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Electronic Supporting Information (ESI)

Edge-Sharing Bi-octahedral Diruthenium(IV,IV) Compounds Containing Ru-Ru Double Bonds Chelated and Bridged by Two Carbonate and Two Oxo Groups

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Table 1. Crystallographic data and structure refinement details for compounds **1**—**3.**

Compounds	**1**	**2**	**3**
Empirical formula	$H_{32}C_{10}N_4O_{16}Ru_2$	$H_{34}C_{12}N_4O_{14}Ru_2$	$H_{52}C_{14}N_4O_{22}Ru_2$
M_r	666.53	660.57	830.73
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a [Å]	7.2244(16)	7.1532(3)	7.8283(6)
b [Å]	13.610(3)	13.3890(5)	14.3445(11)
c [Å]	11.705(3)	11.9650(6)	14.3344(11)
β [°]	94.217(4)	90.039(2)	90.810(2)
V [Å^3]	1147.8(4)	1145.94(9)	1609.5(2)
Z	2	2	2
ρ_{calcd} [g·cm^{-3}]	1.929	1.914	1.722
μ [mm^{-1}]	1.396	1.391	5.674
F(000)	672	668	864
GOF on F^2	0.989	1.087	1.064
Reflections	5689	7170	10852
$R_{(int)}$	0.050	0.0555	0.0234
R_1, wR_2 [$I>2\sigma(I)$][a]	0.0322, 0.0637	0.0449, 0.1111	0.0237, 0.0622
R_1, wR_2 (all data)[a]	0.0521, 0.0712	0.0585, 0.1173	0.0244, 0.0626
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$	0.413, -0.442	1.724, -1.468	0.546, -1.026

[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 2. Crystallographic data and structure refinement details for compounds **4**—**7.**

Compounds	**4**	**5**	**6**	**7**
Empirical formula	$H_{28}C_2O_{24}Mg_2Ru_2$	$H_{24}C_2O_{22}Ni_2Ru_2$	$H_2Cl_5OK_2Ru$	$Cl_{10}OK_4Ru_2$
M_r	687.00	719.77	374.54	729.04
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Tetragonal
Space group	$P2_1/c$	$P2_1/c$	*Pnma*	*I4/mmm*
a [Å]	7.7401(10)	9.2137(9)	13.5704(17)	7.1221(11)
b [Å]	9.3154(12)	5.9918(6)	9.6330(12)	7.1221(11)
c [Å]	14.1849(18)	16.2072(15)	7.0067(9)	17.185(4)
β [°]	98.067(2)	96.8500(10)	90	90
V [Å^3]	1012.6(2)	888.36(15)	915.9(2)	871.7(3)
Z	2	2	4	2
ρ_{calcd} [g·cm^{-3}]	2.253	2.691	2.716	2.778
μ [mm^{-1}]	1.665	3.866	4.002	4.197
F(000)	688	712	708	684
GOF on F^2	1.094	1.073	1.012	1.004
Reflections collected	5431	4778	5036	2008
$R_{(int)}$	0.022	0.017	0.034	0.031
R_1, wR_2 [$I>2\sigma(I)$][a]	0.0187, 0.0497	0.0176, 0.0428	0.0323,	0.0384,
R_1, wR_2 (all data)[a]	0.0213, 0.0511	0.0200, 0.0436	0.0417,	0.0422,
$(\Delta\rho)_{max}$,$(\Delta\rho)_{min}$ [e/Å^3]	0.513, -0.400	0.387, -0.397	1.457, -0.691	3.193, -

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

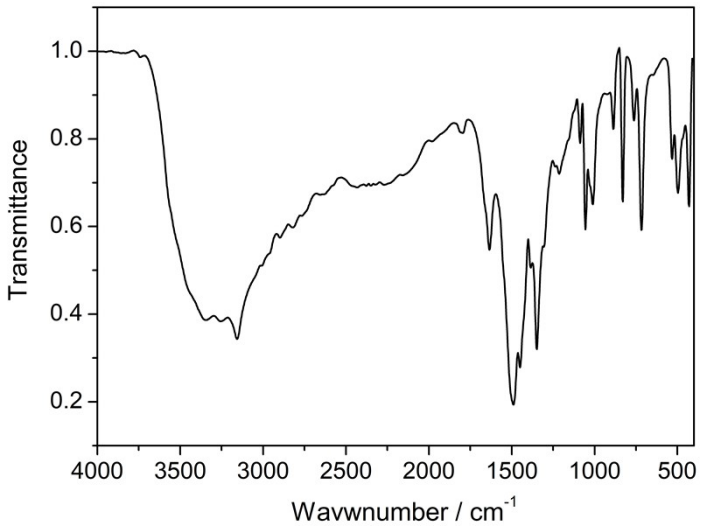

Fig. S1 IR spectrum of compound **1**.

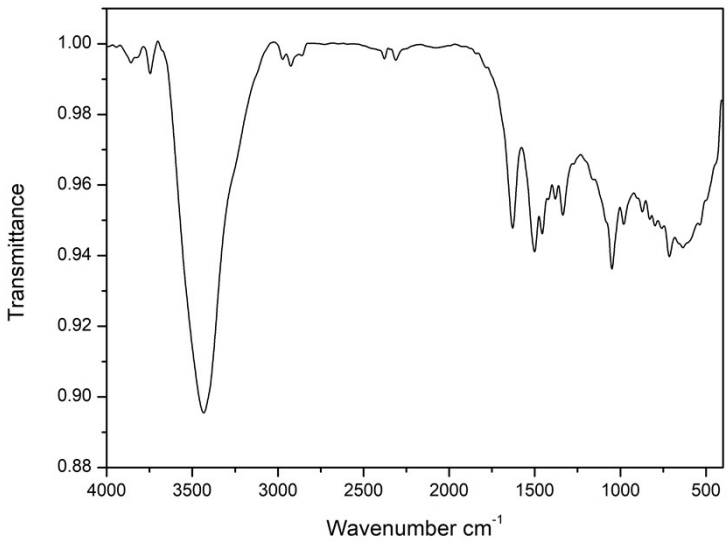

Fig S2. IR spectrum of compound **2**.

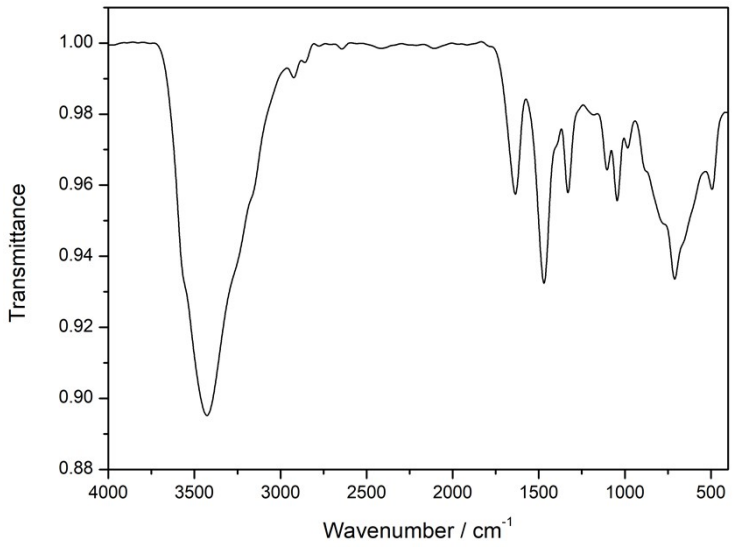

Fig S3. IR spectrum of compound **3**.

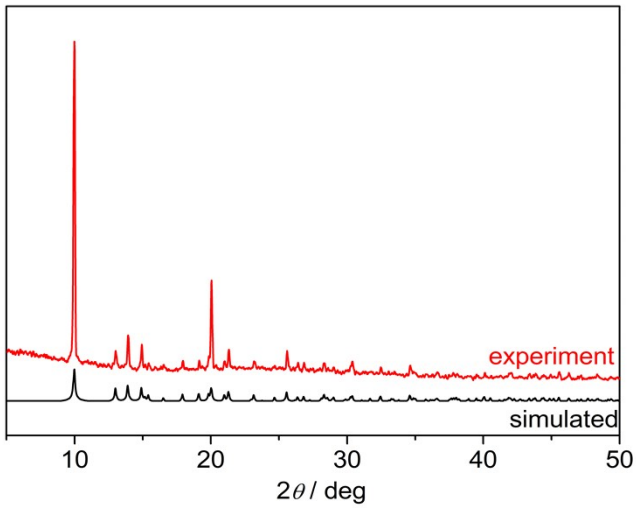

Fig. S4 Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and as-synthesized product of **1.**

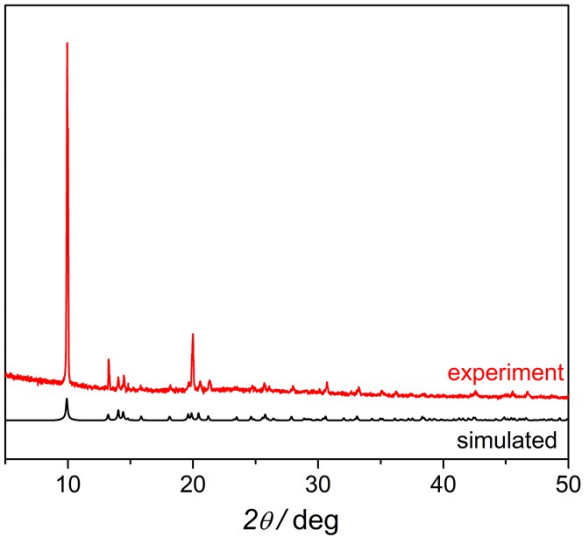

Fig. S5 Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and as-synthesized product of **2**.

