

Nature of Hydration Water in (\pm)-Tris(ethylenediamine)cobalt(III) Chloride Hydrate, (\pm)-[Co(en)₃]Cl₃·*n*H₂O, as Studied by ¹H, ²H, and ¹⁷O Solid State NMR

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The static and dynamics properties of hydration water molecules in (\pm)-[Co(en)₃]Cl₃ were studied by means of ¹H, ²H, and ¹⁷O solid state NMR. By ¹H 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 1.0×10^{-9} m² s⁻¹. The ²H NMR spectrum at 141 K consists of two components, one being a Pake doublet corresponding to a quadrupole coupling constant (QCC) of (226 ± 2) kHz and an asymmetry parameter of the electric field gradient η of 0.08 ± 0.01 , and another being a Gaussian line with a linewidth of 3.5 kHz. The ¹⁷O 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 $\text{QCC} = (6.3 \pm 0.5)$ 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 $\bar{F}\bar{c}1$. From the ratio of the populations at these positions their potential energy difference was estimated to be between (2.7 ± 0.1) and (3.5 ± 0.1) kJmol⁻¹. The ²H NMR spectrum at room temperature indicates a finite quadrupole interaction which is attributable to the rapid rotation of water molecule about the molecular *G*-axis. When the water content exceeds 2.7, the QCC is reduced sharply to (5.0 ± 0.1) kHz at 285 K, suggesting that there occurs rapid rotation of water and rapid exchange of ²H between nonequivalent positions.

Key words: (\pm)-[Co(en)₃]Cl₃; Absorbed Water; Molecular Motion; Hydrogen Bond; Quadrupole Interaction.