**ORTHO-POSITRONIUM LIFETIME AS A DETECTOR OF SPIN-CROSSOVER**

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Positron lifetime parameters were measured for the spin-crossover complexes \([\text{Fe}(\text{R-1H-tetrazole})_6](\text{BF}_4)_2\) (\(R = 1\)-ethyl, 1-\(n\)-propyl) and for the diamagnetic \([\text{Zn}(1-n\text{-propyl-1H-tetrazole})_6](\text{BF}_4)_2\). Positronium forms with significant intensity in the studied compounds. The *ortho-para* conversion of ortho-positronium was used to follow the spin-crossover. Changes of the dynamic structure were found in the propyltetrazole complex between 150 K and 90 K.

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1. Introduction

*ortho*-Positronium (*o*-Ps) lifetime spectra can signal the spin-crossovers of transition metal ions in liquid [1] and solid phases [2]. The lifetime of *o*-Ps is shorter in the presence of unpaired electrons (high-spin state), due to the *ortho-para* conversion initiated by the paramagnetic spin–spin relaxation, and it is longer in the case of paired 3\(d\) electrons (low-spin state), because of the lack of *ortho-para* conversion. The studied \([\text{Fe}(1\text{-alkyl-1H-tetrazole})_6](\text{BF}_4)_2\) compounds are octahedrally coordinated spin-crossover complexes of iron(II) — they undergo a temperature induced high-spin (HS) ↔ low-spin (LS) transition

\[
t^3_{2g} \xrightarrow{\text{cooling}} t^5_{2g}, \quad 3T^1_{2g} \xrightarrow{\text{heating}} 1A^1_{1g}, \quad \Delta S = 2.
\]

The complexes are arranged into electrically neutral layers. There is a cleavage plane parallel to these planes and a pseudotrigonal symmetry axis perpendicular to each layer. In the ethyltetrazole complex (Fe-etz) only 2/3 of the central Fe(II) ions undergo spin-crossover (\(T_{1/2} = 105\) K)*, while the other 1/3 remain in the HS state even at the lowest temperatures [3] while in the propyltetrazole complex (Fe-ptz) the spin-crossover \((T^\dagger_{1/2} = 135\) K and \(T^\dagger_{1/2} = 128\) K, accompanied by a

\(^*\)At \(T_{1/2}\), the HS state fraction of ions undergoing the spin-crossover is equal to 0.5.
crystallographic phase transition at 130 K) is practically complete [4]. The phase transition influences only the relative position of the complex layers. The partial spin-crossover of Fe-etz is traced back to the two inequivalent lattice sites in 2:1 proportion; the Fe(II) sites of Fe-ptz are equivalent [3]. Fe-etz was studied to explore the effects of an incomplete spin-crossover on positron lifetime parameters. Average o-Ps lifetime ($\tau_{o-Ps}$) in Fe-ptz shows unexpected trend at $T > T_{1/2}$ which is also present in the isomorphous but diamagnetic Zn-ptz (Fig. 1a) [2]. Additional NMR spectroscopic analysis ($^1$H, $^{11}$B and $^{19}$F spin–lattice relaxation time ($T_1$) and spectrum measurements) [5] and X-ray diffraction measurements were carried out to reveal the underlying process.

Fig. 1. (a) Single crystal X-ray structure of [Zn(1-n-propyl-1H-tetrazole)$_6$](BF$_4$)$_2$ at 95 K (H-atoms are not shown). (b)–(d) o-Ps lifetime (big circles) and its relative intensity (small circles) for [Fe(1-ethyl-1H-tetrazole)$_6$](BF$_4$)$_2$, spin-crossover temperature $T_{1/2} = 105$ K (b); [Fe(1-n-propyl-1H-tetrazole)$_6$](BF$_4$)$_2$, $T_{1/2} = 135$ K and $T_{1/2} = 128$ K (c); [Zn(1-n-propyl-1H-tetrazole)$_6$](BF$_4$)$_2$ (d). Solid symbols: cooling, open symbols: heating direction. Diamonds in graph (d): $^{19}$F spin-lattice relaxation time ($T_1$) for [Zn(1-n-propyl-1H-tetrazole)$_6$](BF$_4$)$_2$, solid symbols $\omega_0 = 29.0$ MHz, open symbols $\omega_0 = 83.5$ MHz; the minima indicate that BF$_4^-$ rotates above 40 K, analysis of the 90 to 150 K temperature region suggests changing anion dynamics.
2. Experimental

The alkyltetrazole ligands were prepared as described by Franke et al. [6] and the complexes themselves were prepared by the method of Poganiuch et al. [7]. The crude (polycrystalline) products were recrystallized from nitromethane to obtain single crystals. Single crystals were used to avoid the effects of grain boundaries on the positron-annihilation parameters.

The positron source was made by the deposition of $^{22}\text{NaCl}$ solution between two kapton foils. The source was placed between the pair of crystals and the source-sample sandwich was mounted in an evacuated cryostat. The pressure in the cryostat was kept at about $10^{-8}$ bar. The uncertainty of the temperature control was less than 0.1 K. The heating or cooling rate between two measurements was about 1 K min$^{-1}$. For the recording of lifetime spectra a fast-fast coincidence system was used. The spectra were collected in the 4096 channels of a multichannel analyser card with a 10 ps channel time. The time resolution of the system was about 270 ps. The spectrum evaluation was carried out with the computer program RESOLUTION [8].

