Supporting Information For

The first heterometallic examples of 3d–4f heptanuclear [Mn$^{II}_3$Ln$^{III}_4$] complexes with planar disc-like cores and diverse magnetic properties

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Experiment Section

General   All the reagents and solvents are of commercially available and used as received.   [Mn$_6$O$_2$(Piv)$_{10}$(4-Me-Py)$_{2.5}$(PivH)$_{1.5}$]   was   prepared   according   to   the literature.[1]

Elemental analyses (C, H and N) were performed on a Vario EL III CHNOS element analyzer and the content of lanthanide (La, Pr, Nd, and Gd) had been determined by Inductively Coupled Plasma optical emission spectrometer (ICP). Infrared spectra (400–4000 cm^{-1}) were measured on a Nicolet Magna 750 FT-IR spectrophotometer using KBr pellets. Variable temperature direct-current (dc) susceptibility magnetic data for complexes **1–4** were collected on a PPMS-9T superconducting magnetometer under a field of 0.1 T in the temperature range 2–300 K. Alternating-current (ac) magnetic susceptibilities were measured on a Quantum Design MPMS-XL magnetometer. This magnetometer works with an oscillating ac field of 3 Oe and ac frequencies ranging from 311 to 2311 Hz.

Synthesis of [Mn$^{II}_3$La$^{III}_4$(Piv)$_{12}$(tea)$_2$(H$_2$O)$_3$] (1): A mixture of [Mn$_6$O$_2$(Piv)$_{10}$(4-Me-Py)$_{2.5}$(Hpiv)$_{1.5}$] (0.09 g, 0.05 mmol), La(NO$_3$)$_3$·6H$_2$O (0.38 g, 0.1 mmol), teaH$_3$ (0.07 mL, 0.5 mmol), and NEt$_3$ (0.07 mL, 0.5 mmol) in 10 mL MeCN and 5 mL MeOH was added to a 23 mL Teflon-Lined Autoclave and heated to 120 ℃ for 72 h, and then slowly cooled to room temperature at the rate of about 4℃ h^{-1}. The pure colorless prism crystals suitable for the single-crystal X-ray diffraction were collected by filtration. Yield: 0.031 g (52.6% based on La(NO$_3$)$_3$·3H$_2$O). Elemental analysis (%) calcd for C$_{72}$H$_{135}$N$_2$O$_{33}$Mn$_3$La$_4$: C, 37.92; H, 6.10; N, 1.23. Found: C, 37.76; H, 5.97; N, 1.15. ICP analysis calcd (%) for La: 24.37. Found: 24.56. Selected IR data (KBr, cm^{-1}): 3452(mb), 2960(vs), 2872(m), 2832(m), 1553(vs), 1486(vs), 1423(vs), 1376(vs), 1296(m), 1255(m), 1226(vs), 1080(s), 1056(vs), 1029(m), 916(m), 888(vs), 804 (m), 792(m), 599(s), 534(w).

Synthesis of [Mn$^{II}_3$Pr$^{III}_4$(Piv)$_{12}$(tea)$_2$(H$_2$O)$_3$] (2): This complex was obtained by the same procedure as for **1** but Pr(NO$_3$)$_3$·6H$_2$O (0.44g, 0.1 mmol) was used in place of La(NO$_3$)$_3$·6H$_2$O. Yield: 0.028 g (49.1% based on Pr(NO$_3$)$_3$·6H$_2$O). Elemental analysis (%) calcd for C$_{72}$H$_{135}$N$_2$O$_{33}$Mn$_3$Pr$_4$: C, 37.79; H, 6.08; N, 1.22. Found: C, 37.82; H, 5.89; N, 1.20. ICP analysis calcd (%) for Pr: 24.63. Found: 24.44. Selected IR data (KBr, cm^{-1}): 3445 (mb), 2965(s), 2853(m), 1559(vs), 1477(vs), 1420(vs), 1370(m), 1289(m), 1225(vs), 1060(s), 1042(vs), 920(m), 890(s), 805 (m), 792(m), 560(m).

