca2_1$) for BNP showed five inequivalent CN groups, two water molecules per complex anion and $Z = 4$. A later refinement [6] gave the same space group, number of sites and formula

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units but found instead three water molecules per formula unit in BNP. This number of water molecules was also confirmed by means of a thermogravimetric analysis of several samples of BNP [7]. The structure [3, 6] predicted five different but equally populated ^{14}N sites for the CN groups in BNP. The number of NQR lines found in BNP is consistent with the number of sites predicted for the structure of BNP at room temperature.

Figure 1 shows the temperature dependence of the NQR lines of the CN group between 77 K and room temperature. The dependence of the NQR frequencies between room temperature and 233 K is linear for the seven lines of highest frequency and almost linear for the other two. In order to understand the changes in the complex spectrum of BNP, it is convenient to label the lines 1, 2, ... in the order of increasing frequency at the highest temperature of each phase. Below 233 K, lines 1 to 7 showed a noticeable change in their $d\nu/dT$ values. On other hand, lines 1, 2 and 5 exhibited a splitting, thus increasing the total number in the spectrum to twelve lines. Lines 8 and 9 did not show any changes in their slope at or around the transition temperature, as seen in Figure 1. The variations in $d\nu/dT$ in lines 1 to 7 were smooth, and no discontinuities were observed in their frequencies, showing that a second order phase transition occurs at 233 K. All lines except the lines numbered in this phase 11 and 12 showed $d\nu/dT$ values that changed noticeably with the temperature below T_c, and for the lines 5, 7, and 9, an unusual positive $d\nu/dT$ value was found as seen in Figure 1.

At 131 K, line 12 faded out while several new lines appeared, increasing the total in the NQR spectrum to seventeen lines. The discontinuities in frequency showed that the transition at 131 K was first order with a hysteresis of around 4–5 K, depending on the rate of cooling of the sample [8]. Nevertheless, the largest splitting observed was of only a few kHz so that the transition is just weakly first order. Lines 1, 7, 8, and 11 of this phase showed an unusual positive $d\nu/dT$ value, and a very complex pattern of line crossing was found below this temperature, making the identification of some of the lines very difficult.

The complexity grew markedly below 118 K, due to the increase in the number of lines of different intensities. On cooling from 131 K, the line at 2655 kHz formed a doublet composed by a strong and a weak line, and the latter faded out below 118 K. In the range of 131 to 118 K, the highest frequency line was extremely weak, and only at 125 K was a reliable spectrum obtained after many hours of signal averaging. The overall effect of the transition observed at 131 K was to produce only small changes in the $d\nu/dT$ of the highest frequency doublet.

The changes observed in the frequencies and in their $d\nu/dT$ values below 118 K were, in general, smooth and very small, as seen in Figure 1. Therefore, the transition may be classified as pseudo second order, although the fading of one of the weaker lines shows that perhaps it should be classified as very weakly first order.

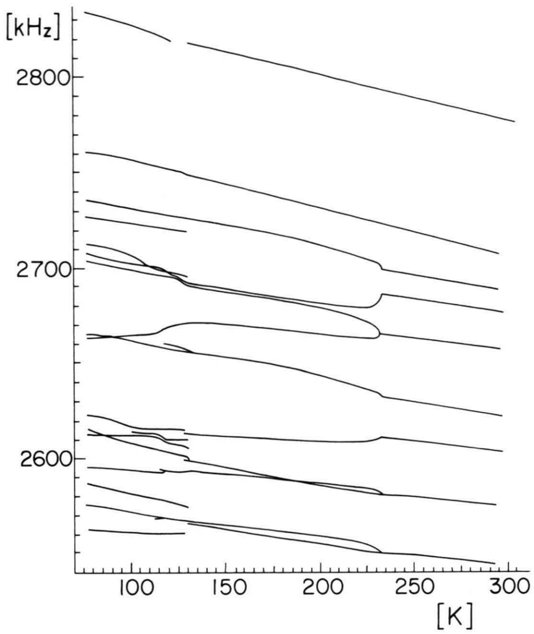

Fig. 1. Temperature dependence of the ^{14}N Nuclear Quadrupole Resonance spectrum of the cyanide groups of $Ba_2[Fe(CN)_5NO]\cdot 3H_2O$.

Table 1. Comparison of the highest frequency doublets of the ^{14}N NQR spectrum of Sodium Nitroprusside (SNP) and Barium Nitroprusside (BND).

^{14}N NQR lines	Temperature Coefficients [kHz/K]	77 K [kHz]	122 K [kHz]	195 K [kHz]	293 K [kHz]
BNP	−0.26	2761	2751	2735	2706
SNP	−0.24	2760	2750	2733	2709
BNP	−0.24	2834	2818	2802	2777
SNP	−0.22	2830	2820	2802	2781

Discussion

The nitroprusside (NPE) ion in BNP shows a distorted octahedral configuration with the Fe atom shifted 0.244 Å to the NO side above the plane determined by the equatorial C atoms [3, 6]. The Fe–C and C–N distances are in the ranges 1.90–1.98(2) and 1.10–1.21(2) Å, respectively [3, 6]. The FeCN bonds are not linear, a deviation of up to 12(2)° having been found for two of the equatorial groups. The NQR spectrum of the CN groups of this NPE ion, when free, will consist therefore of two sets of lines corresponding to the equatorial cyanides plus an additional one belonging to the CN group located along the ONFeCN axis.

In the crystal, the field of the neighboring ions will produce additional frequency shifts depending on the position of each N site within the unit cell [10]. In BNP, at room temperature, NPE anions are stacked along the c axis in double intercalated rows with neighboring NO groups located in a nearly antiparallel fashion [3, 6]. Each NPE anion is coordinated by four Ba^{2+} through the equatorial N atoms [3, 6]. The three water molecules are at distances from the N atoms so that weak $N \cdots H$ bonds are present in BNP at room temperature and are also coordinated with Ba^{2+}. Two of the water molecules showed unusually large anisotropic thermal parameters [3, 6], suggesting the presence of dynamic or static disorder in the position of these molecules.

