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Supporting Information for

Heterometallic Strategy to Achieve Large Magnetocaloric Effect in Polymeric 3d Complexes

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Experimental Section

Materials and methods. All chemicals were reagent grade and used as purchased without further purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). The XRPD spectra were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Simulation of the XRPD spectrum was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge *via* the internet at http://www.iucr.org. IR spectra were measured in the range of 400-4000 cm^{-1} on a Tensor 27 OPUS FT-IR spectrometer using KBr pellets (Bruker, German). Magnetic susceptibility was measured by a Quantum Design MPMS superconducting quantum interference device (SQUID). Diamagnetic corrections were estimated by using Pascal constants and background corrections by experimental measurement on sample holders.

X-ray Crystallography. The single-crystal X-ray diffraction data of **1, 2** and **4** were collected on a Rigaku SCX-mini diffractometer at 293(2) K , but **3** on a Rigaku 007 Saturn 70 diffractometer at 113(2) K, with Mo-Kα radiation (λ = 0.71073 Å) by ω scan mode. The program *CrystalClear*[S1] was used for the integration of the diffraction profiles. The structure was solved by direct method using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL (semi-empirical absorption corrections were applied by using the SADABS program).[S2] The non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic

thermal parameters on F^2. All hydrogen atoms of were generated theoretically at the specific atoms and refined isotropically with fixed thermal factors. The selected bond lengths and angles are given in Tables S1.

References

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S2. CrystalClear and CrystalStructure; Rigaku/MSC: The Woodlands, TX, 2005.

Elemental analysis (%) calcd for **1**, $C_8H_{14}CrMnNO_{12}$ (423.14): C 22.71, H 3.33, N 3.31%; found for **1**: C 22.35, H 3.61, N 3.69%; calcd for **2**, $C_7H_{12}CrMnNO_{12}$ (409.10): C 20.55, H 2.96, N 3.42%; found for **2**: C 20.74, H 3.17, N 3.76%; calcd for **3**, $C_8H_{14}AlMnNO_{12}$ (398.12): C 24.14, H 3.54, N 3.52%; found for **3**: C 24.47, H 3.25, N 3.84%; calcd for **4**, $C_8H_{14}CrMgNO_{12}$ (392.50): C 24.48, H 3.60, N 3.57%; found for **3**: C 24.64, H 3.92, N 3.96%.

IR (KBr) for **1**: 3173(m), 2883(w), 1599(s), 1453(s), 1388(s), 1346(s), 1084(w), 1014(w), 883(w), 828(s), 428(s); for **2**: 3160(m), 2886(w), 1593(s), 1388(s), 1347(s), 1065(s), 968(w), 942(w), 884(w), 830(s), 430(s); for **3**: 3157 (s), 2892(w), 1620(s), 1455(W), 1397(s), 1365(s), 1124(m), 1015(m), 834(s), 605(w), 472(s); for **4**: 3161(m), 2893(w), 1614(s), 1453(m), 1397(s), 1347(s), 1138(m), 1014(w), 832(s), 436(s).

Table S1. Selected bond lengths [Å] for **1 - 4**.

