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Decanuclear Manganese Isobutyrate Clusters Featuring a Novel $Mn^{II}_8Mn^{III}_2$ Core

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Recrystallization of freshly prepared Mn^{II} isobutyrate from PrOH or from EtOH/MeCN mixtures containing pyrazole (pyr) yields neutral mixed-valence decanuclear manganese(II/III) complexes, $[Mn_{10}O_2(O_2CCHMe_2)_{18}(HO_2CCHMe_2)_2(PrOH)_2]$ (**1**) and $[Mn_{10}O_2(O_2CCHMe_2)_{18}(pyr)_4]$ (**2**). The Mn_{10} metal core of both **1** and **2** consists of eight Mn^{II} and two Mn^{III} centers and represents a new motif in the structural organization of polynuclear mixed-valence manganese clusters. Both, **1** and **2** exhibit a net antiferromagnetic exchange coupling resulting in singlet ground states.

Introduction

Within the research on high-nuclearity coordination compounds polynuclear manganese coordination clusters remain a very fruitful area, motivated by the intriguing structural complexity (with nuclearities up to 84),[1] the relevance to bioinorganic functionality,[2] and a tendency of mixed-valence derivatives to exhibit slow magnetization relaxation and quantum tunneling, features characteristic of single-molecule magnets.[3] The latter field in particular has sparked enormous activity since the $Mn^{III/IV}$ compound $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$ was identified as a prototypal single-molecule magnet.[4]

Recently, we aimed to probe whether the use of bulky, flexible ligands such as isobutyrate could result in novel Mn cluster structures, motivated by the success of a similar kinetic "shrink-wrapping" approach in polyoxometalate chemistry.[5] Therefore, we investigated the reactions of manganese(II) isobutyrate, $Mn(O_2CCHMe_2)_2$, with polypyridyl ligands, leading e.g. to the formation of trinuclear linear $[Mn^{II}_3(O_2CCHMe_2)_6(N\text{-}N)_2]$ complexes (N-N = 1,10′-phenanthroline,[6] 2,2′-bipyridine[6] or 2,2′-dipyridylamine[7]) or chain coordination polymers $\{[Mn^{II}_3(O_2CCHMe_2)_6(bpm)]\cdot 2EtOH\}_n$, $[Mn^{II}_2Mn^{III}_2O_2(O_2CCHMe_2)_6(bpm)(EtOH)_4]_n$, and $\{[Mn^{II}Mn^{III}_2O(O_2CCHMe_2)_6(hmta)_2]\cdot EtOH\}_n$ when bridging ligands such as 2,2′-bipyrimidine (bpm) or hexamethylentetramine (hmta) were used.[7] Continuing these studies, we here present a uniform route to higher-nuclearity neutral, mixed-valence (Robin-Day class I) $Mn^{II/III}$ clusters based on isobutyric acid, $[Mn_{10}O_2(O_2CCHMe_2)_{18}(HO_2CCHMe_2)_2(PrOH)_2]$ (**1**) and $[Mn_{10}O_2O_2CCHMe_2)_{18}(pyr)_4]$ (**2**) (pyr = pyrazole). The structures of **1** and **2** comprise condensed core structures, with the motif differing from common structures in Mn coordination clusters.

Results and Discussion

Air oxidation and recrystallization of freshly prepared Mn^{II} isobutyrate from *n*-propanol yields an $\{Mn_{10}\}$ cluster, $[Mn_{10}O_2(O_2CCHMe_2)_{18}(HO_2CCHMe_2)_2(PrOH)_2]$ (**1**), isolated as propanol solvate **1**·2PrOH or water solvate **1**·2H_2O, and comprising eight Mn^{II} and two Mn^{III} ions. Interaction of $Mn(O_2CCHMe_2)_2$ and pyrazole in the mixture of EtOH and MeCN led to $[Mn_{10}O_2(O_2CCHMe_2)_{18}(pyr)_4]$ (**2**), isolated as **2**·2MeCN, which forms a very similar decanuclear core structure.

