

Tumbling motions of $[\text{NH}_2(\text{CH}_3)_2]^+$ ions in $[\text{NH}_2(\text{CH}_3)_2]_2\text{CoCl}_4$ determined by ^1H MAS NMR spectroscopy in the rotating frame

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The structure and phase transition temperatures of $[\text{NH}_2(\text{CH}_3)_2]_2\text{CoCl}_4$ were determined using x-ray diffraction and differential scanning calorimetry (DSC), respectively. While the structure for the $[\text{NH}_2(\text{CH}_3)_2]_2\text{CoCl}_4$ crystals determined using x-ray diffraction is consistent with the previously reported results, the phase transition temperatures using DSC are not. It is possible that the phase transition temperatures of $[\text{NH}_2(\text{CH}_3)_2]_2\text{CoCl}_4$ vary according to the conditions of crystal growth. The local structure was studied using ^1H MAS NMR spectroscopy: the chemical shifts and the spin-lattice relaxation time $T_{1\rho}$ in the rotating frame for the ^1H nucleus in $[\text{NH}_2(\text{CH}_3)_2]_2\text{CoCl}_4$ were observed. The results show that the structural change due to chemical shifts does not occur with a change in the temperature. The temperature dependence of the $T_{1\rho}$ values for ^1H reflect the modulation of the inter- NH_2 and inter- CH_3 dipolar interactions due to $[\text{NH}_2(\text{CH}_3)_2]^+$ motions. The $T_{1\rho}$ values of materials containing paramagnetic ions are shorter than those of pure materials; the influence of the paramagnetic ions is predominant. The relaxation time should be inversely proportional to the square of the magnetic moment of the paramagnetic ions. Therefore, $T_{1\rho}$ of materials containing Co^{2+} ions is shorter than those of materials without paramagnetic ions. Therefore, the ^1H spin-lattice relaxation is driven by the fluctuations of the magnetic dipole of the Co^{2+} paramagnetic ions. A shorter $T_{1\rho}$ indicates that the transfer of energy from the nuclear spin system to the surrounding environment is more facile. On the other hand, $T_{1\rho}$ for ^1H in $[\text{NH}_2(\text{CH}_3)_2]_2\text{CoCl}_4$ showed a minimum, and it is apparent that the $T_{1\rho}$ values for ^1H are governed by the tumbling motions. The long $T_{1\rho}$ for ^1H above T_{C1} may be due to the breakage and replacement of two hydrogen bonds in the dimethylammonium ions. This hypothesis is supported by the results of the x-ray diffraction of $[\text{NH}_2(\text{CH}_3)_2]_2\text{CoCl}_4$. The activation energy was determined from the results of the $T_{1\rho}$ NMR relaxation experiments. The activation energy for ^1H nuclei is lower above T_{C1} than below T_{C1} . The protons exhibit high mobility, and which thus have great potential as proton conductors. In future work, the structural properties of N(1) and N(2) in two inequivalent $[\text{NH}_2(\text{CH}_3)_2]^+$ groups will be discussed on the basis of high field FT NMR results.