[Mn(5-Hal-sal₂323)]₂[ReCl₆] (Hal=Cl, Br): the first Mn(III) molecular complexes to exhibit both spin crossover and single-ion magnet effects

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At present, the main class of Mn(III) spin-crossover compounds are cationic complexes of Mn(III) with the sal₂323 ligand and its derivatives, which were first obtained in 2003, and the first spin transition in this class was discovered in 2006. Since that time, an active investigations of these complexes have begun, aimed at studying the effects of substituents on the phenolate nucleus of the ligand, the nature of counterions and solvate solvents on the spin behavior of the complexes. In this work, we used for the first time a doubly charged paramagnetic anion [ReCl₆]²⁻ as a counterion in the Mn(III) cationic complexes with a monohalosubstituted ligands (5-Cl(Br)-sal₂323). To the best of our knowledge, all complexes of the [Mn(sal₂323]⁺ family synthesized so far contain singly charged anions. An important argument in favor of choosing the [ReCl₆]²⁻ as a counterion magnet, like its analogs [ReBr₆]²⁻ and [ReI₆]²⁻. Thus, one could expect the formation of complexes combining the Mn(III) spin crossover and [ReCl₆]²⁻ single-ion magnetism in the same crystal lattice. Only a few compounds are known in the literature in which the spin transition coexists with single-molecule magnetism.

The bicomponent ion-pair molecule complexes $[Mn(5-Cl-sal_2323)][ReCl_6]$ (1) and $[Mn(5-Br-sal_2323)][ReCl_6]$ (2) were synthesized. Their crystal structures and magnetic properties were studied. The compounds are isostructural and show a thermally induced spin transition at high temperature associated with the cationic subsystem and a field-induced frequency dependent on magnetic susceptibility at low temperature, associated with the anionic subsystem.

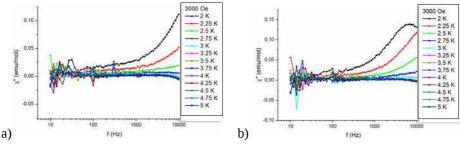


Figure 1. The frequency dependency of the $\chi''(v)$ for complexes **1** (a) and **2** (b) at temperatures of 2-5 K under the magnetic field of H = 3000 Oe.

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