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# Transformation of the $[Mn^{II}_2Mn^{III}_2(hmp)_6]^{4+}$ Core into $[Co^{III}_2Mn^{II}_2(hmp)_6]^{4+}$ in the Reaction of the $[Mn_4(hmp)_6-(NO_3)_2(H_2O)_2]$ Cluster with $[CoX_4]^{2-}$ (X = Cl, Br)

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The reactions of  $[Mn_4(hmp)_6(NO_3)_2(H_2O)_2](ClO_4)_2$  with  $(Bu_4N)_2[CoX_4]$  (X = Cl, Br) in CH\_3CN have been studied and the new heterometallic tetranuclear clusters  $[Co^{\rm III}_2Mn^{\rm II}_2-(hmp)_6Cl_2(CH_3CN)_2]Mn^{\rm II}Cl_4\cdot 3CH_3CN$  and  $[Co^{\rm III}_2Mn^{\rm II}_2-(hmp)_6Br_2(CH_3CN)_2]Mn^{\rm II}Br_4\cdot 4CH_3CN$  have been synthe-

sized and characterized by TGA, electrospray ionization mass spectrometry, single-crystal X-ray diffraction, and magnetic measurements. The magnetic properties of the heterometallic clusters were analyzed by DFT and ab initio calculations.

### Introduction

In the last decade, the design and synthesis of molecular nanomagnets, the so-called single-molecule magnets (SMMs) and single-chain magnets (SCMs), that exhibit the unique features of slow magnetic relaxation and magnetic hysteresis of molecular origin have become the main area of research in the field of molecular magnetism.<sup>[1]</sup> Among the known single-molecule magnets, [Mn<sub>4</sub>] mixed-valence tetranuclear clusters with the 2-(hydroxymethyl)pyridine (hmp) chelating ligand are of considerable interest as building blocks for the design of one-, two-, and three-dimensional magnetic assemblies.<sup>[2]</sup> These clusters possess a similar double-cuboidal [Mn<sub>4</sub>(hmp)<sub>6</sub>]<sup>4+</sup> core containing two inner Mn<sup>III</sup> ions and two outer Mn<sup>II</sup> ions. The hmp<sup>-</sup> ligands

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provide two  $\mu_3$ -O and four  $\mu$ -O bridges between the Mn<sup>III</sup>–Mn<sup>III</sup> and Mn<sup>III</sup>–Mn<sup>II</sup> ions, respectively. The internal Mn<sup>III</sup> ions are hexacoordinated and characterized by the Jahn–Teller elongation typical of a 3<sup>+</sup> oxidation state. The external Mn<sup>II</sup> ions may be hexa- or heptacoordinated and have labile terminal ligands that always coordinate either anions and/or solvent molecules. These ligands are easily exchangeable by appropriate bridging ligands that allow the assembly of the [Mn<sub>4</sub>(hmp)<sub>6</sub>] core into extended coordination networks.

Previously we investigated the reactions of the cluster  $[Mn_4(hmp)_6(NO_3)_2(H_2O)_2](ClO_4)_2$  (I) with the nitroprusside anion  $[FeNO(CN)_5]^{2-}$  and  $[Fe^{III}Cl_4]^-$ . In the former case, the chain cluster  $[Mn_4(hmp)_6(NO_3)_2FeNO(CN)_5]$ ·  $4CH_3CN^{[2i]}$  was synthesized, and in the latter case the oxobridged dinuclear complex  $[Fe^{III}_2(hpm)_2Cl_4]$ .<sup>[3]</sup>

Herein we report the results of our study of the reactions of I with  $(Bu_4N)_2[CoX_4]$  (X = Cl, Br) in CH<sub>3</sub>CN leading to the heterometallic clusters [Co<sup>III</sup><sub>2</sub>Mn<sup>II</sup><sub>2</sub>(hmp)<sub>6</sub>Cl<sub>2</sub>-(CH<sub>3</sub>CN)<sub>2</sub>]Mn<sup>II</sup>Cl<sub>4</sub>·3CH<sub>3</sub>CN (II) and [Co<sup>III</sup><sub>2</sub>Mn<sup>II</sup><sub>2</sub>(hmp)<sub>6</sub>-Br<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]Mn<sup>II</sup>Br<sub>4</sub>·4CH<sub>3</sub>CN (III), which are the first heterometallic clusters containing the [M<sup>III</sup><sub>2</sub>M'<sup>II</sup><sub>2</sub>(hmp)<sub>6</sub>] core. Up to now, the known heterometallic tetranuclear clusters incorporate, in addition to hmp ligands, various carboxylate ligands, and the nuclei include three Mn<sup>III</sup> and one  $M'^{II}$  (M' = Ni, Zn) ions.<sup>[4]</sup> The heterometallic clusters II and III have been isolated in the crystalline form and characterized by single-crystal X-ray diffraction, thermogravimetric analysis (TGA), electrospray ionization mass spectrometry (ESI-MS), and magnetic susceptibility measurements. The analysis of the magnetic properties has been supported by the quantum chemical calculations.