1		**2**		**3**		**4**	
Mn1—O2^{i}	2.1728 (15)	Mn1—O2^{i}	2.179 (2)	Mn1—O2^{i}	2.1533 (16)	Mg1—O2^{i}	2.060 (2)
Mn1—O2^{ii}	2.1728 (15)	Mn1—O2^{ii}	2.179 (2)	Mn1—O2^{ii}	2.1533 (16)	Mg1—O2^{ii}	2.060 (2)
Mn1—O2^{iii}	2.1728 (15)	Mn1—O2^{iii}	2.179 (2)	Mn1—O2^{iii}	2.1533 (16)	Mg1—O2^{iii}	2.060 (2)
Mn1—O2^{iv}	2.1728 (15)	Mn1—O2^{iv}	2.179 (2)	Mn1—O2^{iv}	2.1533 (16)	Mg1—O2^{iv}	2.060 (2)
Mn1—O2	2.1728 (15)	Mn1—O2^{v}	2.179 (2)	Mn1—O2^{v}	2.1533 (16)	Mg1—O2	2.060 (2)
Mn1—O2^{v}	2.1728 (15)	Mn1—O2	2.179 (2)	Mn1—O2	2.1533 (16)	Mg1—O2	2.060 (2)
Cr1—O1^{vi}	1.9782 (13)	Cr1—O1^{vi}	1.983 (2)	Al1—O1^{vi}	1.9022 (14)	Cr1—O1^{vi}	1.973 (2)
Cr1—O1	1.9782 (13)	Cr1—O1	1.983 (2)	Al1—O1	1.9022 (14)	Cr1—O1	1.973 (2)
Cr1—O1^{vii}	1.9782 (13)	Cr1—O1^{vii}	1.983 (2)	Al1—O1^{vii}	1.9022 (14)	Cr1—O1^{vii}	1.973 (2)
Cr1—O1^{viii}	1.9782 (13)	Cr1—O1^{viii}	1.983 (2)	Al1—O1^{viii}	1.9022 (14)	Cr1—O1^{viii}	1.973 (2)
Cr1—O1^{ix}	1.9782 (13)	Cr1—O1^{ix}	1.983 (2)	Al1—O1^{ix}	1.9022 (14)	Cr1—O1^{ix}	1.973 (2)
Cr1—O1^{x}	1.9782 (13)	Cr1—O1^{x}	1.983 (2)	Al1—O1^{x}	1.9022 (14)	Cr1—O1^{x}	1.973 (2)

Symmetry Code: ^{i} *x, x−y+1, −z+1/2;* ^{ii} *−x+y, −x+1, z;* ^{iii} *−x+y, y, −z+1/2;* ^{iv} *−y+1, x−y+1, z;* ^{v} *−y+1, −x+1, −z+1/2;* ^{vi} *−x, −y, −z;*^{vii} *y, −x+y, −z;* ^{viii} *−y, x−y, z;* ^{ix} *x−y, x, −z;* ^{x} *−x+y, −x, z.*

Table S2. Comparison of $-\Delta S_m$ among our complexes (**1** and **2)** and some reported ones with the $-\Delta S_m$ value above 36.0 J kg^{-1} K^{-1} (ΔH = 7 T).

Complexes	Dimensionality	Types of metal ions	$-\Delta S_m$/J$kg^{-1}K^{-1}$ (ΔH=7T)	Refs
$[Mn(glc)_2(H_2O)_2]$	0D	*3d*	60.3	1
$Gd(HCO_2)_3$	3D	*4f*	55.9	2
$[Mn(H_2O)_6][MnGd(oda)_3]_2 \cdot 6H_2O$	3D	*3d-4f*	50.1	3
Complex 2	**3D**	***3d-3d***	**48.2**	**this work**
$[Gd_6(OH)_8(suc)_5(H_2O)_2]_n$	3D	*4f*	48.0	10
$[Gd_2(OAC)_3(H_2O)_{0.5}]_n$	1D	*4f*	47.7	4
$[Gd(C_4O_4)(OH)(H_2O)_4]_n$	3D	*4f*	47.3	12
$Gd(HCOO)(bdc)]_n$	3D	*4f*	47.0	11
$[Gd_6O(OH)_8]_n$	3D	*4f*	46.6	13
$[Gd_{24}(DMC)_{36}(\mu_4\text{-}CO_3)_{18}(\mu_3\text{-}H_2O)_2] \cdot 6H_2O$	0D	*4f*	46.1	5
$[Gd(HCOO)(OAc)_2(H_2O)_2]_n$	2D	*4f*	45.9	6
$[Gd_2(OAC)_3(MeOH)]_n$	1D	*4f*	45.0	4
Complex 1	**3D**	***3d-3d***	**43.93**	**this work**
$[Gd_2(OAC)_6(H_2O)_4] \cdot 4H_2O$	0D	*4f*	41.6	7
$\{Co_{10}Gd_{42}\}$	0D	*3d-4f*	41.26	8
$\{Ni_{10}Gd_{42}\}$	0D	*3d-4f*	38.2	9
$[Gd_4(OAC)_4(acac)_8(H_2O)_4]$	0D	*4f*	37.7	4
$\{Ni_{12}Gd_{36}\}$	0D	*3d-4f*	36.3	9

