

Hydrogen motional disorder in crystalline iron group chloride dihydrates

Brennan J. Walder, Alex M. Patterson, and Philip J. Grandinetti*

Department of Chemistry, Ohio State University, 100 West 18th Avenue, Columbus, OH 43210, USA

Jay H. Baltisberger

Division of Natural Science, Mathematics, and Nursing, Berea College, Berea, Kentucky 40403, USA

The principal components and relative orientation of the ^2H paramagnetic shift and quadrupolar coupling tensors have been measured for the $\text{MCl}_2 \cdot 2\text{D}_2\text{O}$ family of compounds, $\text{M} = \text{Mn, Fe, Co, Ni, Cu}$, using the 2D shifting-d echo NMR experiment in order to determine (1) the degree of unpaired electron delocalization and (2) the number and location of crystallographically distinct hydrogen sites around oxygen and their fractional occupancies. The molecular susceptibilities of the 3d ion systems are combined with various point dipole source configurations modeling unpaired electron delocalization to predict ^2H paramagnetic shift tensors at potential deuterium sites. The instantaneous deuterium quadrupolar coupling and shift tensors are then combined with parameterized motional models, developed for trigonally ($\text{M} = \text{Mn, Fe, Co, Cu}$) and pyramidally ($\text{M} = \text{Ni}$) coordinated D_2O ligands, to fit the experimental 2D spectra. Dipole sources placed onto metal nuclei with a small degree of delocalization onto the chlorine ligands yield best agreement with experiment for $\text{M} = \text{Mn, Fe, Co, Ni}$, while best agreement for $\text{CuCl}_2 \cdot 2\text{D}_2\text{O}$ is obtained with additional delocalization onto the oxygen. Our analysis of the salts with trigonally coordinated water ligands ($\text{M} = \text{Mn, Fe, Co, Ni}$) confirm the presence of bisector flipping and the conclusions from neutron scattering that hydrogen bonding to chlorine on two adjacent chains leads to the water molecule in the $[\text{M}(\text{D}_2\text{O})_2\text{Cl}_4]$ cluster being nearly coplanar with O-M-Cl involving the shortest metal-chlorine bonds of the cluster. In the case of $\text{NiCl}_2 \cdot 2\text{D}_2\text{O}$ the experimental parameters were found to be consistent with a motional model where the D_2O ligands are pyramidally coordinated to the metal and undergo bisector flipping while the water ligand additionally hops between two orientations related by a 120° rotation about the Ni-O bond axis. This restricted water ligand motion is likely due to van Der Waals interactions and is concerted with neighboring water ligands motions.