# **Results and Discussion**

#### Synthesis and Identification

The complexes  $[Co_2Mn_2(hmp)_6Cl_2(CH_3CN)_2]MnCl_4$ · 3CH<sub>3</sub>CN (**II**) and  $[Co_2Mn_2(hmp)_6Br_2(CH_3CN)_2]MnBr_4$ · 4CH<sub>3</sub>CN (**III**) are the products of redox reactions between the cluster  $[Mn_4(hmp)_6(NO_3)_2(H_2O)_2](ClO_4)_2$  (**I**) and the Co complexes  $(Bu_4N)_2[CoX_4]$  (X = Cl, Br). The redox reactions take place between the Mn<sup>III</sup> ions of the starting cluster I and Co<sup>II</sup> ions to yield the heterometallic cation clusters  $[Co^{III}_2Mn^{II}_2(hmp)_6X_2(CH_3CN)_2]$  with anions  $[Mn^{II}X_4]$  (X = Cl, Br). Crystals of **II** and **III** were grown slowly at room temperature from acetonitrile solutions containing the Co complexes **II** and **III** were not formed by using a ratio of 1:1 of **I** and the cobalt complex. The reactions were performed under both aerobic and anaerobic conditions, and the same complexes were obtained in both cases.

Complex II was dissolved in acetonitrile at room temperature and its ESI-MS spectra were recorded. The mass spectrum in the positive-ion mode is shown in Figure 1. Analysis of the isotopic structure of the registered ion peaks and the accurate measurement of the ion masses allowed us to identify all the main ions that were detected. The intense signal at m/z = 472.973 has been assigned to the [MnCo(C<sub>6</sub>H<sub>6</sub>NO)<sub>3</sub>Cl]<sup>+</sup> and [Mn<sub>2</sub>Co<sub>2</sub>(C<sub>6</sub>H<sub>6</sub>NO)<sub>6</sub>Cl<sub>2</sub>]<sup>2+</sup> ions. The presence of these ions in the mass spectrum of II is unambiguous evidence for the formation of a heterometallic (Co,Mn) cation cluster containing Mn and Co ions in the ratio 1:1. The inset in Figure 1 shows the distribution of  $[MnCo(C_6H_6NO)_3Cl]^+$  and  $[Mn_2Co_2(C_6H_6NO)_6Cl_2]^{2+}$  ions. A comparison of this experimental distribution with the results of computer simulations gives the ratio of cation and dication intensities as 3:1. The relative peak intensities of these and other ions in the mass spectrum of **II** are presented in Table 1. In the negative-ion mode, the ESI-MS analysis of a solution of **II** shows the presence of a peak corresponding to the  $[MnCl_3]^-$  anion, which is formed by the in situ fragmentation of the  $[MnCl_4]^{2-}$  complex to  $[MnCl_3]^-$  and  $Cl^-$  anions. Note that these results are in complete agreement with the single-crystal X-ray structural analysis (see below).

Table 1. m/z values (experimental and calculated) and the relative peak intensities of the main ions in the ESI-MS spectrum (positiveion mode) of an acetonitrile solution (ca. 100  $\mu$ M) of the complex [Mn<sub>2</sub>Co<sub>2</sub>(C<sub>6</sub>H<sub>6</sub>NO)<sub>6</sub>Cl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]MnCl<sub>4</sub> (II).

Ion	<i>m/z</i> (exp.)	m/z (calcd.)	Rel. intensity
$\overline{[Mn(C_6H_6NO)_2]^+}$	271.026	271.028	0.95
$[Co(C_6H_6NO)_2]^+$	275.021	275.023	0.18
$[MnCo(C_6H_6NO)_3Cl]^+$	472.973	472.975	0.75
$[Mn_2Co_2(C_6H_6NO)_6Cl_2]^{2+}$	472.973	472.975	0.25
$[Mn_2Co(C_6H_6NO)_4Cl_2]^+$	670.926	670.927	0.05
$[MnCo_2(C_6H_6NO)_4Cl_2]^+$	674.920	674.922	0.46
$[Mn_2Co_2(C_6H_6NO)_6Cl_3]^+$	980.916	980.919	0.12



Figure 1. ESI-MS spectrum for the acetonitrile solution (ca. 100  $\mu$ M) of the [Mn<sub>2</sub>Co<sub>2</sub>(C<sub>6</sub>H<sub>6</sub>NO)<sub>6</sub>Cl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]MnCl<sub>4</sub> complex (II) recorded in the positive-ion mode. The signal from the [Cu(CH<sub>3</sub>CN)<sub>2</sub>]<sup>+</sup> ion is a result of a design feature of our home-made electrospray ion source. Inset: Region of m/z = 472.5-475.5 expanded for clarity.



A special feature of the crystals of II and III is their capacity to readily lose the guest acetonitrile molecules and to absorb water from air. Most likely, water molecules replace acetonitrile in the crystal lattice of II and III. This is evident from the TGA, IR spectroscopic, single-crystal Xray diffraction, and elemental analyses. The TGA experiments were carried out under argon at a heating rate of 10 K min<sup>-1</sup>. In the course of the TGA, the composition of the gas phase was controlled by mass spectrometry. Figure S1 in the Supporting Information displays the thermogram of freshly prepared crystals of III, which were dried for 20 min in air before the TG-DSC measurements. A small weight loss (1.03%) was detected with increasing temperature in the range 50-140 °C. This can be attributed to the loss of residual acetonitrile crystallization molecules  $\{[Co_2Mn_2(hmp)_6Br_2(CH_3CN)_2]MnBr_4 \cdot xCH_3CN, x \approx 0.4\}.$ In the temperature range 170-220 °C, a weight loss of 5.20% was observed, which has been assigned to the loss of two coordinated acetonitrile molecules (calcd. 5.43%). In the mass spectrum recorded in the gas phase (Figure S1 in the Supporting Information) peaks are observed at m/z41, 15 and 26 corresponding to the CH<sub>3</sub>CN molecular ion  $(m/z \ 41)$  and its fragments (CH<sub>3</sub>: m/z = 15; CN: m/z = 26). After heating the sample of III to 220 K, the C=N band of coordinated CH<sub>3</sub>CN at 2270 cm<sup>-1</sup> in the IR spectrum vanished.

