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^{59}Co Nuclear Quadrupole Interaction in Crystalline *Δ*-Tris[*trans*-(1*R*,2*R*)-1,2-diaminocyclohexane]cobalt(III) Chloride Trihydrate

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The lineshape of ^{59}Co NMR was measured on solid $[Co(chxn)_3]^{3+}$ (chxn = *trans*-(1*R*,2*R*)-1,2-diaminocyclohexane) at the Larmor frequencies of 47 and 96 MHz. The ^{59}Co nuclear quadrupole coupling constant and the asymmetry parameter of the electric field gradient were determined to be 7.50 MHz and 0.75, respectively. These values correspond to a very small distortion of the complex cation in the crystal.

The ^{59}Co nuclear magnetic resonance chemical shift and its relaxation time in complex ions in solutions have been known to be highly sensitive to any environmental perturbation, and have thus been used to examine the ion-pairing phenomenon in solutions.[1—5] One of the present authors along with coworkers previously measured the quadrupole splitting (some ten kHz) of ^{59}Co in several complex ions of cobalt in anisotropic environments.[6—8] They also measured the dependence of the spin-lattice relaxation rates (T_1^{-1}) of ^{59}Co for slightly distorted complex ions in $[Co(chxn)_3]^{3+}$, where chxn = *trans*-(1*R*,2*R*)-1,2-diaminocyclohexane, on the concentration of a variety of multivalent anions in aqueous solutions. They found that the relaxation is governed by a nuclear electric quadrupole interaction which is induced by a distortion of the complex cation upon the formation of instantaneous ion-pairs with the anions.[9]

The thus-estimated ^{59}Co quadrupole interaction could be useful for a quantitative discussion of the possible interactions of these big complex ions with the counterions and/or solvent molecules in the solution: In order to do this it seems to be necessary to know how large is the ^{59}Co nuclear quadrupole interaction in the complex cations located in some standard environment. In the present study we measured the ^{59}Co NMR spectrum in polycrystalline *Δ*-$[Co(chxn)_3]Cl_3\cdot 3H_2O$ to deduce the intrinsic nuclear quadrupole interaction for the complex cation, $[Co(chxn)_3]^{3+}$, in the solid state.

Experimental

The complex compound *Δ*-$[Co(chxn)_3]Cl_3\cdot 3H_2O$ was prepared according to the literature.[9] The powder NMR spectrum of ^{59}Co under the static condition was measured by Bruker MSL-200 and MSL-400 spectrometers at the Larmor frequencies of 47.485 and 95.651 MHz, respectively, at room temperature. The MAS (magic angle spinning) spectrum at the MAS rate of 9.6 kHz was collected at 95 MHz at room temperature.

Results and Discussion

The powder NMR spectrum for ^{59}Co under the static condition at 95 MHz is shown in Fig. 1. This spectrum indicates the existence of a weak, but certain, satellite peak at +324 kHz from the strong central component; the satellite could also be observed in the measurements at 47.485 MHz. This fact implies that there is a non-vanishing nuclear quadrupole interaction between the central cobalt atom and its non-cubic electric environment. The lower bound of the quadrupole coupling constant, e^2Qq/h, is estimated according to the first-order perturbation treatment of the line shape; the powder NMR line shape function, $P_\eta(x)$, for a nucleus in an electric field gradient with the asymmetry parameter, η, is given by

$$\begin{aligned}&P_\eta(x) = K(\alpha)/\pi[\eta(1-x)]^{1/2},\\&\sin\alpha = S(x) \quad \text{for } -\frac{1}{2}(1+\eta) \leqq x \leqq -\frac{1}{2}(1-\eta),\\&P_\eta(x) = K(\alpha)/\pi[\eta(1-x)]^{1/2},\\&\sin\alpha = S(x)^{-1} \quad \text{for } -\frac{1}{2}(1-\eta) \leqq x \leqq 1,\end{aligned}$$

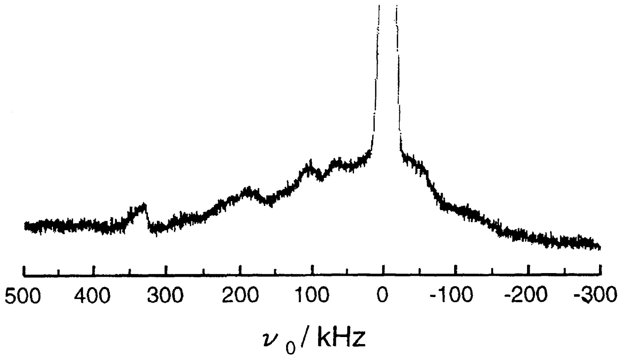

Fig. 1. ^{59}Co broadband NMR spectrum for the polycrystalline specimen of *Δ*-$[Co(chxn)_3]Cl_3\cdot 3H_2O$.

and

$$P_\eta(x) = 0, \qquad \text{elsewhere,}$$

where $K(\alpha)$ stands for the complete elliptic integral, $x = (\nu_m - \nu_L)/|m-\frac{1}{2}|\nu_Q$ $(m \neq \frac{1}{2})$, and we define $S(x) = \frac{1}{2}[(2x+1+\eta) \times (3-\eta)/\eta(1-x)]^{1/2}$. Because $K(\alpha)$ and, hence, the powder line shape has a logarithmic singularity at $\alpha = \pi/2$, i. e., at $x = -\frac{1}{2}(1-\eta)$, the lower bound of e^2Qq/h can be estimated by putting $\eta = 0$ to be 1.5 MHz.[10,11]

The line shape of the central component is shown in Fig. 2. An asymmetric line shape suggests that the cobalt nucleus experiences a finite nuclear electric quadrupole interaction as well as a significant dipolar interaction with the surrounding protons. It suggests also that the chemical shielding for the ^{59}Co is also asymmetric, probably due to an asymmetric conformation of the complex cation or to a non-cubic site symmetry of the cobalt atomic site. The line shape can be treated by the second-order perturbation theory.[10,11] We tried to reproduce the powder ^{59}Co line shape in Fig. 2 using a simulation program provided by Bruker Co., Ltd. by taking e^2Qq/h, the asymmetry parameter of the electric field gradient, η,[10] the principal components of the anisotropic chemical shift tensor, σ_{11}, σ_{22}, and σ_{33}, and the dipolar broadening factor as adjustable parameters. The result of the simulation is given in Fig. 2, and the values of the various parameters are listed in Table 1. We obtained the dipolar broadening of 5 kHz, which may be assigned to the dipolar interaction between the ^{59}Co and the nearby protons in the chxn ligands.

