Electronic Supporting Information (ESI)

Alkali counterions tune diruthenium(III,III)-based ferrimagnetic chain structural antiferromagnets exhibiting step-like hysteresis loops

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Table S1. Crystallographic data and structure refinement details for compounds 1–4.

Compounds	1	2	3	4
Empirical formula	$H_{15}Ru_2P_4O_{20}$	$H_{18}K_2CuRu_2P_4O_{24}$	$H_{18}Rb_2CuRu_2P_4O_{24}$	$H_{20}Cs_2CuRu_2P_4O_{25}$
M_r	661.14	869.90	962.64	1075.52
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	7.4047(14)	7.7337(12)	7.858(2)	8.006(4)
b [Å]	7.6292(16)	8.4478(13)	8.425(2)	8.475(4)
c [Å]	7.6771(15)	9.1576(14)	9.230(3)	9.314(5)
α [°]	94.658(3)	87.824(2)	86.978(6)	85.061(9)
β [°]	98.754(3)	76.102(2)	75.656(5)	74.589(8)
γ [°]	112.864(3)	64.533(2)	64.585(5)	64.129(7)
V [Å^3]	390.25(13)	522.89(14)	533.6(3)	547.9(4)
Z	1	1	1	1
ρ_{calcd} [g·cm^{-3}]	2.813	2.763	2.995	3.205
μ [mm^{-1}]	2.455	3.250	7.325	5.996
F(000)	323	425	461	497
GOF on F^2	1.048	1.083	0.969	1.071
Reflections collected (total/unique)	1592/1353	2153/2079	2249/1584	1897/1289
$R_{(int)}$	0.018	0.0319	0.0413	0.0209
R_1, wR_2 [$I>2\sigma(I)$][a]	0.0295, 0.0637	0.0310, 0.0852	0.0551, 0.1295	0.0626, 0.1737
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ [e/Å^3]	0.597, -0.638	0.966, -1.111	1.402, -1.347	1.834, -0.953

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Selected bond distances (Å) of compounds 1–4.

	1		2	3	4
Ru(1)–Ru(1A)	2.3310(9)	Ru(1)–Ru(1A)	2.3530(5)	2.3549(14)	2.3550(18)
Ru(1)–O(1)	2.005(4)	Ru(1)–O(2)	1.970(3)	1.973(7)	1.979(9)
Ru(1)–O(5)	2.026(4)	Ru(1)–O(5)	1.988(3)	1.977(7)	1.980(9)
Ru(1)–O(9)	2.284(5)	Ru(1)–O(9)	2.261(3)	2.270(8)	2.269(10)
Ru(1)–O(2A)	2.043(4)	Ru(1)–O(1A)	1.976(3)	1.968(7)	1.987(9)
Ru(1)–O(6A)	2.044(4)	Ru(1)–O(6A)	1.998(3)	1.994(7)	1.986(9)
P(1)–O(1)	1.529(5)	Cu(1)–O(4)	1.953(3)	1.941(6)	1.930(11)
P(1)–O(2)	1.549(4)	Cu(1)–O(10)	2.060(3)	2.019(7)	2.008(11)
P(1)–O(3)	1.561(4)	Cu(1)–O(11)	2.313(4)	2.399(11)	2.459(11)
P(1)–O(4)	1.510(4)	P(1)–O(1)	1.564(3)	1.574(7)	1.571(10)
P(2)–O(5)	1.517(5)	P(1)–O(2)	1.563(3)	1.560(8)	1.559(10)
P(2)–O(6)	1.532(5)	P(1)–O(3)	1.520(3)	1.512(8)	1.518(11)
P(2)–O(7)	1.525(5)	P(1)–O(4)	1.520(3)	1.509(7)	1.512(11)
P(2)–O(8)	1.553(5)	P(2)–O(5)	1.555(3)	1.558(8)	1.553(10)
O(3)–H(3)	0.83(4)	P(2)–O(6)	1.549(3)	1.557(8)	1.548(10)
O(4)–H(4)	1.2200	P(2)–O(7)	1.489(3)	1.500(8)	1.486(10)
O(7)–H(7)	0.85(6)	P(2)–O(8)	1.566(4)	1.573(9)	1.561(11)
O(8)–H(8)	0.84(5)	O(8)–H(1)	0.84(3)	0.85(2)	0.84(2)

Symmetry codes: 1. A, 1 - x, 2 -y, 2 - z; B, 1 - x, 1 - y, 1 – z; 2-4. A, 1 - x, 2 -y, 2 - z; B, 2 - x, 2 - y, 1 – z.

Table S3. Selected bond angles (˚) of compound 1.

Ru(1A)–Ru(1)–O(1)	93.34(13)	Ru(1)–O(1)–P(1)	121.0(2)
Ru(1A)–Ru(1)–O(5)	92.69(13)	Ru(1A)–O(2)–P(1)	120.0(3)
Ru(1A)–Ru(1)–O(9)	178.82(12)	Ru(1)–O(5)–P(2)	118.4(3)
Ru(1A)–Ru(1)–O(2A)	92.07(13)	Ru(1A)–O(6)–P(2)	117.5(2)
Ru(1A)–Ru(1)–O(6A)	92.06(13)	O(1)–P(1)–O(2)	110.0(2)
O(1)–Ru(1)–O(5)	90.43(17)	O(1)–P(1)–O(3)	110.7(2)
O(1)–Ru(1)–O(9)	85.49(18)	O(1)–P(1)–O(4)	110.3(3)
O(1)–Ru(1)–O(2A)	174.59(19)	O(2)–P(1)–O(3)	104.7(2)
O(1)–Ru(1)–O(6A)	87.98(17)	O(2)–P(1)–O(4)	110.8(2)
O(5)–Ru(1)–O(9)	87.18(18)	O(3)–P(1)–O(4)	110.4(2)
O(2A)–Ru(1)–O(5)	89.13(17)	O(5)–P(1)–O(6)	110.2(2)
O(5)–Ru(1)–O(6A)	175.08(18)	O(5)–P(1)–O(7)	111.5(3)
O(2A)–Ru(1)–O(9)	89.10(18)	O(5)–P(1)–O(8)	108.8(2)
O(6A)–Ru(1)–O(9)	88.05(18)	O(6)–P(1)–O(7)	109.5(3)