The thermogravimetric analysis was also carried out on dried crystals that had been stored in air (see Figure S2 in the Supporting Information). Complex II showed a weight loss of 4.67% with increasing temperature in the range 40-120 °C corresponding to the loss of three absorbed water 4.22% molecules {calcd. for the composition  $[Co_2Mn_2(hmp)_6Cl_2(CH_3CN)_2]MnCl_4\cdot 3H_2O\}$ . As this takes place, ions with m/z = 18 and 17 (H<sub>2</sub>O and OH, respectively) were observed in the mass spectrum (see Figure S2 in the Supporting Information). In the temperature range 170-210 °C, a weight loss of 5.58% occurred, which can be attributed to the loss of two coordinated acetonitrile molecules (calcd. 6.32%). Similarly to II, complex III absorbs water on storage in air. Its thermogram demonstrates the mass loss of 4.48% in the temperature range 40–120 °C,

which corresponds to the loss of four water molecules {calcd. 4.60% for  $[Co_2Mn_2(hmp)_6Br_2(CH_3CN)_2]MnBr_4$ · 4H<sub>2</sub>O}. After storage in air, the IR spectra of complexes II and III are characterized by the appearance of a broad band in the range of 3500–3200 cm<sup>-1</sup> corresponding to the OH stretch in H<sub>2</sub>O.

#### Crystal Structures of II and III

The crystals of **II** and **III** have the same triclinic system and similar cell parameters. However, their molecular packing in the lattices is different and the crystals are not isostructural. The presence of two crystallographically independent cluster units  $[Mn_2Co_2]$  located in special positions is characteristic of both structures (see Figures 2 and 3).

In the crystals of II and III, the [Mn<sub>2</sub>Co<sub>2</sub>] cores have a double-cuboidal form with metal cations connected by oxygen bridges and surrounded by hmp<sup>-</sup>, CH<sub>3</sub>CN, and halogen ligands. The bond lengths in the clusters clearly indicate the oxidation states of the metals: CoIII for the external core metals and Mn<sup>II</sup> for the internal core metals. Both the Co and Mn cations are six-coordinated. Note that the structures of the [Mn<sub>2</sub>Co<sub>2</sub>] clusters are different to that of the initial  $Mn_4$  cluster  $(I)^{[2d]}$  and to the structures of other known Mn<sub>4</sub> clusters.<sup>[2h]</sup> In the cases of compounds II and III, the internal Mn<sup>II</sup> ions are coordinated by a halogen atom, a CH<sub>3</sub>CN molecule, and by four hmp ligands, whereas the external Co<sup>III</sup> has three hmp ligands. In contrast, the initial Mn<sub>4</sub> cluster has internal Mn<sup>III</sup> and external seven-coordinated Mn<sup>II</sup> cations: the Mn<sup>III</sup> cations are coordinated by hmp ligands, whereas the Mn<sup>II</sup> cations are coordinated by H<sub>2</sub>O, NO<sub>3</sub>, and hmp ligands.

The selected bond lengths and angles for the  $[Mn_2Co_2]$ units (1 and 2) displayed in Figures 2 and 3 for II and III, respectively, are presented in Table 2. The interatomic  $Mn^{II}-N/Mn^{II}-O$  distances are in the range 2.074–2.361 Å (Table 2) for II and III. Note that in the starting compound  $[Mn_4(hmp)_6(NO_3)_2(H_2O)_2](CIO_4)_2 \cdot 4H_2O$  (I), the  $Mn^{II}-N/$  $Mn^{II}-O$  distances are in the range 2.185–2.336 Å.<sup>[2d]</sup> The



Figure 2. Representation of two crystallographically independent (1 and 2) cluster units  $[Mn_2Co_2]$  of the crystal structure of II. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are presented at the 50% probability level.





Figure 3. Representation of two crystallographically independent (1 and 2) cluster units  $[Mn_2Co_2]$  of the crystal structure of III. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are presented at the 50% probability level.

 $Co^{III}$ –O/Co<sup>III</sup>–N bond lengths and  $Co^{III}$ –O–Co<sup>III</sup>/Co<sup>III</sup>–O– Mn<sup>II</sup> angles in the [Mn<sub>2</sub>Co<sub>2</sub>] cores of **II** and **III** are similar to those found in the mixed-valence cores of [Co<sup>III</sup><sub>2</sub>Co<sup>II</sup><sub>2</sub>] of the double-cuboidal complexes<sup>[5]</sup> in which the Co<sup>III</sup>–O coordination bonds are less than 2 Å and the Co<sup>III</sup>–O bond distances are over 2 Å.<sup>[5]</sup> The lengths of the Co<sup>III</sup>–O/Co<sup>III</sup>– N bonds in the [Mn<sub>2</sub>Co<sub>2</sub>] cores of **II** and **III** are typical of Co<sup>III.[5]</sup> The Mn···Mn distances in the [Mn<sub>2</sub>Co<sub>2</sub>] cores (**1** and **2**, respectively) are 3.440 and 3.463 Å in crystals of **II**, and 3.463 and 3.447 Å in crystals of **III**. It is clear that intracluster coupling should play an essential role in the magnetic properties of these complexes.

Figures 4a and b present the projections along the *a* direction of the crystal structures of **II** and **III**, respectively. In the structure of **II**, the core **1** is situated at the [000] position and the core **2** is situated at the  $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$  inversion center. The cores **1** and **2** of **III** occupy positions at the inversion centers  $[0\frac{1}{2}\frac{1}{2}]$  and [000], respectively. The tetrahedral anions MnX<sub>4</sub> (X = Cl or Br) as well as the CH<sub>3</sub>CN molecules that fill the space between the clusters are situated in general positions.