Synthesis of [Mn$^{II}_3$Nd$^{III}_4$(Piv)$_{12}$(tea)$_2$(H$_2$O)$_3$] (3) : This complex was obtained by the same procedure as for **1** but Nd(NO$_3$)$_3$·xH$_2$O (0.33 g, 0.1 mmol) was used in place of La(NO$_3$)$_3$·6H$_2$O. Yield: 0.035 g (61.4% based on Nd(NO$_3$)$_3$·6H$_2$O). Elemental analysis (%) calcd for C$_{72}$H$_{135}$N$_2$O$_{33}$Mn$_3$Nd$_4$: C, 37.57; H, 6.04; N, 1.22. Found: C, 37.56; H, 5.89; N, 1.24. ICP analysis calcd (%) for Nd: 25.07. Found: 25.23. Selected IR data (KBr, cm^{-1}): 3449(mb), 2960(s), 1556(vs), 1484(s), 1460(m), 1423(vs), 1376(m), 1363(m), 1296(w), 1227(m), 1057(m), 891(m), 804 (w), 793(w), 600(m), 561(w).

Synthesis of [Mn$^{II}_3$Gd$^{III}_4$(Piv)$_{12}$(tea)$_2$(H$_2$O)$_3$] (4): This complex was obtained by the same procedure as for **1** but Gd(NO$_3$)$_3$·6H$_2$O (0.45 g, 0.1 mmol) was used in place of

La(NO$_3$)$_3$·6H$_2$O. Yield: 0.037 g (62.7% based on Gd(NO$_3$)$_3$·6H$_2$O). Elemental analysis (%) calcd for C$_{72}$H$_{135}$N$_2$O$_{33}$Mn$_3$Gd$_4$: C, 36.74; H, 5.91; N, 1.19. Found: C, 36.55; H, 5.74; N, 1.07. ICP analysis calcd (%) for Gd: 26.72. Found: 26.59. Selected IR data (KBr, cm^{-1}): 3434(wb), 2960(s), 1560(vs), 1485(vs), 1426(vs), 1377(s), 1363(s), 1229(s), 1082(w), 1056(s), 926(w), 805 (w), 792(w), 602(w), 565(w).

X-ray Crystallograph

Crystal data for complex **3**: C$_{72}$H$_{138}$Mn$_3$Nd$_4$O$_{33}$N$_2$, M=2301.62, hexagonal, space group *R*-3*c*, *a* = *b* = 17.941(6) Å, *c* = 57.790(5) Å, *α* = *β* = 90.00°, *γ* = 120.00° *V* = 16109.2(17) Å^3, *Z* = 6, *D$_c$* = 1.424 Mg m^{-3}, *F*(000) = 6942, *μ*(Mo-K*α*) =2.305 mm^{-1}, total of 32266 reflections were collected, 3150 independent reflections (*R*$_{int}$ = 0.0412), the final *R*1 was 0.1470, for the observed data with *I* > 2*σ*(*I*), GOF on F^2 = 1.098. CCDC: 910760. The X-ray single-crystal data were collected at 293 K on a Rigaku MERCURRY CCD diffractometer with Mo-K*α* radiation (*λ* = 0.71073 Å). The commands of DFIX, SIMU, DELU, ISOR, and PART (for disordered tert–butyl groups) have been used. The absorption correction was performed using the program CrystalClear.[2] The structures of complex **3** were solved by the direct methods with the SHELXTL-97 program package and refined on F^2 using full matrix least-squares techniques.[3] The non-H atoms were refined anisotropically and the hydrogen atoms were located by geometric calculations. The solvent disorder was calculated by the program SQUEEZE[4] of the PLATON package software.

Reference

1. V. M. Mereacre, A. M. Ako, R. Clerac, W. Wernsdorfer, G. Filoti, J. Bartolome, C. E. Anson and A. K. Powell, *J. Am. Chem. Soc.*, 2007, **129**, 9248.

