

# Multinuclear Spin-Lattice Relaxation Study of Molecular Motions in Hexakis(1-Alkyl-1*H*-Tetrazolo)Iron(II) and Zinc(II) Bistetrafluoroborate Crystals

Summary of Mónika Bokor's Ph.D. theses

Department of Nuclear Chemistry, Eötvös Loránd University, Budapest

Research Inst. for Solid State Physics and Optics of the Hungarian Academy of Sciences, Budapest  
1999.

Up to now, methods providing no detailed information on the dynamic behavior of molecules has been applied to study transition metal complexes showing temperature induced spin transition. Considering the temperature dependence of positronium lifetimes in  $[\text{Fe}_x\text{Zn}_{1-x}(1-n\text{-propyl-1H-tetrazole})_6](\text{BF}_4)_2$  single crystals ( $1 \geq x \geq 0$ ), it has been concluded that spin transition takes place in non static surroundings.

Molecular reorientational motions *i.e.* dynamic behavior of molecules can be investigated by means of nuclear spin-lattice relaxation spectroscopy. On purpose to characterize the types of reorientational motions of alkyl chains and anions of  $[\text{M}(1\text{-R-1H-tetrazole})_6](\text{BF}_4)_2$  crystals ( $\text{M} = \text{Fe}, \text{Zn}$ ;  $\text{R} = \text{methyl}, \text{ethyl}, n\text{-propyl}$ ) with their temperatures of occurrence, activation energies and correlation times,  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{11}\text{B}$  spin-lattice relaxation time measurements were carried out. In the case of  $\text{M} = \text{Fe}$  compounds of temperature induced spin transition, the object of the investigations was to analyze the connection between the spin-transition process and the dynamic behavior of molecules. The compounds containing  $\text{Fe}^{\text{II}}$  or  $\text{Zn}^{\text{II}}$  central ions are isomorphic so that the results on molecular motions obtained for a compound of the closed-shell  $\text{Zn}^{\text{II}}$  can be transferred to the appropriate  $\text{Fe}^{\text{II}}$  compound for which molecular motions cannot be studied with satisfying precision in the presence of unpaired electrons.

Analyzing the obtained results of measurement, the following conclusions can be drawn.

The temperature induced spin transition takes place in dynamic surroundings: in the studied compounds, the anion and the alkyl group undergoes reorientational motions. The active molecular motions are characterized with the same (within the errors of measurements) temperatures of occurrence, activation energies and correlation times.

The reorientational motion of the  $\text{BF}_4^-$  anion is a common feature of  $[\text{M}(1\text{-R-1H-tetrazole})_6](\text{BF}_4)_2$  compounds according to our measurements on  $^{11}\text{B}$  and  $^{19}\text{F}$  nuclides.

The propyl chain undergoes three different types of reorientational motions in  $[\text{M}(1-n\text{-propyl-1H-tetrazole})_6](\text{BF}_4)_2$  crystals which become active at different temperatures. A "reorientational structural change" involving the propyl chain and the anion occurs at about 130-140 K which is in a cause and effect relation with the spin transition of the  $\text{M} = \text{Fe}$  compound determining its temperature.

The ethyl chain undergoes five different types of reorientational motions in  $[\text{M}(1\text{-ethyl-1H-tetrazole})_6](\text{BF}_4)_2$  crystals which become active at different temperatures. The active types of reorientation are continuously changing in the temperature range 70-90 K. The different anion sites defined by cation complexes with different symmetry in two nonequivalent lattice sites are reflected by reorientational motions of anions.

The methyl chain undergoes three different types of reorientational motions in  $[\text{M}(1\text{-methyl-1H-tetrazole})_6](\text{BF}_4)_2$  crystals which become active at different temperatures.

For  $\text{M} = \text{Fe}$  compounds, electron spin relaxation a spin diffusion are also active at temperatures characterized by the presence of  $S = 2$  state  $\text{Fe}^{\text{II}}$  ions. The  $^1\text{H}$  relaxation is of rapid diffusion type while  $^{19}\text{F}$  relaxation is of diffusion limited type here. The temperature dependence of nuclear spin-lattice relaxation shows a V-shaped minimum below 50 K. Such phenomena has not been reported yet and it is caused by a collective interaction of  $S = 2$  state  $\text{Fe}^{\text{II}}$  ions.