Synthesis and Characterization of the Heptanuclear \([\text{Mn}^{\text{III}}_6\text{Co}^{\text{III}}]^{3+}\) Triplexalen 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 70th birthday

The reaction of the tert-butyl-substituted triplesalen ligand \(\text{H}_6\text{talen}^{\text{t-Bu}_2}\) with \(\text{Mn}^{\text{II}}(\text{OAc})_2\cdot4\text{H}_2\text{O}\) and \(\text{K}_3[\text{Co}^{\text{III}}(\text{CN})_6]\) results in the formation of the heptanuclear complex \([\{\text{talen}^{\text{t-Bu}_2}\} \cdot \text{Mn}^{\text{III}}(\text{MeOH})])_3\cdot2[\text{Co}^{\text{III}}(\text{CN})_6]\) \((\text{PF}_6)_2(\text{OAc})\cdot11\text{MeOH}\) (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 \([\text{Mn}^{\text{III}}_6\text{Co}^{\text{III}}]^{3+}\) complex is closely related to the already published analogs \([\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}]^{3+}\) and \([\text{Mn}^{\text{III}}_6\text{Fe}^{\text{III}}]^{3+}\). 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 \(J_1 = -(0.50 \pm 0.04)\) cm\(^{-1}\), \(J_2 = + (0.05 \pm 0.02)\) cm\(^{-1}\), and \(D = -(2.5 \pm 0.5)\) cm\(^{-1}\). A detailed analysis of the \(J_1\) coupling taking into account the molecular structures of the three available heptanuclear complexes \([\text{Mn}^{\text{III}}_6\text{M}^{\text{III}}]^{3+}\) (\(\text{M} = \text{Cr}, \text{Fe}, \text{Co}\)) 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

Introduction

The design and synthesis of molecule-based magnets has attracted considerable interest over the past decades [1 – 3]. Beyond the synthesis of magnetic materials based on molecular entities that exhibit a spontaneous long-range ferromagnetic ordering, the observation that the molecular complex \([\text{Mn}^{\text{II}}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_4]_3(\text{OH}_2)_4\), \(\text{Mn}_{12}\) [4], exhibits a hysteresis in the magnetization of purely molecular origin [5,6] opened the field to a new class of molecular magnetic materials called single-molecule magnets (SMMs) [7 – 10]. SMMs possess a superior property in comparison to other paramagnetic polynuclear transition metal complexes: SMMs can be magnetized and retain their polarization in the absence of an external magnetic field. Accordingly, they exhibit a hysteresis in the magnetization in analogy to solid-state magnets. Due to these promising properties, SMMs have attracted a great deal of research attention since their discovery in 1993.

The origin of the slow relaxation of the magnetization at low temperatures is an energy barrier for spin reversal. This energy barrier originates from a
Scheme 1. a) The C₃-symmetric hybrid ligand triplesalen C comprised of phloroglucinol A for ferromagnetic coupling and salen units B for single-site magnetic anisotropy; b) the triplesalen ligand H₆talen⁻Bu₂ used in this study.

ground state with large total spin S and large magnetic anisotropy with an easy axis of magnetization (phenomenologically parameterized by a negative zero-field splitting parameter D). In order to prevent quantum tunnelling through this anisotropy barrier, the rhombicity E/D of the spin should vanish.

In order to match these requirements for SMMs, we have designed the C₃-symmetric triplesalen ligand C (Scheme 1a) [11, 12] which combines the 1,3,5-trihydroxybenzene (phloroglucinol) bridging unit A [13-19] for ferromagnetic couplings by the spin-polarization mechanism [17, 20-26] and thus high-spin ground states with the coordination environment of a salen ligand B for a pronounced magnetic anisotropy [27-29]. We have shown for a series of trinuclear triplesalen complexes of the ligand H₆talen⁻Bu₂ (Scheme 1b) that (i) the C₃ symmetry of the triplesalen ligand is impeded onto the complexes and (ii) a severe ligand folding occurs in [(talen⁻Bu₂)M₃] (M = Cu, Ni) resulting in an overall bowl-shaped molecular structure [12, 15]. An advantage of the ligand folding in the trinuclear complexes [(talen⁻Bu₂)(M(solv))₃]⁺⁻ is the preorganization of the three metal ions for coordination of three facial nitrogen atoms of a hexacyanometallate [M(CN)₆]⁻⁻. Thus, reaction of the molecular building block [(talen⁻Bu₂)(M₃(solv))₃]⁺⁻ – formed in situ by reaction of H₆talen⁻Bu₂ with Mn₃(OAc)₂·4H₂O – with [Cr(CN)₆]⁻⁻ and [Fe(CN)₆]⁻⁻ resulted in the formation of the heptanuclear complexes [(talen⁻Bu₂)M₃Cr₃(CN)₆]₃⁺⁺ [30] and [(talen⁻Bu₂)M₃Fe₃(CN)₆]₃⁺⁺ [31], respectively (note that the weakly bound solvent molecules on the sixth coordination sites of some of the Jahn-Teller-distorted Mn ions have been neglected in this formulation). We could (i) show that [M₆₃Cr₃(CN)₆]⁺⁺ is an SMM and [M₆₃Fe₃(CN)₆]⁺⁺ is not an SMM, and (ii) relate this different behavior to differences in the exchange coupling constants of the Mn ions and the central metal ion.