Single-crystal X-ray analysis of **1** and **2** reveals an elongated twisted complex of approximate S_4 symmetry in both compounds, consisting of ten manganese sites bridged by two central μ_4-O and twelve μ_3-Me_2CHCO_2 groups, with one carboxylate O center bridging two Mn centers and the other O site ligating a third Mn ion. Six other carboxylate groups bind in μ_2 modes. The molecular structures of **1** and **2** are shown in Figures 1 and 2, respectively, and full numbering schemes for these structures are given in the Supporting Information (Figures S1 and S2) along with packing diagrams for **1**·2PrOH, **1**·2H_2O and **2**·2MeCN. Selected bond lengths/angles are given in Tables S2–S4.

The Mn_{10} cores (Figures 1b and 2) are based on a central Mn_6O_2 unit containing two μ_4-O sites, resulting in one par-

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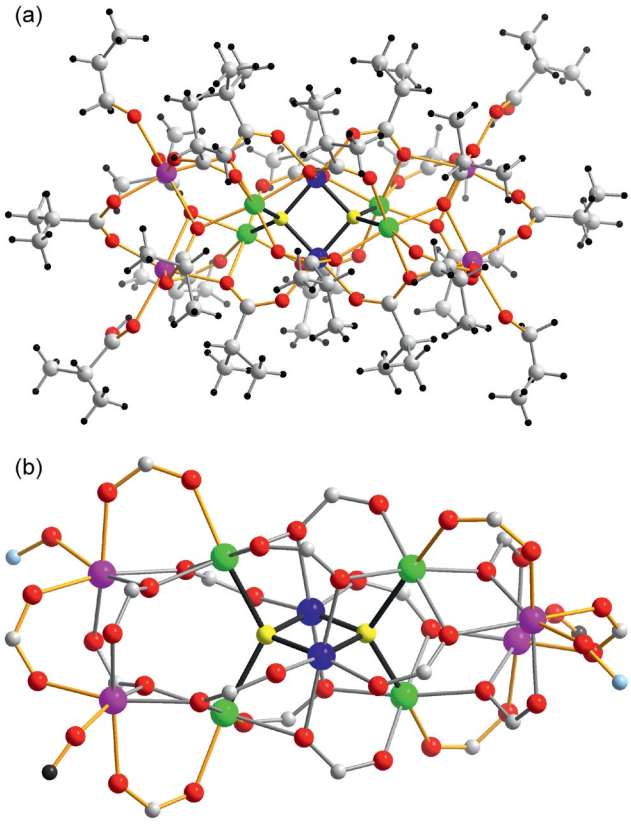

Figure 1. (a) Ball-and-stick representation of the $\{Mn_{10}\}$ cluster **1**. Propyl groups (in gray; H: black) define the solvent-accessible, lipophilic surface of the neutral cluster. (b) Simplified representation of the central Mn coordination environments emphasizing ligand connectivities. The central Mn_6O_2 core (Mn^{III}: blue; Mn^{II}: green; μ_4-O: yellow; μ_4-O–Mn: black bonds) is terminated by four μ_3-*i*PrCOO groups (gray bonds), four more μ_3-*i*PrCOO and six μ_2-*i*PrCOO groups bind the outer Mn^{II} centers (purple). Terminal ligands at these sites are represented by light blue (*n*PrOH) and dark gray (*i*PrCOO) sites.

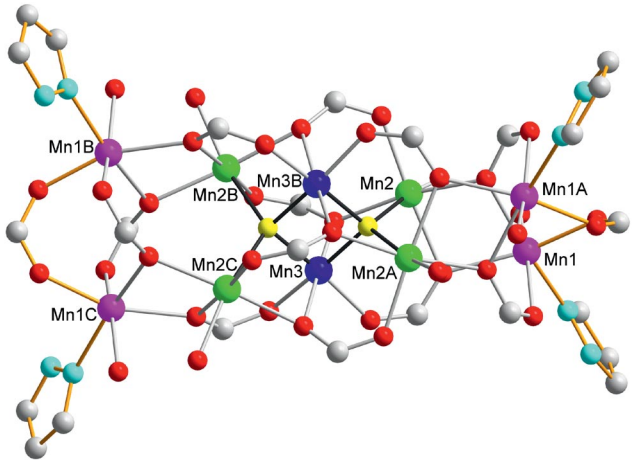

Figure 2. Ball-and-stick representation of the $\{Mn_{10}\}$ cluster **2**. Me_2CH groups and hydrogen atoms are omitted for clarity. Atom color codes as in Figure 1; N: light blue. Pyrazole ligands are coordinated to the outer Mn^{II} centers (purple). Symmetry equivalents: A: $-x + 1$, y, $-z + 3/2$; B: $-x + 1$, $-y + 3/2$, z; C: x, $-y + 3/2$, $-z + 3/2$.