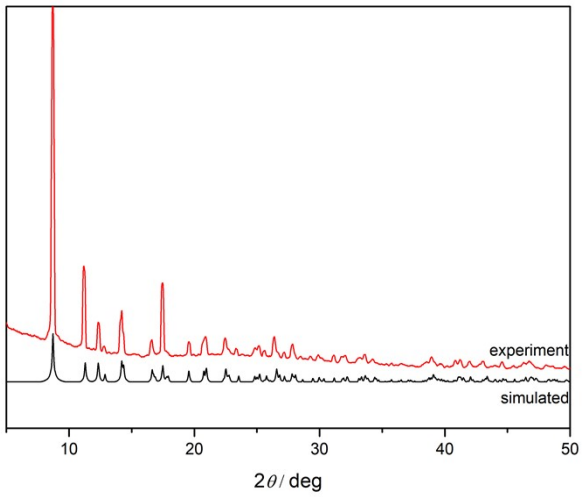

Fig. S6 Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and as-synthesized product of **3.**

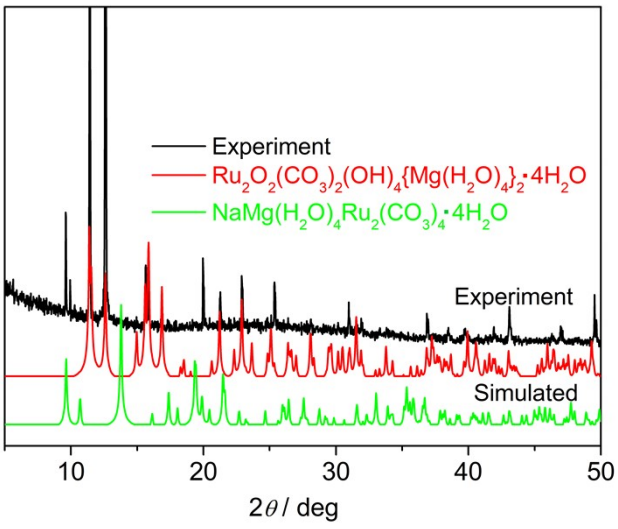

Fig. S7 Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and as-synthesized product of **3.**

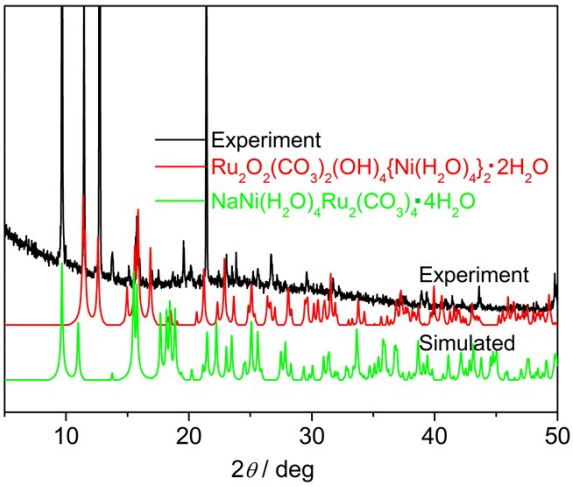

Fig. S8 Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and as-synthesized product of **3.**

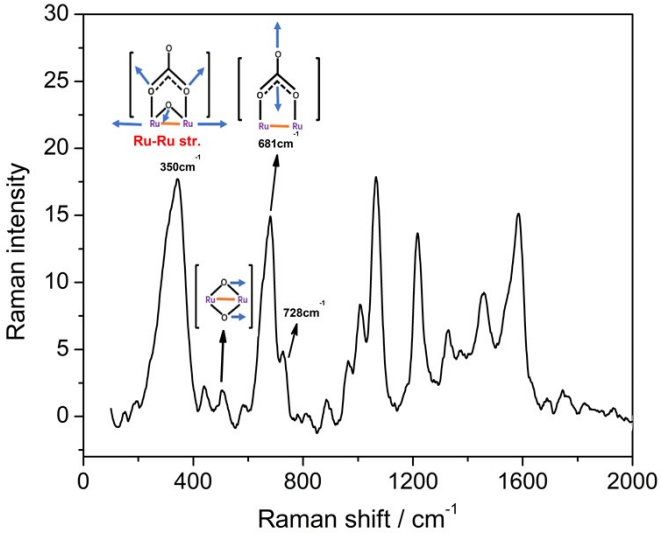

Fig. S9 Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and as-synthesized product of **1.**

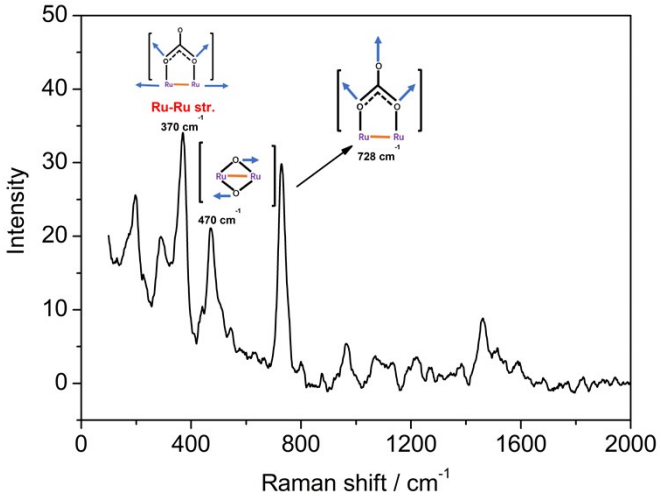

Fig. S10 Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and as-synthesized product of **2.**

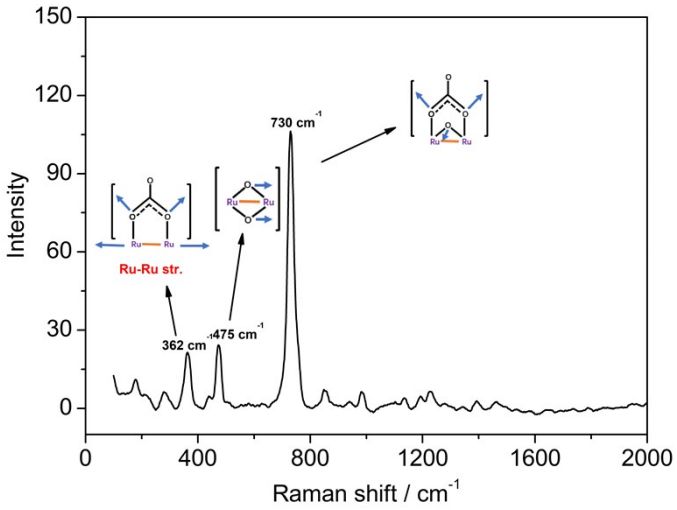

Fig. S11 Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and as-synthesized product of **3.**

