QUADRUPOLE INTERACTION OF CO$^{59}$ IN COBALTIC COMPLEXES

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Received March 27, 1967

(Communicated by Prof. B. V. Thosar, F.A.sc.)

ABSTRACT

Quadrupole coupling constants of Co$^{59}$ has been measured in several octahedral cobaltic complexes. The compounds are diamagnetic and polycrystalline in nature. The magnitudes of the coupling constants were evaluated assuming $\eta$ as zero. The temperature variation of the coupling constants are correlated with the nature of Co-ligand bond and molecular motions in the solid.

INTRODUCTION

Co$^{59}$ has a nuclear spin 7/2 and a high quadrupole moment Q equal to 0.5 barn. The quadrupole interaction would be appreciable compared to Zeeman interaction with the external magnetic field and the magnetic resonance line will be broadened beyond observation, unless the nucleus is in a near cubic environment. This condition is satisfied for Co$^{59}$ in the coordination compounds. The transition metal atoms, because of their unfilled $d$ orbitals, have a tendency to form complexes in which the metal atom is in the octahedral surroundings of the ligands. Trivalent cobalt complexes are diamagnetic. However, large chemical shifts occur due to second order paramagnetism. Quadrupole coupling constants of Co$^{59}$ in a few octahedral cobaltic complexes are reported in this paper. The results have been correlated with the nature of cobalt-ligand bond and molecular motions in these compounds. A brief account of some of the results have been presented earlier.

CALCULATION OF THE QUADRUPOLE COUPLING CONSTANT

The quadrupole coupling constant $[e^2 q Q]/h$ can be determined accurately either by performing a pure quadrupole resonance experiment or by studying the nuclear magnetic resonance in a single crystal. The former method is applied when $e^2 q Q$ is large enough and the latter when the quadrupole energy
is small and could be treated as a perturbation on the Zeeman energy. Co\(^{3+}\) in octahedral surroundings is expected to have a small coupling constant. Hence we shall concern ourselves only with the situation where quadrupole interaction acts as a perturbation on the nuclear magnetic interaction. For an axially symmetric field gradient (i.e., \(\eta = 0\)), with quadrupole perturbation carried to second order, the transition frequencies appropriate to a nucleus of spin I in a single crystal specimen is\(^5,6\)

\[
\nu_{m \rightarrow m-1} = \nu_0 + \frac{1}{2} \nu_Q (3\mu^2 - 1) (m - \frac{1}{2}) \\
+ \frac{\nu_Q}{32\nu_0} (1 - \mu^2) \left\{ [102m (m - 1) - 18I (I + 1) + 39]\mu^2 \\
- [6m (m - 1) - 2I (I + 1) + 3] \right\} 
\]

(1)

where

\[
\nu_Q = \frac{3e^2qQ}{2I(2I-1)} \hbar; \quad \mu = \cos \theta \quad \text{and} \quad \theta
\]

is the angle between the z-axis in the principal axis system of the field gradient tensor and the external magnetic field. \(\nu_0\) is the Larmor frequency or the transition frequency in the absence of the electric quadrupole interaction. From equation (1) it is clear that when quadrupole perturbation is only up to first order (i.e., first order in \(\nu_Q\)) the central transition \(m = \frac{1}{2} \rightarrow m = -\frac{1}{2}\) (for half integer spins) is unshifted from the Larmor frequency \(\nu_0\) \((\because m - \frac{1}{2} = 0)\). When the second order term is also considered the central transition shifts from \(\nu_0\) and the shift is inversely proportional to \(\nu_0\) or the external magnetic field. In a polycrystalline sample all values for \(\mu\) are permissible. The intensity maxima for the resonance absorption lineshape occur at \(\mu = 0\) for quadrupole perturbation up to 1st order. The absorption lineshape consists of (for half integer spins) an unshifted centre line flanked by small maxima separated by

\[
\frac{1}{2} \nu_Q (2m - 1). 
\]

(2)

