

Molecular Motions in Halogen-Bridged One-Dimensional Pt Complexes, [Pt^{II}(en)₂][Pt^{IV}X₂(en)₂](ClO₄)₄ (X = Cl, Br) Studied by ²H and ¹H NMR

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²H and ¹H NMR measurements were performed on crystalline [Pt(en)₂][PtX₂(en)₂](ClO₄)₄ (X = Cl, Br), where the protonated and partially deuterated ethylenediamines (en's), NH₂(CH₂)₂NH₂, NH₂(CD₂)₂NH₂ and ND₂(CH₂)₂ND₂ were used as ligands. Measurements of ²H and ¹H NMR spin-lattice relaxation times showed the presence of motions of en chelate rings at the temperatures near the phase transitions, whereas broad ²H NMR spectra and the reported X-ray diffraction data showed no marked motions. These results were consistently explained by introducing the en puckering motion between highly asymmetric potential wells with an energy difference of 10 - 13 kJ mol⁻¹. This difference was shown to be much larger than 2 - 5 kJ mol⁻¹, reported for the iodo-complex, [Pt(en)₂][PtI₂(en)₂](ClO₄)₄.

Key words: Phase Transition; NMR; Spin-lattice Relaxation; Molecular Motion.