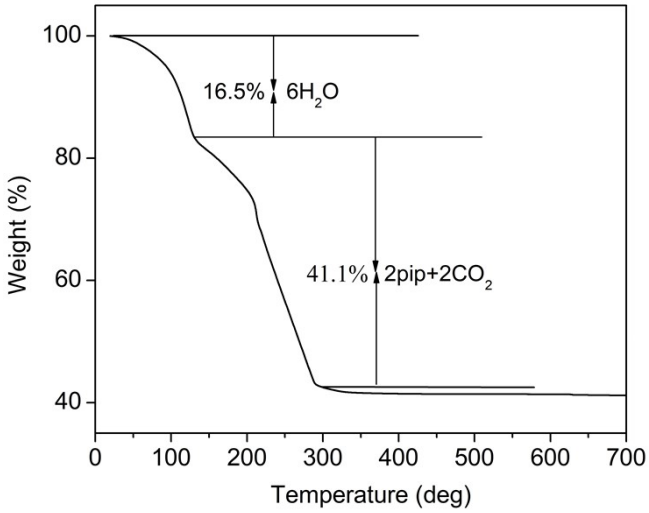

Fig. S12 TG curves of compounds **1.**

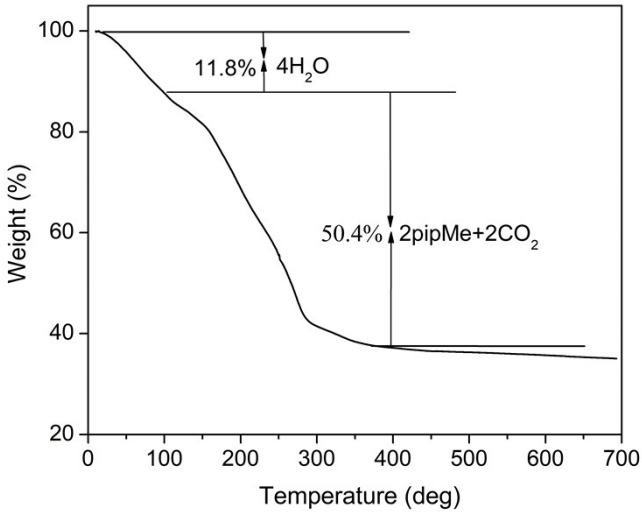

Fig. S13 TG curves of compounds **2.**

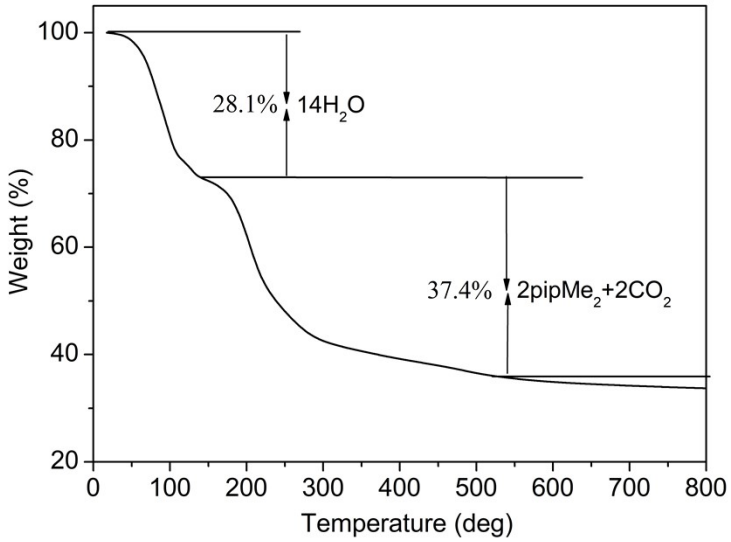

Fig. S14 TG curves of compounds **3.**

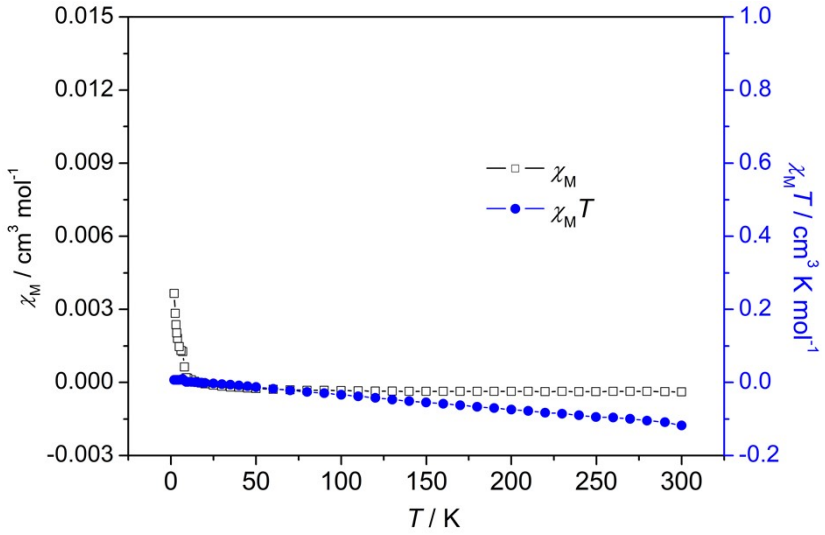

Fig. S15 χ_M and $\chi_M T$ vs. T plots of compound **1.**

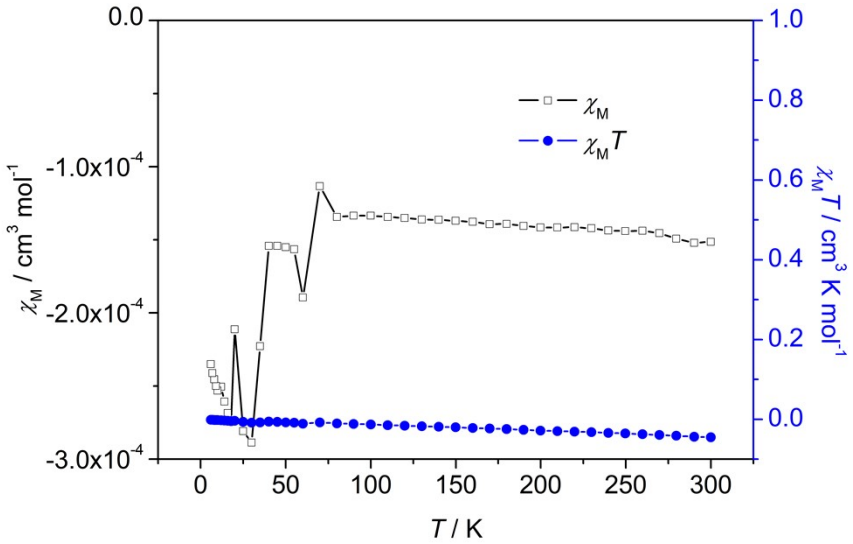

Fig. S16 χ_M and $\chi_M T$ vs. T plots of compound **2.**

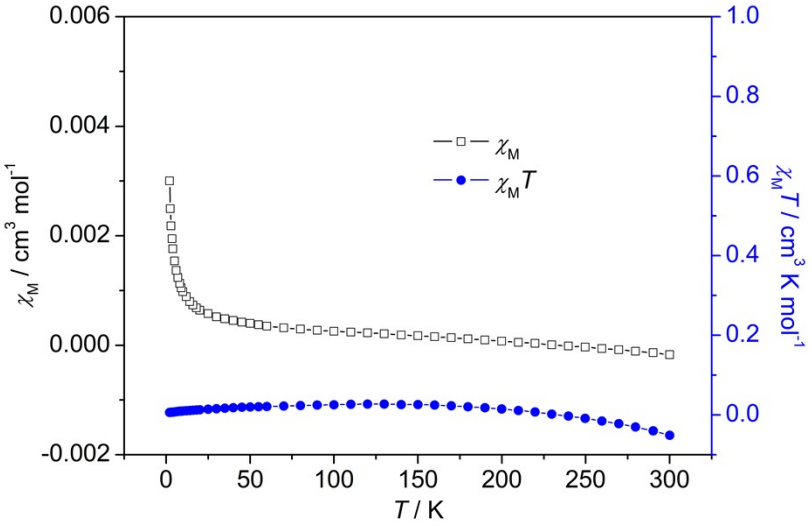

Fig. S17 χ_M and $\chi_M T$ vs. T plots of compound **3.**

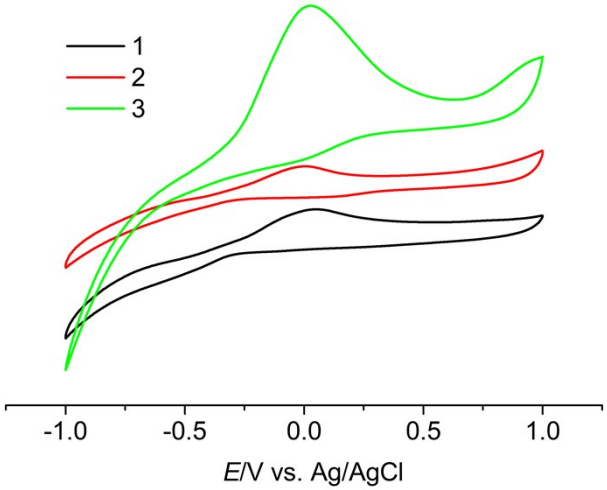

Fig. S18 Cyclic voltammograms of **1**-**3** recorded in 1.0 M KCl aqueous solution**.**