Here, we present the synthesis and characterization of the heptanuclear complex [(talen⁻Bu₂)M₃Co₃(CN)₆]₃⁺⁺ ([M₆₃Co₃(CN)₆]⁺⁺), which is the first member of the heptanuclear triplesalen complex family with a diamagnetic central metal ion. The detailed magnetic characterization and analysis provides in-sight into the interaction between the Mn ions.

Results and Analysis
Synthesis and characterization

The reaction of H₆talen⁻Bu₂, Mn₃(OAc)₂·4H₂O, and K₃[Co(CN)₆] in the molar ratio 2:6:1 in methanolic solution yields dark-brown crystals after addition of NaPF₆. The FT-IR spectrum exhibits the characteristic features of the [Co(CN)₆]⁻⁻ unit. The ESI mass spectrum exhibits a prominent ion at a mass to charge ratio m/z of 918.2 with mass
Heptanuclear \([\text{Mn}^{III}_6\text{Co}^{III}]^{3+}\) Triplesalen Complex

and isotope distribution patterns corresponding to \([\text{Mn}^{III}_6\text{Co}]^{3+}\). The dication \([\text{Mn}^{III}_6\text{Co}]^{2+}\) and the monocation \([\text{Mn}^{III}_6\text{Co}]^{+}\) exhibit weak signals at 1377.4 and 2753.8, respectively. These data are all consistent with the successful formation of \([\text{Mn}^{III}_6\text{Co}^{III}]^{3+}\).

Single-crystal X-ray diffraction established the formulation \([\{(\text{talen}^{r-Bu}_2)(\text{Mn}^{III}(\text{MeOH}))_3\}_2\{\text{Co}^{III}(\text{CN})_6\}_3]^{3+}\) (PF$_6$)$_2$(OAc)-11MeOH (I-

Structural characterization

I-11CH$_3$OH crystallizes in the space group \(P2_1/n\). The asymmetric unit consists of half of the molecule. The other half of the molecule is generated by a crystallographic center of inversion, which is located at the central cobalt ion. The molecular structure of the trication \([\{(\text{talen}^{r-Bu}_2)(\text{Mn}^{III}(\text{CH}_3\text{OH}))_3\}_2\{\text{Co}^{III}(\text{CN})_6\}_3]^{3+}\) (Fig. 1, Table 1) closely resembles those of \([\text{Mn}^{III}_6\text{Cr}^{III}]^{3+}\) [30] and \([\text{Mn}^{III}_6\text{Fe}^{III}]^{3+}\) [31]. Two trinuclear Mn III triplesalen building blocks are connected by the \([\text{Co}^{III}(\text{CN})_6]^{3-}\) bridging unit. The Mn$^{III}$ ions are in an axially elongated octahedral environment. Each Mn$^{III}$ is coordinated by two imine nitrogen atoms and two phenolate oxygen atoms of a triplesalen ligand compartment. The coordination environment is completed by a nitrogen atom of the \([\text{Co}^{III}(\text{CN})_6]^{3-}\) unit and an oxygen atom of a coordinated methanol molecule. The mean values for the Mn–O bond lengths for the central PhO$^-$ and the terminal PhO$^-$ are 1.89 and 1.88 Å, respectively, while the mean Mn–N bond length is 1.98 Å for both the central and the terminal imine donors. These values are in accord with \([\text{Mn}^{III}_6\text{Cr}^{III}]^{3+}\) [30] and \([\text{Mn}^{III}_6\text{Fe}^{III}]^{3+}\) [31]. The Mn$^{III}$ Jahn-Teller axes point along the N≡C···OMeOH directions, as evidenced by longer mean Mn–N, N–C and Mn–OMeOH bonds of 2.21 Å and 2.37 Å, respectively.

