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Two Novel Heterometallic Chains Featuring Mn^{II} and Na^{I} Ions in Trigonal-Prismatic Geometries Alternately Linked to Octahedral Mn^{IV} Ions: Synthesis, Structures, and Magnetic Behavior

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Supporting Information

ABSTRACT: Two new one-dimensional heterometallic complexes, $[Mn_3Na(L)_4(CH_3CO_2)(MeOH)_2](ClO_4)_2 \cdot 3H_2O$ (**1**), $[Mn_3Na(L)_4(CH_3CH_2CO_2)(MeOH)_2](ClO_4)_2 \cdot 2MeOH \cdot H_2O$ (**2**) [LH_2 = 2-methyl-2-(2-pyridyl)propane-1,3-diol], have been synthesized and characterized by X-ray crystallography. Both complexes feature Mn^{II} and Na^{I} ions in trigonal-prismatic geometries that are linked to octahedral Mn^{IV} ions by alkoxy bridges. Variable-temperature direct- and alternating-current magnetic susceptibility data indicated a spin ground state of $S = {}^{11}/_{2}$ for both complexes. Density functional theory calculations performed on **1** supported this conclusion.

In the last 2 decades, a considerable ongoing research has been directed toward polynuclear manganese complexes in various oxidation states. Primarily, investigations have been concentrated on their novel magnetic properties, namely, the single-molecule-magnetic behavior and associated quantum properties.[1] However, from a structural point of view alone, these polynuclear complexes of different shape, size, and dimensionalities make a very interesting study. At the root of these intriguing structures are the coordination spheres of the metal ions, dominated by the octahedral geometry. So, naturally there is still a high degree of interest in the atypical hexacoordinating trigonal-prismatic geometry especially in molecular complexes.[2] The high-spin (HS) Mn^{II} d^5 ion has been particularly well studied because its reorganizing energy for the two extreme geometries is quite low.[3] However, the trigonal prism still remains an elusive geometry, and the factors preventing or permitting this geometry are not always clear.[2]

Herein, we report two novel one-dimensional (1D) heterometallic complexes, $[Mn_3Na(L)_4(CH_3CO_2)(MeOH)_2](ClO_4)_2 \cdot 3H_2O$ (**1**) and $[Mn_3Na(L)_4(CH_3CH_2CO_2)(MeOH)_2](ClO_4)_2 \cdot 2MeOH \cdot H_2O$ (**2**) [LH_2 = 2-methyl-2-(2-pyridyl)propane-1,3-diol[1k,l]], both featuring octahedral Mn^{IV} ions linked alternately to one trigonal-prismatic Mn^{II} ion and even more interestingly to one trigonal-prismatic Na^{I} ion. The complexes are essentially identical in structure and magnetic behavior, showing a weak ferromagnetic interaction among the neighboring Mn ions. Density functional theory (DFT) studies were also carried out, which supported the $S = {}^{11}/_{2}$ ground state.

Both complexes were crystallized by slow evaporation of a stirred mixture of the triangles $[Mn_3O(CH_3CO_2)_6(py)_3](ClO_4)$ (for **1**), $[Mn_3O(C_2H_5CO_2)_6(py)_3](ClO_4)$ (for **2**), LH_2, Et_3N, and $NaClO_4$ in MeOH. It is interesting to note that the starting complexes contain only Mn^{III} ions, which implies that a disproportionation reaction takes place.

Single-crystal X-ray diffraction (XRD) data showed that both complexes belong to the monoclinic space group *C*2 (see the Supporting Information for details), having essentially identical structures except from the different acid residues. The basic unit contains two unique Mn ions and one Na ion, forming an infinite chain in which Mn1 is alternatively linked to Mn2 and Na1 atoms by alkoxy bridges (Figures 1 and 2). Bond-valence-sum calculations suggest that Mn1 is in a 4+ oxidation state and Mn2 is in a 2+ oxidation state (Supporting Information).[4]

