Electronic Supplementary Information (ESI) for

Enantiopure heterobimetallic single-chain magnets from the chiral Ru^{III} building block

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Caption of Content

Experimental Section

General considerations. All chemicals were reagent grade and used as received. (1*S*,2*S*)-(+)-1,2-diaminocyclohexane and (1*R*,2*R*)-(–)-1,2-diaminocyclohexane were purchased form the Aldrich Chemicals Company. ((*R*,*R*) or (*S*,*S*))-$[Bu_4N][Ru(5\text{-}Cl\text{-}Salcy)](CN)_2]$ was synthesized by a method similar to that for $[Bu_4N][Ru(salen)(CN)_2]$.[1] $[Mn(salen)(H_2O)_2]ClO_4$ was prepared according to the literature method.[2] Although no problems were encountered in this work, cyanides are toxic and perchlorate salts are potentially explosive. Thus, these starting materials should be handled in small quantities and with great caution!

((*R*,*R*) or (*S*,*S*))-Ru(5-Cl-salcy)PPh$_3$Cl: (*R*,*R*) or (*S*,*S*)-(5-Cl-H_2salcy) (978 mg, 2.5 mmol) was dissolved in methanol and excess Et_3N (1.4 mL) added. The solution was heated to boiling and $Ru(PPh_3)_3Cl_2$ (2.39 mg, 2.5 mmol) was added. Air was drawn through the hot suspension until all the solid was dissolved, forming a green solution (c. 10h). After it was cooled to room temperature, the solution was filtered and the filtrate was concentrated to about 5 mL. Addition of diethyl ether (50 mL) produced a dark green precipitate which was collected by filtration and washed with water and then diethyl ether. Yield: 58%. Anal. Calcd for $C_{38}H_{33}N_2O_2PCl_3Ru$: C, 57.91; H, 4.22; N, 3.55. Found: C, 57.68; H, 4.15; N, 3.71.

((*R*,*R*) or (*S*,*S*))-[Bu$_4$N][Ru(5-Cl-Salcy)](CN)$_2$]: (*R*,*R*) or (*S*,*S*) Ru(5-Cl-salcy)PPh_3Cl (1.57 mg, 2 mmol) was refluxed with NaCN (25 mg, 5 mmol) in 50 mL of methanol for 1 h. The solution was evaporated to dryness and the residue then dissolved in 10mL of water. Addition of $[NBu_4]Cl$ (556 mg, 2 mmol) to the aqueous solution produced a dark green precipitate which was collected, washed with water, and dried in vacuo. Yield: 48%. Anal. Calcd for $C_{38}H_{54}N_5O_2Cl_2Ru$: C, 58.15; H, 6.93; N, 8.92. Found: C, 58.32; H, 6.71; N, 8.79. ESI-MS: (*m/z*) 544 (M^-). IR (KBr, cm^{-1}): $\nu(C{\equiv}N)$ 2096.

Synthesis of **1**-(*RR*): A solution of $[Bu_4N][Ru((R,R)\text{-}5\text{-}Cl\text{-}Salcy)](CN)_2]$ (31.2 mg, 0.04 mmol) in MeOH/MeCN (1:1 v/v, 10 mL) was added to a solution of $[Mn(salen)(H_2O)_2]ClO_4$ (18.2 mg, 0.04 mmol) in 10 mL of MeOH/MeCN (v/v=1:1). After 10 min of stirring, the resulting dark-green solution was filtered and then left undisturbed. The slow evaporation of the filtrate gave dark-green needles of **1**-(*RR*) after two weeks. Yield: 78%. Anal. Calcd for $C_{76}H_{64}Cl_4Mn_2N_{12}O_8Ru_2$: C, 52.85; H, 3.73; N, 9.73. Found: C, 52.61; H, 3.58; N, 9.52. IR (KBr, cm^{-1}): *v*(C≡N) 2103. Synthesis of **1**-(*SS*): preparation was similar to that of **1**-(*RR*) with the exception $[Bu_4N][Ru((S,S)$-5-Cl-Salcy$)](CN)_2]$ was used. The slow evaporation of the filtrate gave dark-green needles of **1**-(*SS*) after two weeks. Yield: 78%. Anal. Calcd for $C_{76}H_{64}Cl_4Mn_2N_{12}O_8Ru_2$: C, 52.85; H, 3.73; N, 9.73. Found: C, 52.63; H, 3.59; N, 9.52. IR (KBr, cm^{-1}): *v*(C≡N) 2103.

