

The X-ray crystallographic and Mössbauer study of the halide salts of $[\text{Fe}^{\text{III}}(\text{3-OMe-Sal}_2\text{trien})]^+$ spin-crossover cation

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The four halide salts of $[\text{Fe}^{\text{III}}\text{L}]^+$ ($\text{L}=\text{3-OMe-Sal}_2\text{trien}^{2-}$) spin-crossover cation were synthesized for the first time: $[\text{FeL}]\text{F}\cdot 4\text{H}_2\text{O}$, $[\text{FeL}]\text{Cl}\cdot 5\text{H}_2\text{O}$, $[\text{FeL}]\text{Br}\cdot 5\text{H}_2\text{O}$ and $[\text{FeL}]\text{I}$. Structures of the salts have $P\bar{1}$ symmetry at 150K and iron(III)-ligand bond lengths comply with low-spin state (LS, $S=1/2$). The Mössbauer spectra parameters (ΔE_Q – quadrupole splitting and δ – isomer shift) at room temperature also correspond to the LS electronic configuration of iron(III) center (Fig. 1). Presumably the crystal packing features and the halide anion stabilize the LS spin state of spin-crossover cation. Moreover, the new polymorphic LS phase of $[\text{FeL}]\text{I}$ was revealed while the previously described LS phase in [1] shows a peculiar correlation between structure and magnetic properties.

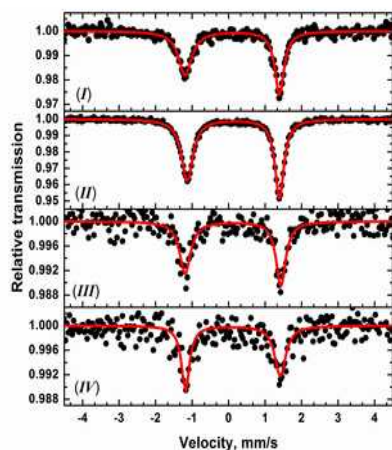


Figure 1. Mössbauer spectra for the $[\text{Fe}(\text{3-OMe-Sal}_2\text{trien})]\text{F}\cdot 4\text{H}_2\text{O}$ [$\Delta E_Q= 2.585(6)$ mm/s, $\delta=0.103(3)$ mm/s] (I); $[\text{Fe}(\text{3-OMe-Sal}_2\text{trien})]\text{Cl}\cdot 5\text{H}_2\text{O}$ [$\Delta E_Q=2.528(2)$ mm/s, $\delta=0.131(1)$ mm/s] (II), $[\text{Fe}(\text{3-OMe-Sal}_2\text{trien})]\text{Br}\cdot 5\text{H}_2\text{O}$ [$\Delta E_Q=2.62(1)$ mm/s, $\delta=0.121(7)$ mm/s] (III), $[\text{Fe}(\text{3-OMe-Sal}_2\text{trien})]\text{I}$ [$\Delta E_Q=2.60(2)$ mm/s, $\delta=0.12(1)$ mm/s] (IV) salts at 296 K. Fit line denotes in red color.

This work was performed in accordance with the state task, state registration No. AAAA-A19-119092390079-8, the instrumental base of the center for collective use and the computer center of the IPCP RAS was used. Partially the study was carried out within the state assignment for the ISSP RAS.

[1] Y.N. Shvachko, N.G. Spitsyna, D.V. Starichenko et al., *Molecules*. **2020**, *25*(21), p. 4922.