Nitrogen-14 Nuclear Quadrupole Resonance in Some Hexanitro Complexes of the Type R₂PbCu(NO₂)₆

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14N NQR Spectra, Hexanitrocuprates(II), Phase Transition, Structure and Bonding

The nuclear quadrupole resonance of nitrogen-14 was observed for potassium, ammonium, rubidium, and thallium lead hexanitrocuprates(II) at various temperatures below the second highest transition temperature of each complex. All the compounds except the ammonium salt yielded two practically same sets of the quadrupole parameters, qQ/h and η, indicating the presence of at least two crystallographically different but very similar kinds of nitrogen atoms in the crystals. For the ammonium salt, three phase transitions at 94.5, 287, and 316 K were located from the experiments of DTA and NQR. The crystals of the highest and the second highest temperature phases were proved to be isomorphous with those of the remaining complexes in their highest and intermediate temperature phases, respectively. The salt yielded two sets of the quadrupole parameters between 287 and 94.5 K, and only one set below 94.5 K down to 4.2 K, indicating that a structural phase transition takes place at 94.5 K. No resonance could be observed in the highest and the second highest temperature phases of all the complexes studied. The covalency of copper-nitrogen bonds in lead hexanitrocuprates(II) is estimated at about 10%, from the quadrupole parameters observed at 4.2 K. The structure of the complex anion is discussed in relation to the Jahn-Teller distortion.

Introduction

Potassium, rubidium, and thallium lead hexanitrocuprates(II) are known to form cubic crystals (Fm3) isomorphous with each other at high temperatures, and to have a regular octahedral complex ion, [Cu(NO₂)₆]⁺² in their crystals [1–5]. Each complex, however, loses its high crystalline symmetry near room temperature through two phase transitions successively taking place [5–10]. According to the recent experiments of X-ray diffraction and EPR carried out at lower temperatures [5, 6, 9–12], the crystal structure consists of a tetragonal or a pseudotetragonal lattice in the intermediate phase of these complexes and a pseudomonoclinic lattice in the lowest temperature phase of the potassium salt. In both phases, the octahedral arrangement of nitrogen atoms around a copper(II) ion is distorted to tetragonal one. Since copper(II) in a cubic field is a Jahn-Teller active ion, the deformation of the complex anion is attributed to the Jahn-Teller effect. The present study by use of the nuclear quadrupole resonance (NQR) of nitrogen-14 has been undertaken in order to obtain information about the deformed structure of the octahedral anions in the low temperature phases, and also to evaluate the covalency of copper-nitrogen bonds in these complexes.

Experimental

All the compounds studied were synthesized by the methods described in the literature [7, 13]. In order to identify the compounds prepared, X-ray powder patterns were taken at room temperature by means of a diffractometer from Rigaku Denki Co. (Model D-3F) equipped with a copper anticathode. The diffraction angles obtained for K₂PbCu(NO₃)₆, Rb₂PbCu(NO₃)₆, and Tl₂PbCu(NO₃)₆ agreed well with those calculated from the reported lattice parameters [5–7]. The measurement of differential thermal analysis (DTA) was carried out by means of a home-made apparatus already described [14] to confirm the existence of the phase transitions of these complexes. Two transition temperatures were determined for each complex in agreement with those reported in the literature [6–10, 12]. Ammonium lead hexanitrocuprate(II) was identified by chemical analysis.

Analysis for (NH₄)₂PbCu(NO₃)₆

Calcd. Pb 35.6 Cu 10.9,
Found Pb 35.9 Cu 10.9.

