Nuclear Quadrupole Resonance of Nitrogen-14 in Potassium Hexathiocyanatoplatinate(IV) and Tetrathiocyanatomercurate(II)

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The nuclear quadrupole resonance of 14N was observed in K3Pt(SCN)6 and K2Hg(SCN)4 at various temperatures. Both compounds yield large asymmetry parameters indicating the existence of asymmetric π-electron distribution about a CN bond axis. The ionic character of metal-ligand bonds in the platinum and mercury complexes is estimated to be 28% and 58%, respectively. The temperature dependence of each component of quadrupole coupling can practically be interpreted in terms of a simple Bayer theory. Both complexes show the quadrupole coupling constant versus temperature curve faintly convex to the abscissa. This anomaly is attributable to vibronic interaction in a thiocyanate group.

** The asymmetry parameter and the quadrupole coupling constant in frequency units are usually expressed as \( \eta = (q_{zz} - q_{yy})/q_{zz} \) and \( eQq/h = |eQq_{zz}/h| \), respectively, where \( q_{yz} \), \( q_{yy} \), and \( q_{zz} \) denote the principal components of electric field gradient (EFG) holding a relation, \( q_{zz} \geq q_{yy} \geq q_{xx} \) and \( eQ \) is a nuclear quadrupole moment.

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Introduction

Previously, we have studied the 14N nuclear quadrupole resonance (NQR) of various alkyl thiocyanates and potassium thiocyanate and found that nitrogen in the alkyl thiocyanates shows considerably larger asymmetry parameters than in KSCN by 0.46-0.47 and also large quadrupole coupling constants (3.5 MHz) than in KSCN \( (\eta = 0.028 \) and \( eQq/h = 2.4 \text{ MHz}. \)). This indicates that the quadrupole resonance parameters of nitrogen are highly sensitive to the electronic state of sulfur in spite of the presence of a carbon atom between them. Consequently, the study of 14N NQR in thiocyanate compounds provides an interesting possibility to obtain more information about bonding between thiocyanate groups and corresponding moieties. Since bonding between sulfur and alkyl carbon can be considered to be almost covalent without noticeable conjugation, NQR data are now available for thiocyanate groups in the two extreme states of bonding, namely, thiocyanate ions, SCN-, and thiocyanate groups bound with a covalent \( \sigma \)-bond, \( \pi \)SCN. These data may be helpful for the elucidation of the electronic structure of thiocyanate groups in various compounds. In this paper, we report the 14N NQR in two thiocyanate complexes and discuss the bonding scheme of thiocyanate groups in metal complexes.

Experimental

Potassium hexathiocyanatoplatinate(IV) was prepared according to the method described in the literature and purified by recrystallization from absolute methanol. Since only one resonance line attributable to \( ^1H \) could be observed at liquid nitrogen temperature for the crystals obtained in this manner, we warmed the sample up to 125 °C in a sealed glass ampoule and then cooled it gradually to room temperature over seven days. Then the sample gave rise to a set of resonance signals, \( ^1H \) and \( ^1H \) strong enough to observe NQR signals even at room temperature.

Potassium tetrathiocyanatomercurate(II) was synthesized by the method reported by ROSENHEIM and COHN, and recrystallized from methanol.

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containing a small amount of potassium thiocyanate. No resonance was observed until the sample was annealed in a similar manner as the former compound. Both compounds were identified by chemical analysis and also checked by infrared spectra.

Analysis for K$_2$Pt(SCN)$_6$
Calcd  Pt 31.4 S 31.0,
Found  Pt 31.4 S 30.5.

Analysis for K$_2$Hg(SCN)$_4$
Calcd  Hg 39.2 SCN 45.5,
Found  Hg 37.9 SCN 46.2.

The NQR of nitrogen was observed by means of a modified POUND-WATKINS type spectrometer already reported$^1$. The ZEEMAN effect of resonance lines was measured in an attempt to assign the observed signals to $v_1$ and $v_{11}$. A chromel-alumel thermocouple calibrated at the standard temperatures was employed for monitoring temperatures above 77 K. Temperatures below 77 K were determined by a chromel-gold (0.03% iron) thermocouple calibrated by the $^{14}$N NQR signals of hexamethylenetetramine$^6$. The accuracy of temperature measurements was estimated to be within ±1 K.