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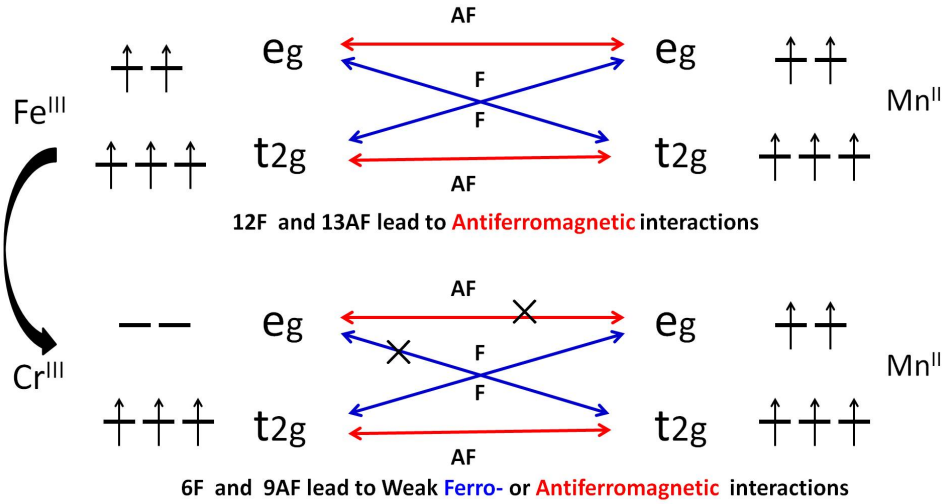
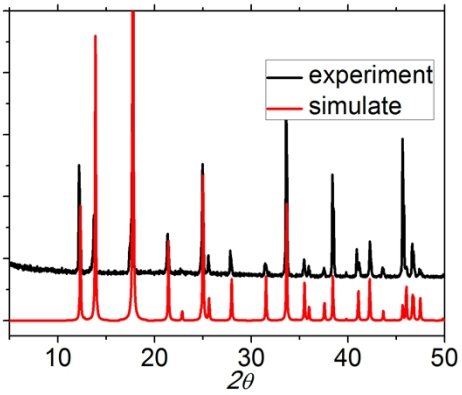
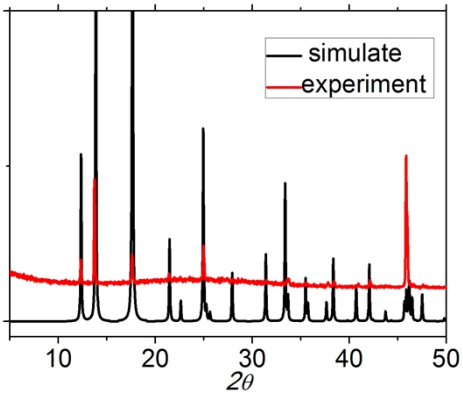


Scheme S1. The magnetic orbital interactions in $[M(HCOO)_6]^{3-}$-Mn^{II} ($M = Fe^{III}$, Cr^{III}) complexes.



(a)



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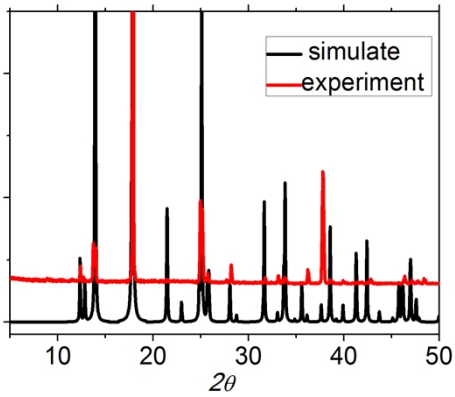
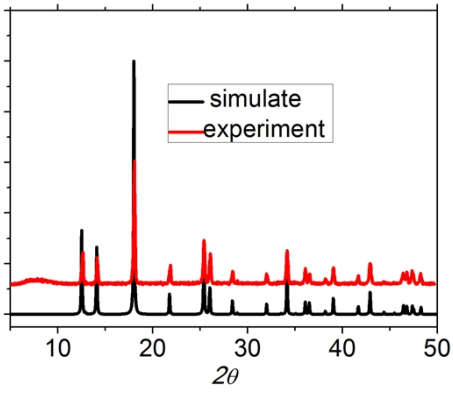


(c)



(d)

Fig. S1 The XRPD patterns of complexes **1** (a), **2** (b), **3** (c) and **4** (d).

