Supporting Information for:

Universal Single Ion Physics in Spin-Orbit Coupled d^5 and d^4 Ions

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Figure S1 Distortion information of Ru octahedra for a) **1**; b) **2**; c) **3**; d) **4**; e) **5**; f) **6**. DI indicates the distortion index value obtained from VESTA software, which is defined as $\mathrm{DI} = \frac{1}{n}\sum_{i=1}^{n}\frac{|d_i - d_{ave}|}{d_{ave}}$, where d_i is a bond length, d_{ave} is the average of bond lengths;[1, 2] the value of δ is calculated by (d_{max}-d_{min})/d_{min}, where d_{max}, d_{min} means longest bond length, shortest bond length in each Ru octahedron, respectively.

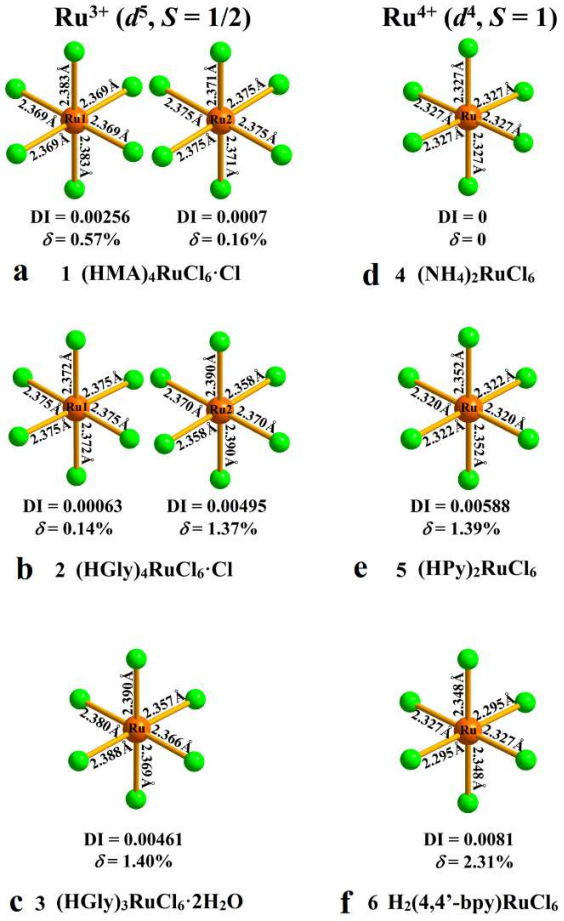

Figure S2 Magnetic susceptibility χ is approximated as $\chi \approx M/H$ at $\mu_0 H$ = 1 T of a) **1-3**, showing paramagnetic behavior, and b) **4-6**, showing roughly temperature independent behavior, indicative of single ion physics.

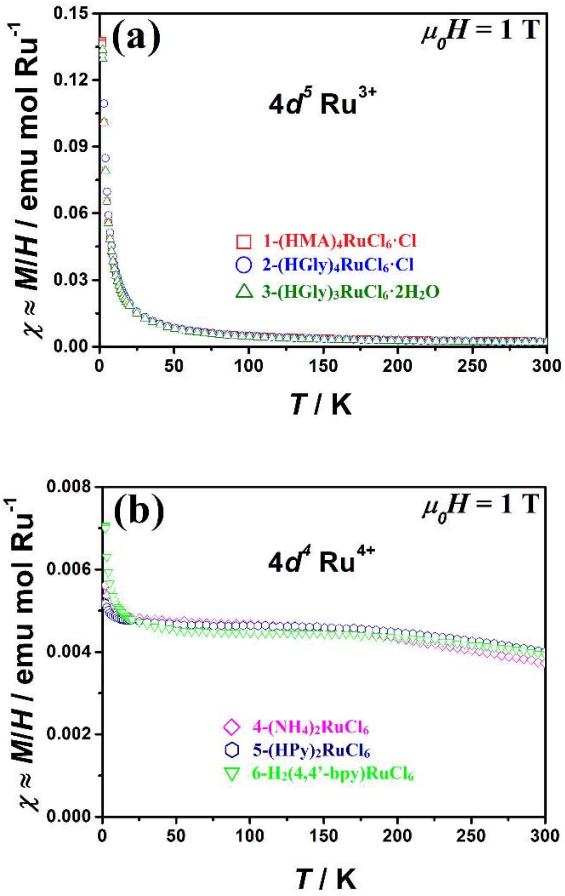

Figure S3 Magnetic field dependence of magnetization at 2 K a) for **1-3** (data of **1** has been amended by 1.2 times based on temperature dependent magnetization data at T = 2 K at $\mu_0 H$ = 1 T); b) for **4-6**.