Results
Since $^{14}$N has a nuclear spin equal to unity, one can usually observe two resonance frequencies $v_1$ and $v_{11}$ for a nitrogen atom having a finite asymmetry parameter $\eta$,

$$v_1 = (eQq/h)(3 + \eta)/4, \quad v_{11} = (eQq/h)(3 - \eta)/4.$$  (1)

Potassium hexathiocyanatoplatinate(IV) gave rise to a pair of resonance lines $v_1$ and $v_{11}$ in the temperature range of 4.2–300 K, while potassium tetra thiocyanatomercurate(II) yielded two sets of the frequencies at various temperatures between 77 and 300 K. Table I shows the resonance frequencies, quadrupole coupling constants, and asymmetry parameters of both complexes determined at 77 K along with those of potassium thiocyanate and methyl thiocyanate for comparison. Fig. 1 indicates the temperature dependence of resonance frequencies in the mercury complex.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$v_1$/kHz</th>
<th>$v_{11}$/kHz</th>
<th>(eQq/h)/kHz</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$SCN</td>
<td>3052.4</td>
<td>2220.7</td>
<td>3515.4</td>
<td>0.4732</td>
</tr>
<tr>
<td>K$_2$Pt(SCN)$_6$</td>
<td>2715.0</td>
<td>2093.5</td>
<td>3205.7</td>
<td>0.3878</td>
</tr>
<tr>
<td>K$_2$Hg(SCN)$_4$</td>
<td>2382.9</td>
<td>2090.1</td>
<td>2982.0</td>
<td>0.1964</td>
</tr>
<tr>
<td>KSCN</td>
<td>2304.6</td>
<td>2046.0</td>
<td>2900.4</td>
<td>0.1783</td>
</tr>
</tbody>
</table>

Fig. 1. Temperature dependence of $^{14}$N NQR Frequencies in K$_2$Hg(SCN)$_4$.

Discussion

1. Structure and bonding
The crystal structure of potassium hexathiocyanatoplatinate(IV) has been reported to form a hexagonal lattice$^7$ with the space group $D_{3d}^7-P\bar{3}m1$ and $Z=1$. All SCN groups in the complex ion are crystallographically equivalent in agreement with the results of the present investigation which yields only one pair of resonance lines $v_1$ and $v_{11}$ at various temperatures studied. However, accurate atomic positions for the light atoms have not been determined as yet.

According to the X-ray analysis carried out by ZVONKOVA$^8$, the mercury complex has a monoclinic lattice belonging to the space group $C_{6h}-C2/c$ with $Z=4$. The complex anion forms a distorted tetrahedron with S–Hg–S angles being 102–108°. Although no accurate atomic positions for light atoms have been determined as yet, a bent Hg–S–C bond with a sulfur valency angle of about 100° is anticipated from the crystal data of analogous complexes,

$$[(C_6H_5)_{3}P]_2Hg(SCN)_4$$ 9 and Cu(en)$_2$Hg(SCN)$_4$ 10. In the complex anion there are two kinds of crystallographically nonequivalent SCN groups.
because of the presence of the C2 site symmetry at the central metal atom. Since four complex ions in a unit cell are crystallographically equivalent, the two sets of resonance lines observed arise from two kinds of SCN groups in the complex ion. In order to determine exact pairing between two \( \nu^I \) and two \( \nu^{II} \) frequencies observed, we measured the saturation recovery rate of resonance signals at liquid nitrogen temperature. The saturation recovery of the \( \nu^I \) and \( \nu^{II} \) lines of higher frequencies is much faster than that of another pair, indicating that nitrogen responsible for the former pair has shorter spin-lattice relaxation time \( T_1 \) than the latter. Therefore, we have assigned the pair of higher frequencies to one kind of SCN groups (site a), and another pair to another kind of SCN groups (site b) in the same complex ion.