O(2A)–Ru(1)–O(6A)	92.01(17)	O(6)–P(1)–O(8)	109.3(3)
		O(7)–P(1)–O(8)	107.5(3)

Symmetry codes: 1. A, 1 - x, 2 -y, 2 - z; B, 1 - x, 1 - y, 1 – z

Table S4. Selected bond angles (˚) of compounds 2–4.

	2	3	4
Ru(1A)–Ru(1)–O(2)	92.52(8)	92.2(2)	92.9(7)
Ru(1A)–Ru(1)–O(5)	92.91(8)	92.8(2)	92.6(7)
Ru(1A)–Ru(1)–O(1A)	92.25(8)	92.5(2)	92.7(7)
Ru(1A)–Ru(1)–O(6A)	91.93(9)	92.2(2)	92.1(8)
Ru(1A)–Ru(1)–O(9)	176.87(8)	177.2(2)	177.7(6)
O(2)–Ru(1)–O(5)	90.92(11)	90.9(3)	90.1(9)
O(2)–Ru(1)–O(9)	87.85(12)	88.5(3)	88.2(9)
O(1A)–Ru(1)–O(2)	175.22(12)	175.3(3)	174.4(9)
O(2)–Ru(1)–O(6A)	88.74(12)	89.1(3)	89.0(10)
O(5)–Ru(1)–O(9)	90.19(11)	90.0(3)	89.5(9)
O(1A)–Ru(1)–O(5)	89.24(11)	89.1(3)	90.7(9)
O(5)–Ru(1)–O(6A)	175.16(12)	175.0(3)	175.3(9)
O(1A)–Ru(1)–O(9)	87.38(12)	86.8(3)	86.3(9)
O(6A)–Ru(1)–O(9)	84.97(12)	85.0(3)	85.8(10)
O(1A)–Ru(1)–O(6A)	90.70(12)	90.6(3)	89.8(10)
O(4)–Cu(1)–O(10)	85.92(12)	86.0(3)	87.6(10)
O(4)–Cu(1)–O(11)	90.26(13)	91.6(3)	93.4(12)
O(4)–Cu(1)–O(4B)	180.00	180.00	180.00
O(4)–Cu(1)–O(10B)	94.08(12)	94.0(3)	92.4(10)
O(4)–Cu(1)–O(11B)	89.74(13)	88.4(3)	86.6(12)
O(10)–Cu(1)–O(11)	89.98(15)	91.8(3)	93.8(11)
O(4B)–Cu(1)–O(10)	94.08(12)	94.0(3)	92.4(10)
O(10)–Cu(1)–O(10B)	180.00	180.00	180.00
O(10)–Cu(1)–O(11B)	90.02(15)	88.2(3)	86.2(11)
O(4B)–Cu(1)–O(11)	89.74(13)	88.4(3)	86.6(12)
O(10B)–Cu(1)–O(11)	90.02(15)	88.2(3)	86.2(11)
O(11)–Cu(1)–O(11B)	180.00	180.00	180.00
O(4B)–Cu(1)–O(10B)	85.92(12)	86.0(3)	87.6(10)
O(4B)–Cu(1)–O(11B)	90.26(13)	91.6(3)	93.4(12)
O(10B)–Cu(1)–O(11B)	89.98(15)	91.8(3)	93.8(10)
Ru(1A)–O(1)–P(1)	121.35(19)	121.0(4)	120.7(15)
Ru(1)–O(2)–P(1)	121.50(14)	121.5(4)	118.7(12)
Ru(1)–O(5)–P(2)	120.56(17)	121.4(4)	120.8(15)

Ru(1A)–O(6)–P(2)	121.14(16)	121.1(4)	122.1(16)
Cu(1)–O(4)–P(1)	130.82(19)	132.4(4)	133.6(15)
O(1)–P(1)–O(2)	107.23(17)	106.8(4)	108.1(13)
O(1)–P(1)–O(3)	109.38(16)	109.2(4)	110.4(15)
O(1)–P(1)–O(4)	108.24(15)	109.4(4)	110.4(14)
O(2)–P(1)–O(3)	108.53(15)	107.8(4)	106.5(14)
O(2)–P(1)–O(4)	110.77(17)	111.1(4)	109.1(16)
O(3)–P(1)–O(4)	112.55(18)	112.5(4)	112.3(16)
O(5)–P(1)–O(6)	108.61(15)	108.4(4)	109.3(14)
O(5)–P(1)–O(7)	111.0(2)	111.7(5)	111.5(15)
O(5)–P(1)–O(8)	108.38(16)	107.8(4)	105.2(15)
O(6)–P(1)–O(7)	113.26(16)	112.9(4)	114.2(15)
O(6)–P(1)–O(8)	104.42(18)	104.7(5)	105.7(15)
O(7)–P(1)–O(8)	110.93(18)	111.0(4)	110.5(15)

Symmetry codes: 2-4. A, 1 - x, 2 -y, 2 - z; B, 2 - x, 2 - y, 1 – z.