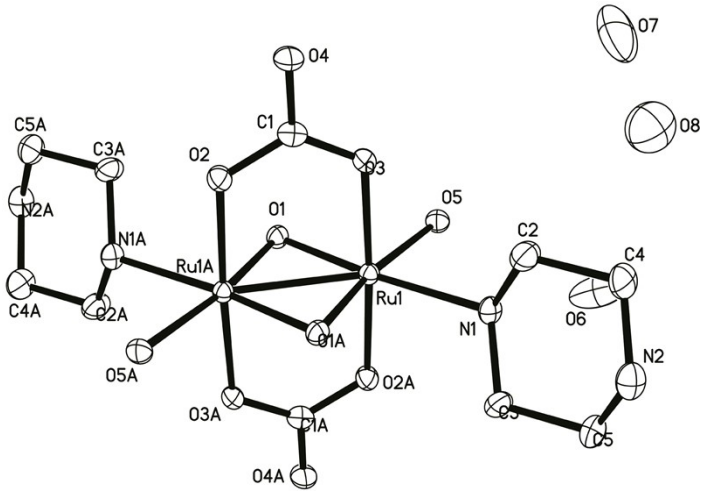

Fig. S19 ORTEP representation of the crystal structure of **1**

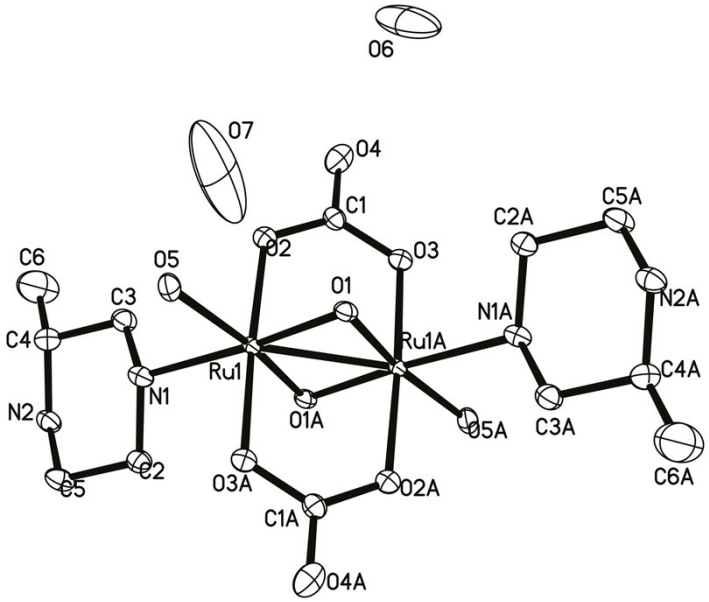

Fig. S20 ORTEP representation of the crystal structure of **2**

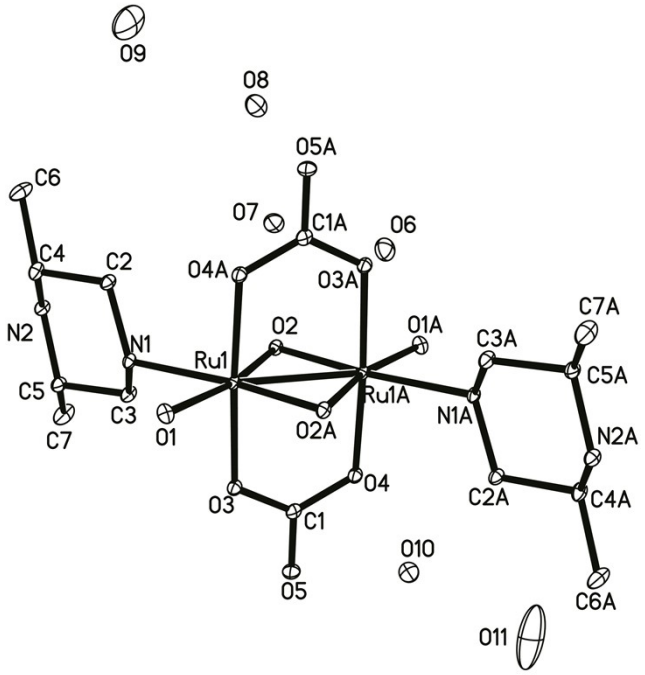

Fig. S21 ORTEP representation of the crystal structure of **3**

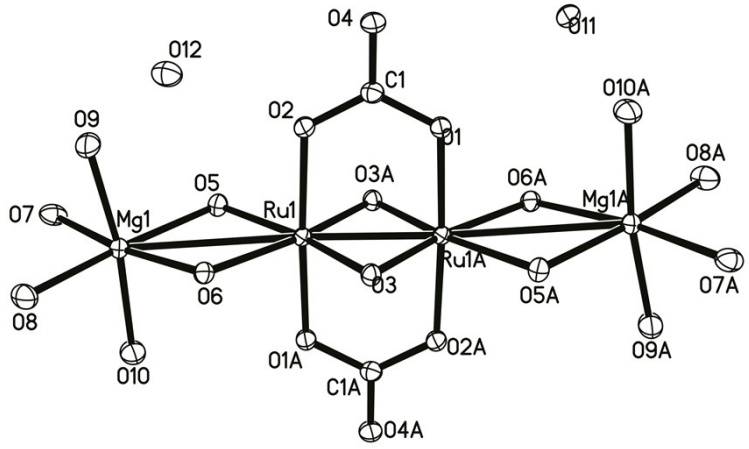

Fig. S22 ORTEP representation of the crystal structure of **4**

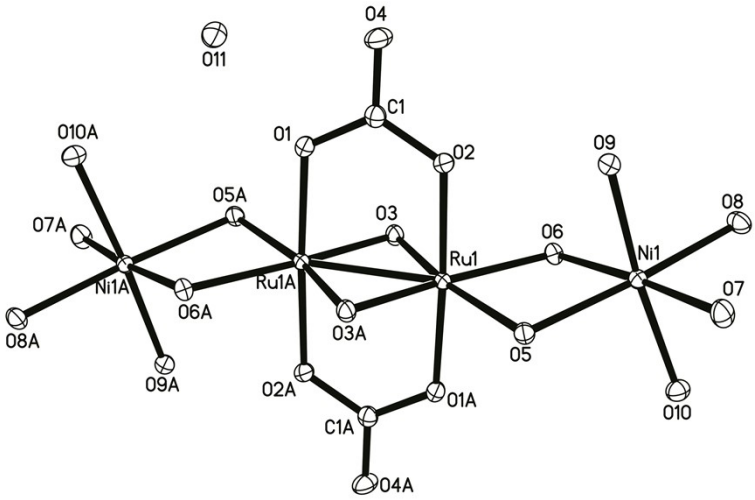

Fig. S23 ORTEP representation of the crystal structure of **5**

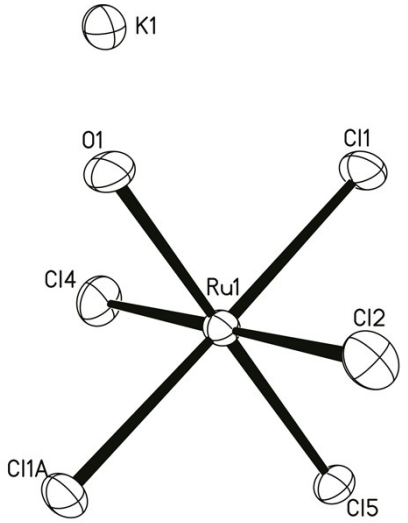

Fig. S24 ORTEP representation of the crystal structure of **6**

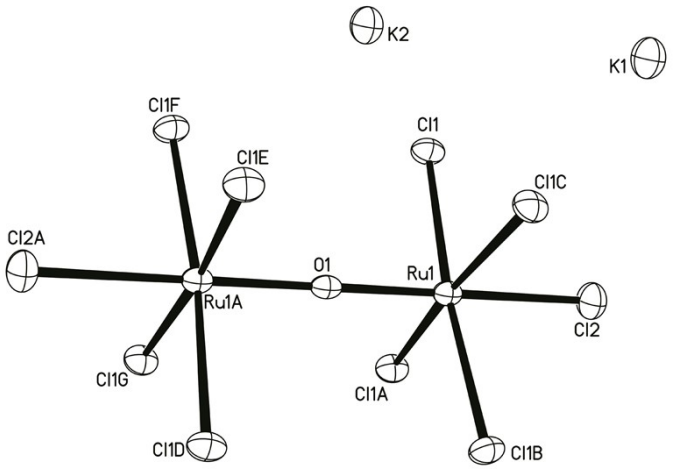

Fig. S25 ORTEP representation of the crystal structure of **7**

Table S3. Selected bond distances (Å) and angles (˚) for compound **1**

Selected bond distances (Å)			
Ru(1)-Ru(1A)	2.3849(8)	O(3)-C(1)	1.282(6)
Ru(1)-O(1)	1.929(3)	O(4)-C(1)	1.260(6)
Ru(1)-O(3)	2.050(3)	N(1)-C(2)	1.470(6)
Ru(1)-O(5)	1.996(3)	N(1)-C(3)	1.485(6)
Ru(1)-N(1)	2.145(4)	N(2)-C(4)	1.481(7)
Ru(1)-O(1A)	1.881(3)	N(2)-C(5)	1.476(7)
Ru(1)-O(2A)	2.037(3)	C(2)-C(4)	1.521(7)
O(2)-C(1)	1.309(5)	C(3)-C(5)	1.512(7)
Selected angles (˚)			
O(1)-Ru(1)-O(3)	87.95(12)	Ru(1A)-Ru(1)-O(1A)	52.15(9)
O(1)-Ru(1)-O(5)	88.07(12)	Ru(1A)-Ru(1)-O(2A)	88.98(8)
O(1A)-Ru(1)-N(1)	170.66(13)	O(1A)-Ru(1)-O(2A)	89.33(13)
Ru(1A)-Ru(1)-O(1)	50.35(9)	Ru(1)-O(1)-Ru(1)#1	77.51(11)
O(1)-Ru(1)-O(1A)	102.49(13)	Ru(1A)-O(2)-C(1)	119.1(3)
O(1)-Ru(1)-O(2A)	89.40(12)	Ru(1)-O(3)-C(1)	119.9(3)
O(3)-Ru(1)-O(5)	89.45(12)	Ru(1)-N(1)-C(2)	114.6(3)
O(3)-Ru(1)-N(1)	93.34(12)	Ru(1)-N(1)-C(3)	114.4(3)
Ru(1A)-Ru(1)-O(3)	88.21(8)	C(2)-N(1)-C(3)	110.3(4)
O(1A)-Ru(1)-O(3)	89.84(13)	C(4)-N(2)-C(5)	110.8(4)
O(2A)-Ru(1)-O(3)	176.98(11)	C(2)-C(1)-O(4)	116.8(4)
O(5)-Ru(1)-N(1)	82.70(13)	O(3)-C(1)-O(4)	119.4(4)
Ru(1A)-Ru(1)-O(5)	138.40(9)	O(2)-C(1)-O(3)	123.8(4)
O(1A)-Ru(1)-O(5)	169.39(13)	N(1)-C(2)-C(4)	112.9(4)
O(2A)-Ru(1)-O(5)	91.91(12)	N(1)-C(3)-C(5)	112.2(5)
Ru(1A)-Ru(1)-N(1)	138.90(10)	N(2)-C(4)-C(2)	110.6(4)
O(1A)-Ru(1)-N(1)	86.77(13)	N(2)-C(5)-C(3)	110.4(4)
O(2A)-Ru(1)-N(1)	89.51(12)		

Symmetry transformations used to generate equivalent atoms: A -x, -y, 2-z

Table S4. Selected bond distances (Å) and angles (˚) for compound **2**

Selected bond distances (Å)			
Ru(1)-Ru(1A)	2.3808(6)	O(4)-C(1)	1.262(7)
Ru(1)-O(1)	1.925(4)	N(1)-C(2)	1.493(7)
Ru(1)-O(2)	2.049(4)	N(1)-C(3)	1.474(8)
Ru(1)-O(5)	2.019(4)	N(2)-C(4)	1.485(9)
Ru(1)-N(1)	2.149(4)	N(2)-C(5)	1.493(9)
Ru(1)-O(1A)	1.874(4)	C(2)-C(5)	1.522(8)
Ru(1)-O(3A)	2.043(4)	C(3)-C(4)	1.530(9)
O(2)-C(1)	1.295(7)	C(4)-C(6)	1.489(13)
O(3)-C(1)	1.303(7)		
Selected angles (˚)			
O(1)-Ru(1)-O(2)	88.70(16)	Ru(1A)-Ru(1)-O(1A)	52.15(12)
O(1)-Ru(1)-O(5)	87.92(18)	Ru(1A)-Ru(1)-O(2A)	89.06(12)
O(1A)-Ru(1)-N(1)	171.58(19)	O(1A)-Ru(1)-O(2A)	89.91(17)
Ru(1A)-Ru(1)-O(1)	50.24(13)	Ru(1)-O(1)-Ru(1A)	77.62(16)
O(1)-Ru(1)-O(1A)	102.39(17)	Ru(1)-O(2)-C(1)	120.1(4)
O(1)-Ru(1)-O(3A)	88.92(16)	Ru(1A)-O(3)-C(1)	119.4(4)
O(3)-Ru(1)-O(5)	90.03(18)	Ru(1)-N(1)-C(2)	113.9(3)
O(3)-Ru(1)-N(1)	92.76(17)	Ru(1)-N(1)-C(3)	114.3(3)
Ru(1A)-Ru(1)-O(2)	88.23(11)	C(2)-N(1)-C(3)	110.1(4)
O(1A)-Ru(1)-O(2)	89.08(17)	C(4)-N(2)-C(5)	111.5(5)
O(2)-Ru(1)-O(3A)	177.16(16)	O(3)-C(1)-O(4)	117.5(5)
O(5)-Ru(1)-N(1)	83.79(18)	O(2)-C(1)-O(4)	119.4(5)
Ru(1A)-Ru(1)-O(5)	138.15(12)	O(2)-C(1)-O(3)	123.1(5)
O(1A)-Ru(1)-O(5)	169.63(17)	N(1)-C(2)-C(5)	111.3(5)
O(3A)-Ru(1)-O(5)	91.43(18)	N(1)-C(3)-C(4)	113.3(5)
Ru(1A)-Ru(1)-N(1)	138.06(13)	N(2)-C(4)-C(3)	109.7(5
O(1A)-Ru(1)-N(1)	85.94(18)	N(2)-C(4)-C(6)	111.1(7)
O(3A)-Ru(1)-N(1)	89.81(17)	N(2)-C(5)-C(2)	109.4(5)

Symmetry transformations used to generate equivalent atoms: A -x, 1-y, -z

Table S5. Selected bond distances (Å) and angles (˚) for compound **3**

Selected bond distances (Å)			
Ru(1)-Ru(1A)	2.3898(4)	O(5)-C(1)	1.260(3)
Ru(1)-O(1)	1.9903(17)	N(1)-C(2)	1.488(3)
Ru(1)-O(2)	1.8883(17)	N(1)-C(3)	1.487(3)
Ru(1)-O(3)	2.0438(17)	N(2)-C(4)	1.504(3)
Ru(1)-N(1)	2.163(2)	N(2)-C(5)	1.497(3)
Ru(1)-O(2A)	1.9239(17)	C(2)-C(4)	1.528(3)
Ru(1)-O(4A)	2.0406(17)	C(3)-C(5)	1.518(4)
O(3)-C(1)	1.301(3)	C(4)-C(6)	1.518(4)