Both complexes show fairly large asymmetry parameters which are too large to be ascribable to the asymmetry of the EFG originating from neighboring ionic charges. Therefore, it is concluded that an anisotropic \( \pi \)-electron distribution in thio cyanate groups produces the large asymmetry parameters of these complexes. This suggests that Pt–SCN and Hg–SCN have a nonlinear structure similar to methyl thio cyanate, and that there exists a considerable amount of covalency in the metal-ligand bonds. The latter statement is confirmed by the fact that both complexes yield larger quadrupole coupling constants than potassium thiocyanate.

In order to quantitatively determine the electronic structure of thio cyanate groups, let the principal axes of the EFG tensor at a nitrogen nucleus be taken with the \( x \)-axis perpendicular to the metal-SCN plane and with the \( z \)-axis directed along the SCN group, which is assumed to be linear. In this coordinate system, one can obtain inequalities among the principal components of the EFG, i.e. \( |q_{zx}| > |q_{yy}| > |q_{xzx}| \) which have already been assured for a methyl thio cyanate molecule by microwave experiments. The inequalities lead to new relations, \( N_x > N_z > N_y \), among the numbers of \( p \)-electrons in the \( 2p_z \)-orbitals of nitrogen along the respective coordinate axes. By assuming that these relations are still valid for the present complexes, one can obtain the following equations according to the Townes–Dailey procedure.

\[
eQq/h = \frac{3}{2} (i\pi_x - i\pi_y)|eQq_p/h|. \tag{3}
\]

Here, \( s \) and \( q_p \) denote the extent of \( sp \)-hybridization in the \( \sigma \)-bonding orbital of nitrogen and the field gradient formed by a single \( 2p \)-electron of nitrogen, respectively. We have also assumed the \( \sigma \)-bonding orbital, the lone-pair orbital, the \( \pi_x \) and the \( \pi_y \) bonding orbitals of nitrogen to accommodate \( 1 + i\sigma, 2, 1 + i\pi_x \), and \( 1 + i\pi_y \) electrons, respectively.

Since these equations involve many unknown parameters in spite of only two observables, \( eQq/h \) and \( \eta \) obtainable from the present experiment, we must remove some of these unknown parameters by making adequate assumptions. The values of \( s + (1 - s)i\sigma \) are approximately constant for the compounds discussed here, because the electron population in both \( \sigma \)-bonding and lone-pair orbitals of nitrogen might be unaltered by the electronic state of the distant sulfur. Under this assumption, the number of excess \( \pi \)-electrons on the nitrogen atom, \( i\pi_x + i\pi_y \), depends linearly on the observed coupling constant. This might be confirmed by the fact that the CN stretching frequency reported \((2166, 2124, 2115, \) and \(2050 \text{ cm}^{-1})^{11,15} \) in the order of compounds listed in Table I) increases linearly with increasing quadrupole coupling constant.

From Equation (3), the value of \( i\pi_x - i\pi_y \) can be calculated by using \( eQq/h \) and \( \eta \) observed as well as \( |eQq_p/h| \) estimated to be 11.3 MHz. The results are shown in Table II. The value of \( i\pi_x - i\pi_y \) is presumed to be zero for thio cyanate ions, because of the essential linear structure of SCN in crystals, and also because of a negligibly small \( \eta \) observed. Accordingly, the 2\( p_x \) and 2\( p_y \) orbitals of nitrogen in an SCN− ion are occupied by the same amount of excess \( \pi \)-electrons, namely \( i\pi_x = i\pi_y = i\pi_{\text{ion}} \). By using Equation (2) with the calculated values of \( i\pi_x - i\pi_y \), the quantity of \( i\pi_{\text{ion}} - i\pi_x \) and \( i\pi_{\text{ion}} - i\pi_y \) can be evaluated for the complexes and methyl thio cyanate as shown in Table II.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( i\pi_x - i\pi_y )</th>
<th>( i\pi_{\text{ion}} - i\pi_y )</th>
<th>( i\pi_{\text{ion}} - i\pi_x )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3SCN</td>
<td>0.098</td>
<td>0.145</td>
<td>0.047</td>
</tr>
<tr>
<td>K2Pt(SCN)6</td>
<td>0.073</td>
<td>0.105</td>
<td>0.032</td>
</tr>
<tr>
<td>K2Hg(SCN)4</td>
<td>0.032</td>
<td>0.061</td>
<td>0.029</td>
</tr>
<tr>
<td>KSCN</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( a \) Calculated from averaged values of \( eQq/h \) and \( \eta \) for the sites a and b.
The electronic structure of an M–SCN group can be represented by resonance among structure I, polarized structure II in SCN, and ionic structures III and IV, consisting of a cation M+ and an anion SCN−. Here, the local polarization of CN has been ignored.