Table S5. Hydrogen bonding distances and angles of O_P—H(1)…O_P in compounds 2–4.

Compound name	O—H (Å)	H…O (Å)	O—H…O_P (Å)	Angles (°)
2(K)	0.84(3)	1.74(3)	2.575(4)	168(5)
3(Rb)	0.85(2)	1.71(3)	2.554(3)	171(7)
4(Cs)	0.84(3)	1.70(4)	2.520(5)	164(8)

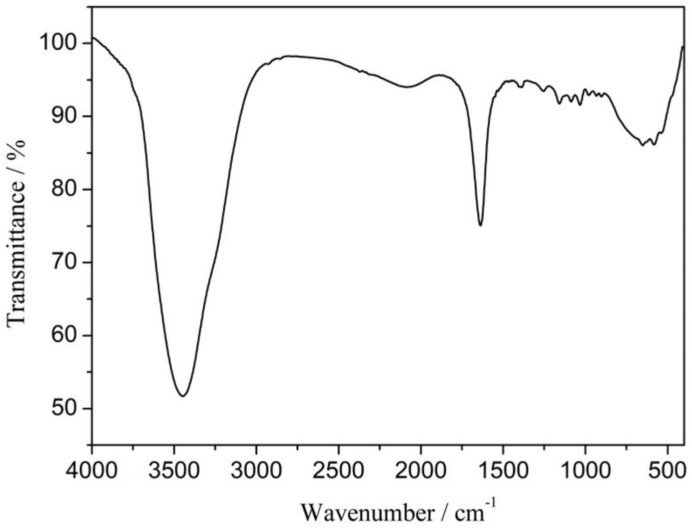

Fig. S1 IR spectra of compound 2.

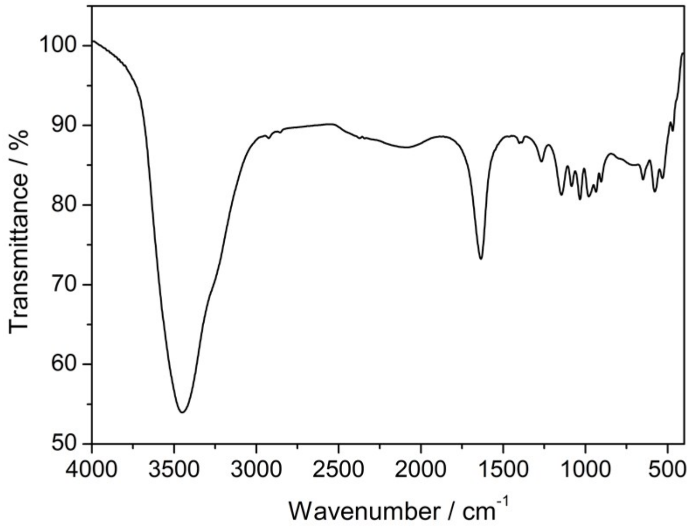

Fig. S2 IR spectra of compound 3.

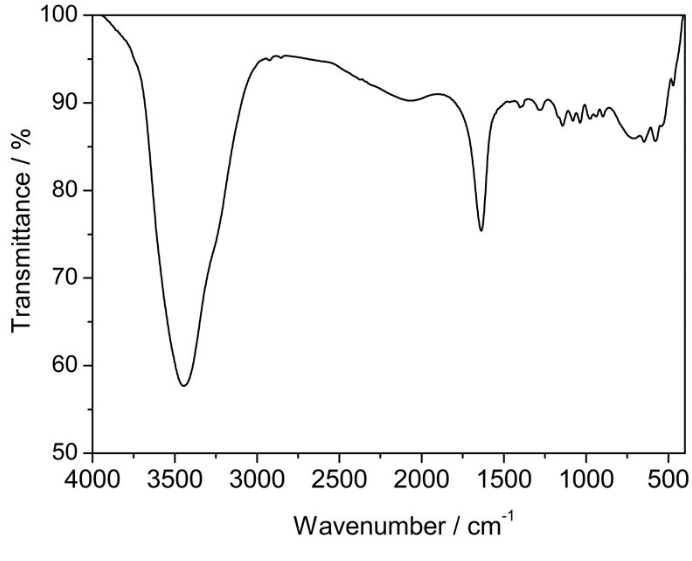

Fig. S3 IR spectra of compound 4.

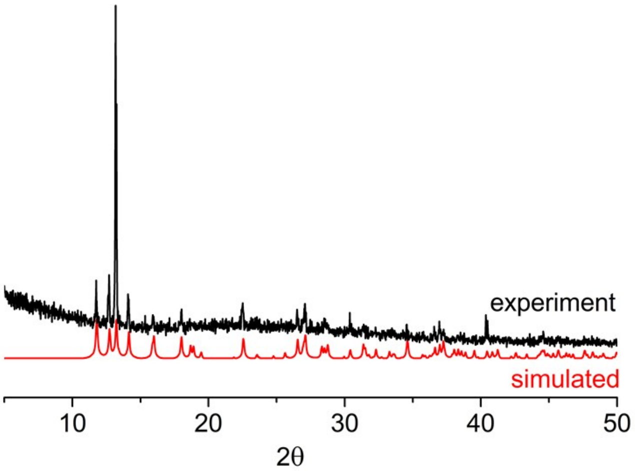

Fig. S4 Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and as-synthesized product of compound 1.