2. RIGAKU/MSC(2004), CrystalClear Version 1.3.6, Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX77381-5209, USA.

3. G. M. Sheldrick, 5.0 ed.; Siemens Analytical X-ray Instruments Inc.: Madison, Wisconsin, USA, 1997.

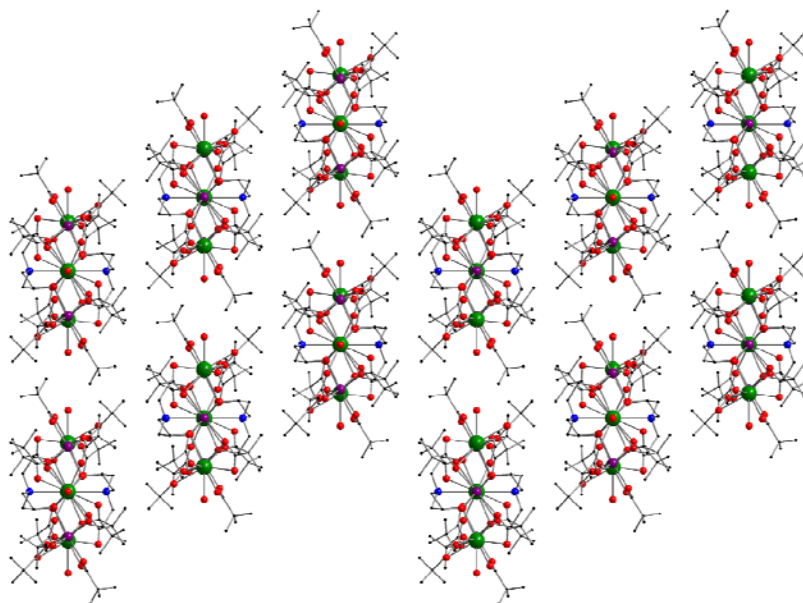4. Vandersluis, P. S., A. L. Acta Crystallogr.; Sect. A 1990, 46, 194.

Fig. S1 Wire-frame representation viewed along the *a*-axis of packing of complex **3**. Color code:

Mn^{II}: violet; Nd^{III}: green; O: red; N: blue; C: black. Hydrogen atoms are omitted for clarity.
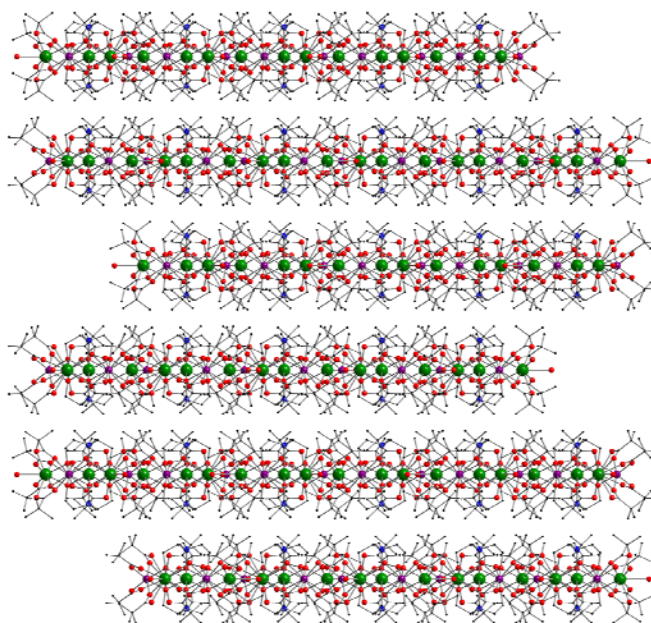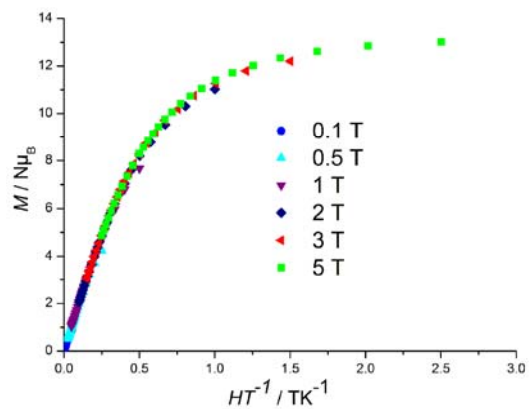

Fig. S2 Wire-frame representation viewed along the *b*-axis of packing of complex **3**. Color code:

Mn^{II}: violet; Nd^{III}: green; O: red; N: blue; C: black. Hydrogen atoms are omitted for clarity.
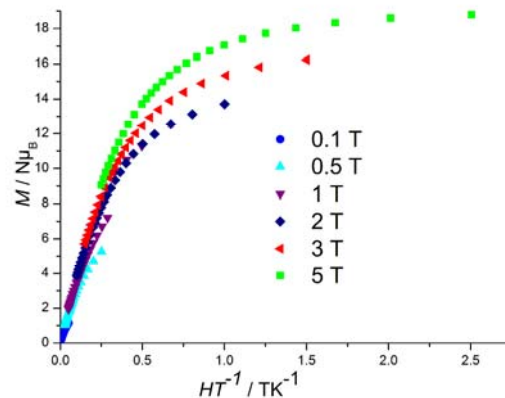
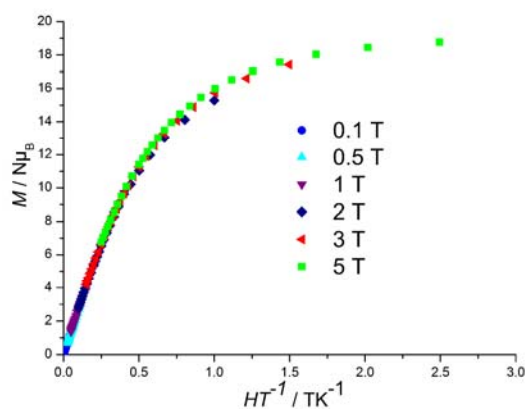**Fig. S3** Plot of *M vs. H/T* of complex **1**

Fig. S4 Plot of *M vs. H/T* of complex **2**

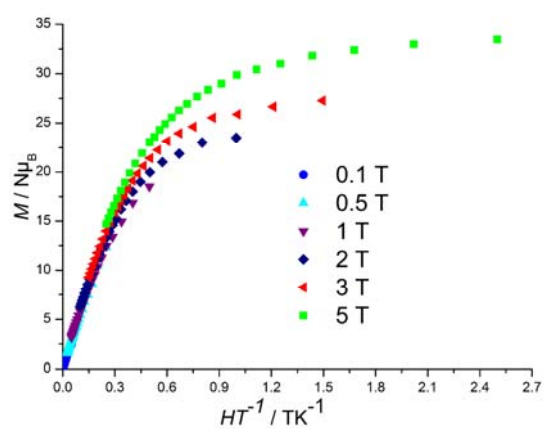**Fig. S5** Plot of *M vs. H/T* of complex **3**

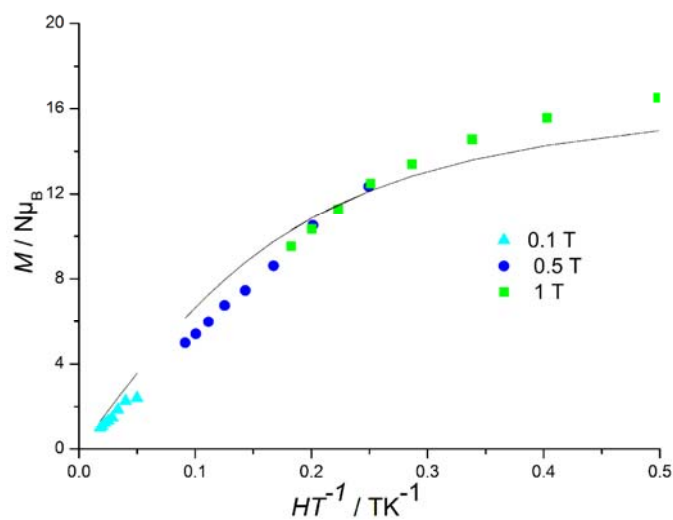**Fig. S6** Plot of *M vs. H/T* of complex **4**