\[
M \quad M+ \quad M+
\]
\[
\text{S}–\text{C}≡\text{N} \quad \text{S}^+\text{C}≡\text{N}^- \quad \text{S}–\text{C}≡\text{N} \quad \text{S}≡\text{C}≡\text{N}^-
\]
I \quad II \quad III \quad IV

Since the structures I and III have a CN triple bond, π-electrons distribute cylindrically symmetric about the bond axis. The same is true for the structure IV, because there exists an isolated SCN bond, π-electrons distribute cylindrically symmetric about the bond axis. The same is true for the structure IV, because there exists an isolated SCN bond.

The local polarization of CN has been considered in the polarized structure II in SCN, and ionic structures III and IV, consisting of a cation M+ and an anion SCN−. Here, the local polarization of CN has been ignored.

\[
q^2_z = q_0\frac{1}{2} - \frac{3}{2} - \frac{3}{2}
\]

\[
<\mathbf{v}=\frac{1}{2}-\frac{3}{2}-\frac{3}{2}
\]

Accordingly, an excess charge of the nitrogen atom in the structure II must occupy the 2p$\sigma$-orbital of nitrogen. This means that the 2p$\pi$ and 2p$\nu$ orbitals of nitrogen are occupied by 2 and 1 electron, respectively, for the structure II, whereas they are equally occupied by 3/2 electrons for the structure IV. Let the contribution of the resonance structure can be calculated as shown in Table III by using the values, $i_{\nu}^\text{ion}$ and $i_{\nu}^\text{coval}$ given in Table II. Here, $i_{\text{MS}}$ (equal to $c + d$) denotes the ionic character of metal-ligand bonds in the platinum and mercury complexes. Jones has reported the same value of 0.71 as the present results for the contribution from III in potassium thiocyanate by the analysis of infrared spectra. For methyl thiocyanate, the present value of 0.10 for b agrees well with that estimated by Lett and Flygare from the results of microwave measurements on gaseous methyl thiocyanate. These facts confirm the adequacy of the present analysis.

Table III. Contributions of the various resonance structures in some thiocyanate compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>$i_{\text{MS}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$SCN</td>
<td>0.90</td>
<td>0.10</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>K$_2$Pt(SCN)$_6$</td>
<td>0.65</td>
<td>0.07</td>
<td>0.20</td>
<td>0.08</td>
<td>0.28</td>
</tr>
<tr>
<td>K$_2$Hg(SCN)$_4$</td>
<td>0.39</td>
<td>0.03</td>
<td>0.41</td>
<td>0.17</td>
<td>0.58</td>
</tr>
<tr>
<td>KSCN</td>
<td>0</td>
<td>0</td>
<td>0.71</td>
<td>0.29</td>
<td>-</td>
</tr>
</tbody>
</table>

2. Temperature dependence of quadrupole coupling constants

A $^{14}$N nucleus is known to have a positive quadrupole moment and the principal field gradient, $q_{zz}$ takes negative values for the compounds discussed owing to concentration of lone-pair electrons in the z-axis. Consequently, the principal values of a quadrupole coupling tensor in energy units can be expressed by,

\[
-eQq_{zz} = eQq_a, eQq_{yy} = \frac{1}{2} eQq (1 + \eta),
\]
\[
eQq_{zz} = \frac{1}{2} eQq (1 - \eta).
\]