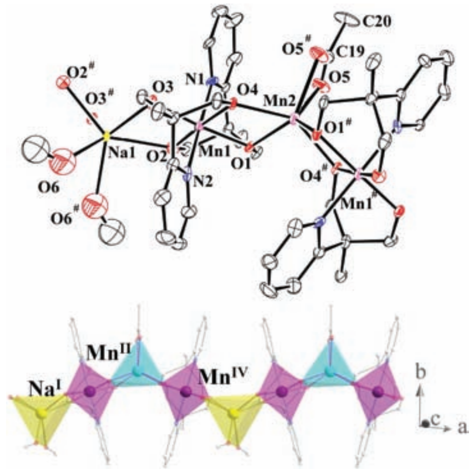

Figure 1. (Top) ORTEP view of the basic unit of **1** (thermal ellipsoids are at the 25% probability level). (Bottom) 1D assembly with coordination geometries. Hydrogen atoms, ClO_4^- ions, and solvent molecules have been removed for clarity. Symmetry code: #1, −*x*, *y*, −*z*.

The geometry around Mn1 is octahedral, with two tridentate L ligands occupying two opposite faces of the octahedron, with the two pyridyl nitrogen atoms in the longer axial sites [Mn1−N1, 1.998(7) Å, and Mn1−N2, 2.023(8) Å, for **1**] and four alkoxy oxygen atoms taking the equatorial positions [Mn1−O_{eq}, 1.812(6)−1.898(5) Å, for **1**]. Two of these oxygen atoms (O1 and O4) are linked on one side to a Mn2 atom, and the other two (O2 and O3) are linked to a Na1 atom. Both Mn2

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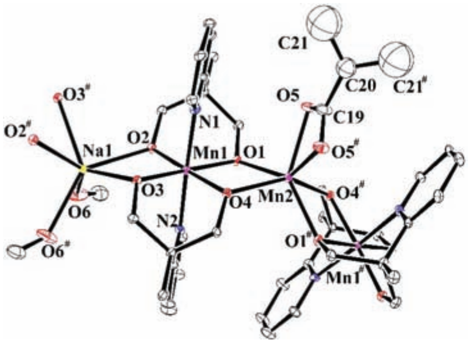

Figure 2. ORTEP view of the basic unit of **2** (thermal ellipsoids are at the 20% probability level). Hydrogen atoms, ClO_4^- ions, and solvent molecules have been removed for clarity. Symmetry code: #1, $-x$, y, $-z$. Note that the bond between C19 and C20 coincides with a 2-fold axis that generates an extra C21 atom in the propionate residue.

and Na1 sit on a 2-fold axis and have very slightly distorted trigonal-prismatic geometries (Figure 3). The trigonal faces of

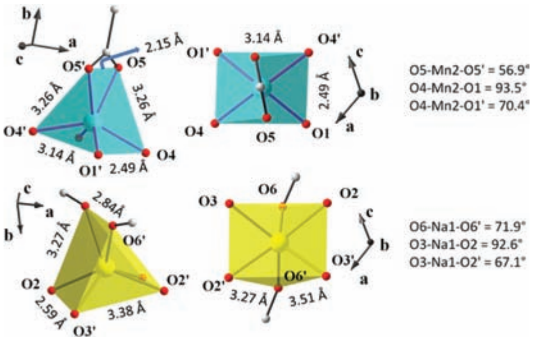

Figure 3. Coordination geometries of Mn^{II} (cyan) and Na^{I} (yellow) ions in complex **1**, with some important geometrical parameters.

Mn2 are occupied by two alkoxy oxygen atoms (O1 and O4) from two sides that bridge with neighboring Mn1 atoms and one oxygen atom (O5) from the acid residue (acetate for **1**; propionate for **2**), with the bonds in the range 2.154(5)–2.252(7) Å (for **1**). The trigonal faces of the Na1-centered prism are occupied by two alkoxy oxygen atoms (O2 and O3) bridging to neighboring Mn1 atoms and one oxygen atom (O6) from a methanol molecule, with the bonds in the range 2.317(6)–2.42(2) Å (for **1**). For both Mn2 and Na1, the trigonal faces are closer than expected for an ideal trigonal-prismatic geometry, but the faces are only very slightly twisted from the ideal value of 0° (see the Supporting Information for details).