When second order perturbation is significant the averaged expression for it possesses for the central transition \((\frac{1}{2} \rightarrow -\frac{1}{2})\), two maxima corresponding to \(\mu = 0\) and \(\mu^2 = 5/9\). These occur at

\[
\nu_1 (\frac{1}{2} \rightarrow -\frac{1}{2}) = \nu_0 + \frac{\nu_Q}{16\nu_0} [I (I + 1) - \frac{3}{4}] 
\]

(3)

\[
\nu_3 (\frac{1}{2} \rightarrow -\frac{1}{2}) = \nu_0 - \frac{\nu_Q}{9\nu_0} [I (I + 1) - \frac{3}{4}]. 
\]

(4)
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Thus the absorption shape consists of two peaks asymmetrically situated about $v_0$ and the peak-to-peak separation $\Delta \nu$ would be,

$$\Delta \nu = v_1 - v_2 = \frac{25v_0^3}{144v_o} [1 (I + 1) - \frac{3}{4}].$$  \hspace{1cm} (5)

Substituting for $I$, which is 7/2 for Co$^{69}$:

$$\Delta \nu = \frac{1}{75.25v_0} \left( \frac{e^2Q}{h} \right)^2.$$  \hspace{1cm} (6)

It should be noted that in the second order only the transition $\frac{1}{2} \rightarrow - \frac{1}{2}$ is observed, the others, e.g., $\pm \frac{1}{2} \rightarrow \pm \frac{3}{2}$, $\pm \frac{1}{2} \rightarrow \pm \frac{1}{2}$, are unobservable by this method.

In the magnetic resonance experiment, one records the derivative of the resonance line. The frequency separation between the derivative maxima, referred to as $\delta \nu$, differs from the absorption peak separation $\Delta \nu$ by $2\sigma$, the dipolar width. It has been shown by Casabella$^7$ that $\sigma$ and a more accurate ($e^2Q/h$) could be obtained by measuring $\delta \nu$ at several fields. The plot of $\delta \nu$ vs. $1/v_0$ will be a straight line for $\Delta \nu/2\sigma > 2$, and is given by

$$\delta \nu = \frac{1.02B}{v_0} + \sigma,$$  \hspace{1cm} (7)

where

$$B = \frac{25}{144} v_0^3 [1 (I + 1) - \frac{3}{4}].$$

The slope of the curve (7) gives the coupling constant accurately and the intercept gives the dipolar contribution.

When $\eta$ is not equal to zero, the peak-to-peak separation in the absorption line shape is modified from equation (5), $\Delta \nu$ is given by,$^8$

$$\Delta \nu = \frac{24}{144} \frac{v_0^3}{v_0} \left[ I (I + 1) - \frac{37}{4} \right] \left[ 1 + \frac{74}{135} \eta + \frac{\eta^2}{45} \right].$$  \hspace{1cm} (8)

Recently, the detailed lineshape for the powder pattern of $\frac{1}{2} \rightarrow - \frac{1}{2}$ transition for $\eta \neq 0$ has been worked out by Narita et al.$^9$

Another method, a more accurate one, would be to measure the pure quadrupole resonance frequencies for the $\pm 7/2 \rightarrow \pm 5/2$, $\pm 5/2 \rightarrow \pm 3/2$,
\[ \nu \left( \frac{7}{2} \rightarrow \frac{5}{2} \right) = \frac{3e^2qQ}{14\hbar} \left( 1 - \frac{\eta^2}{10} - \frac{487}{27000} \eta^4 + \ldots \right) \]
\[ \nu \left( \frac{5}{2} \rightarrow \frac{3}{2} \right) = \frac{2e^2qQ}{14\hbar} \left( 1 - \frac{17}{30} \eta^2 + \frac{50207}{27000} \eta^4 + \ldots \right) \]
\[ \nu \left( \frac{3}{2} \rightarrow \frac{1}{2} \right) = \frac{e^2qQ}{14\hbar} \left( 1 + \frac{109}{30} \eta^2 - \frac{196093}{27000} \eta^4 + \ldots \right). \]

In principle these transitions are observable in quadrupole resonance using nuclear induction. As will be shown below the coupling constants were small and this method could not be used.

**Experimental Results**

The compounds (listed in Table I) were prepared in this laboratory and investigations were made only in polycrystalline compounds. Cobalt forms numerous complexes having different types of ligands as donors. A few compounds having the most symmetrical environment around cobalt atom have been chosen for this study. The environment in the compounds chosen is schematically illustrated in Fig. 1.