O(4)-C(1)	1.302(3)	C(5)-C(7)	1.517(4)
Selected angles (˚)			
O(1)-Ru(1)-O(2)	168.17(7)	O(2A)-Ru(1)-O(4A)	88.54(7)
O(1)-Ru(1)-O(3)	92.98(7)	Ru(1)-O(2)-Ru(1A)	77.63(7)
O(1)-Ru(1)-N(1)	83.11(8)	Ru(1)-O(3)-C(1)	119.68(14)
O(1)-Ru(1)-O(2A)	89.21(7)	Ru(1)-O(4)-C(1)	120.00(15)
Ru(1A)-Ru(1)-O(1)	139.66(5)	Ru(1)-N(1)-C(2)	114.82(15)
O(1)-Ru(1)-O(4A)	88.24(7)	C(2)-N(1)-C(3)	110.24(19)
O(2)-Ru(1)-O(3)	89.82(7)	Ru(1)-N(1)-C(3)	112.16(15)
O(2)-Ru(1)-N(1)	85.38(8)	C(4)-N(2)-C(5)	111.61(19)
Ru(1A)-Ru(1)-O(2)	51.85(5)	O(3)-C(1)-O(5)	118.7(2)
O(2)-Ru(1)-O(2A)	102.37(7)	O(3)-C(1)-O(4)	123.1(2)
O(2)-Ru(1)-O(4A)	89.59(7)	O(4)-C(1)-O(5)	118.3(2)
O(3)-Ru(1)-N(1)	90.30(8)	N(1)-C(2)-C(4)	113.18(19)
Ru(1A)-Ru(1)-O(3)	88.63(5)	N(1)-C(3)-C(5)	113.2(2)
O(2A)-Ru(1)-O(3)	88.48(7)	N(2)-C(4)-C(2)	109.52(19)
O(3)-Ru(1)-O(4A)	176.76(7)	N(2)-C(4)-C(6)	108.9(2)
Ru(1A)-Ru(1)-N(1)	137.21(6)	C(2)-C(4)-C(6)	111.5(2)
O(2A)-Ru(1)-N(1)	172.15(8)	C(3)-C(5)-C(7)	111.1(2)
O(4A)-Ru(1)-N(1)	92.83(8)	N(2)-C(5)-C(7)	109.7(2)
Ru(1A)-Ru(1)-O(2A)	50.52(5)	N(2)-C(5)-C(3)	108.90(19)
Ru(1A)-Ru(1)-O(4A)	88.50(5)		

Symmetry transformations used to generate equivalent atoms: A, 1-x, 1-y, 1-z

Table S6. Selected bond distances (Å) and angles (˚) for compound **4**

Selected bond distances (Å)			
Ru(1)-Ru(1A)	2.4001(4)	Mg(1)-O(6)	2.1069(19)
Ru(1)-O(1A)	2.0185(16)	Mg(1)-O(7)	2.085(2)
Ru(1)-O(2)	2.0648(16)	Mg(1)-O(8)	2.053(2)
Ru(1)-O(3)	1.9004(16)	Mg(1)-O(9)	2.024(2)
Ru(1)-O(5)	2.0568(17)	Mg(1)-O(10)	2.052(2)
Ru(1)-O(6)	2.0439(16)	O(1)-C(1)	1.311(3)
Ru(1)-O(3A)	1.9060(16)	O(2)-C(1)	1.308(3)
Mg(1)-O(5)	2.0839(18)	O(3)-C(1)	1.254(3)
Selected angles (˚)			
Ru(1A)-Ru(1)-O(2)	87.13(5)	O(5)-Mg(1)-O(6)	76.66(7)
Ru(1A)-Ru(1)-O(3)	51.01(5)	O(5)-Mg(1)-O(7)	95.12(8)
Ru(1A)-Ru(1)-O(5)	139.61(5)	O(5)-Mg(1)-O(8)	172.17(9)
Ru(1A)-Ru(1)-O(6)	141.72(5)	O(5)-Mg(1)-O(9)	93.47(8)
Ru(1A)-Ru(1)-O(1A)	89.90(5)	O(5)-Mg(1)-O(10)	94.45(8)
Ru(1A)-Ru(1)-O(3A)	50.81(5)	O(6)-Mg(1)-O(7)	171.43(9)
O(2)-Ru(1)-O(3)	87.89(7)	O(6)-Mg(1)-O(8)	95.54(8)
O(2)-Ru(1)-O(5)	92.18(7)	O(6)-Mg(1)-O(9)	93.01(8)
O(2)-Ru(1)-O(6)	93.13(6)	O(6)-Mg(1)-O(10)	91.60(8)

O(1A)-Ru(1)-O(2)	177.02(6)	O(7)-Mg(1)-O(8)	92.66(9)
O(2)-Ru(1)-O(3A)	88.48(6)	O(7)-Mg(1)-O(9)	85.01(9)
O(3)-Ru(1)-O(5)	169.38(7)	O(7)-Mg(1)-O(10)	91.43(9)
O(3)-Ru(1)-O(6)	90.72(7)	O(8)-Mg(1)-O(9)	86.29(9)
O(1A)-Ru(1)-O(3)	90.14(7)	O(8)-Mg(1)-O(10)	86.26(9)
O(3)-Ru(1)-O(3A)	101.82(7)	O(9)-Mg(1)-O(10)	171.59(9)
O(5)-Ru(1)-O(6)	78.67(7)	Ru(1A)-O(1)-C(1)	120.03(14)
O(1A)-Ru(1)-O(5)	90.16(7)	Ru(1)-O(2)-C(1)	120.69(13)
O(3A)-Ru(1)-O(5)	88.80(7)	Ru(1)-O(5)-Mg(1)	102.28(8)
O(1A)-Ru(1)-O(6)	89.13(6)	Ru(1)-O(6)-Mg(1)	101.93(7)
O(3A)-Ru(1)-O(6)	167.41(7)	O(1)-C(1)-O(2)	122.3(2)
O(1A)-Ru(1)-O(3A)	89.73(7)	O(1)-C(1)-O(4)	118.3(2)
Ru(1)-O(3)-Ru(1A)	78.18(6)	O(2)-C(1)-O(4)	119.40(18)

Symmetry transformations used to generate equivalent atoms: A, 1-x, -y, -z

Table S7. Selected bond distances (Å) and angles (˚) for compound **5**

Selected bond distances (Å)			
Ru(1)-Ru(1A)	2.3848(4)	Ni(1)-O(6)	2.0598(18)
Ru(1)-O(1A)	2.0398(17)	Ni(1)-O(7)	2.0574(19)
Ru(1)-O(2)	2.0417(17)	Ni(1)-O(8)	2.0347(18)
Ru(1)-O(3)	1.8879(17)	Ni(1)-O(9)	2.0766(18)
Ru(1)-O(5)	2.0625(17)	Ni(1)-O(10)	2.0860(18)
Ru(1)-O(6)	2.0440(17)	O(1)-C(1)	1.296(3)
Ru(1)-O(3A)	1.8983(17)	O(2)-C(1)	1.304(3)
Ni(1)-O(5)	2.0704(17)	O(4)-C(1)	1.247(3)
Selected angles (˚)			
Ru(1A)-Ru(1)-O(2)	88.23(5)	O(5)-Ni(1)-O(6)	78.37(7)
Ru(1A)-Ru(1)-O(3)	51.16(5)	O(5)-Ni(1)-O(7)	96.43(8)
Ru(1A)-Ru(1)-O(5)	140.67(5)	O(5)-Ni(1)-O(8)	175.59(7)
Ru(1A)-Ru(1)-O(6)	140.36(5)	O(5)-Ni(1)-O(9)	88.13(7)
Ru(1A)-Ru(1)-O(1A)	88.62(5)	O(5)-Ni(1)-O(10)	94.33(7)
Ru(1A)-Ru(1)-O(3A)	50.77(5)	O(6)-Ni(1)-O(7)	174.81(8)
O(2)-Ru(1)-O(3)	88.52(7)	O(6)-Ni(1)-O(8)	97.49(7)
O(2)-Ru(1)-O(5)	92.64(7)	O(6)-Ni(1)-O(9)	93.79(7)
O(2)-Ru(1)-O(6)	87.53(7)	O(6)-Ni(1)-O(10)	93.65(7)
O(1A)-Ru(1)-O(2)	176.80(7)	O(7)-Ni(1)-O(8)	87.71(8)
O(2)-Ru(1)-O(3A)	89.25(7)	O(7)-Ni(1)-O(9)	86.08(7)
O(3)-Ru(1)-O(5)	168.12(7)	O(7)-Ni(1)-O(10)	86.60(7)
O(3)-Ru(1)-O(6)	89.34(7)	O(8)-Ni(1)-O(9)	90.63(8)
O(1A)-Ru(1)-O(3)	89.04(7)	O(8)-Ni(1)-O(10)	87.44(7)
O(3)-Ru(1)-O(3A)	101.92(7)	O(9)-Ni(1)-O(10)	172.50(7)
O(5)-Ru(1)-O(6)	78.91(7)	Ru(1A)-O(1)-C(1)	120.36(16)
O(1A)-Ru(1)-O(5)	90.17(7)	Ru(1)-O(2)-C(1)	120.52(15)
O(3A)-Ru(1)-O(5)	89.92(7)	Ru(1)-O(5)-Ni(1)	99.68(7)

O(1A)-Ru(1)-O(6)	94.52(7)	Ru(1)-O(6)-Ni(1)	100.65(8)
O(3A)-Ru(1)-O(6)	168.21(7)	O(1)-C(1)-O(2)	121.9(2)
O(1A)-Ru(1)-O(3A)	89.22(7)	O(1)-C(1)-O(4)	118.8(2)
Ru(1)-O(3)-Ru(1A)	78.08(7)	O(2)-C(1)-O(4)	119.3(2)

Symmetry transformations used to generate equivalent atoms: A, 1-x, -y, -z

Table S8. Selected bond distances (Å) and angles (˚) for compound **6**

Selected bond distances (Å)			
Ru(1)-O(1)	2.104(6)	Ru(1)-Cl(4)	2.3451(17)
Ru(1)-Cl(1)	2.3661(11)	Ru(1)-Cl(5)	2.3283(16)
Ru(1)-Cl(2)	2.363(2)	Ru(1)-Cl(1A)	2.3661(11)
Selected angles (˚)			
Cl(1)-Ru(1)-Cl(2)	89.71(3)	Cl(5)-Ru(1)-O(1)	179.67(16)
Cl(1)-Ru(1)-Cl(4)	90.29(3)	Cl(1A)-Ru(1)-Cl(2)	89.71(3)
Cl(1)-Ru(1)-Cl(5)	90.78(3)	Cl(4)-Ru(1)-Cl(5)	90.22(6)
Cl(1)-Ru(1)-O(1)	89.22(3)	Cl(4)-Ru(1)-O(1)	90.11(16)
Cl(1)-Ru(1)-Cl(1A)	178.33(5)	Cl(1A)-Ru(1)-Cl(4)	90.29(3)
Cl(2)-Ru(1)-Cl(4)	179.81(6)	Cl(1A)-Ru(1)-Cl(5)	90.78(3)
Cl(2)-Ru(1)-Cl(5)	89.97(6)	Cl(1A)-Ru(1)-O(1)	89.22(3)
Cl(2)-Ru(1)-O(1)	89.70(16)		

Symmetry transformations used to generate equivalent atoms: A x, 3/2-y, z.

