

NMR · NQR and DTA · DSC Studies of Phase Transitions in Pyridinium Tetrachloropalladate(II) and Pyridinium Tetrachloroplatinate(II)*

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From the measurements of DTA · DSC and the temperature dependences of ³⁵Cl NQR frequencies, phase transitions were detected at 150 K, 168 K, and 172 K for (pyH)₂[PtCl₄], and at 241 K for (pyH)₂[PdCl₄]. In order to elucidate the motional state of the constituent ions in the crystals in connection with the structural phase transitions, the ³⁵Cl NQR and ¹H NMR spin-lattice relaxation times and the second moment of the ¹H NMR line were measured as functions of temperature. For both compounds, the potential wells for the cationic reorientation are suggested to be highly nonequivalent at low temperatures. Above 168 K, the pyridinium ions in (pyH)₂[PtCl₄] are expected to reorient between almost equivalent potential wells. As for (pyH)₂[PdCl₄], it is expected that the orientational order of the cation still remains even above the second order transition at 241 K. A change of the potential curve from two-unequal to three-unequal wells is proposed as a possible mechanism of the second order transition. The activation energies for the cationic motion in the respective model potential are derived for both compounds at high and low temperatures.

Key words: Phase transition, NQR, NMR, Spin-lattice relaxation, DSC.

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