The cobalt ion is coordinated octahedrally by the six carbon atoms of the six bridging cyanide ligands. The mean Co–C bond length of 1.90 Å is smaller in comparison to that of \([\text{Mn}^{III}_6\text{Cr}]^{3+}\) (2.07 Å) [30] and \([\text{Mn}^{III}_6\text{Fe}]^{3+}\) (1.93 Å) [31]. In accordance with the other heptanuclear triplesalen complexes, the mean \(\angle(\text{Co–C–N})\) angle is almost linear (178.9°) whereas the mean \(\angle(\text{C–N–Mn})\) angle is bent (163.1°). This bending does not occur randomly but all six C≡N–Mn units bend towards the molecular C$_3$ axis.
Table 1. Selected interatomic distances (Å) and angles (deg) in 1-11MeOH.

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Dist/Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn1–O11</td>
<td>1.891(2)</td>
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<tr>
<td>Mn1–O12</td>
<td>1.880(2)</td>
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<tr>
<td>Mn1–N11</td>
<td>1.984(3)</td>
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<tr>
<td>Mn1–N12</td>
<td>1.982(3)</td>
</tr>
<tr>
<td>Mn1–N41</td>
<td>2.210(3)</td>
</tr>
<tr>
<td>Mn1–O401</td>
<td>2.377(3)</td>
</tr>
<tr>
<td>Mn2–O21</td>
<td>2.167(2)</td>
</tr>
<tr>
<td>Mn2–O22</td>
<td>2.187(2)</td>
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<tr>
<td>Mn2–N21</td>
<td>2.214(3)</td>
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<td>Mn2–N22</td>
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<td>Mn3–N33</td>
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<tr>
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<tr>
<td>O22–C3</td>
<td>1.312(4)</td>
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<td>175.79(9)</td>
</tr>
<tr>
<td>C41#1–Co1–C41</td>
<td>89.94(13)</td>
</tr>
<tr>
<td>C41#1–Co1–C41</td>
<td>91.06(13)</td>
</tr>
<tr>
<td>C41#1–Co1–C41</td>
<td>88.81(13)</td>
</tr>
</tbody>
</table>

Note: Symmetry transformations used to generate equivalent atoms: #1 −x + 1, −y + 1, −z + 1.

An important aspect for the Mn-Mn exchange interaction is the exact structure of the trinuclear triple-salen building block. We have applied several parameters for a quantitative description of the ligand folding in the study of the trinuclear triple-salen complexes [12, 15]. It turned out that the best parameters to quantitatively describe the ligand folding are the bent angles $\phi_{\text{central}}$ and $\phi_{\text{terminal}}$. The bent angle $\phi$ is defined by $\phi = 180^\circ - \angle (\text{M} - \text{XNO} - \text{XR})$ ($\text{XNO}$, midpoint of adjacent N and O donor atoms; $\text{XR}$, mid-
point of the six-membered chelate ring containing
the N and O donor atoms) [35]. This bent angle is
best suited to differentiate between a bending along
an idealized line through neighboring N and O lig-
ands and a line perpendicular to the former, resulting
in a helical distortion of the salen subunit. In the trinu-
clear NiII and CuII complexes, $\varphi_{\text{central}}$ is in the range
of 20°–30° while $\varphi_{\text{terminal}}$ is significantly smaller in
the range of 3°–9°. Coordination of the hexacyanomet-
allate increases the bent angle $\varphi_{\text{central}}$ to 36.0° in
$[\text{Mn}^\text{III}]^{3+}$ [31], 46.7° in $[\text{Mn}^\text{III}]^{3+}$ [30], and
38.1° in $[\text{Mn}^\text{III}]^{3+}$. The terminal bent angle is
still small with 7.9, 8.5, and 10.0° for $[\text{Mn}^\text{III}]^{3+}$,
$[\text{Mn}^\text{III}]^{3+}$, and $[\text{Mn}^\text{III}]^{3+}$, respectively. The
larger $\varphi_{\text{central}}$ for $[\text{Mn}^\text{III}]^{3+}$ correlates with the
longer Cr–C bond of 2.07 Å in comparison to 1.93 Å
in $[\text{Mn}^\text{III}]^{3+}$ and 1.90 Å in $[\text{Mn}^\text{III}]^{3+}$.

