Effect of dihalide substituents on crystal structure and magnetic properties of cation $[Mn^{III}(3,5\text{-diHal-sal}_2323)]^+$ complexes with BPh_4 anion

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A series of tetraphenylborates of mononuclear Mn(III) cation complexes with hexadentate ligands, the products of the reaction between a N,N′-bis(3-aminopropyl)ethylenediamine and salicylaldehydes with the different haloid substitutions at 3,5 positions, have been synthesized: $[Mn(3,5\text{-diCl-sal}_2323)]BPh_4$ (**1**) and $[Mn(3,5\text{-Br,Cl-sal}_2323)]BPh_4$ (**2**), $[Mn(3,5\text{-diF-sal}_2323)]BPh_4$ (**3**) and two polymorphic modifications (**4** and **5**) of $[Mn(3,5\text{-Br,F-sal}_2323)]BPh_4$. Their crystal structure, dielectric constant (ε) and magnetic properties have been studied. Ligand substituents have a dramatic effect on the structure and magnetic properties of the complexes. The complexes **1** and **2** are isostructural, but have fundamentally different properties. Complex **1** demonstrates two structural phase transitions related to sharp spin crossovers from the high spin (HS) state to the HS:LS intermediate phase at 137 K and from the intermediate phase to the low spin (LS) state at 87 K, while complex **2** exhibits only one spin transition from the HS to the HS:LS intermediate phase at 83 K. The complex **3** exhibits a gradual and complete spin conversion with $T_{1/2}$ = 141 K between a high spin (S = 2) and low spin (S = 1) states. Two polymorphic modifications of the complex $[Mn(3,5\text{-Br,F-sal}_2323)]BPh_4$ have fundamentally different magnetic properties: one of the modifications (monoclinic**,** **4**) shows a gradual and complete spin transition with $T_{1/2}$ = 137 K, while the other (triclinic, **5**) remains in a high spin state over the entire investigated temperature range of 2 - 300 K. The magneto-structural relationships were traced in comparison with dichloro-, dibromo- difluoro- and mixed Br,Cl- and Br,F-substituted $[Mn(3,5\text{-R,R'-sal}_2323)]$ complexes with tetraphenylborate anion [1].

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[1] A.V. Tiunova, A.V. Kazakova, D.V. Korchagin, G.V. Shilov, L.V. Zorina, S.V. Simonov, K.V. Zakharov, A.N. Vasiliev, E.B. Yagubskii, *Chem. Eur. J.* **2021**, *27*, pp. 17609-17619.