X-ray Crystallography. Crystal structures were determined on a Bruker AXS SMART APEX II CCD-based diffractometer using monochromated Mo Kα radiation (λ = 0.71073 Å) at 291 K. Cell parameters were retrieved using SMART software and refined using SAINT[3] on all observed reflections. Data was collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 10 s/frame. Data were integrated using SAINT [3] and SADABS [4]. Structures were solved by direct methods using the program SHELXL-97.[5] Positions of metal atoms and their first coordination spheres were located from direct-methods E-maps. Other nonhydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated positions and refined as riding atoms with a uniform value of U_{iso}.

Physical measurements. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. CD spectra were recorded on a Jasco J-810 spectropolarimeter. IR and VCD spectra in the region of 1800–800 cm^{-1} were recorded on a VERTEX 80v Fourier transform infrared spectrometer equipped with a PMA 50 VCD/IRRAS module (Bruker, Germany) using previous procedures.[6, 7] The solid samples were prepared by mixing the compound and KBr in a 1:200 ratio, and pressing the pellet in a Perkin Elmer hydraulic pellet press for 5 min under 10 tons of pressure. The photo elastic modulator (PEM) was set to 1500 cm^{-1}, and the spectral resolution was 4 cm^{-1}. All VCD measurements were collected for 1 h composed of 4 blocks in 15 min. Baseline correction was performed with the spectra of pure KBr pellet using the same measurement setup. Magnetic susceptibilities for polycrystalline samples were measured with the use of a Quantum Design MPMS-SQUID-VSM magnetometer in the temperature range 1.8–300 K. Field dependences of magnetization were measured using Quantum Design MPMS-SQUID-VSM system in an applied field up to 70 kOe. X-ray powder diffractometry study of the complex was performed on a Bruker D8 ADANCE diffractometer with Cu Kα radiation.

Table S1. Selected bond lengths (Å) and angles (°) in **1-**(*RR*) and **1**-(*SS*).

1-(*RR*)