Table S9. Selected bond distances (Å) and angles (˚) for compound **7**

Selected bond distances (Å)			
Ru(1)-O(1)	1.8209(14)	Ru(1)-Cl(1A)	2.3653(15)
Ru(1)-Cl(1)	2.3653(15)	Ru(1)-Cl(1B)	2.3653(15)
Ru(1)-Cl(2)	2.304(5)	Ru(1)-Cl(1C)	2.3653(15)
Selected angles (˚)			
Cl(1)-Ru(1)-Cl(2)	86.94(7)	Cl(1C)-Ru(1)-Cl(2)	86.94(7)
Cl(1)-Ru(1)-O(1)	93.06(7)	Cl(1A)-Ru(1)-O(1)	93.06(7)
Cl(1)-Ru(1)-Cl(1A)	89.84(5)	Cl(1B)-Ru(1)-O(1)	93.06(7)
Cl(1)-Ru(1)-O(1B)	173.88(11)	Cl(1C)-Ru(1)-O(1)	93.06(7)
Cl(1)-Ru(1)-Cl(1C)	89.84(5)	Cl(1A)-Ru(1)-Cl(1B)	89.84(5)
Cl(2)-Ru(1)-O(1)	179.98(4)	Cl(1A)-Ru(1)-Cl(1C)	173.88(11)
Cl(1A)-Ru(1)-Cl(2)	86.94(7)	Cl(1B)-Ru(1)-O(1C)	89.84(5)
Cl(1B)-Ru(1)-Cl(2)	86.94(7)	Ru(1)-O(1)-Ru(1D)	180.00

Symmetry transformations used to generate equivalent atoms: A 1-y, -1+x, z; b 2-x, -y, z; c 1+y, 1-x, z; d x, -y, 1-z.

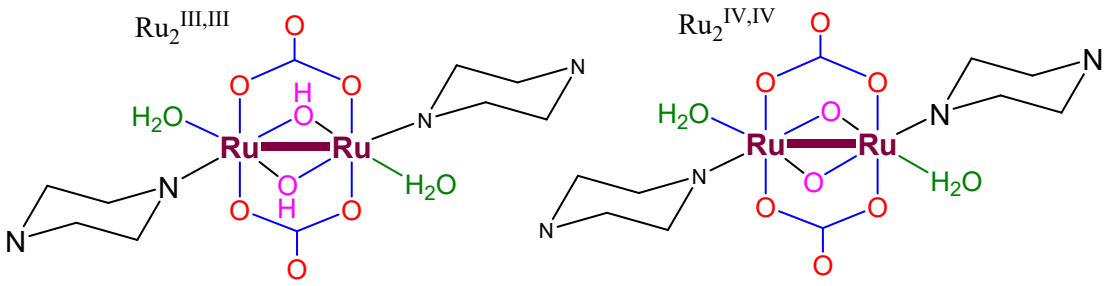

Table S10 Selected structural parameters of compound **1**. Experiments and DFT-computed values for Models $Ru_2^{III,III}$ and $Ru_2^{IV,IV}$

	Exp.	$Ru_2^{III,III}$	$Ru_2^{IV,IV}$
Ru(1)-Ru(1A）	2.3849(8)	2.471	2.400
Ru(1)-O(1)(b)	1.881(3)	2.027	1.900
Ru(1)-O(1A)(b)	1.929(3)	2.077	1.973
Ru(1)-O(3)(a)	2.050(3)	2.101	2.079
Ru(1)-O(2A)(a)	2.037(3)	2.115	2.081
Ru(1)-N(1)(t)	2.145(4)	2.108	2.133
Ru(1)-O(8)(t)	1.996(3)	2.027	2.178
O(1)-Ru(1)-O(1A)	102.49(13)	105.900	103.442
N(1)-Ru(1)-O(5)	82.70(13)	85.725	81.050
Ru(1)-O(1)-Ru(1A)	77.51(11)	74.044	76.562
Ru(1)-O(3)-C(1)	119.9(3)	122.356	120.135
Ru(1A)-O(2)-C(1)	119.1(3)	121.097	120.213

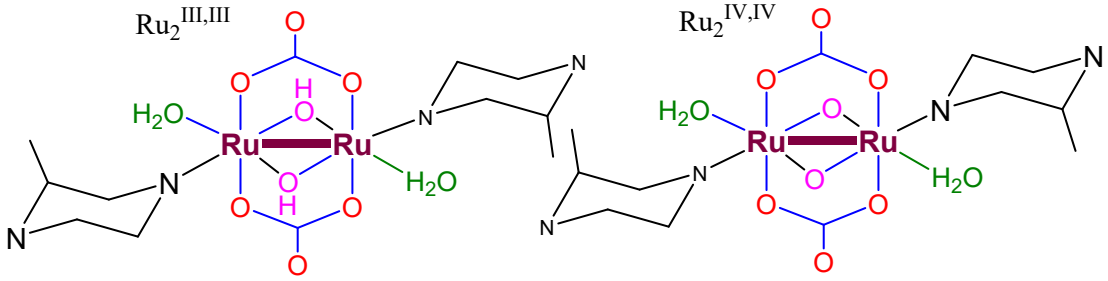

Table S11 Selected structural parameters of compounds **2**. Experiments and DFT-computed values for Models $Ru_2^{III,III}$ and $Ru_2^{IV,IV}$

	Exp.	$Ru_2^{III,III}$	$Ru_2^{IV,IV}$
Ru(1)-Ru(1A)	2.3808(6)	2.498	2.401
Ru(1)-O(1)(b)	1.925(4)	2.064	1.974
Ru(1)-O(1A)(b)	1.874(4)	2.025	1.898
Ru(1)-O(3A)(a)	2.043(4)	2.095	2.080
Ru(1)-O(2)(a)	2.049(4)	2.105	2.080
Ru(1)-N(1)(t)	2.149(4)	2.114	2.132
Ru(1)-O(5)(t)	2.019(4)	2.133	2.178
O(1)-Ru(1)-O(1A)	102.39(17)	104.692	103.381
N(1)-Ru(1)-O(5)	83.79(18)	82.213	80.919

Ru(1)-O(1)-Ru(1A)	77.62(16)	75.308	76.619
Ru(1)-O(2)-C(13)	120.1(4)	122.825	120.205
Ru(1A)-O(3)-C(13)	119.4(4)	121.994	120.160

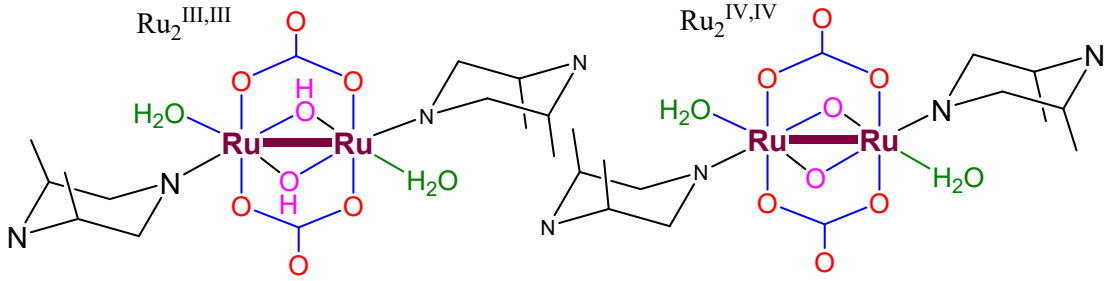

Table S12 Selected structural parameters of compound **3**. Experiments and DFT-computed values for Models $Ru_2^{III,III}$ and $Ru_2^{IV,IV}$

Atom	Exp.	$Ru_2^{III,III}$	$Ru_2^{IV,IV}$
Ru(1)-Ru(1A)	2.3898(4)	2.469	2.400
Ru(1)-O(2)(b)	1.8883(17)	2.018	1.898
Ru(1)-O(2A)(b)	1.9239(17)	2.054	1.974
Ru(1)-O(3)(a)	2.0438(17)	2.096	2.081
Ru(2)-O(4A)(a)	2.0406(17)	2.096	2.081
Ru(1)-N(1)(t)	2.163(2)	2.129	2.132
Ru(1)-O(1)(t)	1.9903(17)	2.119	2.179
O(2)-Ru(1)-O(2A)	102.37(7)	105.349	103.436
N(1)-Ru(1)-O(1)	83.11(8)	81.797	81.073
Ru(1)-O(2)-Ru(2)	77.63(7)	74.651	76.564
Ru(1)-O(3)-C(1)	119.68(14)	122.225	120.197
Ru(1A)-O(4)-C(1)	120.00(15)	122.042	120.193

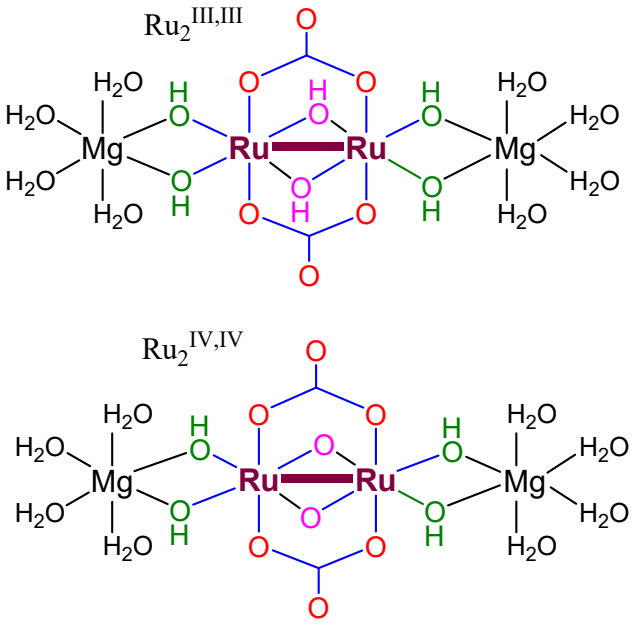

Table S13 Selected structural parameters of compounds **4**. Experiments and DFT-computed values for Models $Ru_2^{III,III}$ and $Ru_2^{IV,IV}$