A comparison of the NQR spectrum of the CN groups in SNP and in BNP shows that the highest frequency doublets have practically the same frequencies [9] and temperature dependence (see Table 1). A single crystal ^{14}N NMR study of SNP [11] showed that such a doublet corresponded to the *trans* CN groups of NPE. The striking similarities found between these lines led us to assign the high frequency doublet of BNP to one of the *trans* cyanides and the remaining lines to the other CN groups of NPE. In SNP, the equatorial N sites are divided into two sets of identical CN groups, while in BNP these atoms are all inequivalent at room temperature. The change in the number of inequivalent sites is related to the crystal field contribution to the EFG observed in the ^{14}N NQR [10]. NPE occupies a general position in the BNP structure [3, 6], so a different crystal field acts on each ^{14}N [10]. The NQR frequencies of the cyanides in NPE show only very small changes when Na^+ is replaced by Ba^{2+}. Even if the substitution of the cation produces a different and a slightly more open structure, the resulting frequencies show that only small changes in the crystal field contribution to the EFG occur. The charge distribution within NPE itself is therefore expected to be only slightly perturbed by Ba^{2+} substitution.

The structure of BNP may be described as consisting of relatively large and nearly spherical NPE anions in a closed-packed arrangement with water molecules and Ba^{2+} filling some of the interstices between the large ions [3, 6]. This structure will be stable if the cations are able to maximize the number of contacts with the anions and if H-bonds involving the water molecules take advantage of all the acceptor centers. H-bonds found in BNP are weak [3, 6], except for one between two of the water molecules, so the lattice energy will depend mostly on the electrostatic interaction between the ions. A stable structure of an ionic crystal will accept cations of a diameter sufficiently large so that they will not "rattle" in the interstices [12]. This stability requirement is reflected in the radius ratio of the ions forming the structure. The maximum number of large ions (B) that can surround and touch a second ion (A) depends on their relative size [12] or (r_A/r_B). As this number decrease toward zero, the number of B ions touching A also decreases and different types of coordination polyhedra around A become stable [12]. The presence of hydration water in BNP modifies this requirement, as this molecule occupies different interstices and is coordinated with itself and with Ba^{2+} and NPE ions [3, 6].

As the temperature is lowered, the mobility of the water molecules in BNP decreases [6]. Rapidly rotating and tumbling water molecules occupy an effective volume larger than a molecule with restricted motion such as that found in hydrides at low temperature [6, 12]. If the change in the effective radius is sufficiently large, a new coordination polyhedron becomes more stable and a phase transition occurs. These structural rearrangements are brought about by soft modes involving rotatory or lattice translational modes [13]. In BNP, the temperature dependence of the NQR spectrum of the equatorial CN group shows the changes that reflect a second order phase transition below 233 K. As seen in Fig. 1, the EFG of one of the *trans* N sites is not perturbed by the transition. This means that the distance of Ba^{2+} and water molecules to this N atom remains unchanged by the transition, and only the usual thermal averaging operates in this site. A softening of a translational lattice phonon, involving the ions near the other cyanides of NPE, produces changes in the EFG that may explain the features observed below 233 K. Unfortunately, the NQR data do not provide clues to decide which mode is operative in this transition.

Further information about the second order transition may be obtained from the splitting (δv) of the lines or the departure from the linear high temperature behavior [13] below T_c. In this case, we can plot $\delta v = \alpha(T_c - T)^\beta$, where α is a constant, T_c the transition temperature, and β the critical exponent. For the transition observed at 233 K, β in BNP was equal to 0.42 ± 0.01 for lines 3 and 4 and 0.33 ± 0.02, for line 5. The wide range of β values shows that the transition found at 233 K is quite complex and can not be interpreted in terms of the simple mean field theory [13].

The transition found at 131 K is first order, as shown by the discontinuites in frequency of lines 1, 4, 5, and by the appearence of several additional lines that increased the total number to 17 lines. Also, hysteresis was found in lines 4 and 5 while a splitting was shown by line 6. First order transitions proceed by nucleation and growth [14]. In these transitions, the low temperature phase LTP, can not be obtained by continuously varying the position and/or orientation of the ions of the high temperature phase (HTP). Therefore, a boundary or wall separates regions of LTP from the surrounding HTP matrix. The required nucleation for the transition occurs if a suitable density of appropriate defects is present in the crystal [14]. The dependence of the density of these defects on the crystal growth process, impurities and thermal treatment will produce a spread in the transition temperature of the microcrystals present in the sample [14]. Upon cooling, the transition in the microcrystals takes place at different times depending on their defect concentration, thus extending the transition over a noticeable temperature range [14]. At each temperature within this range, a mixture of the two phases coexists and, if the cooling is slow enough, the relative quantity does not depend on the rate of cooling [14]. The results obtained in BNP below 131 K show that the density of defects that are able to produce nucleation is high, as the extension of the hysteresis is small. On the other hand, the small discontinuities in the frequencies of some of the lines show that the two phases are quite similar, so that the boundary regions can move without requiring a large amount of energy, thus favoring a small hysteresis effect [8]. In several lines, the discontinuities were observed only in the dv/dT values below 131 K, showing that the structural changes around these sites were smooth as in a second order phase transition. This indicates that around these sites no significant change in the ion arrangement occurs at T_c.

The transition found at 118 K produces very small effects in the frequencies and in the dv/dT values, indicating the existence again of only minor structural modifications in BNP below that temperature.

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