ticularly short separation of the central two Mn sites of 2.791(3) Å for **1** and 2.773(4) Å for **2**. Bond valence sums (BVS; Table S5) identify these two sites as Mn^{III} [**1**: Mn–O distances: 1.873(6)–2.235(8) Å, avg. BVS: 3.019; **2**: Mn–O distances: 1.883(5)–2.201(5) Å, avg. BVS: 3.159]. All other Mn sites are assigned as Mn^{II} with longer Mn–O bond lengths [**1**: Mn–O 2.089(9)–2.279(7) Å, avg. BVS: 1.860; **2**: Mn–O 2.103(6)–2.243(3) Å, avg. BVS: 1.937].[8] Note that this Mn_6O_2 motif is common to several other Mn clusters or coordination polymers.[9] Four peripheral Mn^{II} centers expand this Mn_6 core in **1** and **2**, each connected to one of the four outer Mn sites of the Mn_6O_2 core by two η^1,μ_2-carboxylate groups.

Whereas the slightly distorted octahedral environments of the central six Mn sites are completed by ligation of μ_4-O and carboxylate ligands, in **1** one *n*-propanol ligand binds to each of the four outer Mn positions, in addition to bridging and terminal isobutyrate ligands [Mn–O distances: 2.089(9)–2.276(7) Å]. The latter are both protonated and participate in intra- and intermolecular hydrogen bonding. Within the accuracy limits of the X-ray data, terminal carboxylate groups display elongated C–O distances [1.318(2) and 1.325(2) Å], which corresponds to the OH group of coordinated, neutral isobutyric acid, with the protons involved in hydrogen bonds to neighboring isobutyrates [O41···O43 2.559(2) and O44···O21 2.551(2) Å]. *n*PrOH ligands form hydrogen bonds to lattice *n*PrOH molecules with the distance of 2.690(3) Å (O33···O45), which are also involved in hydrogen bonds with the nearest isobutyrate groups [O45···O26 2.809(4) Å].

In contrast, in complex **2** all four outer Mn sites (Mn1, Mn1A, Mn1B and Mn1C) are situated in distorted octahedral NO_5 coordination environments comprised of five oxygen atoms from bridging isobutyrates [Mn–O 2.089(9)–2.276(7) Å] and a nitrogen atom of the pyrazole ligand [Mn–N 2.242(9) Å].

Based on the charge neutrality of **1** and **2** and the BVS (Table S5 in Supporting Information) the Mn oxidation states in the core are assigned as $Mn^{II}_8Mn^{III}_2$. Until now, a few decanuclear Mn complexes have been reported with $Mn^{II}_2Mn^{III}_8$,[10] $Mn^{II}_2Mn^{III}_8Na$,[11] $Mn^{II}_4Mn^{III}_6$,[12–15] $Mn^{II}_6Mn^{III}_4$,[16] Mn^{III}_{10},[17–21] $Mn^{III}_4Mn^{IV}_6$,[22] and Mn^{II}_{10} configurations,[23] but no $Mn^{II}_8Mn^{III}_2$ core has yet been reported.