As the simple assumption that a smaller hexa-
cyanoantimoneallate unit forces the triplesalen unit to bend
more does not hold, we have identified a stronger helical distortion in $[\text{Mn}^\text{III}]^{3+}$ in comparison to
$[\text{Mn}^\text{II}]^{3+}$ [31]. This distortion may be best visual-
ized by the angle between the benzene plane of the central phloroglucinol and the vector formed by the central phenolate oxygen atom and the cen-
tral ketimine nitrogen atom (Fig. 2a). This angle is
only 1.3° in $[\text{Mn}^\text{II}]^{3+}$ [30], whereas it is 11.7° in
$[\text{Mn}^\text{III}]^{3+}$ [31] and 9.0° in $[\text{Mn}^\text{II}]^{3+}$. The stron-
ger helical distortion in $[\text{Mn}^\text{II}]^{3+}$ and $[\text{Mn}^\text{III}]^{3+}$ comes along with a slighter distortion of the central phloroglucinol ring and its six direct substituents. These twelve atoms are all in an ideal-
ized plane, whereas in $[\text{Mn}^\text{II}]^{3+}$ the three oxygen
atoms lie below the plane, and the three ketimine carbon atoms lie above the plane (Fig. 2a).

Magnetic measurements

Temperature-dependent magnetic susceptibility measurements (2–290 K, 0.1 T) on powdered sam-
ples of 1·7H2O reveal $\mu_{\text{eff}} = 11.88 \mu_B$ at 290 K,
which decreases monotonically with temperature to
a minimum of 6.52 $\mu_B$ at 1.9 K (Fig. 3a). The room
temperature value is close to the spin-only value of
12.0 $\mu_B$ of six uncoupled MnIII high-spin ions
($S_i = 2$, $g_i = 2.0$). The continuous decrease of $\mu_{\text{eff}}$
dicates dominating antiferromagnetic interactions
between the MnIII ions. In order to probe the magnetic
anisotropy, we have performed variable-temperature
variable-field (VTVH) magnetization measurements
for 1·7H2O at 1, 4, and 7 T (Fig. 3b). The iso-field
lines exhibit a strong nesting behavior which is indica-
tive of strong magnetic anisotropy [36]. The saturation
magnetization at the highest field of 7 T is 16.78 $\mu_B$.

In order to obtain some quantitative insight into
magnitudes and ratios of the exchange couplings $J_{ij}$
and zero-field splittings $D_i$, we have performed a
full-matrix diagonalization of the appropriate spin-
Hamiltonian including isotropic HDV exchange,
zero-field splitting, and Zeeman interaction (see Experi-
mental Section for details). A frequently used simpli-
ification in such spin-Hamiltonians is a collinearity of
the local D tensors, which is not always the case. We
have incorporated the zero-field splitting for the MnIII
ions including the relative orientations of the individ-
ual D tensors by the angle $\theta$ of the Jahn–Teller axes
with the molecular axis.

As the central metal ion is a diamagnetic low-spin
CoIII ion, our first coupling scheme only incorporated
the MnIII-CoIII exchange interaction $J_1$ (Fig. 4a) of
MnIII ions belonging to the same trinuclear triplesalen
building block. Using this coupling scheme, we have
not been able to satisfactorily reproduce both experi-
mental data sets, the temperature dependence of $\mu_{\text{eff}}$
and the results of the VTVH measurements. The tem-
perature dependence of $\mu_{\text{eff}}$ required a coupling con-
stant $J_1$ of about $-0.5 \text{ cm}^{-1}$ without providing a good
reproduction of the experimental data. Contrarily, the
VTVH data indicated a weaker coupling. However, no
satisfactory reproduction of the VTVH data was possi-
ble. The iso-field lines at 4 and 7 T could be reproduced
qualitatively. The 1 T data could not even qualitatively
be reproduced as the simulations exhibited saturation
behavior whereas the experimental data do not.