Both crystal structures are stabilized by hydrogen bonds. Intercluster interactions are in the (011) plane for II and in the (011) and (001) planes for III (Figures S3–S5 in the Supporting Information). In the case of II, these interactions are formed by C-H···Cl contacts (2.649, 2.857, and 2.862 Å) with C-H···Cl angles greater than 125°. For III, the C-H. Br contacts have lengths of 2.946–2.994 Å with angles greater than 124°. There are many contacts between clusters and anions: C-H···Cl for II (H···Cl distances are in the range 2.607–2.890 Å with angles greater than 125°) and C-H···Br for III (H···Br distances are in the range 2.807-3.050 Å with angles in the range of 120–150°). In addition, there are a number of C-H···Cl (in II), C-H···Br (in III), and C-H ... N contacts between solvent molecules and clusters/anions. The shortest intermolecular Mn...Mn distances are rather large: 6.806 and 7.087 Å (Mn1····Mn3) in the crystal of II and 7.441 (Mn2···Mn3), 7.793 (Mn1···Mn1), and 7.845 Å (Mn1····Mn3) in the crystal of III {Mn3 is the atom

Table 2. Selected bond lengths [Å] and angles [°] of the two crystal-
lographically independent [Mn <sub>2</sub> Co <sub>2</sub> ] cores (1 and 2) in the crystals
of <b>II</b> and <b>III</b> .

Crystal II				
1	2			
Co1–O2 1.873(1)	Co2-O4 1.874(1)			
Co1–O1 1.894(1)	Co2–O6 1.895(1)			
Co1-O3 1.902(1)	Co2–O5 1.905(1)			
Co1-N2 1.935(1)	Co2-N5 1.927(1)			
Co1-N3 1.936(1)	Co2–N6 1.929(1)			
Co1–N1 1.949(1)	Co2-N7 1.950(1)			
Mn1–O2 2.091(1)	Mn2–O4 2.096(1)			
Mn1–O1 2.165(1)	Mn2–O6 2.165(1)			
Mn1–O3 2.248(1)	Mn2–O5 2.248(1)			
Mn1–O3 2.296(1)	Mn2–O5 2.291(1)			
Mn1–N4 2.296(2)	Mn2–N8 2.287(1)			
Mn1-Cl1 2.4136(4)	Mn2–Cl2 2.4324(5)			
Co-O1-Mn 101.57(5)	Co-O4-Mn 106.30(5)			
Co-O2-Mn 105.34(5)	Co-O5-Mn 98.82(4)			
Co–O3–Mn 98.42(4)	Co-O5-Mn 98.12(4)			
Co–O3–Mn 96.98(4)	Mn–O5–Mn 99.47(4)			
Mn–O3–Mn 98.40(4)	Co-O6-Mn 102.07(5)			
Crystal III				
1	2			
Co1–O3 1.874(3)	Co2–O4 1.882(3)			
Co1–O2 1.896(2)	Co2–O6 1.892(3)			
Co1-O1 1.909(2)	Co2-O5 1.896(3)			
Co1-N3 1.930(3)	Co2-N6 1.933(3)			
Co1-N2 1.935(3)	Co2–N5 1.934(3)			
Co1-N1 1.946(3)	Co2-N7 1.951(3)			
Mn1–O3 2.074(2)	Mn2–O4 2.084(3)			
Mn1–O1 2.151(3)	Mn2–O6 2.168(3)			
Mn1–O2 2.199(2)	Mn2–O5 2.188(3)			
Mn1–O2 2.349(3)	Mn2–O5 2.361(3)			
Mn1–N4 2.261(3)	Mn2-N8 2.240(3)			
Mn1–Br1 2.5717(7)	Mn2–Br2 2.6041(7)			
Co-O1-Mn 100.1(1)	Co-O4-Mn 108.0(1)			
Co–O2–Mn 98.8(1)	Co-O5-Mn 99.6(1)			
Co–O2–Mn 96.9(1)	Co-O5-Mn 97.3(1)			
Mn–O2–Mn 99.1(1)	Mn-O5-Mn 98.5(1)			
Co-O3-Mn 107.8(1)	Co-O6-Mn 100.4(1)			

in the anion  $[MnCl(Br)_4]^{2-}$ , see Figure S6 in the Supporting Information}.



Figure 4. Projections of the crystal structures of II (a) and III (b) along the a direction (hydrogen atoms have been omitted for clarity).

#### Quantum Chemical Calculations

To understand on a molecular level and for correct simulation of the magnetic properties of the clusters II and III, the pair exchange interactions in their spin systems containing Mn<sup>II</sup> ions with S = 5/2 were calculated for the XRD structures. The calculations were performed by using the spin-unrestricted broken-symmetry approach. As mentioned earlier, the crystallographically independent [Mn<sub>2</sub>Co<sub>2</sub>] cores have Mn<sup>II</sup>...Mn<sup>II</sup> pairs with slightly different distances (Table 3). Thus, we calculated J values for both types of pairs. Table 3 demonstrates that the differences in J values for clusters of types 1 and 2 are not large. Moreover, the J values calculated for the  $[Mn_2Co_2]$  cores of crystals II and III at the UBP86/def2-SVP level of theory are also very similar. In the case of cluster II, we also performed calculations by using a much larger basis set (TZVP) and hybrid functional (B3LYP). These calculations were considerably more time- and resource-consuming and resulted in similar, although noticeably larger, J values.

Thus, we did not recalculate the J values for cluster III at this level of theory.

Table 3. Parameters of the pair exchange interactions (J) between Mn<sup>II</sup> cations of the [Mn<sub>2</sub>Co<sub>2</sub>] cores calculated by using the spinunrestricted broken-symmetry approach at the UBP86/def2-SVP and UB3LYP/def2-TZVP (in parentheses) levels of theory.