A Varian wide line spectrometer with variable temperature accessories has been utilised. Measurements were made at different field strengths ranging from 3 to 12 k-gauss and at varied temperatures in favourable cases. The chemical shifts in these compounds have been studied by Dharmatti et al. and the data were utilised to fix the frequency of Co\(^{59}\) resonances. An asymmetric line due to \( \frac{1}{2} \rightarrow - \frac{1}{2} \) transition was observed in all the compounds. The linewidth (i.e., derivative peak-to-peak separation) decreased with increasing field indicating the presence of second order quadrupole interactions. The peak separation in frequency \( \delta \nu \), was plotted against \( 1/\nu_0 \) and from this curve \((e^2qQ)/\hbar\) and dipolar contribution to width have been evaluated. The values are given in Table I. The resonances were extremely weak for 'trans' \([Co (NH_3)_4(NO_2)_2]NO_2\), \(Co (NH_3)_3 (NO_2)_3\), \(Na_3 [Co (NO_2)_6]\) and \(Co (dipy)_3 (ClO_4)_3\). Mean of a few traces at 12 kg. was used to calculate the coupling constants \((e^2qQ)/\hbar\). For \(Co (en)_3 Cl_3\cdot3H_2O\) coupling constant obtained on putting \( \delta \nu \) for \( \Delta \nu \) in equation (6) compares well with the value obtained from \( \delta \nu \) vs. \( 1/\nu_0 \) plot. This is of course understandable for in these compounds the dipole interactions contribute much less to the width compared to quadrupolar interaction. It has been assumed throughout that \( \eta \) is zero.
In trans Co(NH$_3$)$_4$(NO$_2$)$_2$NO$_3$ and Co(NH$_3$)$_3$(NO$_2$)$_3$ the lineshape indicates that $\eta$ may not be zero. As we have not been able to determine $\eta$, the coupling constant has been calculated for $\eta = 0$.

In the hexammines the high field side of the resonance spectrum shows a few extra humps indicative of non-equivalent sites for cobalt. These
### Table I

**Quadrupole coupling constants and the chemical shifts of Co$^{59}$ in cobalt complexes**

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Chemical shifts at 10 K. gauss (in liquid)</th>
<th>Coupling constant $(e^2qQ)/h$ in Mc/s (in solids)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>K$_3$Co (CN)$_6$</td>
<td>0 (Reference)</td>
<td>2.7±0.1</td>
</tr>
<tr>
<td>2</td>
<td>Co (dipy)$_3$ (ClO$_4$)$_3$</td>
<td>-66.2</td>
<td>11.2</td>
</tr>
<tr>
<td>3</td>
<td>Co (NH$_3$)$_3$ (NO$_2$)$_3$</td>
<td>-69.4 (s)$^b$ -71.0 (w)</td>
<td>3.6</td>
</tr>
<tr>
<td>4</td>
<td>Co (en)$_3$ Cl$_3$</td>
<td>-70.1</td>
<td>3.3±0.1</td>
</tr>
<tr>
<td>5</td>
<td>' Trans' [Co (NH$_3$)$_4$ (NO$_2$)$_2$] NO$_3$</td>
<td>-71.5</td>
<td>5.6$^a$</td>
</tr>
<tr>
<td>6</td>
<td>Na$_3$Co (NO$_2$)$_6$</td>
<td>-73.5</td>
<td>8.4</td>
</tr>
<tr>
<td>7</td>
<td>Co (NH$_3$)$_6$ Cl$_3$</td>
<td>-80.8</td>
<td>1.5±0.1</td>
</tr>
<tr>
<td>8</td>
<td>Co (NH$_3$)$_4$ (NO$_2$)$_8$</td>
<td>-80.8</td>
<td>1.8±0.1</td>
</tr>
<tr>
<td>9</td>
<td>Cobalt Oxinate</td>
<td>-94.2</td>
<td>4.3</td>
</tr>
<tr>
<td>10</td>
<td>Cobalt acetyl acetonate</td>
<td>-122.9</td>
<td>5.7±0.2$^e$</td>
</tr>
</tbody>
</table>

