ELECTRON SPIN RELAXATION IN TWO POLYAMINOPOLYPYRIDINECARBOXYLATE COMPLEXES OF GD (III)

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Introduction

In the search for highly efficient magnetic resonance imaging (MRI) contrast agents, polyaminopolypyridinecarboxylate complexes of Gd(III) have shown unusual properties with both very rapid and very slow electron spin relaxation in solution observed by electron paramagnetic resonance. We studied two such complexes, $[Gd(tpaen)]^-$ and $[Gd(bpatcn)(H_2O)]$ (see Fig. 1), in liquid aqueous solutions using EPR at multiple temperatures and frequencies between 9.5 and 325 GHz. We analyzed the results using the model of random zero-field splitting modulations through Brownian rotation and molecular deformations.[1]

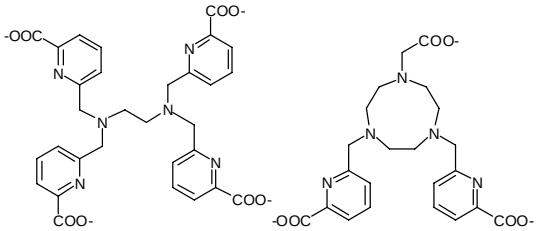

Fig. 1. The $tpaen^{4-}$ and $bpatcn^{3-}$ ligands

Experimental

EPR spectra of both Gd(III) complexes in aqueous solutions were recorded using conventional continuous-wave spectrometers at W-band (Bruker Elexsys E680, Tallahassee), Q-band and X-band (Elexsys E500, Lausanne) at temperatures between 273 and 350 K. Very high-frequency spectra (218 and 325 GHz) were acquired using the homodyne quasi-optical setup on the 17 T magnet of the NHMFL EMR facility.

Results and Discussion

Both complexes exhibit line widths between 150 and 300 G depending on temperature at X-band. At higher frequencies, the lines become much sharper (as narrow as 4 G at 325 GHz). We could estimate the effect of concentration using diluted samples and found it to be ca. 0.1 G/mM.

In comparison with other chelates, the electron spin relaxation of both complexes, as manifested by the EPR peak-to-peak width, is moderate at X-band and slow at higher frequencies and magnetic fields. From that particular point of view, they are possible candidates as building blocks for high-efficiency MRI contrast agents. At very high EPR frequencies, we find that the modern model of the electron spin relaxation of Gd(III) complexes, taking into account the modulation of the zero-field splitting by rotation and molecular deformations, is apparently not able to account for the observed line widths. We suggest that the rotational modulation of the g-tensor anisotropy might become effective under such conditions.

Acknowledgements

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References

[1] Rast, S., *et al*., Journal of the American Chemical Society, **123**, 2637-2644 (2001).