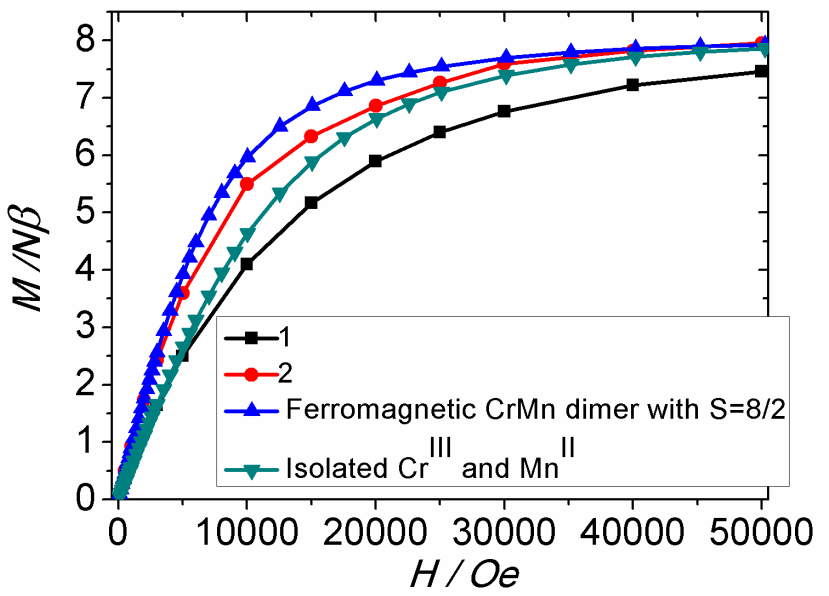
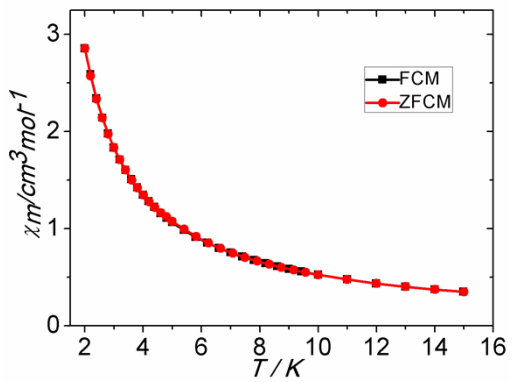
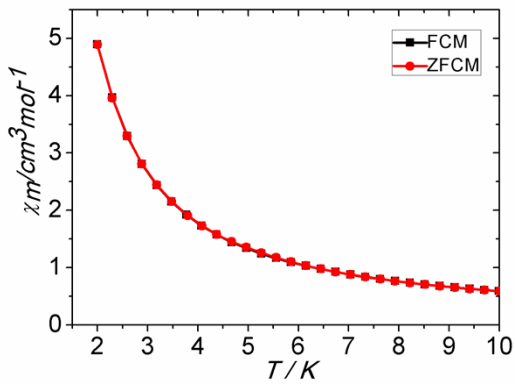


Fig. S2 $M/N\,\mu_B$ vs H plots of **1** and **2** at 2 K as well as the Brillouin function of ferromagnetic Cr^{III}-Mn^{III} dimer with S = 8/2 and two isolated ions high spin Cr^{III} and Mn^{II} with g = 2.0.



(a)



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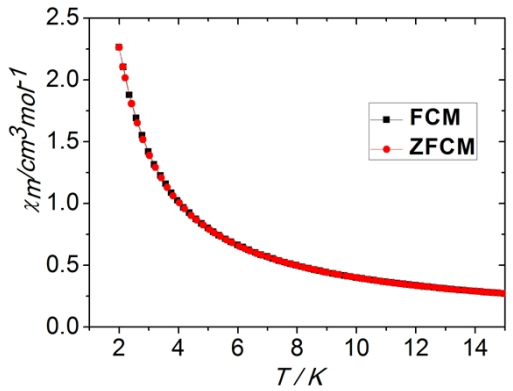