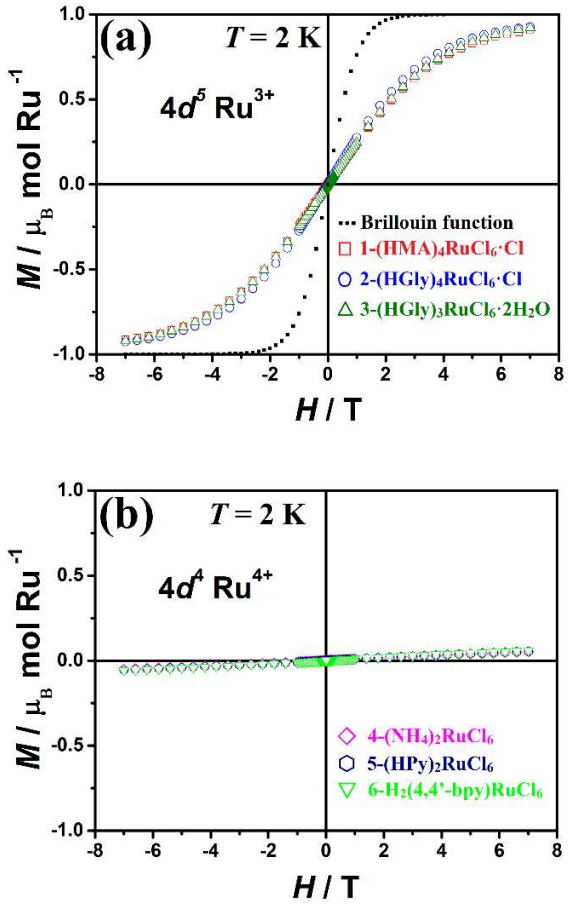

Table S1 Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **1**-**6**.

1					
Atom	**Site**	***x***	***y***	***z***	U_{eq}
Ru1	2a	0.5	0	0.5	0.00958(4)
Ru2	2d	0	0	0.5	0.00945(4)
Cl1	4g	0.52869(3)	0.22215(6)	0.39917(3)	0.01537(8)
Cl6	4g	0.10046(3)	0.22350(7)	0.47257(3)	0.01668(8)
Cl5	4g	-0.06434(3)	-0.01185(7)	0.34973(3)	0.01652(8)
Cl3	4g	0.48524(3)	0.24130(6)	0.59689(3)	0.01630(8)
Cl4	4g	0.09651(3)	-0.24123(7)	0.48230(3)	0.01702(8)
Cl2	4g	0.34943(3)	0.01596(7)	0.43670(3)	0.01675(8)
Cl8	2e	0.75	0.61345(12)	0.75	0.02999(17)
Cl7	2f	0.25	0.61881(12)	0.75	0.03035(17)
N2	4g	0.63626(12)	0.5165(3)	0.56345(13)	0.0198(3)
N1	4g	0.06632(14)	0.4945(3)	0.63762(12)	0.0221(4)
N3	4g	0.8821(15)	0.9282(4)	0.72659(14）	0.0286(4)
N4	4g	0.27059(14)	0.9383(4)	0.61020(16)	0.0293(4)
C1	4g	0.02030(17)	0.5097(4)	0.70726(15)	0.0248(4)
C4	4g	0.28464(15)	1.1264(4)	0.64550(16)	0.0252(4)
C3	4g	0.85316(16)	1.1181(4)	0.71689(15)	0.0255(4)
C2	4g	0.70900(15)	0.4808(3)	0.52292(17)	0.0233(4)
H2BC	4g	0.743(2)	0.584(5)	0.532(2)	0.035
H4BN	4g	0.270(2)	0.846(5)	0.651(2)	0.035
H2CN	4g	0.657(2)	0.543(5)	0.618(2)	0.035
H2AC	4g	0.687(2)	0.451(5)	0.459(2)	0.035

