

## Electronic Supporting Information (ESI)

### Toward a new type of heterometallic systems based on paddle-wheel Ru<sub>2</sub> dimer: first results derived from the use of high spin diruthenium(III,III) buiding block

Bing-Bing Yang, Li-Na Feng, Xiao-Meng Fan, Kai-Xiang Zhang, Jian-Hui Yang\* and Bin Liu\*

*Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, Shaanxi Key Laboratory of Physico-Inorganic Chemistry, College of Chemistry & Materials Science, Northwest University, Xi'an 710127, P. R. China.*

Table S1. Selected bond distances (Å) and angles (°) for compound **1**

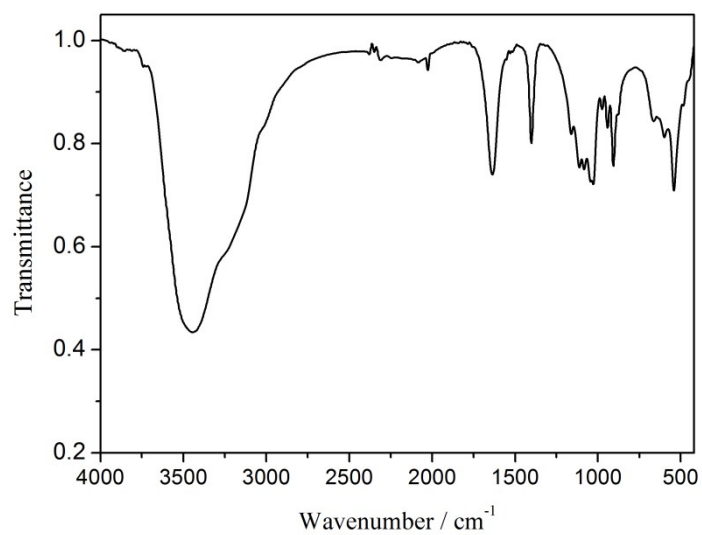
Selected bond distances (Å)			
Ru(1)–Ru(1A)	2.3400(8)	Cu(1)–O(4)	1.944(4)
Ru(1)–O(1)	1.988(4)	Cu(1)–O(3B)	1.920(4)
Ru(1)–O(5)	1.978(4)	Cu(1)–O(7C)	1.980(4)
Ru(1)–O(2A)	1.971(4)	Cu(1)–O(8B)	1.992(4)
Ru(1)–O(6A)	1.977(4)	Cu(1)–O(10)	2.296(6)
Ru(1)–O(9)	2.263(5)		
P(1)–O(1)	1.560(4)	P(2)–O(5)	1.569(5)
P(1)–O(2)	1.558(4)	P(2)–O(6)	1.572(4)
P(1)–O(3)	1.519(4)	P(2)–O(7)	1.518(4)
P(1)–O(4)	1.515(4)	P(2)–O(8)	1.509(5)

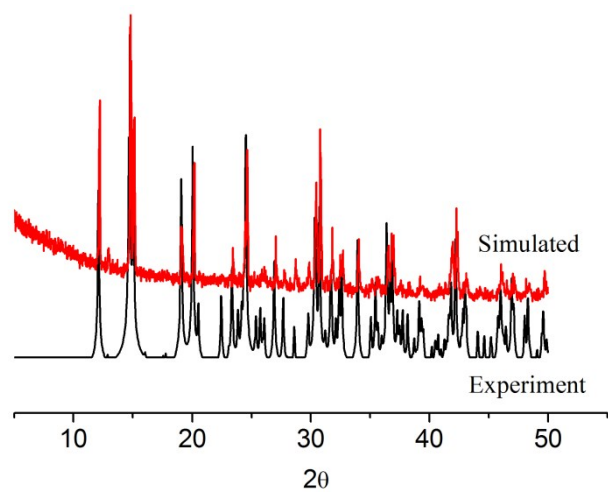
Selected bond angles (°)			
Ru(1A)–Ru(1)–O(1)	91.58(11)	O(4)–Cu(1)–O(10)	96.4(2)
Ru(1A)–Ru(1)–O(5)	93.23(12)	O(3B)–Cu(1)–O(10)	93.54(19)