As the chosen coupling scheme did not provide a
reasonable reproduction of the experimental data, our
next approach was to take into account a coupling of
MnIII ions belonging to different trinuclear triplesalen
subunits. However, a consideration of the full $S_6$ sym-
metry would require incorporation of two additional
coupling constants, e.g. $S_1$ couples with $S_4$ ($J_{14}$)
equally with $S_5$ and $S_6$ ($J_{15} = J_{16}$). As the incorpo-
ration of two additional coupling constants between
the building blocks would overparametrize the system,
we arbitrarily have chosen to incorporate only the ex-
change coupling between a spin on one building block
and the spin of the other building block in trans posi-
tion, i.e., $J_{14} = J_2$. The two cis pathways have been
neglected. This results in the coupling scheme pro-
vided in Fig. 4b. Using this improved coupling scheme,
Fig. 3. a) Temperature dependence of $\mu_{\text{eff}}$ at 0.1 T and b) VTVH at 1, 4, and 7 T for 1·7H2O. The lines correspond to simulations based on the complete spin-Hamiltonian by full matrix diagonalization. The simulations provided are a selection of a thorough search in the $J_1$, $J_2$, and $D$ parameter space.

we have performed an intensive search in the $J_1$, $J_2$, and $D$ parameter space. The $\mu_{\text{eff}}$ vs. $T$ data prove to be highly insensitive to the zero-field splitting. Taking into account a slightly ferromagnetic $J_2$ interaction yielded a good reproduction of the experimental temperature dependence. More sensitive to a change of all three parameters are the VTVH data. Especially the curvature of the 1 T data set has only been reproduced by taking into account a ferromagnetic coupling constant of $+0.05$ cm$^{-1}$ for $J_2$. Evaluating the whole parameter search, the best values are given by $J_1 = -(0.50 \pm 0.04)$ cm$^{-1}$, $J_2 = +(0.05 \pm 0.02)$ cm$^{-1}$, and $D = -(2.5 \pm 0.5)$ cm$^{-1}$. A limited number of simulations is incorporated in Fig. 3.

Discussion

The detailed analysis of the experimental magnetic data suggests a $\text{Mn}^{\text{III}}-\text{Mn}^{\text{III}}$ coupling constant within a trinuclear triplesalen subunit of only $J_1 =$
−0.50 cm⁻¹. This coupling is significantly weaker in comparison to \( J_1 = -1.03 \) cm⁻¹ in \([\text{Mn}^{III} \text{Cr}^{III}]^{3+}[30]\) and \( J_1 = -0.85 \) cm⁻¹ in \([\text{Mn}^{III} \text{Fe}^{III}]^{3+}[31]\). In other trinuclear \text{Mn}^{III}\text{triplesalen subunits the following Mn^{III}-Mn^{III} coupling constants have been established:}

\[
J = -0.30 \text{ cm}^{-1} \text{ in } ([\text{talen}^{\text{NO}_2}]\langle\text{Mn}^{III}(\text{DMSO})_2\rangle_2)\langle\text{ClO}_4\rangle_3[37] \quad \text{and } J = -0.70 \text{ cm}^{-1} \text{ in } ([\text{talen}^{\text{Bu}_2}]\langle\text{Mn}^{III} \cdot \text{MeOH}\rangle_3)\langle\text{ClO}_4\rangle_3[33] \quad \text{and } J = -0.60 \text{ cm}^{-1} \text{ in } ([\langle\text{talen}^{\text{Bu}_2}\rangle\text{Mn}(\text{MeOH})_2][\mu_2-\text{OAc}])_2[\text{SbP}h_3]_2[34].
\]

This comparison indicates that the \text{Mn}^{III} \text{Mn}^{III} coupling depends on steric and electronic effects. However, in the series of heptanuclear complexes of the \text{tert-butyl}\-substituted ligand \text{H}_6\text{talen}^{\text{Bu}_2}, the coupling in \([\text{Mn}^{III} \text{Co}^{III}]^{3+}\) is relatively weak. We have tried to relate the differences between the coupling constants to structural differences. As analyzed in the previous section, the helical distortion in \([\text{Mn}^{III} \text{Co}^{III}]^{3+}\) is close to that found in \([\text{Mn}^{III} \text{Fe}^{III}]^{3+}\), and significantly stronger than that found in \([\text{Mn}^{III} \text{Cr}^{III}]^{3+}\). Therefore, the coupling constant in \([\text{Mn}^{III} \text{Cr}^{III}]^{3+}\) should be exceptional within this series and not the coupling constant in \([\text{Mn}^{III} \text{Co}^{III}]^{3+}\), as found experimentally. We have compared more structural parameters (distances, angles, torsion angles), finding that the molecular structures of \([\text{Mn}^{III} \text{Co}^{III}]^{3+}\) and \([\text{Mn}^{III} \text{Fe}^{III}]^{3+}\) are almost super-imposable (Fig. 2b) due to the same size of the central hexacyanometallate unit. Therefore, it might be reasonable to assume that the difference in the coupling constant between these two complexes is of electronic nature.