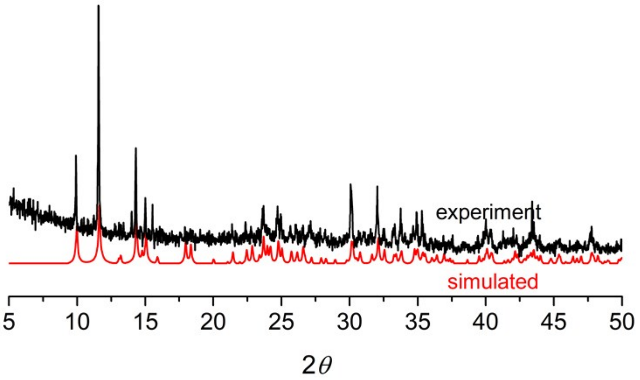

Fig. S5 Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and as-synthesized product of compound 2.

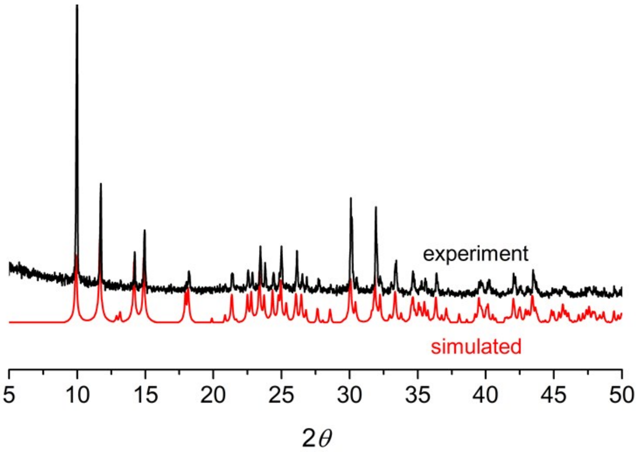

Fig. S6 Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and as-synthesized product of compound 3.

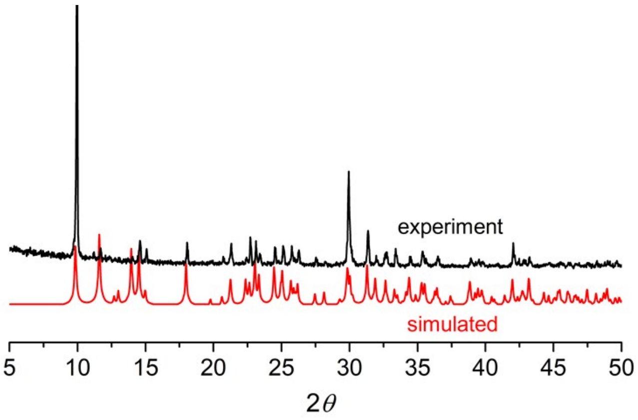

Fig. S7 Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and as-synthesized product of compound 4.