The NQR spectra of nitrogen-14 were observed by means of a modified Pound-Watkins type spectrometer [15], operated in a frequency modulation mode. Resonance frequencies were determined by use of a model TR-5104 frequency counter from Takeda Riken Co. A chromel vs alumel thermocouple and a chromel vs gold (0.03% iron) thermo-
Table I. $^{14}$N Quadrupole resonance frequencies ($v_1$, $v_{11}$, and $v_{111}$) and S/N ratios at 4.2 and 77 K in some hexanitrocuprates(II) along with their transition temperatures ($T_{tr}$).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T/K$</th>
<th>$v_1$/kHz (S/N)</th>
<th>$v_{11}$/kHz (S/N)</th>
<th>$v_{111}$/kHz (S/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_2$PbCu(NO$_2$)$_6$</td>
<td>4.2</td>
<td>4525.7(80)</td>
<td>3519.5(260)</td>
<td>1006.2(10)</td>
</tr>
<tr>
<td>[281, 273 K]$^8$</td>
<td>77</td>
<td>4531.2(80)</td>
<td>3516.3(4)</td>
<td>1001.5(10)</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>4436.8(120)</td>
<td>3507.4(290)</td>
<td>929.5(25)</td>
</tr>
<tr>
<td>$Tl_2$PbCu(NO$_2$)$_6$</td>
<td>77</td>
<td>4515.0(3)</td>
<td>3516.3(4)</td>
<td>925.7(24)</td>
</tr>
<tr>
<td>[291, 245 K]$^8$</td>
<td>4.2</td>
<td>4428.7(4)</td>
<td>3503.7(10)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>4425.2(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Rb_2$PbCu(NO$_2$)$_6$</td>
<td>4.2</td>
<td>4511.7(35)</td>
<td>3510.7(30)</td>
<td>1001.0(7)</td>
</tr>
<tr>
<td>[313, 274 K]$^{12}$</td>
<td>77</td>
<td>4506.5(35)</td>
<td>3511.7(30)</td>
<td>994.9(7)</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>4499.3(4)</td>
<td>3507.3(10)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>4506.5(35)</td>
<td>3508.3(10)</td>
<td></td>
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<tr>
<td>($NH_4$)$_2$PbCu(NO$_2$)$_6$</td>
<td>4.2</td>
<td>4519.6(25)</td>
<td>3516.7(140)</td>
<td></td>
</tr>
<tr>
<td>[316, 287, 94.5 K]$^*$</td>
<td>77</td>
<td>4506.5(5)</td>
<td>3510.7(9)</td>
<td></td>
</tr>
</tbody>
</table>

* Data of the present work.

coupled calibrated by the $^{14}$N NQR frequency of hexamethylenetetramine [16] were employed above and below liquid nitrogen temperature, respectively, for the determination of the temperature of specimen. The observed temperature was estimated to be accurate within ±1 K.

Results

The $^{14}$N NQR frequencies and their signal-to-noise ratios (S/N) of the hexanitro copper(II) complexes determined at 4.2 and 77 K are given in Table I, in which three resonance frequencies, $v_1$, $v_{11}$, and $v_{111}$ are defined by

\[
\begin{align*}
  v_1 &= \frac{\varepsilon Q q}{h} (3 + \eta)/4, \\
  v_{11} &= \frac{\varepsilon Q q}{h} (3 - \eta)/4; \\
  v_{111} &= v_1 - v_{11} = \frac{\varepsilon Q q}{h} \eta/2.
\end{align*}
\]

Here, $\varepsilon Q q/h$ and $\eta$ stand for the nuclear quadrupole coupling constant and the asymmetry parameter, respectively. It is noteworthy that the present copper(II) complexes showed unsaturated resonance lines even at liquid helium temperature although saturation of resonance absorptions is quite commonly observed for diamagnetic compounds at low temperatures. The intensity of all the lines observed increased with decreasing temperature even below 77 K and very large S/N ratios could be obtained at liquid helium temperature as given in Table I.

Potassium and thallium lead hexanitrocuprates(II) yielded two closely spaced $v_1$ lines with almost the same intensity and a single stronger $v_{11}$ line at 4.2 K. With increasing temperature from 4.2 K, the single $v_{11}$ line gradually became broad and clearly splitted into two component lines of equal intensity at about 100 and 80 K for the potassium and thallium salts, respectively, as shown in Figs. 1 and 2. Hence, the single $v_{111}$ line observed below the respective temperatures can be regarded as a line consisting of two component lines accidentally overlapping each other. In order to confirm the existence of two sets of $v_1$ and $v_{11}$ in both complexes, we measured $v_{111}$ frequencies at 4.2 K.