C(149)-Ru(3)	2.059(4)	Mn(2)-N(8)	1.998(4)	Mn(4)-N(18)	2.013(4)
C(150)-Ru(3)	2.117(5)	Mn(2)-N(7)	2.089(4)	Mn(4)-N(17)	2.044(4)
C(151)-Ru(4)	2.133(5)	Mn(2)-N(12)	2.315(4)	Mn(4)-N(22)	2.325(4)
C(152)-Ru(4)	2.095(4)	Mn(2)-N(11)	2.393(4)	Mn(4)-N(23)	2.342(4)
Mn(1)-O(3)	1.904(3)	Mn(3)-O(9)	1.907(3)	N(1)-Ru(1)	2.030(4)
Mn(1)-O(4)	1.934(3)	Mn(3)-O(10)	1.911(3)	N(2)-Ru(1)	2.016(4)
Mn(1)-N(3)	1.986(4)	Mn(3)-N(13)	1.995(4)	N(5)-Ru(2)	2.089(4)
Mn(1)-N(4)	2.020(4)	Mn(3)-N(14)	2.058(4)	N(6)-Ru(2)	1.994(4)
Mn(1)-N(9)	2.306(4)	Mn(3)-N(21)	2.301(4)	N(15)-Ru(3)	2.046(4)
Mn(1)-N(10)	2.355(4)	Mn(3)-N(24)#1	2.317(4)	N(16)-Ru(3)	2.073(4)
Mn(2)-O(8)	1.875(3)	Mn(4)-O(14)	1.927(3)	N(19)-Ru(4)	1.990(4)
Mn(2)-O(7)	1.927(3)	Mn(4)-O(13)	1.948(3)	N(20)-Ru(4)	2.035(4)
N(24)-Mn(3)#2	2.317(4)	Ru(1)-C(76)#2	2.119(5)	C(83)-N(13)-Mn(3)	121.7(4)
O(1)-Ru(1)	2.052(3)	N(9)-C(73)-Ru(1)	178.0(5)	C(84)-N(13)-Mn(3)	114.4(3)
O(2)-Ru(1)	2.015(3)	N(10)-C(74)-Ru(2)	170.3(4)	C(86)-N(14)-C(85)	122.6(4)
O(5)-Ru(2)	2.023(3)	N(11)-C(75)-Ru(2)	176.7(4)	C(86)-N(14)-Mn(3)	126.3(3)
O(6)-Ru(2)	2.006(3)	N(12)-C(76)-Ru(1)#1	171.1(5)	C(85)-N(14)-Mn(3)	111.1(3)
O(11)-Ru(3)	2.076(3)	C(7)-N(1)-Ru(1)	121.4(4)	C(99)-N(15)-Ru(3)	121.7(3)
O(12)-Ru(3)	2.012(3)	C(8)-N(1)-Ru(1)	111.7(3)	C(100)-N(15)-Ru(3)	110.8(3)
O(15)- Ru(4)	2.044(3)	C(14)-N(2)-Ru(1)	125.2(3)	C(106)-N(16)-Ru(3)	126.6(3)
O(16)-Ru(4)	2.025(3)	C(13)-N(2)-Ru(1)	110.2(3)	C(105)-N(16)-Ru(3)	110.4(3)
C(28)-N(3)-Mn(1)	115.1(3)	C(43)-N(6)-Ru(2)	122.5(3)	C(28)-N(3)-Mn(1)	115.1(3)
C(30)-N(4)-Mn(1)	126.4(4)	C(44)-N(6)-Ru(2)	110.4(3)	C(30)-N(4)-Mn(1)	126.4(4)
C(29)-N(4)-Mn(1)	112.1(3)	C(63)-N(7)-Mn(2)	123.5(3)	C(65)-N(8)-Mn(2)	112.6(3)
C(50)-N(5)-Ru(2)	122.5(3)	C(64)-N(7)-Mn(2)	111.7(3)	C(73)-N(9)-Mn(1)	167.8(4)
C(49)-N(5)-Ru(2)	111.3(3)	C(66)-N(8)-Mn(2)	124.1(3)	C(74)-N(10)-Mn(1)	147.3(4)

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

1-(*SS*)

