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ORTHO-POSITRONIUM LIFETIME AS A DETECTOR OF SPIN-CROSSOVER

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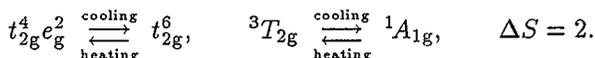
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Positron lifetime parameters were measured for the spin-crossover complexes $[\text{Fe}(\text{R}-1H\text{-tetrazole})_6](\text{BF}_4)_2$ ($\text{R} = 1\text{-ethyl, } 1\text{-}n\text{-propyl}$) and for the diamagnetic $[\text{Zn}(1\text{-}n\text{-propyl-}1H\text{-tetrazole})_6](\text{BF}_4)_2$. 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 $[\text{Fe}(1\text{-alkyl-}1H\text{-tetrazole})_6](\text{BF}_4)_2$ compounds are octahedrally coordinated spin-crossover complexes of iron(II) — they undergo a temperature induced high-spin (HS) \leftrightarrow low-spin (LS) transition



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 ($T_{1/2} = 105 \text{ K}$)*, 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 ($T_{1/2}^\uparrow = 135 \text{ K}$ and $T_{1/2}^\downarrow = 128 \text{ K}$, 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 (τ_{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 (^1H , ^{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.

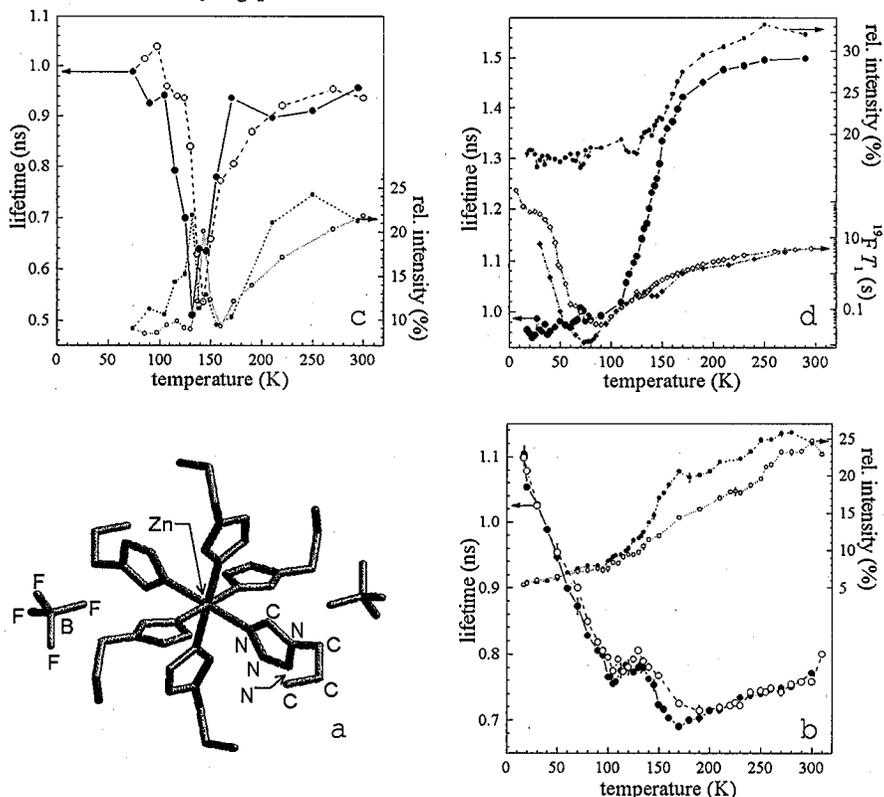


Fig. 1. (a) Single crystal X-ray structure of $[\text{Zn}(1\text{-}n\text{-propyl-1}H\text{-tetrazole})_6](\text{BF}_4)_2$ at 95 K (H-atoms are not shown). (b)–(d) *o*-Ps lifetime (big circles) and its relative intensity (small circles) for $[\text{Fe}(1\text{-ethyl-1}H\text{-tetrazole})_6](\text{BF}_4)_2$, spin-crossover temperature $T_{1/2} = 105$ K (b); $[\text{Fe}(1\text{-}n\text{-propyl-1}H\text{-tetrazole})_6](\text{BF}_4)_2$, $T_{1/2}^\uparrow = 135$ K and $T_{1/2}^\downarrow = 128$ K (c); $[\text{Zn}(1\text{-}n\text{-propyl-1}H\text{-tetrazole})_6](\text{BF}_4)_2$ (d). Solid symbols: cooling, open symbols: heating direction. Diamonds in graph (d): ^{19}F spin-lattice relaxation time (T_1) for $[\text{Zn}(1\text{-}n\text{-propyl-1}H\text{-tetrazole})_6](\text{BF}_4)_2$, 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 ($6\% < I_{o\text{-Ps}} < 26\%$). $I_{o\text{-Ps}}$ 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 $\tau_{o\text{-Ps}}$ 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 $\tau_{o\text{-Ps}}$ becomes longer. The residual HS state Fe(II) ions ($\gamma_{\text{HS}} = 1/3$) induce *ortho-para* conversion even at temperatures well below $T_{1/2}$ and therefore $\tau_{o\text{-Ps}}(T)$ 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 ($8\% < I_{o\text{-Ps}} < 25\%$). $I_{o\text{-Ps}}$ 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 $\tau_{o\text{-Ps}}$ of Fe-ptz between $T_{1/2}$ and 200 K where the $\tau_{o\text{-Ps}}(T)$ is controlled by the pick-off annihilation. The shape of the $\tau_{o\text{-Ps}}(T)$ 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 $\tau_{o\text{-Ps}}$ 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 $\tau_{o\text{-Ps}}$.

3.3. $[Zn(1-n-propyl-1H-tetrazole)_6](BF_4)_2$

τ_{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. 1H 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 τ_{o-Ps} with decreasing temperature indicates an increase in the electron density in the surroundings of *o*-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, τ_{o-Ps} is influenced — results of NMR analysis support this version.

4. Conclusions

τ_{o-Ps} is strongly influenced by the abundance of unpaired electrons which can produce *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 *ortho-para* conversion decreases and therefore τ_{o-Ps} becomes longer. As a consequence, if there is a significant intensity of positronium, τ_{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 τ_{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.

Acknowledgments

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