![Fig. 1. Temperature dependence of $^{14}$N NQR frequencies in potassium lead hexanitrocuprate(II).](image)
A pair of $v_{III}$ lines having an equal intensity was observed for both complexes at the frequencies expected from Equation (2), indicating that there exist at least two crystallographically different kinds of nitrogen sites in crystals. A more careful examination on the thallium salt revealed that each $v_{III}$ line has a triplet structure barely resolvable as shown in Fig. 3. The frequency separation between the neighboring components of the triplet structure is smaller than 0.2 kHz. The appearance of the triplet structure suggests the presence of nitrogen atoms having three slightly different surroundings in both crystalline sites of the thallium salt. Since each $v_{III}$ triplet consists of very closely spaced component lines, it may be reasonable that only unresolved resonance absorptions are detected for the corresponding $v^I$ and $v^{II}$ lines which appear in a considerably higher frequency range than $v_{III}$.

All the resonance lines, $v^I$ and $v^{II}$ of the potassium and thallium salts gradually weakened with increasing temperature and disappeared in the noise level below the respective lowest transition temperature ($T_{tr}$) known to date. Since the spectrometer employed had a high sensitivity below about 4 MHz, the $v^{II}$ signals of each compound could be detected even in a high temperature region where $v^I$ lines were undetectable. The $v^{II}$ lines of the thallium salt could be observed up to its lowest $T_{tr}$, 245 K [6], while those of the potassium salt disappeared at 196 K far below the lowest $T_{tr}$, 273 K [8–10]. Since the temperature variation curves obtained for both salts are smooth, it is concluded that no phase transition takes place in the respective temperature range where NQR signals are detectable. Although we carefully carried out experiments in search of NQR signals at higher temperatures, no resonance was observed in the intermediate and the highest temperature phases of both salts.

Rubidium lead hexanitrocuprate(II) yielded two sets of $v^I$ and $v^{II}$ in the temperature range 4.2–182 K, although two $v^{II}$ lines could be detected up to 242 K. This indicates that there exist at least two kinds of crystallographically nonequivalent nitrogen atoms in the crystals below 242 K. The observed temperature dependence curves are smooth indicating that no phase transition takes place between 4.2 and 242 K. The latter temperature can be replaced by 274 K which is the lower $T_{tr}$ already reported [12], because the rubidium salt shows no detectable heat anomaly below this temperature on the measurements of DTA carried out.

Ammonium lead hexanitrocuprate(II) gave rise to a pair of $v^I$ and $v^{II}$ lines below 77 K. With increasing temperature, both lines abruptly disappeared at 94.5 K and a doublet of lines with an equal intensity appeared on the high frequency side of each singlet as shown in Fig. 4. The $v^I$ doublet and the $v^{II}$ doublet, all resonance frequencies of which have a normal negative temperature coefficient, disappear in the noise level at about 244 and 287 K, respectively, after becoming gradually weak with increasing temperature. When the sample is cooled down, both doublets disappear at 92.5 K and the signals of the low temperature phase appear at the same temperature. To confirm the presence of phase transition at around 94 K and to locate
phase transitions expected at higher temperatures as well, we carried out an experiment of DTA over a fairly wide range of temperature. Endothermic peaks were detected at 93.5, 287, and 316 K on warming, while exothermic peaks appeared at 92.5, 287.5, and 314 K on cooling. Accordingly, it is evident that the ammonium salt undergoes three phase transitions among which the highest and the lowest are the first order phase transition because of thermal hysteresis observed in NQR and DTA measurements.

Since no crystal data are available for the ammonium salt, we have recorded X-ray powder patterns at 298 and about 332 K to compare them with those of the other salts. The diffraction patterns of the ammonium and rubidium salts recorded at 298 K are shown in Fig. 5, indicating that there is a close resemblance between the two. The rubidium salt is known to form orthorhombic crystals in its intermediate phase belonging to the space group Fmmm with $a = 10.8296$, $b = 10.8196$, and $c = 10.6113$ Å at 295 K [5]. This lattice, however, can be regarded as pseudotetragonal one, and the two powder patterns obtained can be well interpreted as arising from a pseudotetragonal lattice having the same lattice constant, $a = 10.8$ and $c = 10.6$ Å. Consequently, the ammonium salt in the second highest phase is clearly isomorphous with the rubidium salt in its intermediate phase and, therefore, with the potassium and thallium salts in their intermediate phase. The powder pattern of the highest temperature phase of the ammonium salt observed at 332 K can be interpreted (see Table II) as resulting from the same cubic structure [1-5]