To the best of our knowledge, **1** and **2** are the first molecular complexes to feature sodium ions in this unique geometry. However, Mn^{II} ions do appear in geometries that lie closer to the trigonal-prismatic structure, but most of them are mononuclear or have softer coordinating atoms.[3] The general explanation for this geometry changeover is not always clear, but for the HS d^5 ion, the energy barrier is expected to be very low (no LFSE loss). For **1** and **2**, however, a very distinct packing effect is seen, when the bond lengths and angles are closely examined. $Mn1^{IV}$ is joined to $Mn2^{II}$ by O1 and O4 atoms, which take up the cis positions in the equatorial plane of Mn1, are bonded quite strongly to the highly charged ion with small bond lengths (~1.9 Å), and create only an angle of ~82° at the metal center. So, O1 and O4 can be considered to be fixed in space at a distance of ~2.5 Å (behaving as a bidentate ligand with a small bite angle) from each other, and bonds with Mn2 with these two atoms are expected to be quite longer (~2.2 Å) because Mn^{II} has a higher ionic radius. Hence, the two oxygen atoms cannot produce an angle near 80–90° at the Mn2 center, and this is also true for the other two oxygen bridges from the opposite side. So, Mn2 fails to adopt an octahedral geometry, but it can still take an acid residue to compensate for it by having six bonds around in a trigonal-prismatic fashion.

The variable-temperature (1.8–300 K) magnetic susceptibility data for **1** and **2** were measured under a 0.2 T applied field. The magnetic behaviors of **1** and **2** are essentially identical, and therefore those of the former will be discussed in detail (for **2**, the data can be found in the Supporting Information). The obtained data for **1** are shown in Figure 4 as both χ_M versus T and $\chi_M T$ versus T plots. The room temperature $\chi_M T$ value of 8.14 cm^3 K mol^{-1} is just above the expected (8.125 for $g = 2$) value for a noninteracting $Mn^{IV}{}_2Mn^{II}$ unit. The $\chi_M T$ value gradually increases upon a lowering of the temperature and shows a rapid jump below 100 K, to reach a maximum value of 16.15 cm^3 K mol^{-1} at 8 K. Below this temperature, the $\chi_M T$ value rapidly drops to 10.10 cm^3 K mol^{-1} at 1.8 K, probably because of saturation effects or weak intercluster interactions. Above 50 K, the $1/\chi_M$ versus T plot obeys the Curie–Weiss law with θ = 19.4(4) K, which along with the nature of the $\chi_M T$ versus T plot suggests a dominant ferromagnetic interaction among the metal ions.

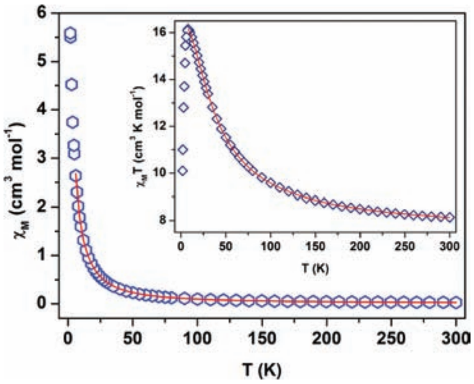

Figure 4. Plots of χ_M versus T and $\chi_M T$ versus T (inset) for **1** in the temperature range 1.8–300 K. The red lines indicate the fitting using the theoretical model (see the text and Supporting Information).