H1AC	4g	-0.043(2)	0.514(5)	0.682(2)	0.035
H2AN	4g	0.599(2)	0.415(5)	0.561(2)	0.035
H1BN	4g	0.049(2)	0.582(5)	0.595(2)	0.035
H1BC	4g	0.036(2)	0.422(5)	0.745(2)	0.035
H1CC	4g	0.034(2)	0.625(5)	0.734(2)	0.035
H3AN	4g	0.847(2)	0.850(5)	0.727(2)	0.035
H1CN	4g	0.120(2)	0.514(5)	0.657(2)	0.035
H1AN	4g	0.058(2)	0.393(5)	0.612(2)	0.035
H2BN	4g	0.606(2)	0.596(5)	0.537(2)	0.035
H4AN	4g	0.227(2)	0.925(5)	0.570(2)	0.035
H3NB	4g	0.932(2)	0.917(5)	0.774(2)	0.035
H3CC	4g	0.837(2)	1.160(5)	0.769(2)	0.035
H4CC	4g	0.334(2)	1.133(5)	0.691(2)	0.035
H3AC	4g	0.802(2)	1.121(5)	0.672(5)	0.035
H4AC	4g	0.233(2)	1.161(5)	0.669(20	0.035
H2CC	4g	0.739(2)	0.372(5)	0.546(2)	0.035
H4BC	4g	0.291(2)	1.192(5)	0.602(2)	0.035
H3BC	4g	0.89992)	1.191(5)	0.705(2)	0.035
H4CN	4g	0.313(2)	0.904(5)	0.581(2)	0.035
H3CN	4g	0.910(2)	0.889(5)	0.685(2)	0.035

2

Atom	**Site**	***x***	***y***	***z***	U_{eq}
Ru1	1d	0.5	0	0	0.00698 (3)
Ru2	1c	0	0.5	0	0.00717 (3)

Cl3	2i	0.50998(3)	0.21395(2)	0.01053(2)	0.00984 (4)
Cl4	2i	0.24929(3)	0.54817(3)	-0.04432(2)	0.01123 (5)
Cl1	2i	0.24770(3)	-0.00189(3)	0.02635(2)	0.01125 (5)
Cl6	2i	0.03991(3)	0.27420(3)	0.02837(2)	0.01218 (5)
Cl2	2i	0.52046(3)	-0.11410(3)	0.21213(2)	0.01128 (5)
Cl5	2i	-0.03211(3)	0.56106(3)	-0.20860(2)	0.01211 (5)
Cl7	2i	0.74254(3)	0.73027(3)	0.51705(2)	0.01367 (5)
O2A	2i	0.02105(9)	0.27777(9)	0.71908(8)	0.01399 (15)
O3B	2i	0.51464(9)	0.50270(9)	0.73588(8)	0.01428 (15)
O1A	2i	0.51246(9)	0.12878(9)	0.36191(7)	0.01332 (15)
O4B	2i	0.95778(9)	0.06910(9)	0.61377(8)	0.01426 (15)
O2B	2i	-0.04636(10)	0.35653(9)	0.52639(8)	0.01502 (16)
O4A	2i	1.11095(10)	-0.08816(9)	0.60434(8)	0.01526 (16)
O1B	2i	0.3443(1)	-0.03382(9)	0.43258(8)	0.01562 (16)
O3A	2i	0.44701(10)	0.61909(10)	0.54603(8)	0.01884 (18)
N2	2i	-0.23476(11)	0.31758(11)	0.80593(9)	0.01306 (17)
N4	2i	1.23287(11)	-0.11728(10)	0.80836(9)	0.01249 (17)
N3	2i	0.26928(11)	0.35762(11)	0.80373(9)	0.01260 (17)
N1	2i	0.33901(12)	0.29891(10)	0.19796(9)	0.01376 (18)
C2A	2i	-0.06729(12)	0.32410(11)	0.64357(10)	0.01113 (18)
C1B	2i	0.29137(13)	0.15802(12)	0.26261(10)	0.01312 (19)
C4B	2i	1.13258(13)	-0.00469(11)	0.75755(10)	0.01195 (19)
C4A	2i	1.06584(12)	-0.01296(11)	0.65021(10)	0.01132 (18)
C3A	2i	0.42902(12)	0.52784(11)	0.6573(1)	0.01152 (18)
C1A	2i	0.39521(12)	0.08270(11)	0.35759(10)	0.01147 (18)