Fig. S7 The reduced magnetization $M/N\mu_B$ vs H/T plots for complex **4** at 0.1–1 T. The solid lines show the best fit using the $S = 17/2$, $g = 2.06$, and $D = -0.011$ cm^{-1}.
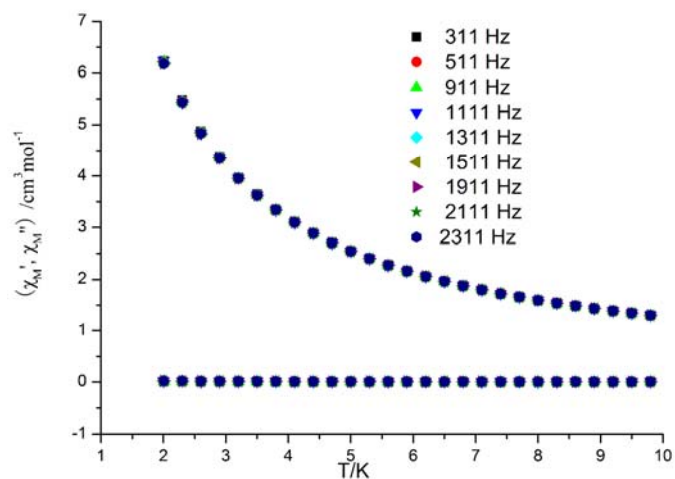
Fig. S8 Ac susceptibility in-phase χ'_m and out-of-phase χ''_m signals of complex **1** in a 3.0 G field oscillating at the indicated frequencies.

Fig. S9 Ac susceptibility in-phase χ'_m and out-of-phase χ''_m signals of complex **2** in a 3.0 G field oscillating at the indicated frequencies

Fig. S10 Ac susceptibility in-phase χ'_m and out-of-phase χ''_m signals of complex **3** in a 3.0 G field oscillating at the indicated frequencies.
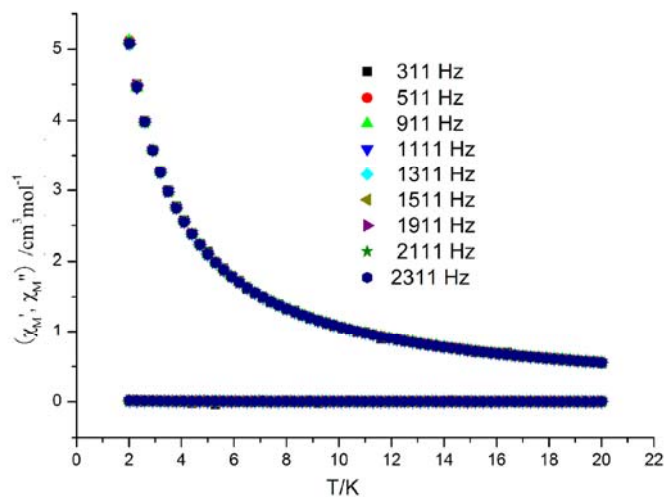

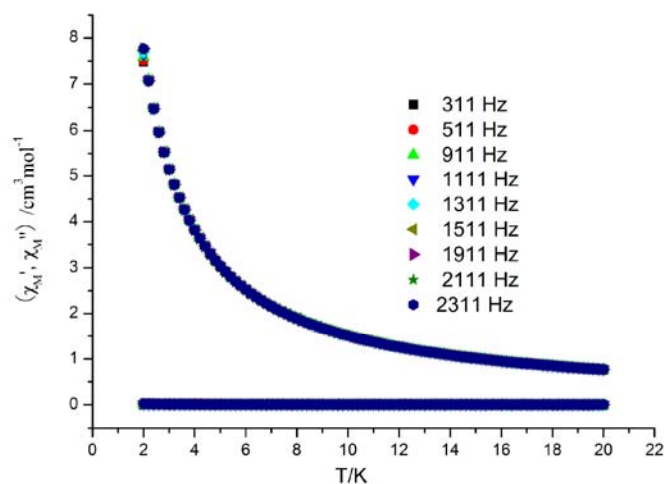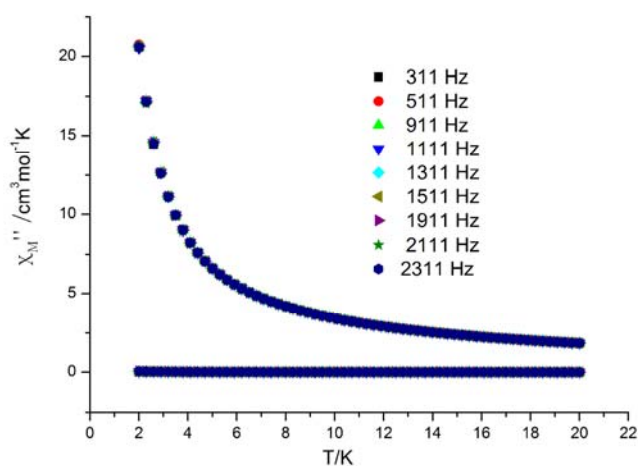**Fig. S11** Ac susceptibility in-phase χ'_m and out-of-phase χ''_m signals of complex **4** in a 3.0 G field oscillating at the indicated frequencies.