<table>
<thead>
<tr>
<th>$(h k l)$</th>
<th>$2\theta_{\text{obs}}$</th>
<th>$2\theta_{\text{calc.}}$</th>
<th>Relative Int.</th>
</tr>
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<tr>
<td>(1 1 1)</td>
<td>14.20</td>
<td>14.23</td>
<td>29</td>
</tr>
<tr>
<td>(2 0 0)</td>
<td>16.41</td>
<td>16.45</td>
<td>100</td>
</tr>
<tr>
<td>(2 2 0)</td>
<td>23.32</td>
<td>23.34</td>
<td>53</td>
</tr>
<tr>
<td>(3 1 1)</td>
<td>27.43</td>
<td>27.44</td>
<td>23</td>
</tr>
<tr>
<td>(2 2 2)</td>
<td>28.68</td>
<td>28.69</td>
<td>5</td>
</tr>
<tr>
<td>(4 0 0)</td>
<td>33.23</td>
<td>33.25</td>
<td>32</td>
</tr>
<tr>
<td>(3 3 1)</td>
<td>36.32</td>
<td>36.33</td>
<td>16</td>
</tr>
<tr>
<td>(4 2 0)</td>
<td>37.30</td>
<td>37.31</td>
<td>38</td>
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<tr>
<td>(4 2 2)</td>
<td>41.02</td>
<td>41.02</td>
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</tr>
<tr>
<td>(5 1 1)</td>
<td>43.64</td>
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<tr>
<td>(3 3 3)</td>
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<td>8</td>
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<tr>
<td>(5 3 1)</td>
<td>50.07</td>
<td>50.06</td>
<td>5</td>
</tr>
<tr>
<td>(6 0 0)</td>
<td>50.82</td>
<td>50.82</td>
<td>13</td>
</tr>
<tr>
<td>(4 4 2)</td>
<td>53.79</td>
<td>53.79</td>
<td>5</td>
</tr>
</tbody>
</table>

Table II. Comparison of calculated and observed 2θ values for ammonium lead hexanitrocuprate(II) at 332 K ($a = 10.77$ Å).

Fig. 4. Temperature dependence of $^{14}$N NQR frequencies in ammonium lead hexanitrocuprate(II).

Fig. 5. X-ray powder patterns of ammonium and rubidium lead hexanitrocuprates(II) recorded at 298 K.
Discussion

Covalency of copper-nitrogen bonds

The quadrupole coupling constant and the asymmetry parameter calculated from the resonance frequencies observed at 4.2 K for the compounds studied are given in Table III together with those of sodium nitrite [17] for comparison. All the eQq/h values obtained resemble each other and smaller by about 500 kHz than that of sodium nitrite. This decrease in eQq/h seems to originate from covalency of copper-nitrogen bonds formed in the complex anion.

In an analogous way to our earlier calculation of the electronic population of an NO$_2^-$ ion [17], let the valence orbitals of nitrogen in an -NO$_2$ group be expressed by

\[ \psi_{N-O} = 2^{-1/2}(1 - \cot \theta)\sigma_{p} + \phi_{z}, \]

\[ \psi_{N-O''} = 2^{-1/2}(1 + \cot \theta)\sigma_{p} - \phi_{z}, \]

\[ \psi_{N-Cu} = (\cot \theta)\phi_{z} + (1 - \cot \theta)\phi_{p}, \]

\[ \psi_{\pi} = \phi_{\pi}. \]