C3B	2i	0.28770(12)	0.45631(12)	0.67725(10)	0.01291 (19)
C2B	2i	-0.21818(12)	0.35210(12)	0.67465(10)	0.0135 (2)
H2A	2i	-0.2380(18)	0.4422(18)	0.6329(15)	0.02
H3D	2i	0.1849(19)	0.3216(18)	0.8171(15)	0.02
H2C	2i	-0.322(2)	0.3346(18)	0.8259(15)	0.02
H2B	2i	-0.2842(19)	0.3008(18)	0.6516(15)	0.02
H4A	2i	1.1824(19)	0.0801(18)	0.7312(15)	0.02
H2D	2i	-0.2174(19)	0.2303(18)	0.8484(15)	0.02
H3A	2i	0.2821(18)	0.4104(18)	0.6260(15)	0.02
H3B	2i	0.2115(19)	0.5187(18)	0.6617(15)	0.02
H4B	2i	1.0641(19)	-0.0091(17)	0.8161(15)	0.02
H1D	2i	0.3534(19)	0.3390(18)	0.2463(16)	0.02
H1B	2i	0.2018(19)	0.1576(17)	0.3005(15)	0.02
H2E	2i	-0.1761(19)	0.3651(18)	0.8276(15)	0.02
H4C	2i	1.2918(19)	-0.1219(18)	0.7521(16)	0.02
H1A	2i	0.2870(19)	0.1196(18)	0.2083(16)	0.02
H4D	2i	1.2868(19)	-0.1046(17)	0.8633(16)	0.02
H1	2i	0.3903(19)	-0.0666(18)	0.4861(16)	0.02
H3C	2i	0.3309(19)	0.2882(18)	0.8200(15)	0.02
H2	2i	0.0325(19)	0.3340(18)	0.5142(16)	0.02
H1C	2i	0.2748(19)	0.3474(18)	0.1483(16)	0.02
H3	2i	0.525(2)	0.6508(18)	0.5388(16)	0.02
H3E	2i	0.2769(19)	0.3988(18)	0.8517(16)	0.02
H4E	2i	1.1873(19)	-0.1952(18)	0.8470(16)	0.02
H1E	2i	0.4167(19)	0.3035(18)	0.1535(16)	0.02

H4	2i	0.9299(19)	0.0720(18)	0.5476(16)	0.02

3

Atom	**Site**	***x***	***y***	***z***	U_{eq}
Ru	4a	0.90869(2)	-0.00553(2)	0.31005(2)	0.00694 (3)
Cl2	4a	0.83302(3)	-0.26287(5)	0.35886(2)	0.01130 (7)
Cl5	4a	0.80464(3)	0.17036(5)	0.38134(2)	0.00994 (7)
Cl3	4a	1.04919(3)	-0.01454(5)	0.38629(2)	0.01031 (7)
Cl6	4a	1.01192(3)	-0.18445(5)	0.23769(2)	0.01178 (7)
Cl4	4a	0.98200(3)	0.25704(5)	0.26538(2)	0.01065 (7)
Cl1	4a	0.76760(4)	0.01146(5)	0.23218(2)	0.01173 (8)
O2A	4a	0.57153(12)	0.8650(2)	0.50056(7)	0.0180 (3)
O3B	4a	0.34555(11)	0.63693(18)	0.64912(7)	0.0145 (2)
O1A	4a	0.71506(14)	0.3414(2)	0.50430(8)	0.0238 (3)
N2	4a	0.59071(13)	0.9275(2)	0.37065(8)	0.0119 (3)
O2W	4a	0.44920(14)	0.99288(18)	0.63360(8)	0.0169 (3)
O1W	4a	0.34931(13)	0.5619(2)	0.50845(7)	0.0216 (3)
O2B	4a	0.46239(11)	1.0998(2)	0.51417(7)	0.0163 (3)
N3	4a	0.27491(13)	0.5660(2)	0.76806(8)	0.0118 (3)
O1B	4a	0.75273(12)	0.6095(2)	0.54634(9)	0.0220 (3)
O3A	4a	0.24130(17)	0.4303(3)	0.60309(8)	0.0331 (4)
C3B	4a	0.22820(15)	0.4636(3)	0.71454(9)	0.0128 (3)
N1	4a	0.56574(15)	0.6269(2)	0.61121(9)	0.0158 (3)
C2B	4a	0.53241(15)	1.0567(2)	0.41127(9)	0.0117 (3)