As we have found some influence on the experimental magnetic data of the long-range coupling \( J_2 \) from one building block to the other, facilitated by the exchange pathway \( \text{Mn}^{III}-\text{C}=\text{N}-\text{Co}^{III}-\text{C}=\text{N}-\text{Mn}^{III} \), it might be possible that there is an exchange pathway not only between \text{Mn}^{III} ions of two different trinuclear building blocks but also of the same building block through the central diamagnetic \text{Co}^{III} ion. That would result in two independent exchange pathways for one \text{Mn}^{III} \text{Mn}^{III} coupling constant \( J_1 \); one pathway through the central phosphoroglucinol unit and one pathway through the central metal ion. The latter should depend on the electron configuration of the central metal ion which is \( d^8 \) 1 s. in \([\text{Mn}^{III} \text{Co}^{III}]^{3+}\) and \( d^9 \) 1 s. in \([\text{Mn}^{III} \text{Fe}^{III}]^{3+}\).

In conclusion, the synthesis, structural and magnetic characterization of \([\langle\text{talen}^{\text{Bu}_2}\rangle\langle\text{Mn}^{III}(\text{MeOH})\rangle_3][\text{Co}^{III}(\text{CN})_6]\)^{3+} provides evidence for a \text{Mn}^{III}-\text{Mn}^{III} exchange interaction through the central metal ion. In order to test this working hypothesis, we will carefully analyze more members of this family of heptanuclear triplesalen complexes.

**Experimental Section**

**Preparation of compounds**

A solution of \text{H}_6\text{talen}^{\text{Bu}_2} (222 mg, 0.200 mmol) and \text{Mn}^{III}(\text{OAc})_2 \cdot 4\text{H}_2\text{O} (147 mg, 0.600 mmol) was heated at reflux in \text{CH}_3\text{OH} (75 mL) for 20 min. The resulting dark-brown solution was cooled to r.t. and filtered. The filtrate was treated with a solution of \text{K}_3[\text{Co}^{III}(\text{CN})_6] (33 mg, 0.099 mmol) and 18-crown-6 (200 mg, 0.767 mmol) in \text{CH}_3\text{OH} (25 mL) and stirred for 30 min. After addition of a solution of \text{NaPF}_6 (70 mg, 0.417 mmol) and 18-crown-6 (200 mg, 0.767 mmol) in \text{CH}_3\text{OH} (25 mL), stirring was continued for further 15 min. The resulting solution was filtered using very fine filter paper (Blauband). Slow evaporation of the filtrate caused the deposition of dark-brown crystals, which were separated, washed twice with cold \text{MeOH}/\text{H}_2\text{O} (1 : 1), and air-dried. The sample used for magnetic measurements was analyzed as \([\langle\text{talen}^{\text{Bu}_2}\rangle\langle\text{Mn}(\text{MeOH})\rangle_2][\text{Co}(\text{CN})_6]\)[\text{PF}_6]_2-\text{OAc}\). Yield: 172 mg (25 %). IR (KBr): \nu = 2955, 2906, 2870, 2155 (C–N), 1613, 1570, 1535, 1493, 1275, 845, 575, 554 cm⁻¹. – MS (+)-ESI, \text{MeOH}: \text{m/z} = 918.2 [\text{Mn}_6\text{Co}]^{3+}; 1377.4 [\text{Mn}_5\text{Co}]^{2+}; 2753.8 [\text{Mn}_6\text{Co}]^{–}. – MS (+)-ESI, \text{MeOH}: \text{m/z} = 918.2 [\text{Mn}_6\text{Co}]^{3+}; 1377.4 [\text{Mn}_5\text{Co}]^{2+}; 2753.8 [\text{Mn}_6\text{Co}]^{–}.

