

## **NMR study of intramolecular chemical exchange in the La(III) complex of triethylenetetraaminehexaacetic acid in aqueous solution**

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In coordination complexes containing central metal atoms, structures with more than six ligands generally rearrange so rapidly on the NMR time scale, even at low temperatures, that it is impossible to distinguish symmetrically non-equivalent sites occupied by similar ligands. On the other hand, a few macrocyclic ligands, most notably 1,4,7,10-tetraazacyclododecane -N,N,N,N-tetraacetic acid (DOTA) and 1,4,7,10-tetrakis(2-carbamoyl-ethyl)-1,4,7,10-tetraazacyclododecane, are known to form very rigid complexes with lanthanum(III) ion so that slow exchange NMR spectra may be observed. NMR line-shape analysis of these spectra is consistent with exchange due solely to conformational changes.

In this lecture, an intramolecular ligand rearrangement taking place via a bond-breaking process in lanthanum(III) complex of triethylenetetraaminehexaacetic acid will be presented by dynamic NMR experiments. Evidence that the ligands are exchanging derives from the observation of temperature and mixing time ( $\tau_m$ ) dependent cross peaks between the diastereotopic protons on each side of the complex in the 2D EXSY experiment. The exchange rate coefficient,  $k$ , were determined to be  $7.1 \times 10^{-2}$ ,  $29.1 \times 10^{-2}$ ,  $70.0 \times 10^{-2}$ , and  $140.4 \times 10^{-2} \text{ s}^{-1}$  at 295, 310, 320, and 330 K, respectively, corresponding to the activation parameters  $E_a = 69.6 \text{ kJ}$ ,  $\Delta H^\ddagger = 66.9 \text{ kJ/mol}$  and  $\Delta S^\ddagger = -39.6 \text{ J/mol}$ . The paramagnetic lanthanide complexes of this and related ligands are being employed extensively in magnetic resonance as MRI contrast reagents and as shift reagents for alkali metal nuclei.