Ru(1A)–Ru(1)–O(2A)	93.60(11)	O(7C)–Cu(1)–O(10)	99.5(2)
Ru(1A)–Ru(1)–O(6A)	91.42(11)	O(8B)–Cu(1)–O(10)	85.3(2)
Ru(1A)–Ru(1)–O(9)	178.69(12)		
Ru(1)–O(1)–P(1)	123.8(2)	Cu(1)–O(4)–P(1)	125.9(2)
Ru(1)–O(5)–P(2)	120.5(2)	Cu(1D)–O(3)–P(1)	119.0(2)
Ru(1A)–O(2)–P(1)	122.9(2)	Cu(1D)–O(8)–P(2)	141.6(3)
Ru(1A)–O(6)–P(2)	121.4(2)	Cu(1E)–O(7)–P(2)	130.5(3)

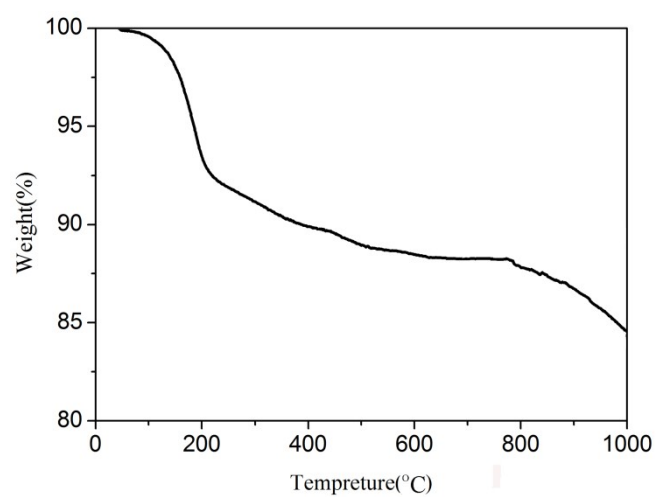
Symmetry codes: A -x, 1 - y, 2 - z; B 1/2 - x, -1/2 + y, 2/3 - z; C x, -1 + y, z; D 1/2 - x, 1/2 + y, 3/2 - z; E x, 1 + y, z;



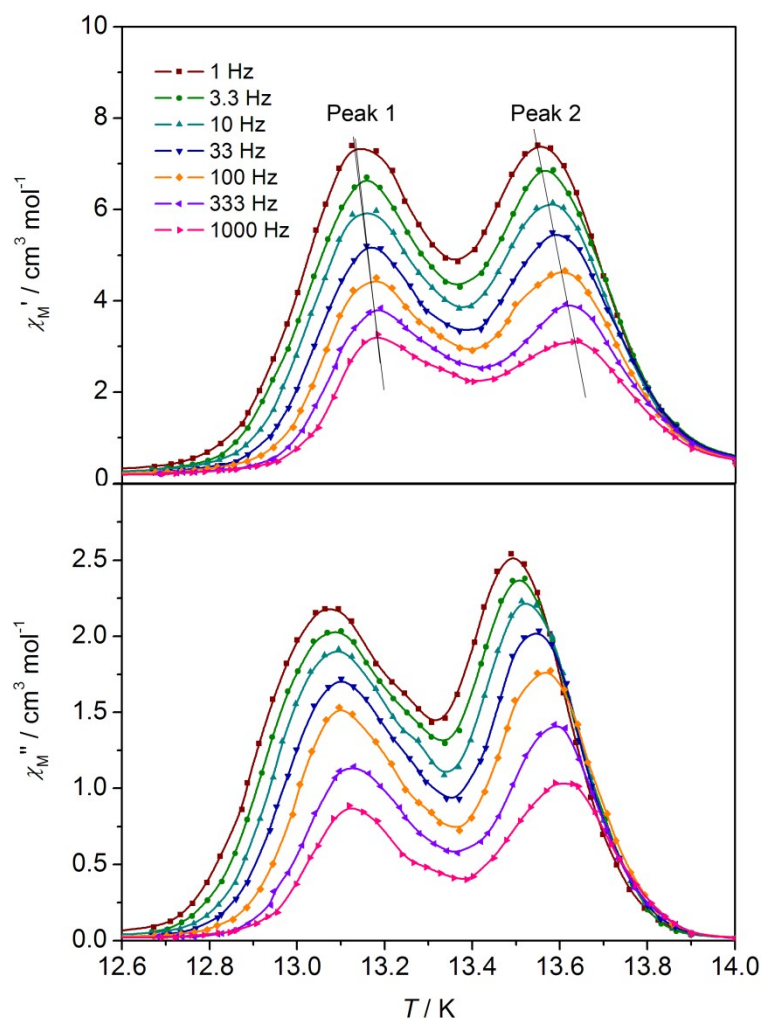
**Fig. S1** IR spectra of compound **1**.