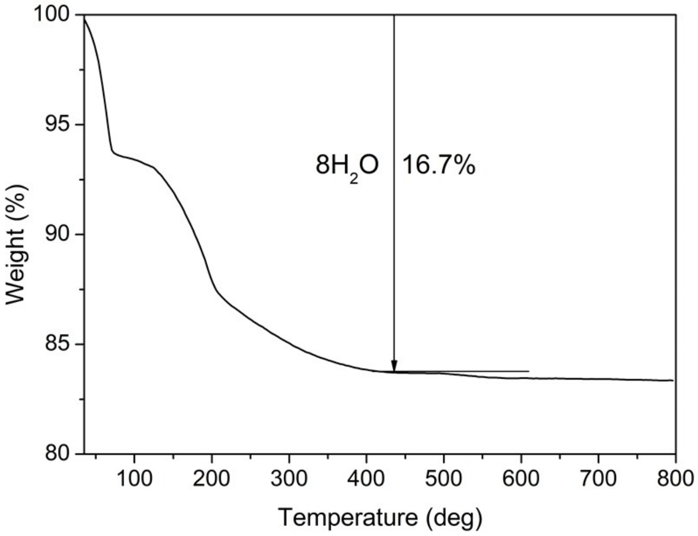

Fig. S8 TG curve of compound 2. 16.6%

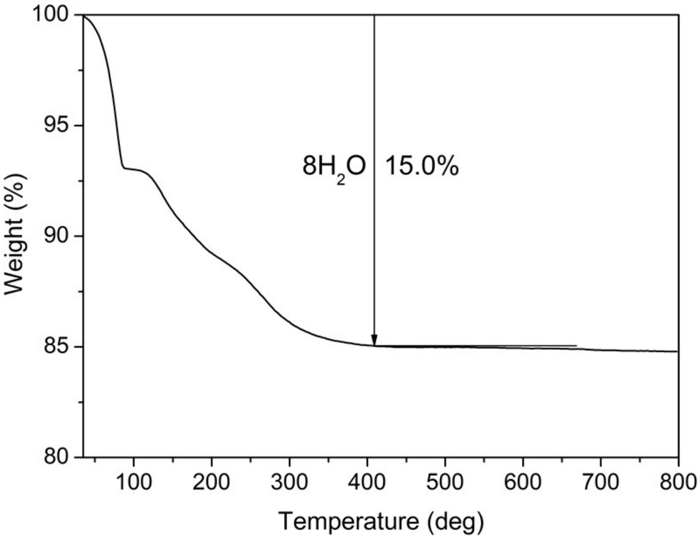

Fig. S9 TG curve of compound 3. 15.0%

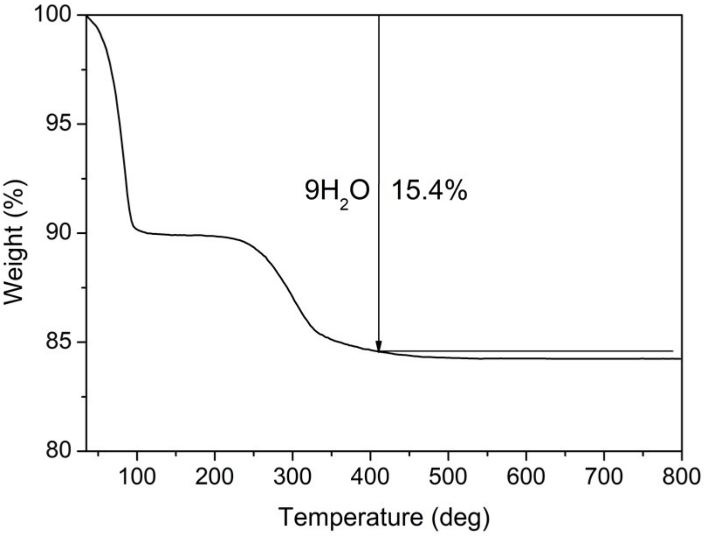

Fig. S10 TG curve of compound 4. 13.6%

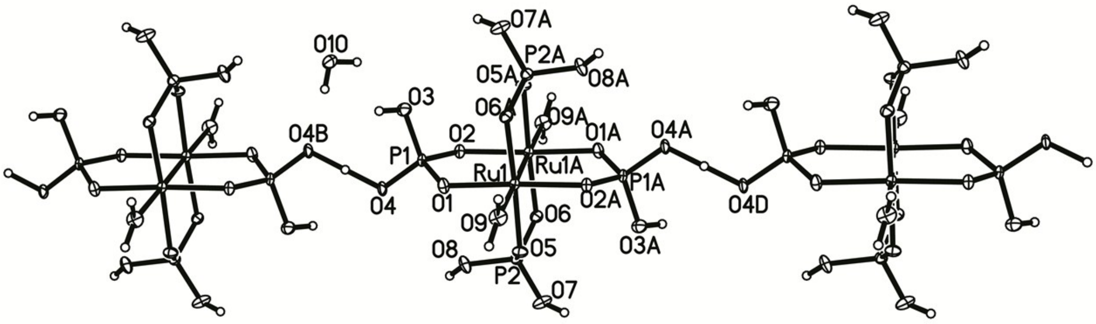

Fig. S11 ORTEP representation (30% thermal probability ellipsoids) of the crystal structure of compound 1.

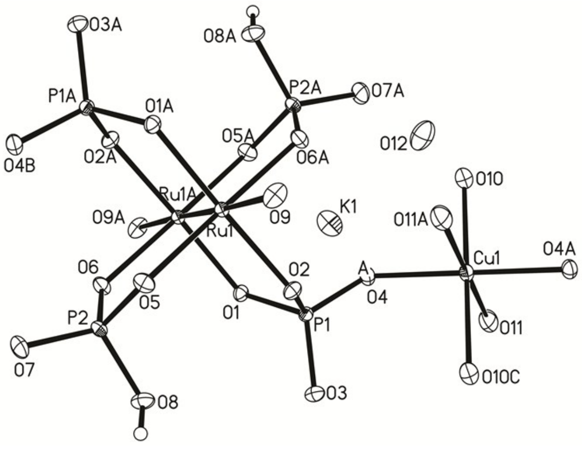

Fig. S12 ORTEP representation (30% thermal probability ellipsoids) of the crystal structure of compound 2.

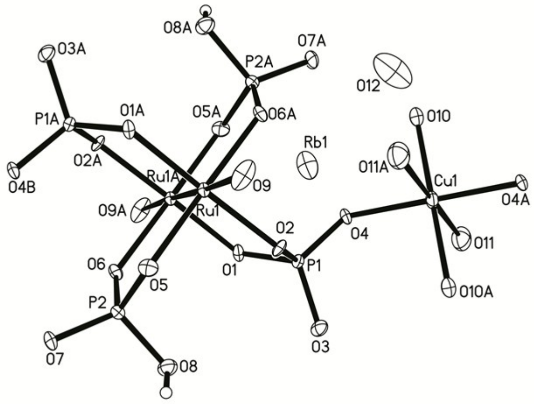

Fig. S13 ORTEP representation (30% thermal probability ellipsoids) of the crystal structure of compound 3.

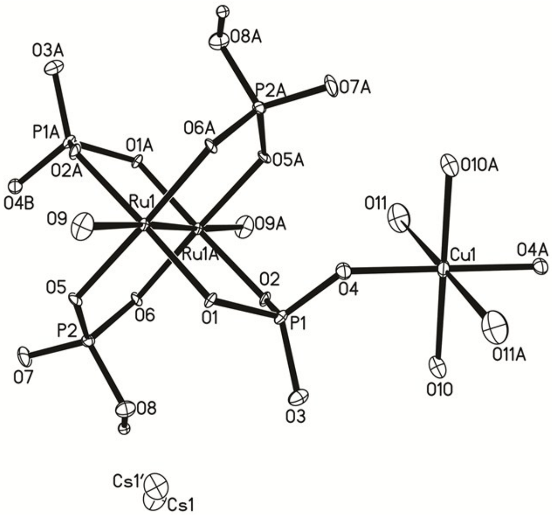

Fig. S14 ORTEP representation (30% thermal probability ellipsoids) of the crystal structure of compound 4.