Magnetic Properties

Measurements of the low-field magnetic susceptibility data for compounds **1**·2PrOH and **2**·2MeCN in the temperature range 2–290 K indicate dominating antiferromagnetic exchange coupling (Figure 3). At 290 K the effective magnetic moments for **1**·2PrOH and **2**·2MeCN reach values of 15.8 and 16.8, respectively. Both high-temperature values are slightly lower than the expected spin-only value of 19.12 for ten isolated magnetic centers (8 Mn^{II} with $s = 5/2$ and 2 Mn^{III} with $s = 2$ and $g_{iso} = 2.0$; horizontal dashed line in Figure 3). For both compounds **1** and **2** μ_{eff} continually

decreases towards lower temperatures (μ_{eff} = 3.56 at 2.0 K) due to antiferromagnetic exchange coupling, which correspondingly results in a maximum in the molar susceptibility χ_m at T_{max} = 8.0 K (**1**) and 9.0 K (**2**). For both **1** and **2**, the susceptibility data follows a Curie–Weiss-type expression with Weiss temperatures of Θ(**1**·2PrOH) = –21.9 K and Θ(**2**·2MeCN) = –25.8 K (determined for 50 K < T < 300 K). Dominant antiferromagnetic exchange is also observed for other mixed-valence $\{Mn^{II/III}_{10}\}$-type clusters.[10,14,22]

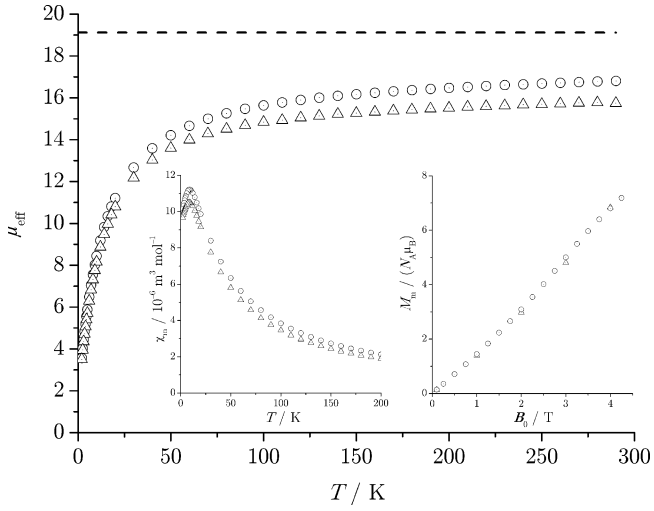

Figure 3. Experimental μ_{eff} vs. T plots (SI units) of **1**·2PrOH (circles) and **2**·2MeCN (triangles) at B_0 = 0.1 Tesla. Insets: χ_m vs. T (at 0.1 Tesla) and M vs. B_0 (at 2.0 K). The dashed horizontal graph represents the spin-only value for an uncoupled system of eight spin-5/2 and two spin-2 centers.

The existence of seven nearest-neighbor exchange pathways (assuming maximum symmetry of the Mn_{10} core) and, thus, seven exchange energies J_1–J_7 (Table S6) preclude a meaningful least-squares fit to a model Hamiltonian based on the available susceptibility data due to overparametrization. Note that even with additional magnetic data (e.g. inelastic neutron scattering, high-field magnetization and high-field EPR) the complexity of the coupling scheme in both clusters renders an unambiguous quantitative analysis of the magnetic properties nearly impossible. This problem is aggravated by the fact that several possibly competing exchange pathways are involved in the individual interactions between the Mn centers. However, based on the near-linear field dependence of the magnetization (Figure 3, inset), we postulate singlet ground states for **1** and **2**.

Conclusions

Bulky ligands such as isobutyrate allow access to new high-nuclearity $Mn^{II/III}$ cluster types such as **1** and **2** with a lipophilic surface (and corresponding solubilities in non-polar media) and an unprecedented Mn^{II}/Mn^{III} ratio. The structure-directing effect of these ligands is also evident from similar reactions employing less flexible ligands such as, for example, acetate, which results in entirely different coordination structures, in the case of acetate in an $\{Mn_4\}$-based coordination polymer.[24] The magnetism of clusters **1** and **2** is complex due to a multitude of coupling pathways and ligand-field effects and is characterized by overall antiferromagnetic coupling and singlet ground states.

Supporting Information (see footnote on the first page of this article): Experimental section, IR spectra, TGA/DTA graphs, packing diagrams, selected bond lengths and angles, BVS calculations, crystal data and structural refinements details.

CCDC-691857 (**1**·2PrOH), -698242 (**1**·2H_2O), and -717551 (**2**·2MeCN) 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.

Acknowledgments

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