**X-Ray crystallographic data collection and refinement**

Crystal data for \( \text{I-11MeOH} : M = 3649.42 \text{ g mol}^{-1}, \text{C}_{163}\text{H}_{263}\text{CoF}_{12}\text{Mn}_{18}\text{O}_{31}\text{P}_{2}\), monoclinic, space group \( P2_1/n, a = 18.594(4) \text{ Å}, b = 25.628(5) \text{ Å}, c = 19.504(4) \text{ Å}, \beta = 93.89(3) ^\circ, V = 9273(3) \text{ Å}^3, Z = 2, \rho = 1.31 \text{ g cm}^{-3}, \mu = 0.6 \text{ mm}^{-1}, F(000) = 3860, \text{crystal size} = 0.40 \times 0.20 \times 0.11 \text{ mm}^3. \text{Crystals of I-11MeOH were removed from the mother liquor and immediately cooled to 100(2) K on a Nonius KappaCCD diffractometer (four circle goniometer, MoKα radiation, graphite monochromator, detector distance 35.90 mm). A total of 116546 reflections (2.16 < θ < 25.00°) were collected of which 16270 reflections were unique (Rint = 0.0605). An empirical absorption correction using equivalent reflections was performed with the program SADABS 2.10[38]. The structure was solved with SHELX-97[39] and refined using SHELXL-97[39] to R = 0.0538 for 12996 reflections with I ≥ 2σ(I), R = 0.0711 for all reflections; Max/min residual electron density 1.00 and −1.00 e Å⁻³. All F atoms of the \text{PF}_6^- ion were located and refined on two positions. The OH hydrogen atoms of solvent \text{MeOH} molecules were not located. The acetate anion was found disordered with a MeOH molecule at a center of inversion. The unit cell contains four voids with a vol-
volume of approx. 130 Å³. Originally, two disordered MeOH molecules were found in the region of each void, but could not be refined properly. Thus, their scattering power was removed from the data set using the PLATON/SQUEEZE routine [40]. They are, however, included in the given sum formula.

CCDC 75929 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Other physical measurements

Temperature-dependent magnetic susceptibilities were measured on powdered samples by using a SQUID magnetometer (Quantum Design MPMS XL-7 EC) at 0.1 T (2 – 200 K). VTVH measurements were performed at 1, 4, and 7 T in the range 2 – 10 K with the magnetization equidistantly sampled on a 1/T temperature scale. For calculation of the molar magnetic susceptibilities, χm, the measured susceptibilities were corrected for the underlying diamagnetism of the sample holder and the sample by using tabulated Pascal’s constants. Infrared spectra (400 – 4000 cm⁻¹) of the sample holder and the sample by using tabulated Paschen susceptibilities were corrected for the underlying diamagnetism of the molar magnetic susceptibility, T.

Computational details

The magnetic properties of [Mn⁶CoIII]³⁺ were simulated by a full-matrix diagonalization of the spin-Hamiltonian in Eq. 1.

\[
\hat{H} = -2 \sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j + \sum_i D_i (\hat{S}_i \cdot \mathbf{e}_i (\theta_i, \phi_i))^2 + \mu_B \sum_i \mathbf{B} \cdot \mathbf{g} \cdot \hat{S}_i
\]

Here the first sum reflects the isotropic exchange interaction between spins given by the spin vector operators \( \hat{S}_i \), at sites i. A negative value of \( J_{ij} \) corresponds to an antiferromagnetic coupling. The anisotropic magnetization behavior of the manganese ions is accounted for by local anisotropy tensors in the second sum. The tensors are parameterized by a strength factor \( D_i = D \), which is the same for all six manganese ions. The local unit vector \( \mathbf{e}_i \), which is parameterized by the polar angles \( \theta_i \) and \( \phi_i \), points along the local Jahn-Teller axis and represents an easy or a hard axis depending on the sign of \( D \). Due to the \( S_6 \) symmetry all six local unit vectors \( \mathbf{e}_i \) can be parameterized by the common polar angle between the Jahn-Teller axis and the \( S_6 \) symmetry axis, which is \( \theta = 39.2^\circ \). The relative \( \phi_i \) angles are determined by the \( S_6 \) symmetry. The third term models the interaction with the applied magnetic field. \( \mathbf{B} \) represents the local g-tensor at site i. For the Mn³⁺ ions an isotropic value of 2.0 was assumed.

The Hilbert space of the full spin-Hamiltonian has a dimension of 15625. In the presence of a magnetic field we employed inversion symmetry. This reduced the average matrix size to roughly 7800 × 7800. Since the measurements were performed with powder samples we also employed an orientational average using a Lebedev grid with 50 orientations [41, 42].

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