C2A	4a	0.52594(16)	0.9942(2)	0.47982(10)	0.0114 (3)
C1A	4a	0.69445(16)	0.4836(2)	0.53995(9)	0.0140 (3)
C3A	4a	0.27841(15)	0.5208(2)	0.65228(9)	0.0127 (3)
C1B	4a	0.58692(16)	0.4664(3)	0.57208(10)	0.0150 (3)
H2B	4a	0.564(2)	1.165(4)	0.4092(14)	0.022
H2C	4a	0.571(2)	0.822(4)	0.3805(15)	0.022
H3B	4a	0.242(2)	0.342(4)	0.7196(14)	0.022
H2D	4a	0.660(2)	0.930(4)	0.3785(14)	0.022
H2A	4a	0.463(2)	1.071(4)	0.3943(14)	0.022
H3E	4a	0.338(2)	0.570(4)	0.7633(15)	0.022
H2AW	4a	0.457(2)	1.062(3)	0.663(1)	0.018
H3C	4a	0.251(2)	0.521(3)	0.8082(19)	0.022
H3D	4a	0.258(2)	0.689(4)	0.7634(14)	0.022
H1E	4a	0.610(2)	0.634(4)	0.6489(15)	0.022
H2	4a	0.459(2)	1.067(4)	0.5469(16)	0.022
H3A	4a	0.158(3)	0.481(3)	0.7127(15)	0.022
H1D	4a	0.574(2)	0.715(4)	0.5853(15)	0.022
H2E	4a	0.581(2)	0.951(4)	0.3325(15)	0.022
H1C	4a	0.501(2)	0.621(4)	0.6240(13)	0.022
H3	4a	0.270(3)	0.472(4)	0.5741(16)	0.022
H1A	4a	0.535(2)	0.456(4)	0.5430(16)	0.022
H1B	4a	0.587(2)	0.355(4)	0.5952(15)	0.022
H1	4a	0.777(2)	0.346(4)	0.4880(14)	0.022
H2BW	4a	0.4016(16)	0.921(3)	0.6425(13)	0.018
H1AW	4a	0.351(2)	0.522(3)	0.4722(8)	0.018

H1BW	4a	0.3321(19)	0.6652(19)	0.5113(14)	0.018

4

Atom	**Site**	***x***	***y***	***z***	U_{eq}
Ru	4b	0.5	0.5	0.5	0.00675(9)
Cl	24e	0.5	0.5	0.73831(3)	0.01132(9)
N	8c	0.75	0.75	0.75	0.0139(4)
H	32f	0.6994(6)	0.6994(6)	0.8006(6)	0.131(17)

