Supporting Information

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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Experimental Section

Synthesis

$[\text{Mn}_3\text{O}(\text{CH}_3\text{CO}_2)_6(\text{py})_3]\text{ClO}_4$, $[\text{Mn}_3\text{O}(\text{CH}_3\text{CH}_2\text{CO}_2)_6(\text{py})_3]\text{ClO}_4$ and the ligand LH_2 were prepared as described earlier in the literature.¹

Complex 1. To a 10 mL MeOH solution of $[\text{Mn}_3\text{O}(\text{CH}_3\text{CO}_2)_6(\text{py})_3](\text{ClO}_4)$ (0.25 mmol, 218 mg) a 5 mL methanolic solution of LH_2 (0.5 mmol, 84 mg) was added slowly. After stirring this mixture for 10 minutes 1 mmol of Et_3N (101 mg) and 1 mmol (141 mg) of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ were added and stirred for 1 hour. Slow evaporation of the resulting brown solution (after filtration) gave thin rectangular shaped brown crystals within 48 hours. Isolated Yield: ~ 25 % (based on Mn). Anal. Calcd for **1**, $\text{C}_{40}\text{H}_{61}\text{N}_4\text{O}_{23}\text{Cl}_2\text{Mn}_3\text{Na}$: C, 39.23; H, 5.02; N, 4.57. Found: C, 39.01; H, 5.22; N, 4.61. Selected IR data (KBr, cm^{-1}): 3337(broad), 2839(m), 1598(s), 1560(s), 1470(s), 1290(m), 1167(m), 1082(vs), 1041(vs).

Complex 2. Thin brown rectangular shaped crystals of **2** were obtained by a similar method using $[\text{Mn}_3\text{O}(\text{CH}_3\text{CH}_2\text{CO}_2)_6(\text{py})_3](\text{ClO}_4)$ (0.25 mmol, 222 mg) instead of the acetate triangle. Isolated Yield: ~ 20 % (based on Mn). $\text{C}_{43}\text{H}_{67}\text{N}_4\text{O}_{23}\text{Cl}_2\text{Mn}_3\text{Na}$: C, 40.77; H, 5.33; N, 4.42. Found: C, 40.47; H, 5.55; N, 4.52. Selected IR data (KBr, cm^{-1}): 3342(broad), 2837(m), 1600(s), 1542(s), 1469(s), 1292(m), 1166(m), 1081(vs), 1043(vs).

Physical Measurements. Elemental analyses of C, H, and N were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded as KBr pellets using a Magna 750 FT-IR spectrophotometer. The measurements of variable-temperature magnetic susceptibility were carried out on a Quantum Design MPMS-XL7 SQUID magnetometer. The experimental susceptibility data were corrected for diamagnetism (Pascal's tables).²

X-Ray Crystallographic Data Collection and Refinements. Single crystal X-ray data for **1** and **2** were collected on a Bruker SMART APEX CCD diffractometer using the SMART/SAINT software.³ Intensity data were collected using graphite-monochromatized Mo-K α radiation (0.71073 Å) at 293 K. The structures were solved by direct methods using the SHELX-97⁴ program incorporated into WinGX.⁵ Empirical absorption corrections were applied with SADABS.⁶ All non-hydrogen atoms were refined with anisotropic displacement coefficients (in a few cases the disordered atoms were treated isotropically). The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Crystallographic data and refinement parameters are been shown in Table S1, and important inter-atomic distances and angles are given in Table S2.

Table S1. Crystallographic Data and Refinement Parameters for **1** and **2**.

	1	2
empirical formula	C ₄₀ H ₆₁ N ₄ O ₂₃ Cl ₂ Mn ₃ Na	C ₄₃ H ₆₇ N ₄ O ₂₃ Cl ₂ Mn ₃ Na
Fw	1224.63	1266.71
<i>T</i> (K)	293 (2)	293(2)
crystal system	monoclinic	monoclinic
space group	<i>C</i> 2	<i>C</i> 2
<i>a</i> /Å	12.856(2)	12.847(3)
<i>b</i> /Å	22.321(4)	22.558(5)
<i>c</i> /Å	10.5277(14)	10.458(2)
β /deg	120.980(4)	120.78(3)
<i>V</i> /Å ³	2590.1(7)	2603.8(13)
<i>Z</i>	2	2
ρ_{calcd} (g cm ⁻³)	1.573	1.630

μ (Mo K α) (mm ⁻¹)	0.917	0.916
$\lambda/\text{\AA}$	0.71073	0.71073
F (000)	1254.0	1308.0
collected reflns	14733	6565
unique reflns	7450	3890
GOF (F^2)	0.974	1.059
R_I^a	0.0752	0.0606
wR_2^b	0.2334	0.1665

Table S2. Selected Bond Distances (Å) and Angles (°) for **1** and **2** in the **1/2** format.

