

Gadolinium Complexes Exhibiting Ultra-fast Ligand Self-exchange in Ionic Liquids for Application in NMR Field Probes

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The technology used in Magnetic Resonance Imaging (MRI) relies on the observation of nuclear magnetic resonance (NMR) during complex choreographies of time-varying magnetic fields. Hardware imperfections as well as other external perturbances influence these field evolutions, limiting image quality and the feasibility of high-performance methods. Continuous concurrent magnetic field monitoring¹ is a method for probing the spatiotemporal magnetic field evolution in an MR system by the usage of a set of NMR field sensors. For these sensors, highly homo-perfluorinated liquid compounds with short fluorine NMR relaxation times (T_1 and $T_2 < 1$ ms) are required. Effective relaxation enhancement requires a close contact between the ^{19}F atoms and a paramagnetic centre – ideally in the first coordination sphere. Herein we present that a homo-perfluorinated ionic liquid in which the anions also act as ligands for the paramagnetic metal complex, offers such a possibility. The model Gd(III) complex $[\text{N}^n\text{Bu}_4][\text{Gd}(\text{Tf}_2\text{N})_4]$ ($\text{Tf}_2\text{N}^- = \text{bis}(\text{trifluoromethylsulfonyl})\text{imide}$), obtained from the reaction of its precursor $[\text{Gd}(\text{NTf}_2)_3]$ with $[\text{N}^n\text{Bu}_4](\text{NTf}_2)$, shows the extension of the coordination sphere from six to eightfold with transoid configuration of the NTf_2 ligands. Hence, the solution of the $[\text{Gd}(\text{NTf}_2)_3]$ in ionic liquids of the triflimide type $[\text{cat}^+][\text{Tf}_2\text{N}^-]$ ($\text{cat}^+ = \text{AMIm} = 1\text{-allyl-3-methylimidazolium}$, EthylMIm or $\text{PR}_3\text{R}'^+$) is shown (by evaluation of exchange rates of the non-paramagnetic parent Yttrium compound) to yield a single ^{19}F signal, reflecting rapid ligand self-exchange, and relaxation times in the sub-millisecond range as targeted.

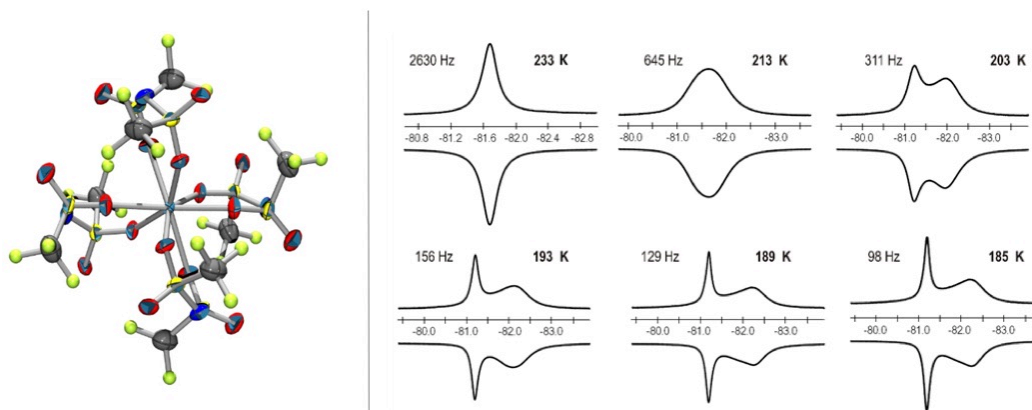


Figure 1. ORTEP of $[\text{N}^n\text{Bu}_4][\text{Gd}(\text{Tf}_2\text{N})_4]$. Cation omitted and fluorides shown as spheres for clarity. The transoid configuration is clearly visible for the $[\text{NTf}_2^-]$ ligands. Ellipsoids except for fluorides are drawn on the 30% probability level.

Figure 2. Comparison of observed (upper) with calculated (lower) ^{19}F NMR (282.39 MHz) spectra of a mixture of $[\text{Y}(\text{NTf}_2)_3]$ with $[\text{EthylMIm}][\text{NTf}_2]$ (1:1.5) in CD_2Cl_2 displaying line broadening, coalescence and splitting into two signals upon cooling.

[1] C. Barmet, N. De Zanche, B. J. Wilm and K. P. Pruessmann, *Magnetic Resonance in Medicine*, **2009**, 62, 269.