C(149)-Ru(3)	2.029(8)	Mn(4)-N(18)	2.017(6)	Mn(4)-N(23)	2.286(6)
C(150)-Ru(3)	2.083(8)	Mn(4)-N(17)	2.028(6)	N(1)-Ru(1)	2.050(6)
C(151)-Ru(4)	2.098(8)	Mn(4)-N(22)	2.262(7)	N(2)-Ru(1)	1.992(6)
C(152)-Ru(4)	2.056(7)	Mn(4)-N(23)	2.286(6)	N(5)-Ru(2)	2.047(6)
Mn(1)-O(3)	1.895(5)	N(1)-Ru(1)	2.050(6)	N(6)-Ru(2)	2.010(6)
Mn(1)-O(4)	1.932(5)	N(2)-Ru(1)	1.992(6)	N(15)-Ru(3)	2.065(6)
Mn(1)-N(3)	1.977(6)	N(5)-Ru(2)	2.047(6)	N(16)-Ru(3)	2.042(5)
Mn(1)-N(4)	2.015(6)	N(6)-Ru(2)	2.010(6)	N(19)-Ru(4)	2.004(6)
Mn(1)-N(9)	2.275(7)	N(15)-Ru(3)	2.065(6)	N(20)-Ru(4)	2.030(6)
Mn(1)-N(10)	2.304(7)	N(16)-Ru(3)	2.042(5)	N(24)-Mn(3)#2	2.280(7)
Mn(2)-O(8)	1.848(5)	N(19)-Ru(4)	2.004(6)	O(1)-Ru(1)	2.027(5)
Mn(2)-O(7)	1.934(5)	N(20)-Ru(4)	2.030(6)	Mn(4)-N(23)	2.286(6)
Mn(2)-N(8)	1.999(6)	N(24)-Mn(3)#2	2.280(7)	N(1)-Ru(1)	2.050(6)
Mn(2)-N(7)	2.071(6)	O(1)-Ru(1)	2.027(5)	N(2)-Ru(1)	1.992(6)
Mn(2)-N(12)	2.254(7)	O(2)-Ru(1)	2.034(5)	O(16)-Ru(4)	2.025(5)
Mn(2)-N(11)	2.345(6)	O(5)-Ru(2)	1.977(4)	Mn(4)-N(18)	2.017(6)
Mn(3)-O(10)	1.891(5)	O(6)-Ru(2)	2.014(5)	Mn(4)-N(17)	2.028(6)
Mn(3)-O(9)	1.913(5)	O(11)-Ru(3)	2.041(4)	Mn(4)-N(22)	2.262(7)
Mn(3)-N(13)	1.984(6)	O(12)-Ru(3)	2.031(5)	Mn(3)-N(21)	2.245(6)
Mn(3)-N(14)	2.056(6)	Mn(4)-O(14)	1.920(5)	Mn(3)-(24)#1	2.280(7)
C(7)-N(1)-Ru(1)	121.7(5)	C(8)-N(1)-Ru(1)	112.1(5)	C(50)-N(5)-Ru(2)	122.0(5)
C(14)-N(2)-Ru(1)	124.3(5)	C(13)-N(2)-Ru(1)	111.2(5)	C(49)-N(5)-Ru(2)	110.1(4)
C(27)-N(3)-Mn(1)	128.4(5)	C(28)-N(3)-Mn(1)	115.5(4)	C(43)-N(6)-Ru(2)	123.5(5)
C(30)-N(4)-Mn(1)	126.5(5)	C(29)-N(4)-Mn(1)	112.8(5)	C(44)-N(6)-Ru(2)	110.7(4)
C(63)-N(7)-Mn(2)	123.1(5)	C(64)-N(7)-Mn(2)	109.9(4)	C(66)-N(8)-Mn(2)	125.9(5)
C(85)-N(14)-Mn(3)	113.0(4)	C(86)-N(14)-Mn(3)	125.4(5)	C(65)-N(8)-Mn(2)	112.3(4)
C(84)-N(13)-Mn(3)	115.6(5)	C(83)-N(13)-Mn(3)	120.8(6)	C(76)-N(12)-Mn(2)	166.3(6)
C(75)-N(11)-Mn(2)	148.1(6)	C(74)-N(10)-Mn(1)	146.5(6)	C(73)-N(9)-Mn(1)	167.4(7)

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

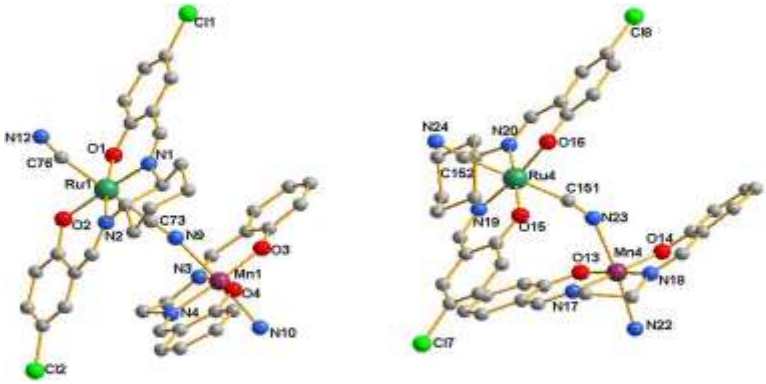

Fig. S1. Perspective drawing of the crystallographically structural unit of **1-**(*SS*)**.** H atoms are omitted for clarity.