	Exp.	$Ru_2^{III,III}$	$Ru_2^{IV,IV}$
Ru(1)-Ru(1A)	2.4001(4)	2.469	2.406
Ru(1)-O(3)(b)	1.9004(16)	2.045	1.934
Ru(1)-O(3A)(b)	1.9060(16)	2.052	1.937
Ru(1)-O(1A)(a)	2.0185(16)	2.093	2.095
Ru(2)-O(2)(a)	2.0648(16)	2.0126	2.088
Ru(1)-O(5)(t)	2.0568(17)	2.071	2.091
Ru(1)-O(6)(t)	2.0439(16)	2.062	2.087
Mg(1)-O(5)(t)	2.0839(18)	2.014	2.027
Mg(1)-O(6)(t)	2.1069(19)	2.019	2.026
O(3)-Ru(1)-O(3A)	101.82(7)	105.881	103.132
O(5)-Ru(1)-O(6)	78.67(7)	85.095	83.159
Ru(1)-O(3)-Ru(2)	78.18(6)	74.120	76.868
Ru(1A)-O(1)-C(1)	120.03(14)	121.448	121.413
Ru(1)-O(2)-C(1)	120.69(13)	122.448	121.671

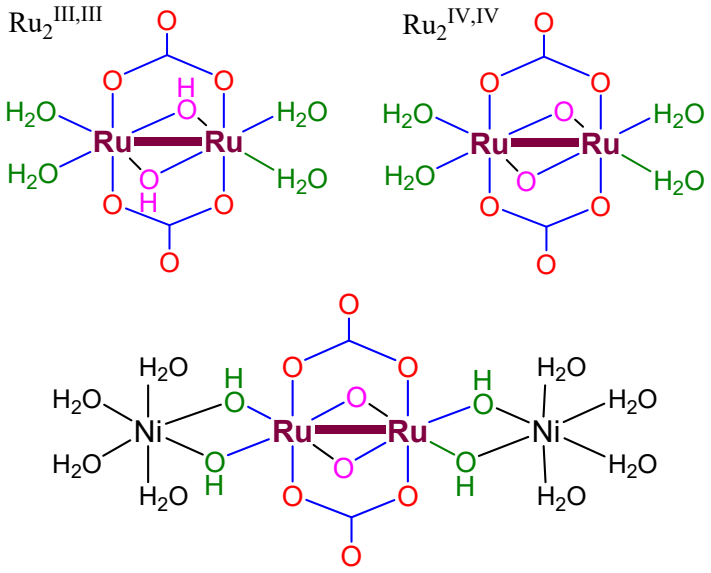

Table S14 Selected structural parameters of compounds **5**. Experiments and DFT-computed values for Models $Ru_2^{III,III}$, $Ru_2^{IV,IV}$ and without omitting.

	Exp.	$Ru_2^{III,III}$	$Ru_2^{IV,IV}$	Without omitting
Ru(1)-Ru(1A)	2.3848(4)	2.456	2.384	2.390
Ru(1)-O(3)(b)	1.8879(17)	2.033	1.924	1.918
Ru(1)-O(3A)(b)	1.8983(17)	2.038	1.923	1.916
Ru(1)-O(1)(a)	2.0398(17)	2.095	2.051	2.079
Ru(2)-O(2)(a)	2.0417(17)	2.098	2.065	2.085
Ru(1)-O(5)(t)	2.0625(17)	2.137	2.187	2.075
Ru(1)-O(6)(t)	2.0440(17)	2.135	2.169	2.072
O(3)-Ru(1)-O(3A)	101.820	105.784	103.503	102.871
O(5)-Ru(1)-O(6)	78.660	84.370	83.347	82.402

Ru(1)-O(3)-Ru(1A)	78.180	74.214	76.570	77.129
Ru(1)-O(3)-C(1)	120.690	122.814	120.237	121.673
Ru(1A)-O(3A)-C(2)	120.030	122.866	120.780	121.360

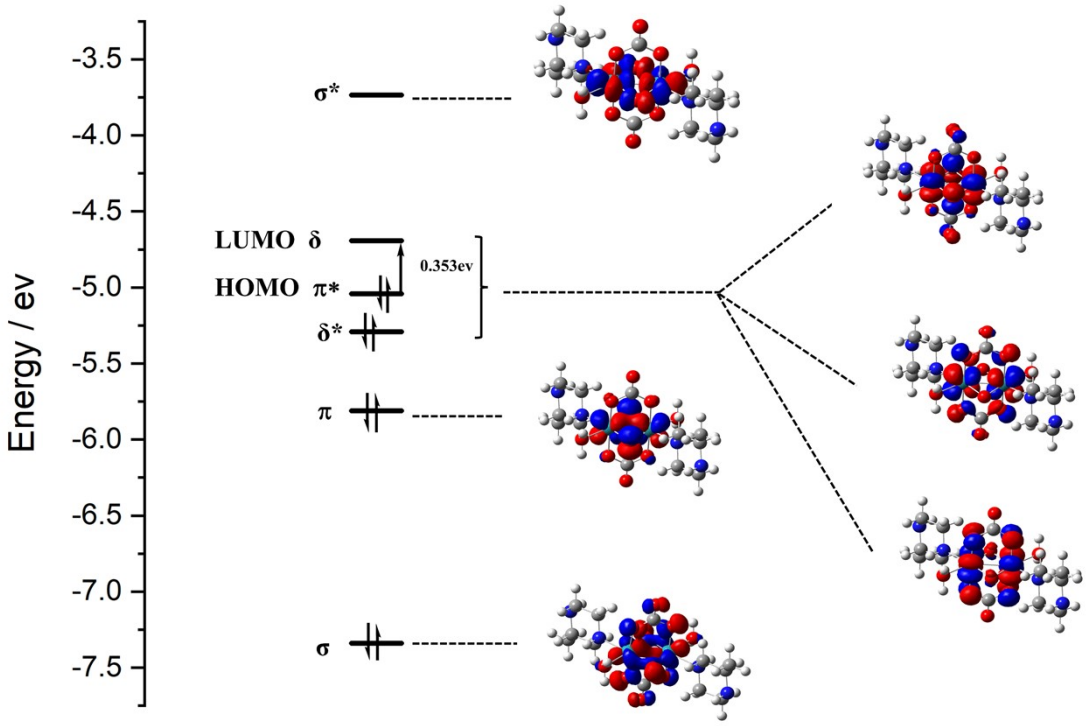

Fig. S23 Molecular orbital diagram of compound **2** with corresponding energies (eV).

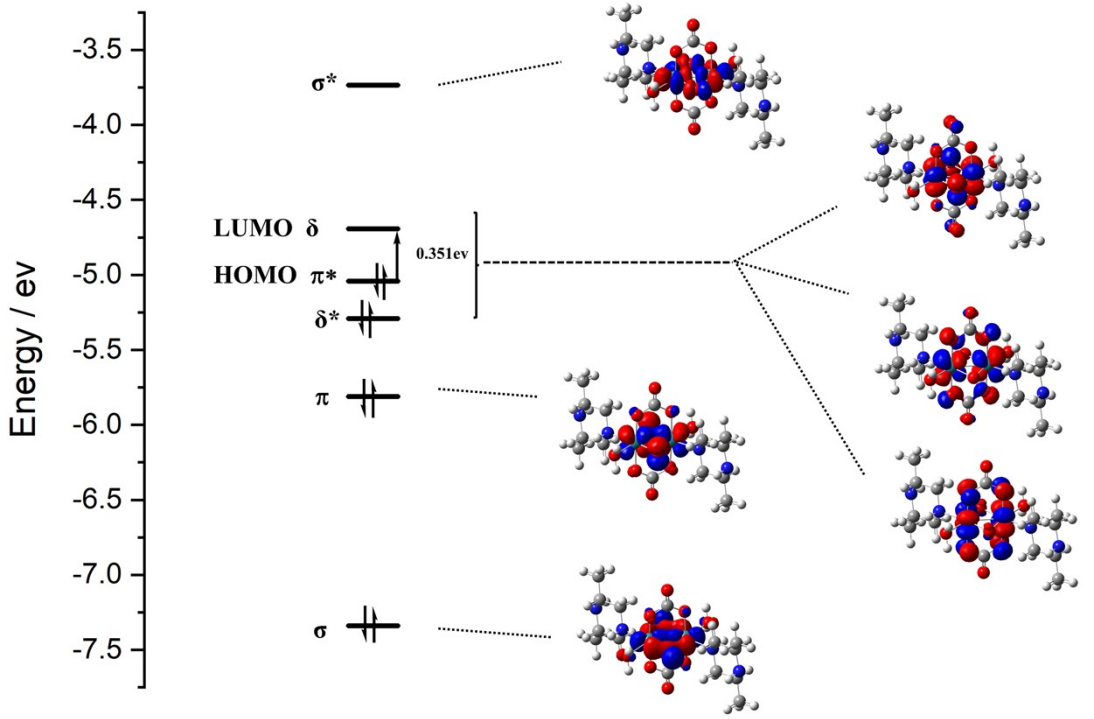

Fig. S26 Molecular orbital diagram of compound **3** with corresponding energies (eV).

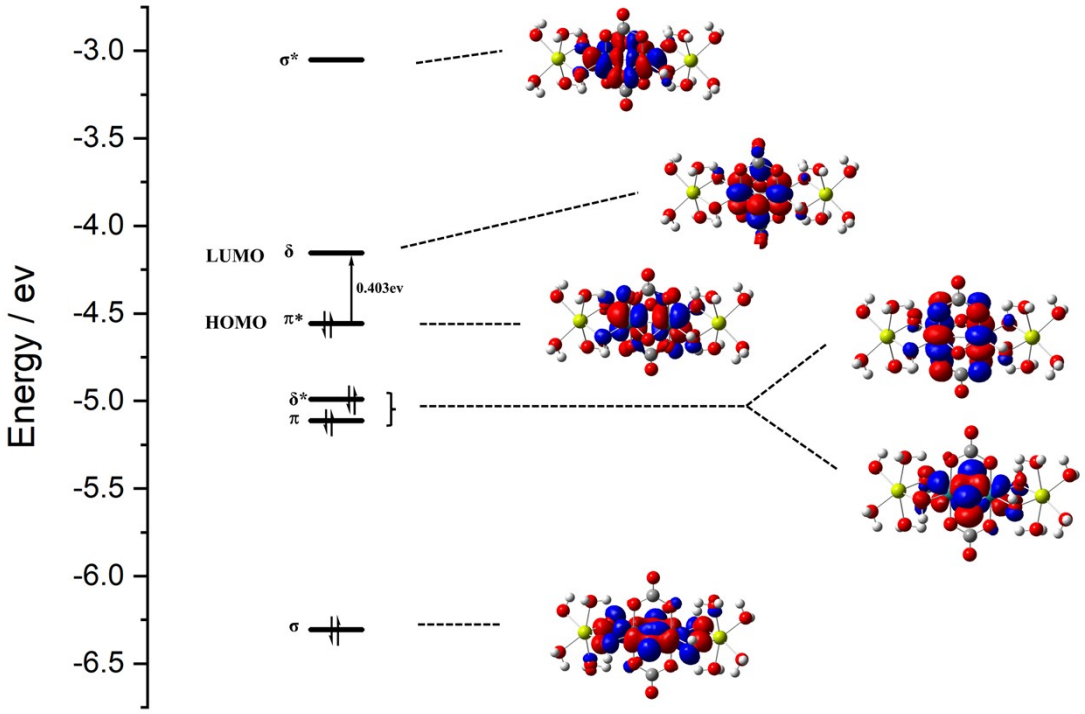

Fig. S27 Molecular orbital diagram of compound **4** with corresponding energies (eV).