3. Results and discussion

3.1. $[\text{Fe}(1\text{-ethyl-1H-tetrazole})_6](\text{BF}_4)_2$

Fe-etz shows Ps formation (Fig. 1b) with a significant intensity both in the HS- and LS-state region ($6\% < I_{o-Ps} < 26\%$). $I_{o-Ps}$ decreases with decreasing temperature throughout the whole temperature range, with two break-points: one at 170 K and the other at $T_{1/2}$. The most characteristic feature of the temperature dependence is the strong and monotonous increase in $\tau_{o-Ps}$ with the decrease in the temperature from the spin-crossover point (Fig. 1a). As the spin transition makes unpaired electrons disappear gradually upon cooling, the probability of the *ortho-para* conversion decreases and therefore $\tau_{o-Ps}$ becomes longer. The residual HS state Fe(II) ions ($\gamma_{HS} = 1/3$) induce *ortho-para* conversion even at temperatures well below $T_{1/2}$ and therefore $\tau_{o-Ps}(T)$ changes gradually instead of producing a steplike trend in the vicinity of $T_{1/2}$ (see Fe-ptz, Fig. 1c).

3.2. $[\text{Fe}(1\text{-n-propyl-1H-tetrazole})_6](\text{BF}_4)_2$

Ps forms (Fig. 1c) with high intensity also in Fe-ptz both in the HS- and LS-state region ($8\% < I_{o-Ps} < 25\%$). $I_{o-Ps}$ shows globally the same temperature dependence as in Fe-etz except the peaks at $T_{1/2}$ which can be attributed to the phase transition in the ptz complex. The $o$-Ps lifetime increases below $T_{1/2}$ (Fig. 1c). There is a pronounced step in $\tau_{o-Ps}$ of Fe-ptz between $T_{1/2}$ and 200 K where the $\tau_{o-Ps}(T)$ is controlled by the pick-off annihilation. The shape of the $\tau_{o-Ps}(T)$ curves are the same in both Zn-ptz (Fig. 1d) and in Fe-ptz at $T > T_{1/2}$ (Fe-ptz). The Fe-ptz and Zn-ptz are isomorphous but there is no spin-crossover in Zn-ptz. Consequently, this lifetime trend between the $T_{1/2}$ and 200 K is not connected to the spin-crossover. (Probable underlying processes are discussed in Sec. 3.3.) The steplike increase in $\tau_{o-Ps}$ below $T_{1/2}$ in Fe-ptz is a clear sign of the spin-crossover since the disappearing of HS state Fe(II) ions reduces the probability of *ortho-para* conversion resulting in longer $\tau_{o-Ps}$.
3.3. \([Zn(1-n-propyl-1H-tetrazole)\_6](BF\_4)\_2\]

\(\tau_{o-Ps}\) decreases by 30% when cooled from 200 to 90 K (Fig. 1d) and it is nearly constant at \(T < 90\) K. Comparing \(\tau_{o-Ps}(T > 130\) K) for Fe-ptz (Fig. 1c) and Zn-ptz (Fig. 1d), the trends are the same and the difference of the lifetime values is explained by the presence of unpaired \(e^-\) spins in Fe-ptz. To explain \(\tau_{o-Ps}(T)\) for Zn-ptz above 90 K, NMR spectroscopic [5] and X-ray diffraction methods were applied. \(^1\)H and \(^{19}\)F \(T_1(T)\) (Fig. 1d) suggested that several changes of the dynamic structure — i.e. changes of the reorientational dynamics of propyl groups and anions — occur at 90 K < \(T < 150\) K. The most likely sites where Ps exists are open spaces surrounded by the central ion, ligands, and anions. The observed decrease in \(\tau_{o-Ps}\) with decreasing temperature indicates an increase in the electron density in the surroundings of \(\sigma\)-Ps. Possible origins of this change in the electron density are the following. The contraction of Ps sites caused by slight changes in the structure of the crystal — X-ray structures rule this out. Changes in the dynamics of propyl chains and anions result in changed electron density distribution and so, \(\tau_{o-Ps}\) is influenced — results of NMR analysis support this version.

4. Conclusions

\(\tau_{o-Ps}\) is strongly influenced by the abundance of unpaired electrons which can produce \textit{ortho-para} conversion of the Ps. For the two investigated Fe-compounds it is understood that as the spin-crossover makes unpaired electrons disappear gradually as the sample is cooled down, the probability of the \textit{ortho-para} conversion decreases and therefore \(\tau_{o-Ps}\) becomes longer. As a consequence, if there is a significant intensity of positronium, \(\tau_{o-Ps}\) detects sensitively the spin-crossover. The differences between the lifetime trends for the two compounds below \(T_{1/2}\) can be explained by the effect of the residual HS state Fe(II) ions of Fe-etz. The increase in \(\tau_{o-Ps}\) in Fe-ptz and Zn-ptz above 130 K and 90 K, respectively, can be explained by changes of the dynamic structure of the molecular groups in the vicinity of the Ps atoms.

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References