(4)

Figs. 2 and 3 show the temperature dependence of $eQq/h$, $eQq_{yy}/h$, and $eQq_{zz}/h$ in both complexes. All of these values decrease almost linearly with increasing temperature in a higher temperature region than 77 K. By applying the BAYER theory to the present systems, the principal values of the EFG are given by the following equations, where the amplitudes of libration about the x-, y-, and z-axes are denoted by $\theta_x$, $\theta_y$, and $\theta_z$, respectively.

\[
q_{zz} = q_0[1 - (3 + \eta_0)(\theta_x^2)]/2 - (3 - \eta_0)(\theta_y^2)/2
\]
\[
q_{yy} = -q_0[(1 + \eta_0)/2 - (3 + \eta_0)(\theta_x^2)/2 - \eta_0(\theta_y^2)]
\]

(5a)

(5b)
Here, $|eQq_0/h|$ and $\eta_0$ are the quadrupole coupling constant and the asymmetry parameter, respectively, in a fictitious lattice performing no vibration. The mean square amplitude, $\langle \theta^2 \rangle$ of harmonic oscillations with a frequency $\omega$ can be calculated under a high temperature approximation by,

$$\langle \theta^2 \rangle = \left( \frac{1}{2} + kT/\hbar\omega \right) \hbar/\hbar\omega,$$

where $I$ is the moment of inertia.

For the calculation of the temperature variation of the EFG, both of the structural and the vibrational data of crystals are indispensable. Unfortunately, no accurate structural analysis has been performed for the platinum and mercury complexes as yet, and moreover, no vibrational data can be available for the former. Therefore, we have estimated contributions only from librational motion of thiocyanate groups for the latter complex. Contributions from the other vibrational modes, except libration of a complex ion as a whole, usually give small vibrational amplitudes and can be ignored.

TRAMER has carried out the experiments of Raman scattering on a single crystal of $K_2Hg(SCN)_4$ and has assigned the bands at 78 and 138 cm$^{-1}$ to bending modes of Hg–SCN perpendicular and parallel, respectively, to the Hg–SCN plane. These modes can be approximated as libration of SCN groups. We have evaluated $|eQq_0/h|$ and $\eta_0$ as 3.010 MHz and 0.194 for nitrogen in the site a, and as 2.910 MHz and 0.177 for that in the site b by extrapolating observed values in Fig. 3 to 0 K. The moment of inertia of an SCN group is estimated to be $2.44 \times 10^{-38}$ g $\cdot$ cm$^2$ from the bond distances reported for KSCN$^{17}$. One can calculate the temperature coefficients of $eQq_{xx}/h$, $eQq_{yy}/h$, and $eQq/h$ from Equations (5) and (6) with the values estimated. The results are given in Table IV.

The agreement between the observed and calculated temperature coefficients is extremely well for nitrogen at the site b, indicating that the temperature variation can be interpreted mostly in terms of the bending motion of Hg–SCN rather than the
libration of complex ions. On the other hand, each of the calculated values for the site a is less than half of the corresponding observed one. This suggests that the libration of complex ions contributes considerably to averaging of the EFG of nitrogen at the site a.

The temperature variation curves of $eQq_{xx}/h$ and $eQq/h$ of the platinum complex and those of $eQq_{yy}/h$ and $eQq/h$ for the site b of the mercury complex are slightly convex to the abscissa in a high temperature region. This is anomalous because the observed coupling constant versus temperature curve normally has downward curvature owing to the anharmonicity of thermal vibrations in addition to the BAYER term. The anomaly might be interpreted in terms of a partial scission of $S=C$ bonds taking place at high temperatures due to the excitation of thermal motion. In other words, contributions from the resonance structures I and/or III slightly increase with increasing temperature, whereas those from II and/or IV decrease in compensation. This is due to a vibronic interaction.

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