Table S1 Bond–Valence Sums for the Mn and O[a] Atom of Complex **3**

Atom	BVSs	Assigned ox. state	Atom	BVSs	Assignment	Group
Mn1	1.97	2	O1	1.81	O^{2-}	Piv^-
Nd1	2.87	3	O2	1.65	O^{2-}	Piv^-
Nd2	2.86	3	O3	1.89	O^{2-}	Piv^-
			O4	1.89	O^{2-}	Piv^-
			O5	1.91	O^{2-}	tea^{3-}
			O6	0.22	H_2O	H_2O

[a] BVS values for O atoms of O^{2-}, O^- and H_2O groups are typically 1.8–2.0, 1.0–1.2 and 0.2–0.4, respectively, but can be affected by hydrogen bonding.

Table S2 Selected Bond Lengths (Å) for Complex **3**

Nd(1)–O(3)	2.417(4)	Nd(2)–O(5)#4	2.443(3)
Nd(1)–O(3) #3	2.417(4)	Nd(2)–O(5)#2	2.442(3)
Nd(1)–O(5) #1	2.467(3)	Nd(2)–O(5)#5	2.442(3)
Nd(1)–O(5)#4	2.467(3)	Nd(2)–O(5)#3	2.442(3)
Nd(1)–O(1)	2.468(4)	Nd(2)–N(5)#5	2.712(6)
Nd(1)–O(1)#3	2.468(4)	Mn(1)–O(4)#2	2.106(3)
Nd(1)–O(6)	2.661(8)	Mn(1)–O(4)#3	2.106(3)
Nd(1)–O(2)	2.679(3)	Mn(1)–O(2)	2.219(3)
Nd(1)–O(2)#3	2.679(3)	Mn(1)–O(2)#4	2.219(3)
Nd(2)–O(5)#1	2.442(3)	Mn(1)–O(5)	2.311(3)
Nd(2)–O(5)	2.442(3)	Mn(1)–O(5) #4	2.311(3)

Symmetry transformations used to generate equivalent atoms: #1 –x+y+1, –x+1, z #2 –y+1, x–y, z#3 –x+4/3, –x+y+2/3, –z+1/6 #4 x–y+1/3, –y+2/3, –z+1/6.

Table S3 Summary of Direct Current Magnetic Data for the Mn_3Ln_4

compounds	ground state of Ln	g for non-interacting	expected $\chi_M T$ at 300 K[a]	observed $\chi_M T$ at 300 K [a]	observed $\chi_M T$ at 2 K [a]	Curie constant at 300 K [a]	Weiss constant θ [b,c]
$Mn_3La_4(1)$	$^7F_6$	0	13.13	13.11	13.21	13.09	1.33
$Mn_3Pr_4(2)$	$^3H_4$	4/5	19.53	18.04	12.79	18.22	–4.58
$Mn_3Nd_4(3)$	$^4I_{9/2}$	8/11	19.67	18.43	18.18	18.34	–4.18
$Mn_3Gd_4(4)$	$^8S_{7/2}$	2	44.63	43.22	44.45	43.52	–1.93

Unites: [a] $cm^3 K mol^{-1}$, [b] K; [c] θ is obtained by fitting of the Curie–Weiss law from 50 to 300 K.