Here, $2\theta$ denotes the angle of the NO'-NO'' of the NO$_2$ group, and a cartesian coordinate system ($x$, $y$, $z$) is taken as the $z$-axis along the N-Cu bond direction and the $y$-axis along the $p_{\pi}$ orbital of nitrogen. Let the number of electrons occupying the N-O $\sigma$-orbital, the N-Cu $\sigma$-orbital, and the $\pi$-orbital of nitrogen be denoted by $1 + i_0$, $1 + i_{Cu}$, and $1 + i_{\pi}$, respectively. Then, one can obtain inequalities among the components of the quadrupole coupling tensor, $|eQ_{\pi\pi}/h| > |eQ_{\pi\sigma}/h| > |eQ_{\pi z}/h|$ leading to $i_0 > i_{\pi}$ in the present system [17, 18]. Calculations along the Townes-Dailey procedure [19] give

\[ eQ_{q}/h = [(1 - \cot \theta)i_{Cu} - (1/2 - \cot \theta)i_{0} + i_{\pi}/2] \times |eQ_{\pi}/h|/(1 + i \epsilon), \]

where,

\[ i = 2i_0 + i_{\pi} + i_{Cu} - 1. \]

In these equations, $i$, $\epsilon$, and $q_{\pi}$ are the extra negative charge of the nitrogen atom, the screening constant estimated by Townes and Schawlow at 0.3 [20], and the field gradient formed by a single 2p electron along its symmetry axis, respectively. The angle $2\theta$ is estimated to be 117° by taking an average of the angles determined by structural analyses for the potassium, thallium, and rubidium salts [3–5, 21]. The $|eQ_{\pi}/h|$ value is given as 11.3 MHz for nitrogen-14 [22]. Putting the numerical values of $\epsilon$, $|eQ_{\pi}/h|$, and $2\theta$ as well as the observed eQq/h and $\eta$ values into Equations (7–9), one can get only two equations still involving three unknown parameters, $i_{Cu}$, $i_0$, and $i_{\pi}$. Therefore, an additional assumption is required in order to evaluate the covalency of the metal-ligand bonds. Since the Cu-N bond in the present complexes is expected to be fairly weak, the value of $i_0$ can be approximated to be equal to that of an NO$_2^-$ group. Then, the $i_0$ value can be calculated for sodium nitrite as 0.17 from Equations (7–9) by use of $i_{Cu} = 1$ and $2\theta = 114.9^\circ$ [23]. Finally, one can obtain $i_{\pi} = 0.05$ and $i_{Cu} = 0.89$ for the thallium salt and $i_{\pi} = 0.04$ and $i_{Cu} = 0.89$ for the other three complexes.

When a pure ionic bond is defined by $i_{Cu} = 1$ where an electron pair occupies the "lone pair" orbital $\psi_{N-Cu}$ of nitrogen, and a pure covalent one by $i_{Cu} = 0$, the covalent bond character of the Cu–N bond can be estimated to be about 10%. This may be compared with those determined by the measurements of $^{14}$N NQR on a similar kind of compounds having trivalent nitrogen atoms. There are only few of compounds for which the nature of metal-nitrogen bonds has been evaluated by nitrogen NQR. They are dimethylglyoxime (DMG) complexes of palladium and nickel [24] and pyridine (py) complexes of zinc and cadmium [25]. Hsieh et al. reported the metal-nitrogen covalent character as 35 and 25% for Ni(DMG)$_2$ and Pd(DMG)$_2$, respectively [24], and about 20 and 13% for ZnCl$_2$(py)$_2$ and CdCl$_2$(py)$_2$, respectively [25]. The covalent character of 10% of the present complexes is much smaller than these values. This is rather unexpected, because copper has about the same or greater electronegativity than nickel and zinc [26]. However, the weak covalency observed for the

<table>
<thead>
<tr>
<th>Compound</th>
<th>(eQq/h)/kHz</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$PbCu(NO$_2$)$_6$*</td>
<td>5362.0</td>
<td>0.3744</td>
</tr>
<tr>
<td>Tl$_2$PbCu(NO$_2$)$_6$*</td>
<td>5294.9</td>
<td>0.3504</td>
</tr>
<tr>
<td>Rb$_2$PbCu(NO$_2$)$_6$*</td>
<td>5346.9</td>
<td>0.3753</td>
</tr>
<tr>
<td>(NH$_4$)$_2$PbCu(NO$_2$)$_6$</td>
<td>5357.5</td>
<td>0.3744</td>
</tr>
<tr>
<td>NaN$_2$**</td>
<td>5815</td>
<td>0.4075</td>
</tr>
</tbody>
</table>

* Averaged values.