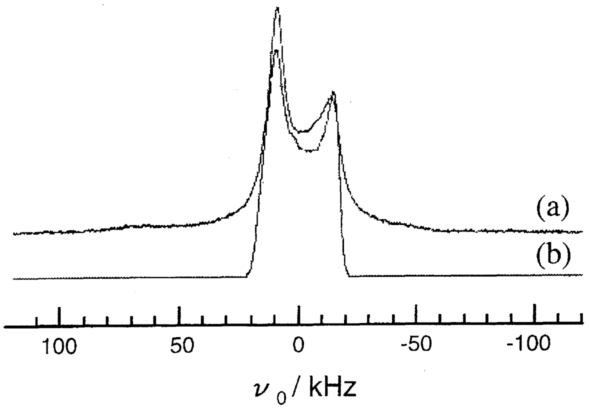

Fig. 2. (a) The spectral line shape of the ^{59}Co central transition $(-1/2 \longleftrightarrow +1/2)$ under the static condition: (b) Simulated spectrum with the parameters listed in Table 1.

Table 1. The Quadrupole Coupling Constant and Its Asymmetry Parameter, and the Values of the Principal Components of the Chemical Shift Tensor Employed to Reproduce the Second-Order Quadrupolar Line Shape for ^{59}Co in Polycrystalline Δ-$[Co(chxn)_3]Cl_3 \cdot 3H_2O$ Estimated uncertainties are given in the parentheses.

e^2Qq/h	7.50(0.5) MHz
η	0.75(0.05)
σ_{11}	165(5) ppm.
σ_{22}	100(5) ppm.
σ_{33}	145(5) ppm.
Dipolar broadening	5.00 kHz

The simulated values of e^2Qq/h and η given in Table 1 predict that the singularity in the line shape, i. e., the satellite transition, appears at a frequency separated from the central line by about 470 kHz, being considerably different from the observed separation of 320 kHz. However, the order of magnitudes of the present e^2Qq/h and η may be accepted considering that the system is so complicated that both the anisotropic quadrupolar and chemical shielding interactions contribute simultaneously, and in a complicate manner, to the ^{59}Co line shape and the line width.

The ^{59}Co MAS NMR spectrum for the central component is shown in Fig. 3(a); it indicates that the MAS works to remove any broadening caused by the anisotropic chemical shielding interaction from the ^{59}Co central line, resulting in a line shape dominated by the partially averaged quadrupole interaction. We calculated the MAS line shape for the central component by using the quadrupole parameters, e^2Qq/h and η, listed in Table 1,[11,12] and obtained the result shown in Fig. 3(b), which is in excellent agreement with the experimental spectrum.

The quadrupole coupling constants in some hexa-coordinated cobalt complexes that are similar to the present complex range from 1 to 8 MHz, and η from 0 to 0.75.[13] Therefore, the values of the present quadrupole parameters imply that the central cobalt ion is coordinated by three chxn ligands nearly octahedrally; however, the crystal field that it experiences is significantly asymmetric. Similar asymmetric coordination of the chxn ligands to the central cobalt ion was observed for the complex cations in $(+)_{589}$-$[Co\{(+)\text{-}chxn\}_3]Cl_3 \cdot 5H_2O$[14] and $(+)_{589}$-$[Co\{(-)\text{-}chxn\}_3]Cl_3 \cdot H_2O$.[15] The present value of e^2Qq/h for Δ-$[Co(chxn)_3]Cl_3 \cdot 3H_2O$ is extremely small compared with those in other numerous cobalt compounds.[13] However, it still seems to be large compared with the estimated values of e^2Qq/h deduced from the relaxation measurements for some complex cobalt salts in solutions,[6,7] implying that the probable ion-pairing between the cobalt complex ions and its counterions contributes only

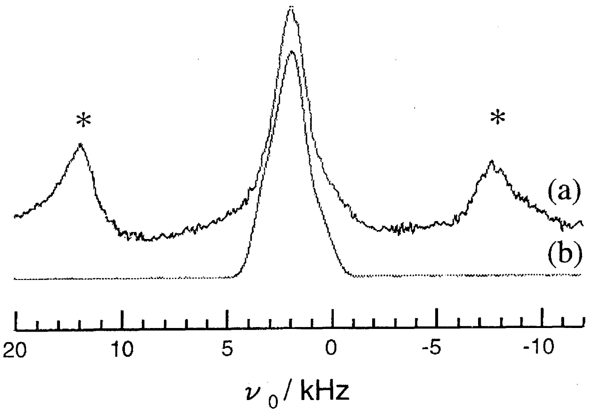

Fig. 3. (a) The spectral line shape of the ^{59}Co central transition $(-1/2 \longleftrightarrow +1/2)$ under the MAS with the spinning rate of 9.6 kHz. The asterisks indicate the spinning side bands: (b) Simulated spectrum with the parameters listed in Table 1.

weakly to the electric field gradients at the central cobalt site in solution.

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