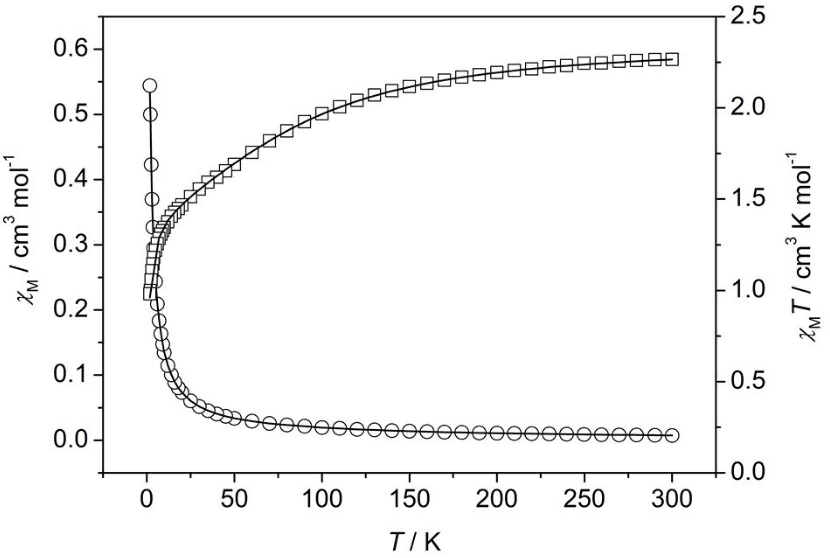

Fig. S15 χ_M and $\chi_M T$ vs T plots for compound 1. Theoretical fitting of the data in the temperature range 2-300 K, based on the equation for zero-field splitting (D) arising from the ground state $S = 3/2$, results in the parameters $g = 2.23$, $D = 100.2$ cm^{-1}, z$J = -0.85$ cm^{-1} and $R = 3.0 \times 10^{-5}$ for 1 (R is defined as $\sum(M_{\text{obsd}} - M_{\text{calcd}})^2 / \sum M_{\text{obsd}}^2$)

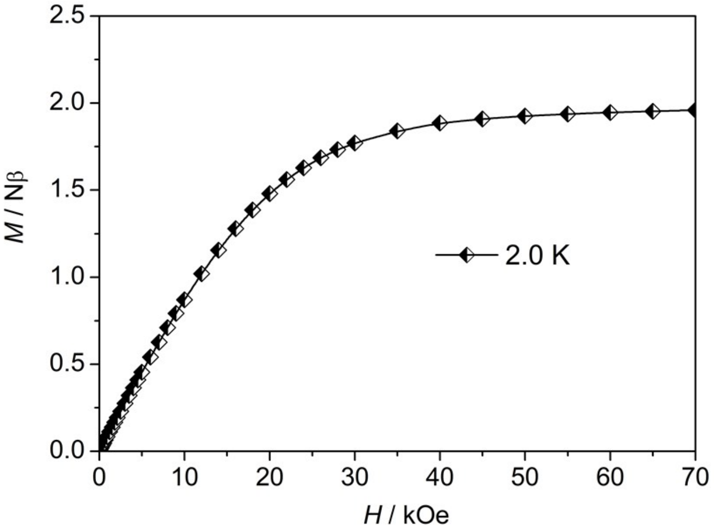

Fig S16. Field dependence of magnetization at 2.0 K for compound 1

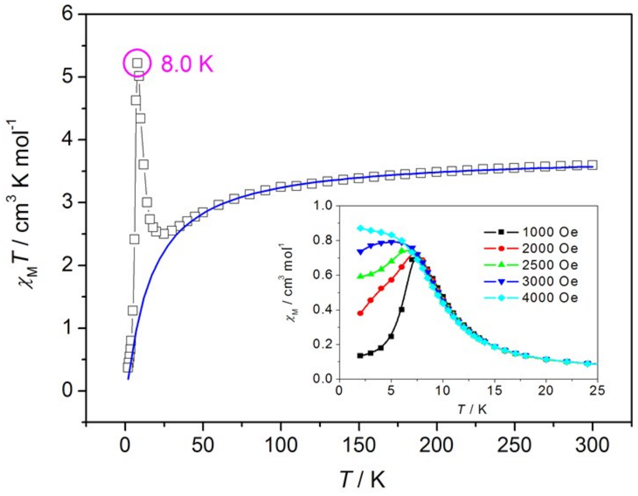

Fig. S17 χ_M and $\chi_M T$ vs T plots for compound 2.

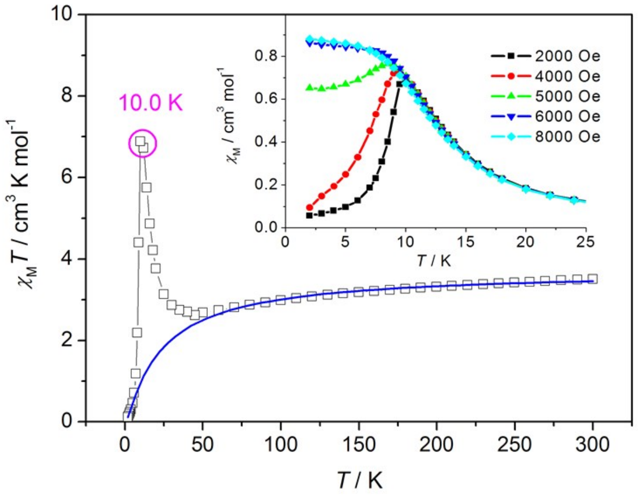

Fig. S18 χ_M and $\chi_M T$ vs T plots for compound 3.