(a) $\eta$ assumed to be zero.
(b) In liquid samples two lines, one weak and the other strong were observed.
(c) At 100°K. $(e^2qQ)/h = 3.8$ Mc/s.
(d) Weak line hence error is bound to be large. Lineshape indicates that $\eta$ may not be zero as assumed.
(e) Only the dispersion mode could be observed.

humps become prominent at low fields. The width of the centre line and separation between one pair of outer humps at 6 Mc./s. correspond to the coupling constants 1.2 and 2.2 Mc/s. respectively. As the field (or $\nu_0$) is increased $\Delta \nu.\nu_0$ also increases instead of remaining constant. This shows overlap and the coupling constant calculated from the width of centre line at 7.5 Mc/s. is found to be 1.5 Mc/s. At this frequency the first order satellites were observed. The coupling constant obtained by using equation (2) is 1.1 Mc/s. for Co (NH$_3$)$_6$ Cl$_3$. 


In pentammines, e.g., \([\text{Co} (\text{NH}_3)_5 \text{Cl}] \text{Cl}_2\), cobalt is in the environment of five ammine ligands and one chlorine ligand. The octahedron around cobalt would be distorted and cationic reorientation is absent as observed from proton resonances. A large field gradient would be present at the cobalt site owing to the asymmetry of charge distribution. For these reasons no \(\text{Co}^{59}\) resonance could be traced in any of the pentammines. In ‘trans’ \([\text{Co} (\text{NH}_3)_4 (\text{NO}_2)_2] \text{NO}_3\), there is an axial symmetry around cobalt which is lacking in the ‘Cis’ isomer. The cationic motion was observed in the former and it was found to be absent in the latter. This explains the failure in recording the nuclear magnetic resonance of \(\text{Co}^{59}\).

Fig. 2. Lineshape of \(\text{Co}^{59}\) resonance in (i) \(\text{Co} (\text{NH}_3)_6 (\text{NO}_2)_6\) and (ii) \(\text{Co} (\text{en})_3 \text{Cl}_3 3\text{H}_2\text{O}\). In ‘trans’ \([\text{Co} (\text{NH}_3)_4 (\text{NO}_2)_2] \text{NO}_3\) the resonance shape is like (i), and in the others like (ii).

As mentioned in Section 2 if one could trace the quadrupole resonance of at least two transitions \(\eta\) could be determined. The induction method could be used for obtaining the quadrupole resonance line. The minimum radio frequency available in the spectrometer used by us was 2 Mc/s. Hence this method could be used (vide equation 9) only for the \(7/2 \rightarrow 5/2\) transition of \(\text{Co} (\text{dipy})_3 (\text{ClO}_4)_3\). A broad line was observed at 2.38 Mc/s which confirms the coupling constant obtained from the powder sample. \(\eta\) could not
be determined as it is not possible to observe other transitions. Search for the quadrupole resonance of Co\(^{59}\) in pentammines was not successful.

Temperature dependence measurements were carried out in hexammines, Co\((en)\sub{3}Cl\sub{3}.3H\sub{2}O\), K\(_3\)Co(CN)\(_6\) and cobalt acetyl acetonate. In the last two the coupling constant remained practically unchanged whereas in the former ones large change was noticed and is shown in Fig. 3.

![Graphs showing temperature dependence](image)

**Fig. 3.** Correlation between the temperature dependence of second moment and quadrupole coupling constants. *(a), (b)*. Second moment and \((e^2\nu Q)/\hbar\) against T in Co\((NH\sub{3})\sub{6}\) (NO\(_2\)\(_2\)). *(c), (d)*. Second moment, and \((e^2\nu Q)/\hbar\) against T in Co\((en)\sub{3}Cl\sub{3}.3H\sub{2}O\).

**DISCUSSION**

The factors that appreciably affect the quadrupole coupling constant are the nature of bond associated with the nucleus concerned and molecular motions in the solid.