** Values extrapolated to absolute zero [17].

\[ \eta \cdot eQ_{q}/h = (3/2)(i_0 - i_{\pi})|eQ_{\pi}|/h(1 + i \epsilon), \]

where,
hexanitrocuprates(II) may be understandable in view of the fact that the Cu–N bond distance of 2.11 Å determined for the potassium and thallium salts [2–4] in their cubic phase is longer than those of similar type compounds containing Cu–N bonds [27].

**On the Crystalline Structure of \( \text{R}_2\text{PbCu(NO}_2\text{)}_6 \)**

The present complexes yield no NQR signals in their second highest temperature phase. This agrees well with the incommensurate model proposed by Noda et al. [12] for this phase of the potassium salt based on the measurements of neutron scattering and X-ray diffraction. According to this model, a large amount of spacial disorder which will prevent detection of NQR signals is expected to develop in the crystals. No resonance could be observed also for the highest temperature cubic phase of these complexes in spite of our careful search for signals. This is presumably due to the dynamic Jahn-Teller effect of the complex anions.

For the lowest temperature phase of the potassium, rubidium, and thallium salts as well as for the second lowest phase of the ammonium salt, the present results indicate that there exist two kinds of nitrogen lattice sites in the respective phase. If the complex ion is axially deformed in these phases as predicted by the Jahn-Teller theorem [28, 29], the ion itself should contain two kinds of \( \text{NO}_2 \) groups, namely, axial and equatorial \( \text{NO}_2 \) groups. Therefore, one can simply expect two NQR lines with an intensity ratio 2:1 for each of \( \nu^I \) and \( \nu^{III} \), provided that all the complex ions in a unit cell are equivalent. The predicted number of resonance lines agrees with the present results, but the observed intensity ratio of almost 1:1 for both \( \nu^I \) and \( \nu^{III} \) doublets of each complex disagrees with the prediction. Our measurements of intensity were done at various temperatures mostly by determining the peak-to-peak height of the recorded derivative curves of resonance absorptions. At liquid helium temperature, however, we carefully measured the linewidth of the \( \nu^I \) and \( \nu^{III} \) absorptions of the potassium salt and the \( \nu^{III} \) absorptions of the thallium and rubidium salts under a reduced modulation width. The results indicated that the two component lines of the \( \nu^I \) doublet and \( \nu^{III} \) doublet as well in these complexes have almost the same integrated intensity.

According to Noda et al. [12], the crystal of the potassium salt in its lowest temperature phase has a pseudomonoclinic symmetry with space group \( \text{C2/n} \) if oxygen atoms are neglected, and contain the tetragonally deformed complex anions in which the axial Cu–N bond length is longer by about 0.2 Å than the equatorial one. The former statement indicates that in the pseudomonoclinic unit cell there is no proper lattice site occupied by the elongated complex anion with four crystallographically equivalent equatorial nitrogen atoms. In other words, all of the equatorial nitrogen atoms are no longer equivalent in the unit cell when the surroundings of each nitrogen atom are taken into account. Presumably, there exist two kinds of the equatorial nitrogen atoms as if the complex ion has the orthohombic symmetry. Consequently, at least three different sets of \( ^{14}\text{N} \) NQR frequencies should be observed for the complexes belonging to this structural model as contradicted with the present results. It may be possible, however, to assign the observed signals to two crystallographically different kinds of the equatorial nitrogen atoms. To examine the adequacy of this possibility, we carried out a supplemental experiment at liquid helium temperature in an attempt to detect additional NQR signals for the thallium salt which yielded the strongest signals among the complexes studied. However, no NQR signals could be detected in the frequency range 1.8–5.1 MHz other than two \( \nu^I \) and one \( \nu^{III} \) frequencies already observed. It is highly desirable, therefore, that more detailed structural analysis for the low temperature phases of these complexes will be carried out and the problem in the interpretation of the NQR results will be solved.