The symmetry of the trinuclear basic magnetic unit implies that the magnetic exchange can be described by a single exchange parameter J (Mn^{IV}–J–Mn^{II}–J–Mn^{IV}). The Heisenberg spin Hamiltonian for this exchange scheme is given by

$$H = -J(S_1 \cdot S_2 + S_2 \cdot S_3)$$

In this Hamiltonian, $S_1 = S_3 = {}^3/_2$ and $S_2 = {}^5/_2$, and the effect of zero-field splitting has not been considered. A theoretical expression for χ_M was derived using the van Vleck equation and assuming an isotropic g value (fittings of both χ_M versus T and $\chi_M T$ versus T in the whole temperature range are provided in the Supporting Information). The least-squares fitting of the experimental data above 7 K gives J = 8.12(19) cm^{-1} and g = 1.898(2) with $R = 6.76 \times 10^{-5}$ for **1** and J = 7.90(25) cm^{-1} and g = 1.912(3) with $R = 1.28 \times 10^{-4}$ for **2**.

Variable-field magnetization measurements (up to 7 T) at 1.8 K did not show any hysteresis (Figure 5), but the reduced magnetization value quite rapidly saturates to ∼11 Nβ, suggesting a spin ground state of $S = {}^{11}/_2$, which is expected for ferromagnetically aligned spins of two Mn^{IV} (${}^3/_2$) ions and one Mn^{II} (${}^5/_2$) ion. The plots of the magnetization data as a function of the temperature (1.8−10 K) in varying fields (1−7 T) showed no evidence for the presence of anisotropy (Supporting Information). To further probe the ground state, ac susceptibility data were collected for both complexes in the 1.8−15 K range using a 5 G ac field oscillating at frequencies in the 10−1000 Hz range. The ac in-phase $\chi'_{\text{M}}T$ values for both complexes slowly rise from 15 K up to about 8 K, clearly heading to ∼16 cm^3 K mol^{-1} at 0 K (Figure 5), which is consistent with a $S = {}^{11}/_2$ ground state (the expected value with $g = 1.9$ is 16.13), and a small dip is observed below 8 K (frequency-independent) because of weak intercluster interactions.[5]

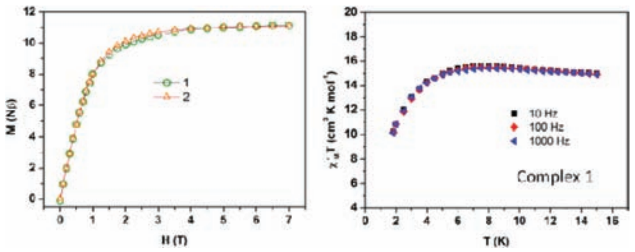

Figure 5. Plots of *M* versus *H* data at 1.8 K for **1** and **2** (left) and the in-phase ac susceptibility data plotted as $\chi'_{\text{M}}T$ versus *T* in the range 1.8−15 K at the indicated frequencies for **1** (right).

DFT (UB3LYP and LANL2DZ) calculations of the $\text{Mn}^{\text{II}}\text{Mn}^{\text{IV}}_2$ unit in **1** show that the spin ground state is $S = {}^{11}/_2$ (Figure S10). The complex nature of the spin structures and the relative energies of the six spin states ($2S + 1 = 2, 4, 6, 8, 10, 12$) make it rather difficult to obtain a reliable value for the exchange parameter *J*.[6]

In summary, two new heterometallic 1D complexes have been synthesized, in which a Mn^{IV} ion bonded to 2 equiv of the pyridyldialkoxide ligand generates trigonal-prismatic pockets on both sides occupied by Mn^{II} and Na^{I} ions. The resulting Mn^{IV}−Mn^{II}−Mn^{IV} units exchange ferromagnetically to give a spin ground state of ${}^{11}/_2$. This work demonstrates that the rare hexacoordinate trigonal-prismatic geometry can be accessed by introducing geometrical constraints by suitable choices of ligands, and not only transition metals but also alkali metals can adopt this geometry in molecular complexes. We are currently investigating the unique properties of the $[\text{Mn}^{\text{IV}}(\text{L})_2]$ moiety by substituting the sodium ion with other alkali metals and the Mn^{II} ion with other transition-metal ions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, details of experimental procedures, powder XRD data, dc and ac magnetic data with fitting, and the results of DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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