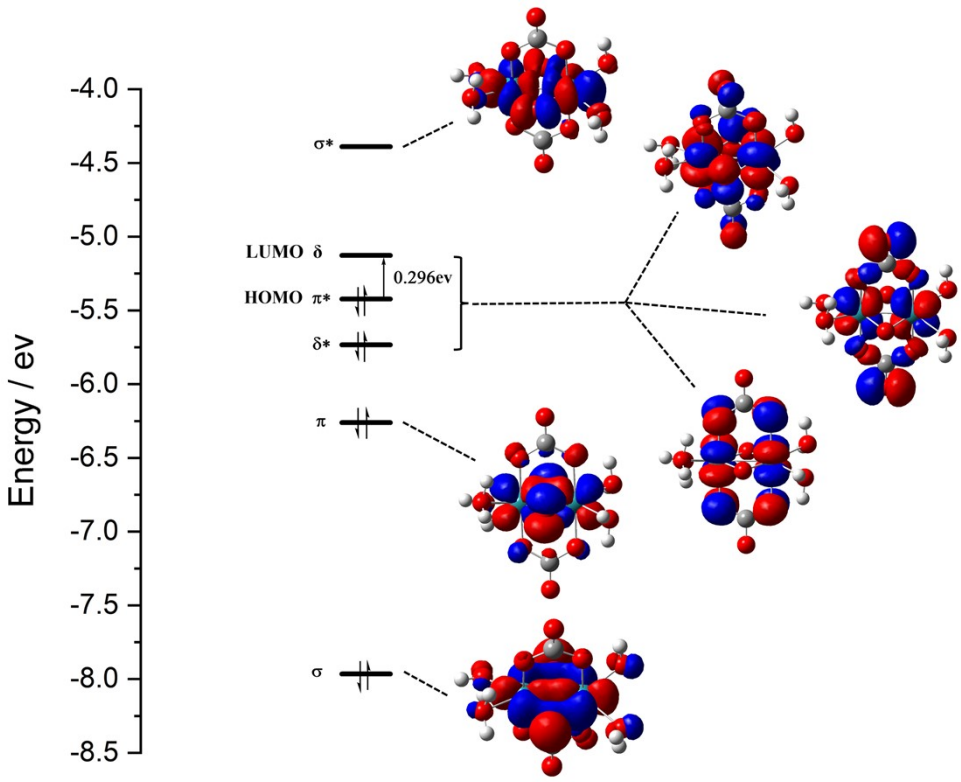

Fig. S28 Molecular orbital diagram of model $Ru_2O_2(CO_3)_2(H_2O)_4$ from compound **5** with corresponding energies (eV).

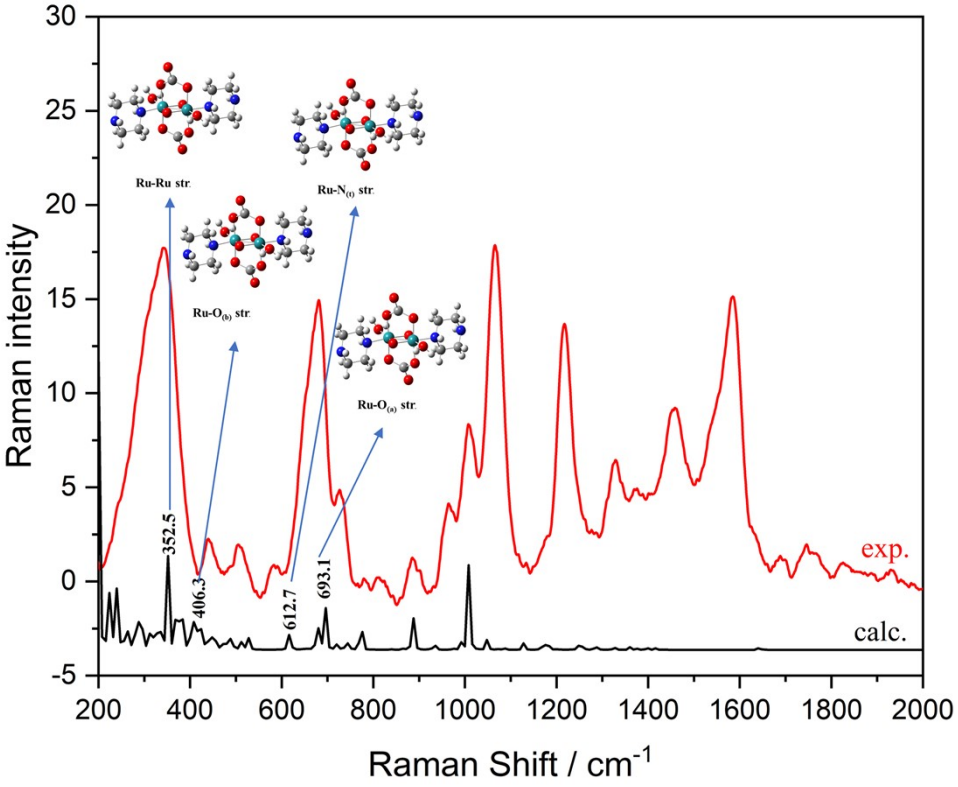

Fig. S29 Experimental and calculated Raman spectra for compound **1.**

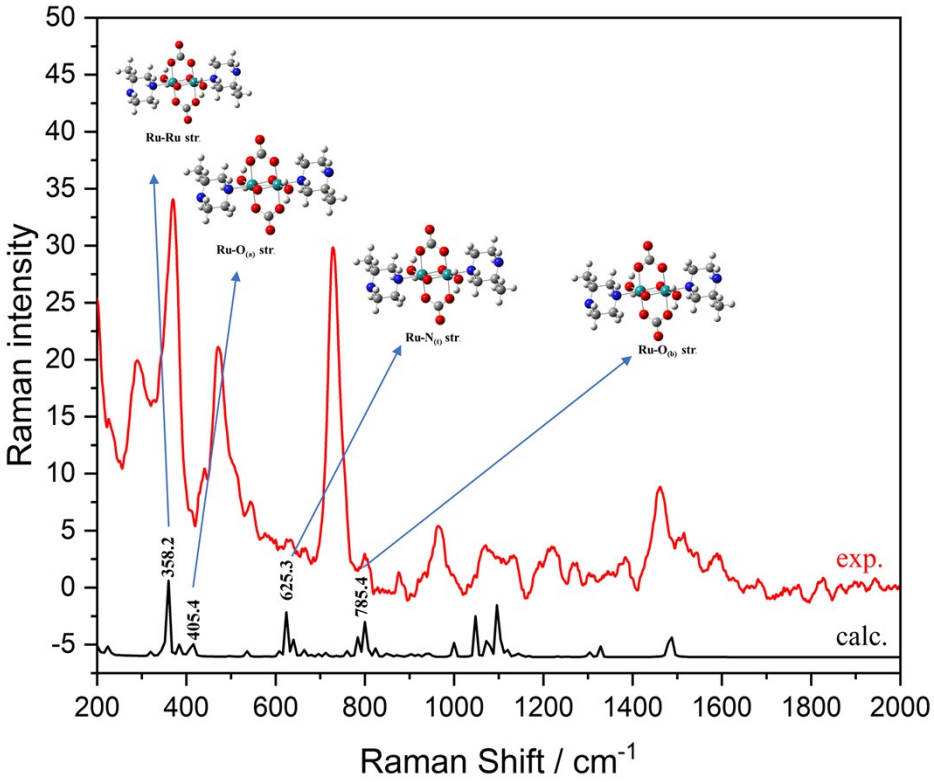

Fig. S30 Experimental and calculated Raman spectra for compound **2.**

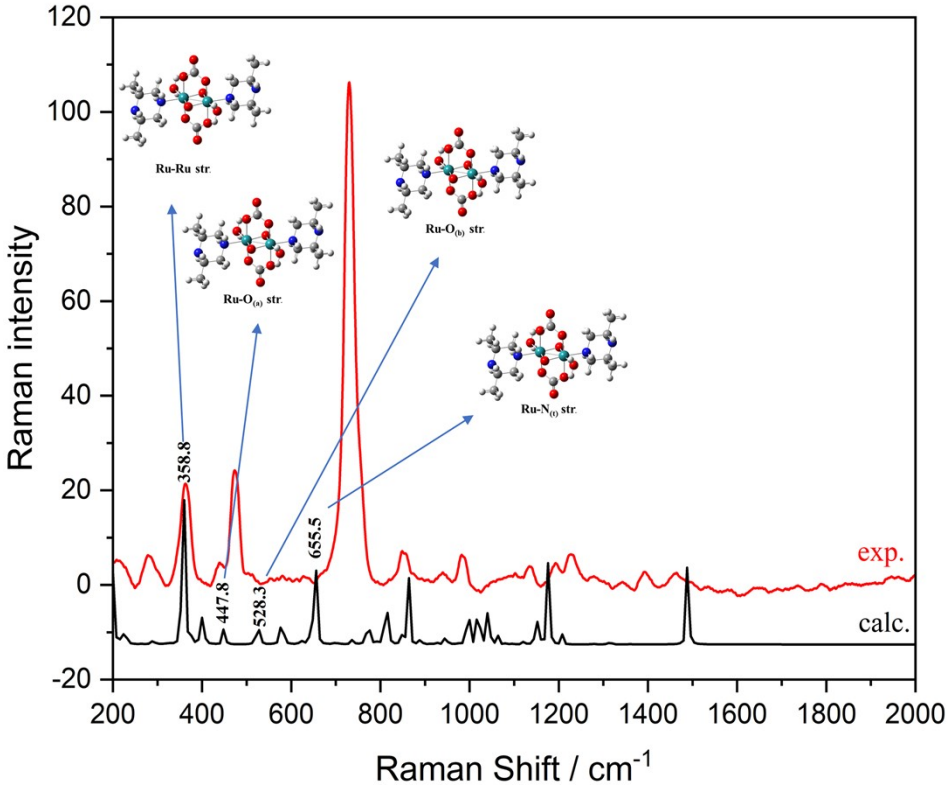

Fig. S31 Experimental and calculated Raman spectra for compound **3.**