Mn(1)-O(1)	1.898(5)/1.899(4)	Mn(1)-O(2)	1.812(6)/1.841(5)
Mn(1)-O(3)	1.841(5)/1.845(4)	Mn(1)-O(4)	1.893(5)/1.895(5)
Mn(1)-N(1)	1.998(7)/2.005(6)	Mn(1)-N(2)	2.023(8)/2.009(5)
Mn(2)-O(1)	2.156(5)/2.166(5)	Mn(2)-O(1) ^{#1}	2.156(5)/2.166(5)
Mn(2)-O(4)	2.154(5)/2.139(4)	Mn(2)-O(4) ^{#1}	2.154(5)/2.139(4)
Mn(2)-O(5)	2.252(7)/2.251(5)	Mn(2)-O(5) ^{#1}	2.252(7)/2.251(5)
Na(1)-O(2)	2.317(6)/2.332(5)	Na(1)-O(2) ^{#2}	2.317(6)/2.332(5)
Na(1)-O(3)	2.360(6)/2.419(5)	Na(1)-O(3) ^{#2}	2.360(6)/2.419(5)
Na(1)-O(6)	2.42(2)/2.370(7)	Na(1)-O(6) ^{#2}	2.42(2)/2.370(7)
Mn(1)-Mn(2)	3.184(2)/3.171(2)	Mn(1)-Na(1)	3.218(2)/3.291(2)
O(1)-Mn(1)-O(2)	93.7(3)/93.8(2)	O(2)-Mn(1)-O(3)	90.1(3)/88.5(2)
O(3)-Mn(1)-O(4)	94.3(2)/95.3(2)	O(4)-Mn(1)-O(1)	81.9(2)/82.5(2)
O(1)-Mn(2)-O(4)	70.4(2)/71.1(2)	O(1) ^{#1} -Mn(2)-O(4) ^{#1}	70.4(2)/71.1(2)
O(5)-Mn(2)-O(5) ^{#1}	56.9(4)/58.3(3)	O(2)-Na(1)-O(3)	67.1(2)/65.5(2)
O(2) ^{#2} -Na(1)-O(3) ^{#2}	67.1(2)/65.5(2)	O(6) ^{#2} -Na(1)-O(6)	71.8(9)/76.9(4)

Symmetry transformations used to generate equivalent atoms: ^{#1} -x,y,-z. ^{#2} -x+1,y,-z+1.

Table S3. Bond Valence Sum (BVS)^a calculations for Mn of **1** and **2** in the **1/2** format.

atom	Mn ^{II}	Mn ^{III}	Mn ^{IV}
Mn1	4.39/4.09	4.09/4.00	<u>4.17/4.29</u>
Mn2	<u>1.92/1.95</u>	1.76/1.79	1.85/1.88
^a The underlined value is the one closest to the charge for which it was calculated. The oxidation state can be taken as the nearest whole number to the underlined value. ⁷			

Computational Methodology

The single point energies of the six possible spin states were calculated for **1** forming the geometry of the Mn₃ unit from the crystallographic data (Figure S7), by density functional theory. The hybrid B3LYP functional⁸ has been used in all calculations as implemented in *Gaussian 03* package,⁹ mixing the exact Hartree-Fock-type exchange with Becke's expression for the exchange functional¹⁰ and that proposed by Lee-Yang-Parr for the correlation contribution.¹¹ The use of the nonprojected energy of the broken-symmetry solution as the energy of the low spin state within the DFT framework provides more or less satisfactory results avoiding the cancellation of the nondynamic correlation effects.¹² The broken symmetry approach along with electron correlations at the B3LYP level has been widely used to investigate magnetic properties in a large number of magnetic systems. We have used LanL2DZ basis set for all the atoms. All of the energy calculations were performed including 10⁻⁸ density-based convergence criterion.

Figure S1. Powder XRD of the complexes carried out in D8 Advance X-ray diffractometer. The experimental patterns match very well with the simulated ones obtained from X-ray single crystal structure.

Figure S2. Ball and stick diagram of the 1D assembly of complex **2**. Color code : yellow = Na^{I} , cyan = Mn^{II} , purple = Mn^{IV} . Hydrogen atoms have been removed for clarity.

Figure S3. Twist angles of the trigonal faces and the s/h ratio in the octahedral and trigonal prismatic coordination geometries of the metal atoms for **1** and **2**. [s = average length of the sides of the trigonal faces of the polygon, h = distance between the trigonal faces] s/h ratio for an ideal octahedron is 1.22, while it is 1.00 for an ideal trigonal prism. The twist angle for an ideal octahedron is 60° (staggered), while it is 0° (superimposed) for an ideal trigonal prism. Note that the presence of a two-fold axis through the Mn2 atom in trigonal prismatic geometry creates two different set of twist angles as the faces cannot be superimposed on each other. For the Na atoms two sides of the faces can be superimposed but they have different lengths, so instead of the twist angle the crossing angle of the other side provide a better picture of its geometry.