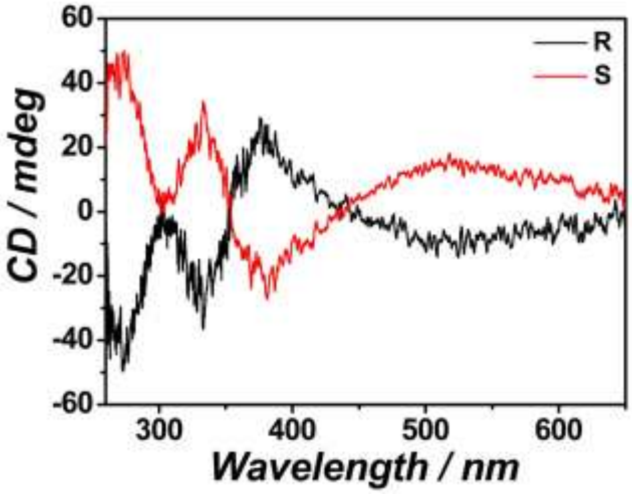

Fig. S2. CD spectra of **1-**(*RR*) (black) and **1-**(*SS*) (red) in KBr pellets.

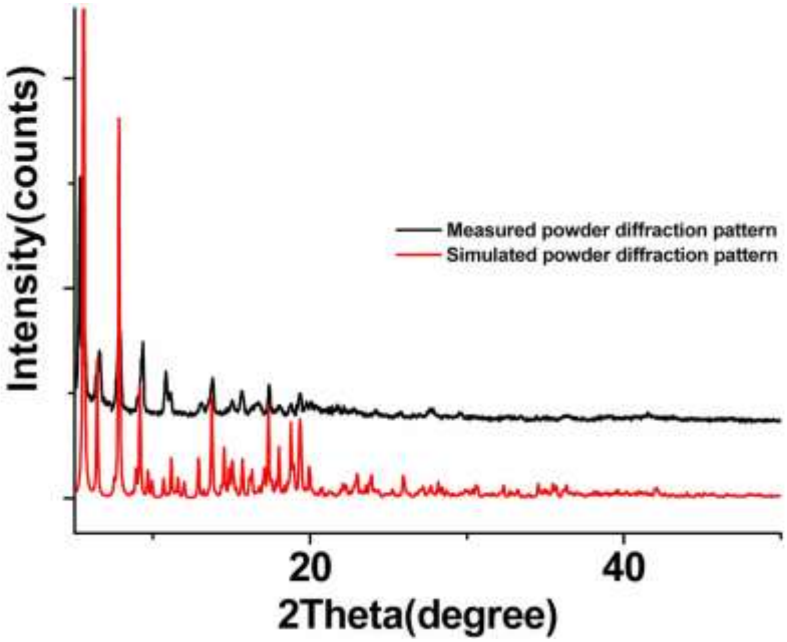

Fig. S3. The measured and simulated X-ray powder diffraction patterns of **1**-(*RR*).

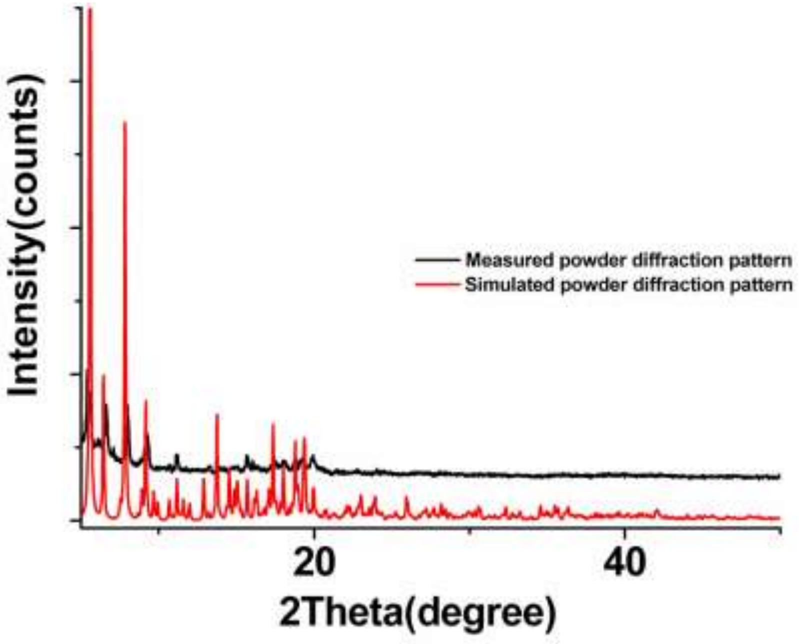

Fig. S4. The measured and simulated X-ray powder diffraction patterns of **1**-(*SS*).

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