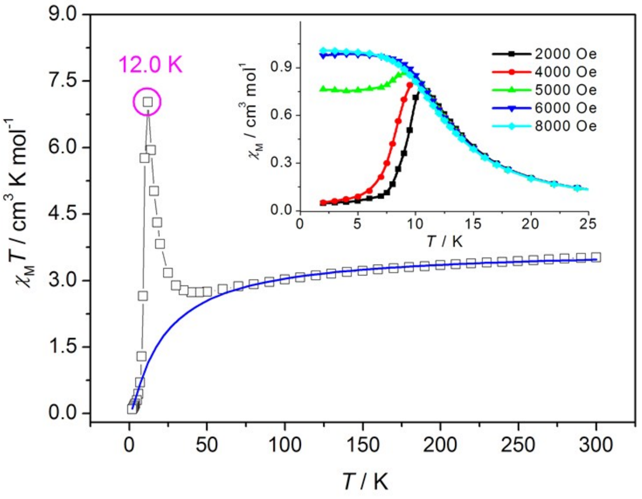

Fig. S19 χ_M and $\chi_M T$ vs T plots for compound 4.

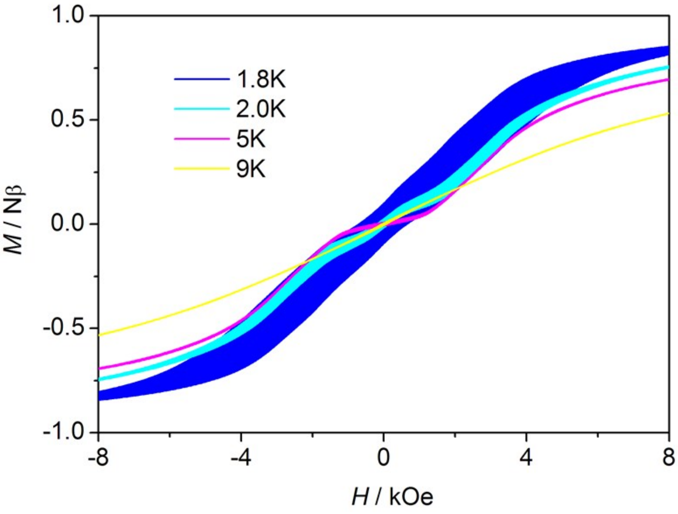

Fig. S20 Magnetic hysteresis loops at different temperature for compound 2.

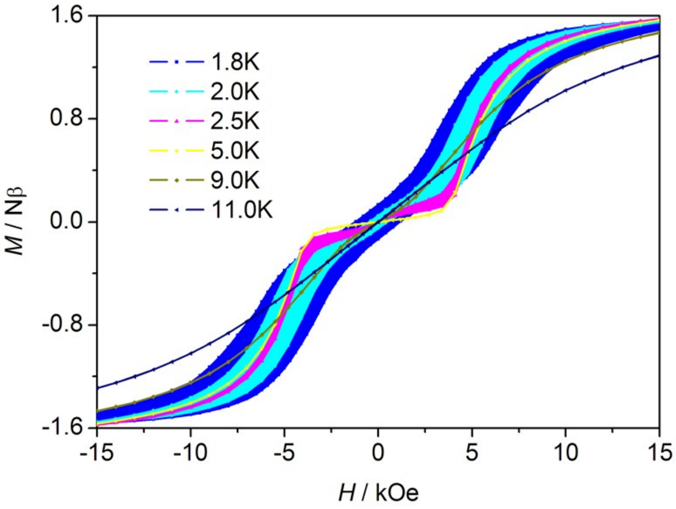

Fig. S21 Magnetic hysteresis loops at 2 K for compound 3 with different sample particle sizes

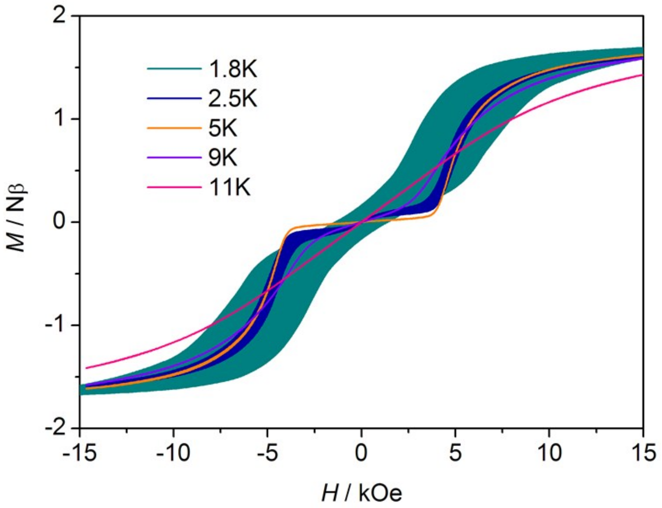

Fig. S22 Magnetic hysteresis loops at 2 K for compound 3 with different sample particle sizes