Figure S4. Curie-Weiss fitting (red solid line) of complex **1** and **2**.

Figure S5. Plots of χ_M vs T and $\chi_M T$ vs T (inset) for complex **1** and **2** in the temperature range of 1.8-300 K. The red lines indicate the fitting using theoretical model *I* and the green line using theoretical model *II* (see below).

Equation used for fitting:

Theoretical Model I (isolated trinuclear units)

$$\chi_M = (Ng^2\beta^2/3kT)[A/B]$$

Theoretical Model II (interacting trinuclear units)

$$\chi_M = \chi_M' / \{1 - \chi_M'(2zJ'/Ng^2\beta^2)\} \quad [zJ' = \text{inter-cluster interaction term}]$$

$$\chi_M' = (Ng^2\beta^2/3kT)[A/B]$$

where,

$$A = 1.5[286 + 165e^{(-2.5J/kT)} + 165e^{(-5.5J/kT)} + 84e^{(-5J/kT)} + 84e^{(-7J/kT)} + 84e^{(-10J/kT)} + 35e^{(-7.5J/kT)} + 35e^{(-8.5J/kT)} + 35e^{(-10.5J/kT)} + 35e^{(-13.5J/kT)} + 10e^{(-11J/kT)} + 10e^{(-13J/kT)} + 10e^{(-16J/kT)} + e^{(-14.5J/kT)} + e^{(-17.5J/kT)}]$$

$$B = 2[6 + 5e^{(-2.5J/kT)} + 5e^{(-5.5J/kT)} + 4e^{(-5J/kT)} + 4e^{(-7J/kT)} + 4e^{(-10J/kT)} + 3e^{(-7.5J/kT)} + 3e^{(-8.5J/kT)} + 3e^{(-10.5J/kT)} + 3e^{(-13.5J/kT)} + 2e^{(-11J/kT)} + 2e^{(-13J/kT)} + 2e^{(-16J/kT)} + e^{(-14.5J/kT)} + e^{(-17.5J/kT)}]$$

Table S4. Results of the susceptibility data fitting.

Complex	Theoretical Model	J (cm ⁻¹)	g	zJ' (cm ⁻¹)	R
1	I (χ_M vs T)	8.12(19)	1.898(2)	-	6.76×10^{-5}
	I ($\chi_M T$ vs T)	8.06(33)	1.900(3)	-	7.54×10^{-5}
	II (χ_M vs T)	8.17(8)	1.95(2)	- 0.030(2)	5.55×10^{-2}
	II ($\chi_M T$ vs T)	8.19(9)	1.95(2)	- 0.039(3)	2.66×10^{-1}
2	I (χ_M vs T)	7.90(25)	1.912(3)	-	1.28×10^{-4}
	I ($\chi_M T$ vs T)	7.77(37)	1.923(3)	-	1.77×10^{-4}
	II (χ_M vs T)	8.1(9)	1.96(1)	- 0.029(1)	7.84×10^{-2}
	II ($\chi_M T$ vs T)	8.2(8)	1.96(2)	- 0.026(5)	1.68×10^{-1}

Figure S6. Magnetization data for **1** and **2**, in the temperature range 1.8 – 10 K, plotted as magnetization vs. H/T , for the indicated fields. The plots show no sign of the presence of any significant anisotropy in these complexes.

Figure S7. In-phase ac susceptibility plotted as $\chi'_M T$ vs T , in the temperature range 1.8-15 K for complex **2**, at the indicated frequencies.

Figure S8. Model of complex **1**, $[\text{Mn}_3(\text{L})_4(\text{CH}_3\text{CO}_2)]^{+1}$ used for the DFT calculations (geometry obtained from the single crystal XRD data). Color code : black = C , white = H , red = O , blue = N , purple = Mn.

Figure S9. Spin density maps calculated for model complex **1** at B3LYP level for the six possible spin states. Positive and negative spin populations are represented as yellow and green surfaces. The isodensity surfaces correspond to a value of 0.01 e/b^3 .

Figure S10. Spin density map of the ground state ($S = 11/2$) of model complex **1**. Positive and negative spin populations are represented as yellow and green surfaces. The spin densities on the bridging atoms show the path of exchange. Note that spin density on the central Mn^{II} ion is almost spherical as all five d orbitals are occupied, whereas for Mn^{IV} ions

the spins are concentrated in between the axes as the three electrons are expected to be occupying the t_{2g} symmetric orbitals.

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