

# Nature of Hydration Water in ( $\pm$ )-Tris(ethylenediamine)cobalt(III) Chloride Hydrate, ( $\pm$ )-[Co(en)<sub>3</sub>]Cl<sub>3</sub>·nH<sub>2</sub>O, as Studied by <sup>1</sup>H, <sup>2</sup>H, and <sup>17</sup>O Solid State NMR

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The static and dynamics properties of hydration water molecules in ( $\pm$ )-[Co(en)<sub>3</sub>]Cl<sub>3</sub> were studied by means of <sup>1</sup>H, <sup>2</sup>H, and <sup>17</sup>O solid state NMR. By <sup>1</sup>H pulsed field gradient (PFG) NMR the apparent diffusion coefficient of mobile water through a micropore along the crystalline unique *c*-axis was found to be  $1.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ . The <sup>2</sup>H NMR spectrum at 141 K consists of two components, one being a Pake doublet corresponding to a quadrupole coupling constant (QCC) of  $(226 \pm 2) \text{ kHz}$  and an asymmetry parameter of the electric field gradient  $\eta$  of  $0.08 \pm 0.01$ , and another being a Gaussian line with a linewidth of 3.5 kHz. The <sup>17</sup>O NMR spectrum at 300 K also consists of a narrow Gaussian peak and a broad powder pattern with a second order quadrupole effect corresponding to  $\text{QCC} = (6.3 \pm 0.5) \text{ MHz}$  and  $\eta = 0.55 \pm 0.02$ . The broad and narrow components are assigned to water molecules accommodated at general 12g positions and special 2a and 2b positions in the trigonal lattice with space group  $\bar{R}3c1$ . From the ratio of the populations at these positions their potential energy difference was estimated to be between  $(2.7 \pm 0.1)$  and  $(3.5 \pm 0.1) \text{ kJmol}^{-1}$ . The <sup>2</sup>H NMR spectrum at room temperature indicates a finite quadrupole interaction which is attributable to the rapid rotation of water molecule about the molecular  $C_2$ -axis. When the water content exceeds 2.7, the QCC is reduced sharply to  $(5.0 \pm 0.1) \text{ kHz}$  at 285 K, suggesting that there occurs rapid rotation of water and rapid exchange of <sup>2</sup>H between nonequivalent positions.

*Key words:* ( $\pm$ )-[Co(en)<sub>3</sub>]Cl<sub>3</sub>; Absorbed Water; Molecular Motion; Hydrogen Bond; Quadrupole Interaction.