Experimental Section

Reagents and Physical Measurement: $K_3[Ru_2(CO_3)_4]\cdot 4H_2O$ was prepared according to the methods described previously.[1] All chemicals and solvents are of reagent grade and used as purchased. IR spectra (Fig. S1—S3) were recorded within the range of 400–4000 cm^{-1} on an EQUINOX55 FT/IR spectrophotometer by using KBr pellets. Powder X-ray diffraction measurements were recorded on a Rigaku RU200 diffractometer at 60 KV, 300 mA and Cu Kα radiation (λ = 1.5406 Å), with a scan speed of 5°/min and a step size of 0.02° in 2θ (Fig. S4—S7). Thermal analysis (N_2 atmosphere, heating rate: 5 ℃·min^{-1}) was performed on an Netzsch STA 449C microanalyzer (Fig. S8—S10). Magnetic measurements were carried out on polycrystalline samples using a Quantum Design MPMS-XL7 SQUID magnetometer. Alternating current (AC) susceptibility measurements were accomplished by using an oscillating AC field of 3.5 Oe. The data were corrected for the diamagnetic contributions of both the sample holder and the complexes obtained from Pascal's constants.[2]

Crystallographic Data Collection and Refinement: Single-crystal diffraction data of compounds 1—4 were collected on a Bruker SMART APEX Ⅱ CCD diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at room temperature. The data integration and reduction were processed with SAINT software. Multiscan absorption correction was performed using SADABS program. The structures were solved by direct method of SHELXS-97 and then refined by the full matrix least-squares technique on F^2 with anisotropic thermal parameters to describe the thermal motions of all nonhydrogen atoms. The hydrogen atoms were generated geometrically and refined isotropically through the riding model.

[1] (a) F. A. Cotton, L. Labella and M. Shang, *Inorg. Chem.* 1992, 31, 2385. (b) A. J. Linday, G. Wilkinson, M. Motevalli and M. B. Hursthouse, *Dalton Trans.* 1987, 11, 2723.

[2] (a) G. A. Bain and J. F. Berry, J. Chem. Educ. 2004, 85 532. (b) O. Kahn, Molecular Magnetism; VCH Publishers: New York, 1993.

Synthesis of compounds 1-4.

Compound 1 was synthesized by mixing 100 mL of an aqueous solution of $K_3[Ru_2(CO_3)_4]_3\cdot 4H_2O$ (10.0 mmol) and 15 ml H_3PO_4 solution. After it was stirred for 1 hours, the solution tuned clear. The solution was filtered and kept at 25°C for a week, and dark-brown block crystals were obtained with a yield of 89% (based on Ru). Elemental analysis (%) calcd for $H_{15}Ru_2P_4O_{20}$: H, 2.29; P, 18.74; Ru, 30.57. Found H, 2.5; P, 18.3; Ru, 30.0.

Compound 2 was synthesized by mixing 20 mL of an aqueous solution of 1 (0.17 mmol) with 10 mL of an aqueous solution of $CuSO_4$(0.64 mmol) and 10 mL of an aqueous solution of KNO_3 (1.58 mmol), and then 0.15 mL H_2O_2 and 0.15 mL 2 mol/L H_3PO_4 solution were added to the solution. Stirring for 4 hours, filtered and kept at 25°C for about a week, the red-brown crystals were isolated with a yield of 76% (based on Ru). Elemental analysis (%) calcd for $H_{18}K_2CuRu_2P_4O_{24}$: H, 2.08; P, 14.24; K, 8.99; Cu, 7.30; Ru, 23.24. Found H, 2.3; P, 13.8; K, 9.1; Cu, 7.5; Ru, 23.0. IR (KBr, cm^{-1}): 3422.55(br,s), 1636.28(m), 1472.67(m), 1071.76(m), 830.50(w), 754.87(w), 660.93(w).

Compound 3 was synthesized by mixing 20 mL of an aqueous solution of 1 (0.085 mmol) with 0.25 mL H_2O_2 and 0.5 mL 2 mol/L H_3PO_4 solution. When the solution tuned claret-red, 10 mL of an aqueous solution of $CuSO_4$(0.32 mmol) and 10 mL of an aqueous solution of RbCl (0.41 mmol) were added. Stirring for 1 hours, filtered and kept at 25°C for about three days, the red-brown crystals were isolated with a yield of 33%

(based on Ru). Elemental analysis (%) calcd for $H_{18}Rb_2CuRu_2P_4O_{24}$: H, 1.88; P, 12.87; Rb, 17.76; Cu, 6.60; Ru, 21.00. Found H, 2.0; P, 12.5; Rb, 17.0; Cu, 6.5; Ru, 20.6. IR (KBr, cm^{-1}): 3451.31(br,s), 1635.05(m), 1145.93(w), 1033.57(w), 979.85(w), 936.44(w), 649.97(w).

Compound 4 was synthesized by mixing 20 mL of an aqueous solution of 1 (0.085 mmol) with 0.25 mL H_2O_2 and 0.5 ml 2 mol/L H_3PO_4 solution. Whem the solution tuned claret-red, 10 mL of an aqueous solution of $CuSO_4$(0.32 mmol) and 10 mL of an aqueous solution of CsCl (0.30 mmol) were added to the solution. Stirring for 1 hours, filtered and kept at 25°C for about three days, and the red-brown crystals were isolated with a yield of 45% (based on Ru). Elemental analysis (%) calcd for $H_{20}Cs_2CuRu_2P_4O_{25}$: H, 1.87; P, 11.52; Cs, 24.71; Cu, 5.91; Ru, 18.79. Found H, 1.9; P, 11.2; Cs, 25.1; Cu, 6.0; Ru, 19.0. IR (KBr, cm^{-1}): 3446.42(br,s), 1637.68(m), 1143.52(w), 1036.65(w), 976.29(w), 898.32(w),648.04(w).