	· · ·	<i>,</i>	2
Compound II		Compound III	
<i>R</i> (Mn–Mn) [Å]	$J  [\mathrm{cm}^{-1}]$	R(Mn-Mn) [Å]	$J  [{ m cm}^{-1}]$
3.463	-1.73 (-2.38)	3.463	-1.99
3.440	-2.02 (-3.27)	3.447	-1.92

Recall that  $Mn^{II}$  cations of the  $[Mn_2Co_2]$  core are connected by two O bridges and that the distances between them are about 3.45 Å. In addition to the  $[Mn_2Co_2]$  core, structures II and III contain the tetrahedral  $[Mn^{II}Cl_4]^{2-}$  and  $[Mn^{II}Br_4]^{2-}$  complex anions, respectively. There are no bridges between the  $Mn^{II}$  of the core and the  $Mn^{II}$  of the tetrahedral anions, and the shortest distances between these  $Mn^{II}$  cations are 6.806 and 7.087 Å for compound II and 7.441 and 8.499 Å in the case of III. Unfortunately, due to the problem of convergence, all our attempts to calculate the *J* values for the exchange interactions between the  $Mn^{II}$  of the core and the  $Mn^{II}$  of the tetrahedral complexes failed.

In recent years,<sup>[6]</sup> considerable attention has been directed towards the measurement and quantum chemical calculation of the zero-field splitting (ZFS) parameters (*D* and *E*) of Mn<sup>II</sup> mononuclear complexes. It was found that the ZFS parameters are highly sensitive to the environment.<sup>[6]</sup> For the Mn<sup>II</sup> ions coordinated to only N- and/or O-based ligands, the *D* value does not exceed 0.3 cm<sup>-1</sup> with the only exception the polyoxometallate complex of Mn<sup>II</sup> with D = 1.46 cm<sup>-1</sup>.<sup>[6c]</sup> Note that previously,<sup>[2d-2f,7]</sup> the temperature dependences of the magnetic susceptibility of the Mn<sup>II</sup>-containing clusters have been well reproduced based on the Heisenberg Hamiltonian and neglecting ZFS of individual ions.

Nevertheless, we calculated the g and ZFS tensors for all types of  $Mn^{II}$  ions in the crystals II and III by using DFT. It has previously been demonstrated<sup>[6d]</sup> that the coupledperturbed spin–orbit coupling approach together with hybrid DFT functionals predict reasonably well the *D* values for the  $Mn^{II}$  complexes. The same approach was used in our calculations (see the Computational Details in the Exp. Sect.). The *D* values were found to be very small for the  $[MnX_4]^{2-}$  complex: -0.02 cm<sup>-1</sup> for X = Cl, and -0.05 cm<sup>-1</sup> for X = Br. Larger absolute values (in the range of 0.18-0.96 cm<sup>-1</sup>) were predicted for the  $Mn^{II}$  ions of the  $[Mn_2Co_2]$ clusters (see Table S1 in the Supporting Information for details). In all cases, the g tensors were calculated to be almost isotropic with a  $g_{iso}$  similar to that of the free electron (see Table S1).

#### Magnetic Properties of Clusters II and III

Figure 5 displays the temperature dependence of the dc molar magnetic susceptibility ( $\chi$ ) of powdered samples of **II** 



and III represented in the form of the product  $\chi T$ (curves 1). At 300 K, the  $\chi T$  values are equal to 12.9 and  $12.34 \text{ cm}^3 \text{K} \text{mol}^{-1}$  for II and III, respectively. Both values are close to the expected value of 13.13 cm<sup>3</sup> K mol<sup>-1</sup> for three magnetically noninteracting  $Mn^{2+}$  ions (S = 5/2) with g = 2.0. For both compounds,  $\chi T$  decreases gradually on cooling (Figure 5). The decrease in  $\chi T$  with decrease in temperature indicates the dominance of antiferromagnetic (AF) interactions between the paramagnetic centers in both compounds. Furthermore, above 25 K, the  $\chi^{-1}$  versus T plots obey the Curie-Weiss law (Figure 5); the Curie-Weiss parameters C and  $\Theta$  are 14.4 cm<sup>3</sup> K mol<sup>-1</sup> and -21.6 K for II, and  $13.2 \text{ cm}^3 \text{ K mol}^{-1}$  and -17.4 K for III, respectively. The negative Weiss constants of -21.6 and -17.4 K indicate prevailing antiferromagnetic interactions between the manganese ions. Most likely, the intracluster interactions through the oxo bridges dominate, although exchange interactions between the cations and anions cannot be excluded.



Figure 5. Experimental temperature dependence (red circles) of  $\chi T$  (1) and  $1/\chi$  (2) for compounds III (a) and II (b) and simulation of  $\chi T$  (1, black lines) taking into account only intracluster exchange interactions. The best fittings lead to the following parameters:  $J = -2.46 \text{ cm}^{-1}$  and g = 1.98 for III, and  $J = -2.95 \text{ cm}^{-1}$  and g = 2.07 for II. Blue lines (lines 2) correspond to the Curie–Weiss law.

According to DFT calculations (Table 3), the magnetic interactions in the crystallographically independent [Mn<sub>2</sub>Co<sub>2</sub>] cores (**1** and **2**) are similar. Thus we simulated the  $\chi T$  temperature dependence neglecting the difference between the cores of **1** and **2**. Figure 5 demonstrates that the magnetic susceptibility at high temperature (50–300 K) can be very well reproduced by taking into account only the antiferromagnetic interactions between the oxo-bridged Mn<sup>II</sup> ions (model 1, see the Exp. Sect.). The experimentally determined J values (–2.46 and –2.95 cm<sup>-1</sup> for **II** and **III**, respectively) are in good agreement with calculations (–1.73 to –3.27 cm<sup>-1</sup>, Table 3).