5

Atom	**Site**	***x***	***y***	***z***	U_{eq}
Ru	1g	0	0.5	0.5	0.00856 (7)
Cl2	2i	0.29051(6)	0.21350(5)	0.49720(5)	0.01318 (9)
Cl3	2i	0.20763(6)	0.63820(5)	0.58636(5)	0.01345 (9)
Cl1	2i	0.07125(6)	0.57253(5)	0.21432(5)	0.01352 (9)
N	2i	0.5652(2)	0.2520(2)	0.77839(19)	0.0158 (3)
C3	2i	0.7180(3)	0.0350(2)	1.0693(2)	0.0167 (3)
C4	2i	0.5488(3)	0.2087(2)	1.0771(2)	0.0169 (3)
C1	2i	0.7296(3)	0.0855(2)	0.7660(2)	0.0173 (3)
C5	2i	0.4716(3)	0.3154(2)	0.9273(2)	0.0156 (3)
C2	2i	0.8073(3)	-0.0277(2)	0.9114(2)	0.0172 (3)
H3	2i	0.917(4)	-0.139(4)	0.904(3)	0.026
H2	2i	0.777(4)	0.053(4)	0.660(3)	0.026
H1	2i	0.515(4)	0.310(4)	0.696(4)	0.026
H4	2i	0.766(4)	-0.038(4)	1.164(4)	0.026

H5	2i	0.483(4)	0.248(4)	1.176(4)	0.026
H6	2i	0.351(4)	0.435(3)	0.921(3)	0.026

6

Atom	**Site**	***x***	***y***	***z***	U_{eq}
Ru	4c	0.500	0.500	0.500	0.00978 (7)
Cl2	8h	0.500	0.500	0.65040(3)	0.0159 (1)
Cl3	8j	0.34890(7)	0.33917(4)	0.500	0.0140 (1)
Cl1	8j	0.22136(8)	0.58418(4)	0.500	0.0187 (1)
N	8g	0.500	0.72821(15)	0.750	0.0174 (4)
C1	8g	0.500	0.94177(16)	0.750	0.0115 (4)
C2	16k	0.5546(2)	0.88651(13)	0.82314(10)	0.0140 (3)
C3	16k	0.5538(2)	0.77815(13)	0.82153(11)	0.0165 (3)
H2	16k	0.595(3)	0.9226(17)	0.8735(16)	0.025
H3	16k	0.587(3)	0.7387(19)	0.8681(15)	0.025
H4N	8g	0.500	0.665(3)	0.750	0.025

Table S2 Crystal field splitting Δ_{oct} and electron repulsion U for doublet of **1-3** and triplet of **4-6** calculated by Gaussian 09 using restricted spin density functional theory with B3LYP hybrid functional and def2-SVP basis set excluding SOC.

Compounds		Δ_{oct} (eV)	U (eV)
1	Ru1	4.07	2.59
	Ru2	4.11	2.37
2	Ru1	4.24	2.57
	Ru2	4.24	2.56
3		4.31	2.60
4		4.49	2.57
5		4.41	2.58
6		4.44	2.56

Table S3 Suitable χ_0 values for subtracting core diamagnetism based on data in reported other compounds with d^5 and d^4 ions for Figure 4.

Compounds	**χ_0 (emu/mol ions)**	**Ref.**	**Compounds**	**χ_0 (emu/mol ions)**	**Ref.**
α-$RuCl_3$	-0.0004	Ref. 46	Sr_2YIrO_6	0	Ref. 51
$[Ru(NH_3)_5Cl]Cl_2 \cdot H_2O$	0	Ref. 47	Sr_2YIrO_6	-0.0005	Ref. 52
$[Hbpy][Ru(bpy)Cl_4] \cdot H_2O$	0	Ref. 47	Ba_2YIrO_6	-0.0006	Ref. 52
$[Ru(NH_3)_6]Cl_3$	0	Ref. 47	Ba_2ScIrO_6	-0.0007	Ref. 53
$SrLa_{10}Ir_4O_{24}$	-0.0006	Ref. 19	Sr_2ScIrO_6	-0.0007	Ref. 53
$Ag_3LiRu_2O_6$	0.0007	Ref. 48	$Sr_3CaIr_2O_9$	-0.00045	Ref. 49
$NaIrO_3$	-0.0008	Ref. 49	$Ba_3ZnIr_2O_9$	-0.0008	Ref. 54
Sr_2YIrO_6	-0.00055	Ref. 50	$Sr_5LaIr_4O_{24}$	-0.00075	Ref. 19

Reference

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2. Momma, K.; Izumi, F. VESTA 3 for Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data. *J. Appl. Crystallogr.* **2011,** 44 (6), 1272-1276.