

# Synthesis and Characterization of the Heptanuclear $[\text{Mn}_6^{\text{III}}\text{Co}^{\text{III}}]^{3+}$ Triplesalen Complex: Evidence for Exchange Pathways Involving Low-spin $\text{Co}^{\text{III}}$

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*Dedicated to Professor Rolf W. Saalfrank on the occasion of his 70<sup>th</sup> birthday*

The reaction of the *tert*-butyl-substituted triplesalen ligand  $\text{H}_6\text{talen}^{t\text{-Bu}_2}$  with  $\text{Mn}^{\text{II}}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{K}_3[\text{Co}^{\text{III}}(\text{CN})_6]$  results in the formation of the heptanuclear complex  $[\{\text{talen}^{t\text{-Bu}_2}\}(\text{Mn}^{\text{III}}(\text{MeOH})_3)_2\{\text{Co}^{\text{III}}(\text{CN})_6\}](\text{PF}_6)_2(\text{OAc}) \cdot 11\text{MeOH}$  ( $[\text{Mn}_6^{\text{III}}\text{Co}^{\text{III}}](\text{PF}_6)_2(\text{OAc}) \cdot 11\text{MeOH}$ , **1** · 11MeOH), which has been characterized by FT-IR spectroscopy, elemental analysis, ESI-MS, single-crystal X-ray diffraction, and magnetic measurements. The molecular structure of the  $[\text{Mn}_6^{\text{III}}\text{Co}^{\text{III}}]^{3+}$  complex is closely related to the already published analogs  $[\text{Mn}_6^{\text{III}}\text{Cr}^{\text{III}}]^{3+}$  and  $[\text{Mn}_6^{\text{III}}\text{Fe}^{\text{III}}]^{3+}$ . Variable-temperature variable-field and  $\mu_{\text{eff}}$  vs.  $T$  magnetic data have been analyzed in detail by full-matrix diagonalization of the appropriate spin-Hamiltonian consisting of isotropic exchange, zero-field splitting, and Zeeman interaction, taking into account the relative orientation of the **D** tensors. This allowed a careful inspection of the  $\text{Mn}^{\text{III}}\text{-Mn}^{\text{III}}$  exchange interaction involving a diamagnetic central metal ion. A satisfactory reproduction of the magnetic data required the incorporation not only of an exchange interaction between the  $\text{Mn}^{\text{III}}$  ions belonging to one triplesalen half unit, but also of an exchange coupling between  $\text{Mn}^{\text{III}}$  ions belonging to different triplesalen subunits. Satisfactory reproduction of the experimental data has been obtained for the parameter set  $J_1 = -(0.50 \pm 0.04) \text{ cm}^{-1}$ ,  $J_2 = +(0.05 \pm 0.02) \text{ cm}^{-1}$ , and  $D = -(2.5 \pm 0.5) \text{ cm}^{-1}$ . A detailed analysis of the  $J_1$  coupling taking into account the molecular structures of the three available heptanuclear complexes  $[\text{Mn}_6^{\text{III}}\text{M}^{\text{III}}]^{3+}$  ( $\text{M} = \text{Cr}, \text{Fe}, \text{Co}$ ) indicates that the exchange interaction between the  $\text{Mn}^{\text{III}}$  ions belonging to the same triplesalen subunit involves not only an exchange pathway through the central phloroglucinol unit but also an exchange pathway through the central metal ion.

*Key words:* Magnetic Properties, Heteronuclear Complexes, Exchange Pathways