Unfortunately, it was impossible to fit well the data for  $\chi T$  over the entire temperature range (2–300 K) taking into account only intracluster exchange interactions. Accounting

for the magnetic interactions of the clusters with the neighbors by using the Weiss temperature<sup>[8]</sup> did not lead to good agreement between simulation and experiment (Figure 6, blue lines). Moreover, accounting for the zero-field splitting  $(D \le 1 \text{ cm}^{-1})$  of the Mn<sup>II</sup> ions does not noticeably influence the low-temperature pattern of  $\chi T$  (see Figure S7 in the Supporting Information). Recall that the *D* parameters were calculated to be less than 1 cm<sup>-1</sup>.



Figure 6. Experimental temperature dependence of  $\chi T$  (red circles) for compounds III (a) and II (b) and simulations of  $\chi T$  taking into account intracluster exchange interactions (*J*) and exchange interactions between clusters and surrounding paramagnetic species within a mean field approximation ( $\theta$ , blue lines) or intracluster (*J*<sub>1</sub>) and cation–anion (*J*<sub>2</sub>) exchange interactions (black lines). The best fittings lead to the following parameters:  $J = -2.21 \text{ cm}^{-1}$ ,  $\theta = 0.4 \text{ K}$ , g = 1.98 and  $J_1 = -4.8 \text{ cm}^{-1}$ ,  $J_2 = 1.9 \text{ cm}^{-1}$ ,  $\theta = -1.4 \text{ K}$ , g = 1.97 for III, and  $J = -2.84 \text{ cm}^{-1}$ ,  $\theta = 1.5 \text{ K}$ , g = 2.06 and  $J_1 = -5.4 \text{ cm}^{-1}$ ,  $J_2 = 1.8 \text{ cm}^{-1}$ ,  $\theta = 0 \text{ K}$ , g = 2.06 for II.

Very good agreement between experiment and simulation over the entire temperature range was achieved (Figure 6, black lines) by taking into account both the antiferromagnetic intracluster interactions through the oxo bridges and ferromagnetic interactions between the Mn<sup>II</sup> ions of the cluster and anion (model 2,  $J_1 = -4.8 \text{ cm}^{-1}$ ,  $J_2 = 1.9 \text{ cm}^{-1}$ for III, and  $J_1 = -5.4 \text{ cm}^{-1}$ ,  $J_2 = 1.8 \text{ cm}^{-1}$  for II). Thus, the *J* values for the ferromagnetic interactions between the cation and anion (1.8–1.9 cm<sup>-1</sup>) are about three times smaller than the *J* values for the intracluster antiferromagnetic interactions (about  $-5 \text{ cm}^{-1}$ ). However, the shortest intermolecular Mn···Mn distances are rather large (6.8–7.8 Å in both crystals) compared with the intracluster distances (3.44–3.46 Å). Note also that taking into account only intracluster exchange interactions and interactions between the cluster and one neighboring anion is a simplification.

## Conclusions

In this work new heterometallic tetranuclear complexes  $[Co_2Mn_2(hmp)_6Cl_2(CH_3CN)_2]MnCl_4\cdot 3CH_3CN$  (II) and

 $[Co_2Mn_2(hmp)_6Br_2(CH_3CN)_2]MnBr_4 \cdot 4CH_3CN$  (III) have been synthesized and characterized. The characteristic structural features of II and III are the presence of two crystallographically independent cluster units [Mn<sub>2</sub>Co<sub>2</sub>] (1 and 2) with a double-cuboidal core containing six-coordinated Mn<sup>II</sup> and Co<sup>III</sup> ions connected by oxygen bridges. In contrast to the  $[Mn^{II}_2Mn^{III}_2]$  cluster I with two inner  $Mn^{III}$ and two outer Mn<sup>II</sup> ions in the cuboidal core, the Co<sup>III</sup> ions are external and the Mn<sup>II</sup> ions internal. The intracluster Mn...Mn distances in the [Mn<sub>2</sub>Co<sub>2</sub>] cores (1 and 2, respectively) are 3.440 and 3.463 Å in crystals of II and 3.463 and 3.447 Å in crystals of III. The acetonitrile guest molecules are lightly bonded to the crystal lattice and lost readily during drying. The loss of CH<sub>3</sub>CN molecules of crystallization is accompanied by the absorption of water from air. Magnetic studies in the temperature range 300-4.2 K indicated a rather strong intracluster antiferromagnetic coupling between the oxo-bridged Mn<sup>II</sup> ions. Experimentally determined J values (-2.46 and -2.95 cm<sup>-1</sup> for II and III, respectively) are in good agreement with calculations (-1.7 to) $-3.3 \text{ cm}^{-1}$ ).

# **Experimental Section**

**Materials:** All manipulations were carried out under aerobic conditions using commercial grade chemicals and solvents. To check the possible influence of air oxygen on the composition of products of the reactions between  $[Mn_4(hmp)_6(NO_3)_2(H_2O)_2](ClO_4)_2$ ·4H<sub>2</sub>O (I) and the Co complexes, the syntheses were also performed under anaerobic conditions. The starting cluster (I) was prepared by a previously reported procedure.<sup>[2d]</sup>  $[(C_4H_9)_4N]_2CoCl_4$  was synthesized by the reaction between  $(C_4H_9)_4NCl$  and  $CoCl_2$  (2:1 molar ratio) in a minimum quantity of absolute ethyl alcohol.  $[(C_4H_9)_4N]_2CoBr_4$  was prepared in a similar way by using  $(C_4H_9)_4NBr$  and  $CoBr_2$ .