The electronegativity difference relates to the covalency of cobalt-ligand bond. The bonding atoms of the groups NH\(_3\), ethylene diamine (en) and
NO$_3^-$ have almost the same electronegativity. We find that coupling constants at liquid-air temperature for Co(en)$_3$Cl$_3$, Co(NH$_3$)$_6$(NO$_3$)$_3$ and the room temperature value of Co(NH$_3$)$_3$(NO$_2$)$_3$ are nearly the same, 3.8 Mc/s. For Co(NH$_3$)$_6$Cl$_3$ the coupling constant at 120° K. is 2 Mc/s, but it increases on lowering the temperature showing that it is not the rigid lattice value. In ‘trans’ [Co(NH$_3$)$_4$(NO$_2$)$_2$] NO$_3$ the coupling constant of 5.6 Mc/s is comparatively high. This could be due to the asymmetry introduced by replacing two of the NH$_3$ groups of the hexammine by NO$_2$ groups. The deviation from octahedral symmetry could hence be more. This is also brought out by the fact that whereas in the former compounds $\eta$ appears to be small from the lineshape, in the latter compound $\eta$ appears to be large (Fig. 2). The lineshape is grossly different for $\eta$ close to zero and close to one and it can, therefore, be easily distinguished. Oxygen, nitrogen and carbon are in the decreasing order of electronegativity. When these atoms belonging to a ligand group are bonded to cobalt atoms the coupling constant should also be in this order if the distortion effects are equal or small. As expected in cobalt acetyl acetonate, where cobalt is linked to six oxygen atoms, the coupling constant is 5.6 ± 0.2 Mc/s, and in K$_3$CO(CN)$_6$ where the donor atom is carbon it is 2.7 ± 0.1 Mc/s. In the compounds with nitrogen as donor, the coupling constants are in between these two values. A correlation thus seems to exist between electronegativity difference and the value of coupling constants when all the bonding ligands are alike and distortion affects negligible. This requires confirmation with more compounds having octahedral carbon and oxygen surroundings.

Molecular motions in NH$_4$ is found to have a significant effect on the coupling constant of bromine in NH$_4$Br. A similar situation occurs in the cobaltic complexes. The coupling constant is found to increase in Co(NH$_3$)$_6$Cl$_3$ at lower temperatures when the cationic motion freezes. The corresponding increase is much higher in Co(NH$_3$)$_6$(NO$_3$)$_3$. In Co(en)$_3$Cl$_3$.3H$_2$O the motion of water molecules above 170° K. could account for the decrease in the coupling constant above this temperature. Figure 3, which is the plot of proton resonance second moment and the quadrupole coupling constant against temperature, shows evidently the correlation between protonic motions and the coupling constant decrease. The proton resonance width in cobalt acetyl acetonate is independent of temperature, the coupling constant is also found to be so. Hence it could be concluded that molecular motions such as the cationic motion in the hexammine or the hindered rotation in water molecule reduce the coupling constant of cobalt.

As mentioned in these compounds the chemical shifts are large (Table I) and are directly related to the strength of the crystalline field due to the
ligand. The quadrupole coupling constant depends on the anisotropy of the electric field around cobalt nucleus whereas the chemical shift depends on the magnitude of the crystalline field. Therefore a correlation between the two is not expected.

The only work available on quadrupole coupling constant of Co$^{69}$ is that of Sugawara, who has studied Co(NH$_3$)$_6$Cl$_3$ in the powder form and a twin crystal of K$_3$Co(CN)$_6$ at 4° K. The coupling constant obtained in the former is 1.5 Mc/s. assuming $\eta$ to be zero. This compares favourably with our values. In K$_3$Co(CN)$_6$, $(e^2qQ)/h = 7.3 \pm 0.1$ Mc/s. with $\eta = 0.75$. Both these values are incompatible with our results. In polycrystalline K$_3$Co(CN)$_6$ we find that $(e^2qQ)/h = 2.7 \pm 0.1$ Mc/s. is temperature independent up to 100° K. and $\eta$ from the lineshape is $< 0.5$. The large value obtained by Sugawara at 4° K. could then only be due to some kind of a transition between 4° K. and 100° K.

ACKNOWLEDGEMENT

It is with pleasure we thank Mr. S. Jagannathan for the preparation and analysis of the compounds.

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