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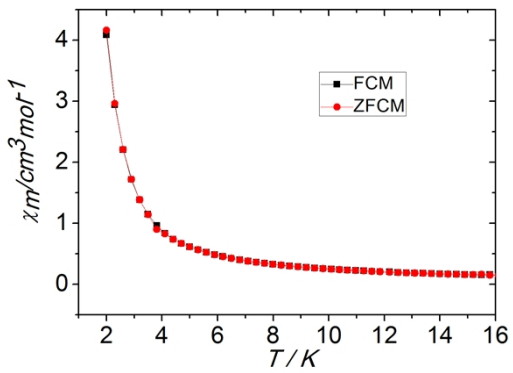

(d)

Fig. S3 ZFCM and FCM plots with external field of 50 Oe for **1** (a), **2** (b), **3**(c), and **4**(d) at low temperature.

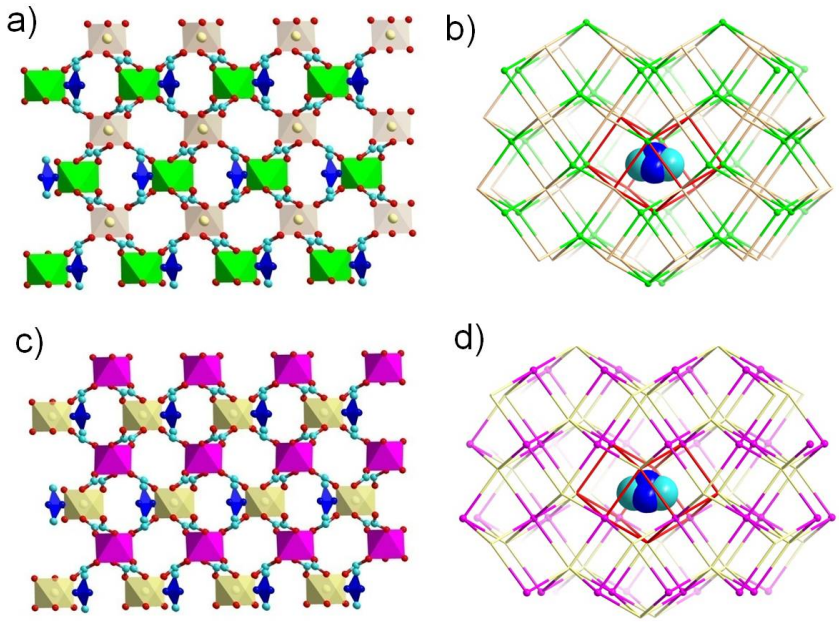

Fig. S4 (a) and (c) The polyhedron view of two sublattices of **3** and **4** with the cations filling in the cavities. (b) and (d) The Niccolite structural topology of **3** and **4** with the two sublattices. Mn^{II} in dark green, Cr^{III} in purple, Al^{III} and Mg^{II} in light yellow, O in red, N in blue and the H atoms omitted for clarity.

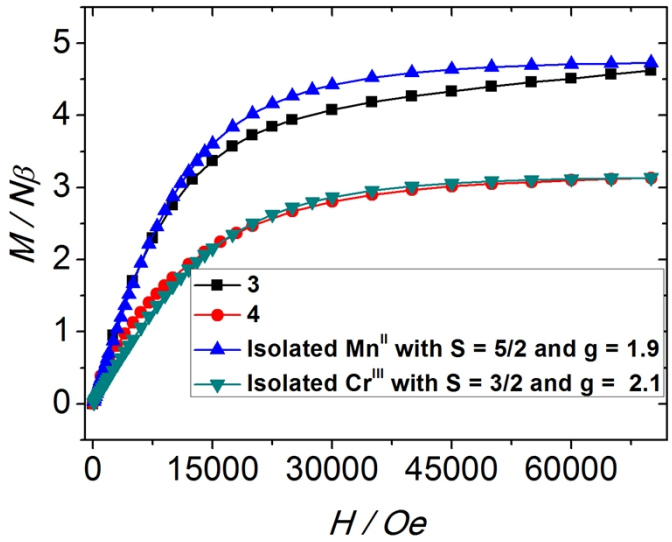

Fig. S5 $M/N\,\mu_B$ vs H plots of **2** and **3** at 2 K as well as the Brillouin function of isolated high spin ions Cr^{III} and Mn^{II} with g = 2.0.