#### Syntheses

[Mn<sub>2</sub>Co<sub>2</sub>(hmp)<sub>6</sub>Cl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]MnCl<sub>4</sub>·3CH<sub>3</sub>CN (II): [Mn<sub>4</sub>(hmp)<sub>6</sub>- $(NO_3)_2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$  (I; 0.065 g, 0.05 mmol) and [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>2</sub>CoCl<sub>4</sub> (0.0685 g, 0.1 mmol) were dissolved separately in a minimum quantity of dry CH<sub>3</sub>CN with stirring. The solution of [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>2</sub>CoCl<sub>4</sub> was added dropwise to the solution of the Mn<sub>4</sub> complex. The color of the solution changed from red-brown to green-brown. The stirring was then continued for a further 20 min at room temperature and the resulting solution was filtered and left to stand undisturbed at room temperature. After several days, black-brown rhombic crystals of II were formed. The crystals were collected by filtration, washed with CH<sub>3</sub>CN, and dried in air. The cooling of the filtrate in a refrigerator provided an additional quantity of crystals; yield 38 mg (44%). The crystals of II lost the guest CH<sub>3</sub>CN molecules very quickly and became unsuitable for crystallographic study. To prevent the solvent loss, the crystals for X-ray diffraction were kept in contact with the mother liquor. The dried solid appeared to be hygroscopic, TGA confirming the formation of the trihydrate. Selected IR data:  $\tilde{v} = 3350.0$  (br), 1611.1 (s), 1477.3 (m), 1441.9 (m), 1284.6 (m), 1157.7 (w), 1045.6 (s), 767.6 (s), 723.2 (m), 669.2 (s), 566.5 (s) cm<sup>-1</sup>.  $C_{40}H_{48}Cl_6Co_2Mn_3N_8O_9$ (1280.27): calcd. C 37.52, H 3.77, N 8.75, Cl 16.61; found C 37.42, H 3.79, N 8.57, Cl 16.65.

[Mn<sub>2</sub>Co<sub>2</sub>(hmp)<sub>6</sub>Br<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]MnBr<sub>4</sub>·4CH<sub>3</sub>CN (III): Complex III was synthesized following the same procedure as used for complex

II except that 2 equiv. of  $[(C_4H_9)_4N]_2CoBr_4$  instead of  $[(C_4H_9)_4-N]_2CoCl_4$  were used. Black-brown crystals of III were formed at room temperature within 2–5 d. The crystals were collected by filtration, washed with CH<sub>3</sub>CN, and dried in air; yield 46.6 mg (57.7%). Similarly to II, the crystals of III lost the guest CH<sub>3</sub>CN molecules very quickly. The dried solid appeared to be hygroscopic, TGA showing the formation of the tetrahydrate. The energy-dispersive X-ray analysis revealed the presence of Mn and Co in a ratio close to 1.5:1. Selected IR data:  $\tilde{v} = 1612.3$  (m), 1471.8 (m), 1442.9 (m), 1284.7 (m), 1035.6 (s), 770.8 (m), 731.1 (m), 668.9 (s) cm<sup>-1</sup>. C<sub>40</sub>H<sub>50</sub>Br<sub>6</sub>Co<sub>2</sub>Mn<sub>3</sub>N<sub>8</sub>O<sub>10</sub> (1564.99): calcd. C 30.69, H 3.22, N 7.16, Br 30.63; found C 30.40, H 3.13, N 6.89, Br 30.78.

Physical Measurements: C, H, N analyses were performed with a vario MICRO cube analyzing device. IR spectra (500-4000 cm<sup>-1</sup>) were recorded with a Varian 3100 FTIR Excalibur Series spectrometer equipped with a ZnS monocrystal cell allowing the spectrum of one crystal or a small amount of a powder sample to be recorded. TGA was performed with a NETZSCH STA 409 C Luxx thermal analyzer interfaced to a QMS 403 Aelos mass spectrometer, which allowed simultaneous thermogravimetry (TG), differential scanning calorimetry (DSC), and mass-spectrometric measurements. Electrospray mass spectra were obtained by using an Exactive Orbitrap mass spectrometer (ThermoFisher Scientific, Germany). Acetonitrile solutions of the samples were electrosprayed and the data were acquired in positive and negative ion modes. The electrospray voltage was held constant at 2.5 kV. The interface ion optic potentials were tuned to minimize original ion fragmentation. Acquisition and data analysis were performed with the Exactive Software, Version 1.1. Dc magnetic susceptibility measurements were performed on powder samples on a home-made SQUID magnetometer (sensitivity 10<sup>-9</sup> emu) in the temperature range 1.9-300 K under an applied magnetic field of 25 and 100 Oe for II and III, respectively. The experimental data were corrected for the magnetization of the sample holder, and diamagnetic corrections were estimated by using Pascal's constants.<sup>[9]</sup>

Simulation of the Temperature Dependence of Magnetic Susceptibility: The temperature dependences of the magnetic susceptibility were fitted by using the Origin 8 software<sup>[10]</sup> or the julX program written by Bill and co-workers.<sup>[11]</sup> Two models and their modifications were used in the simulations. In both models, two crystallographically independent cluster units were proposed to be identical. In the first model, only intracluster exchange interactions were taken into account with the spin Hamiltonian given by Equation (1)

$$\hat{H} = \sum_{i=1}^{3} g_i \, \beta \, \vec{S}_i \vec{B} - 2J_1 \vec{S}_1 \vec{S}_2 \tag{1}$$

in which the indices 1 and 2 refer to the  $Mn^{II}$  ions of the cluster and the index 3 refers to magnetically isolated  $[Mn^{II}Cl_4]^{2-}$  (or  $[Mn^{II}Br_4]^{2-}$ ).

In the second model, the exchange interactions between the  $Mn^{II}$  ions of the cluster and the  $[Mn^{II}Cl_4]^{2-}$  anion were also taken into account by using the spin Hamiltonian given by Equation (2).

$$\widehat{H} = \sum_{i=1}^{3} g_i \beta \vec{S}_i \vec{B} - 2J_1 \vec{S}_1 \vec{S}_2 - 2J_2 \left( \vec{S}_1 \vec{S}_3 + \vec{S}_2 \vec{S}_3 \right)$$
(2)

To analyze the low-temperature behavior of  $\chi T$ , both models were modified to account for interactions of the three-spin unit with paramagnetic neighbors. The latter interactions were considered by



using the Weiss temperature,  $\theta$ , as a perturbation of the temperature scale,  $kT' = k(T - \theta).^{[8]}$ 

Crystal Structure Determination and Refinement: Single-crystal Xray diffraction studies were carried out by using an Oxford Diffraction Gemini-R diffractometer  $[\lambda(Mo-K_{\alpha}) = 0.71073 \text{ Å}, \text{ graphite}$ monochromator and  $\omega$  scans for both experiments]. Because crystals of II and III lose the guest CH<sub>3</sub>CN molecules very quickly and become unsuitable for crystallographic studies, a single crystal was taken from the mother liquor and immediately transferred into the cold nitrogen stream (200 K) on the diffractometer using nylon loop. The data sets for crystals of both II and III were collected at 120 K and treated by CrysAlisPro software for cell refinement, data collection, and data reduction with empirical absorption correction (Scale3AbsPack) of the experimental intensities.<sup>[12]</sup> The structure was solved by direct methods followed by Fourier syntheses and refined by a full-matrix least-squares method in an anisotropic approximation for all non-hydrogen atoms by using the SHELX-97 program.<sup>[13]</sup> The positions of the hydrogen atoms were calculated geometrically. The crystallographic data for II and III are summarized in Table 4.

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	II	III
Formula	C46H51Cl6Co2Mn3N11O6	C <sub>48</sub> H <sub>54</sub> Br <sub>6</sub> Co <sub>2</sub> Mn <sub>3</sub> N <sub>12</sub> O <sub>6</sub>
$M_{\rm r}$	1349.36	1657.17
Space group	$P\overline{1}$	ΡĪ
Ζ	2	2
a [Å]	10.8169(4)	10.6605(6)
b [Å]	14.6619(5)	13.5281(7)
c [Å]	19.6679(7)	21.853(1)
a [°]	71.249(3)	88.687(4)
β [°]	84.527(3)	89.165(4)
γ [°]	72.776(3)	75.299(5)
V[Å <sup>3</sup> ]	2821.2(2)	3047.5(3)
$\rho$ [g/cm <sup>3</sup> ]	1.588	1.806
$\mu$ [cm <sup>-1</sup> ]	15.68	51.25
$\Theta$ range [°]	4.56-30.51	4.59-27.1
N <sub>tot.</sub>	50405	20508
Nindep.	17137	12783
$R_{\rm int}, R_{\sigma}$	0.032, 0.026	0.041, 0.06
N <sub>param.</sub>	672	700
S	1.05	0.961
$R_1 \left[I > 2\sigma(I)\right]$	0.032	0.04

CCDC-937888 (for II) and -937889 (for III) contain 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.

**Computational Details:** All calculations were performed on XRD geometries. The parameters of the exchange coupling, *J*, were calculated by using the spin-unrestricted broken-symmetry approach<sup>[14]</sup> at the UBP86 level of theory<sup>[15]</sup> with the small def2-SVP bases set<sup>[16]</sup> using the ORCA program package.<sup>[17]</sup> Some values were recalculated at the more convenient UB3LYP level<sup>[18]</sup> with the larger def2-TZVP basis set.<sup>[19]</sup> The *J* values were calculated by using Equation (3)<sup>[20]</sup>

$$J = -\frac{E^{HS} - E^{LS}_{BS}}{\left\langle S^2 \right\rangle^{HS} - \left\langle S^2 \right\rangle^{LS}_{BS}} \tag{3}$$

in which  $E^{\text{HS}}$  is the energy of the high-spin state of the pair and  $E^{\text{LS}}_{\text{BS}}$  is the energy of the low-spin state within the broken-symmetry (BS) approach.

The g and D tensors of the  $Mn^{II}$  complexes were calculated by using the coupled-perturbed spin–orbit coupling (CP-SOC) approach<sup>[21]</sup> implemented in the ORCA package and hybrid UB3LYP functional with the SVP basis set (TZVP basis set for selected calculations). To calculate the magnetic properties of the core  $Mn^{II}$ ion, one of the  $Mn^{II}$  ions of the cluster was replaced by a diamagnetic Zn<sup>II</sup> ion.

**Supporting Information** (see footnote on the first page of this article): TG, DTG, DSC, and MS curves for freshly prepared complex **III**, dried complex **II** after storage in air, crystal packing diagrams for complexes **II** and **III** showing intermolecular contacts, molecular structures of the anions of complexes **II** and **III**, and details of the DFT and ab initio calculations of the g and ZFS tensors for Mn<sup>II</sup> ions of the complexes **II** and **III**.

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$$\chi = \frac{\chi_0}{1 - \frac{2zJ'}{Ng^2\mu_R^2}\chi_0}$$
(4)

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