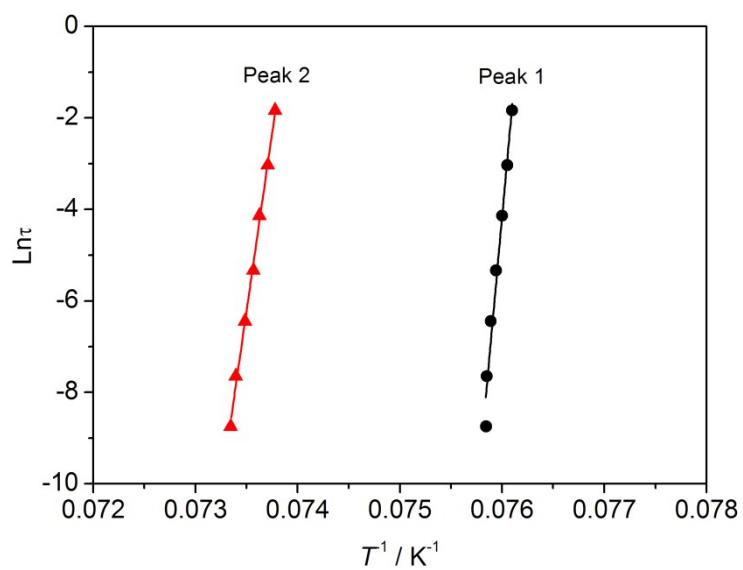
**Fig. S2** Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and as-synthesized product of **1**.



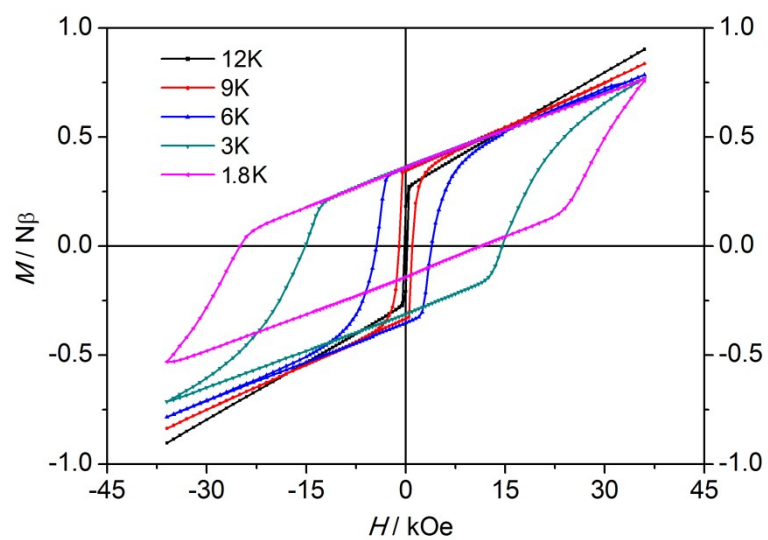
**Fig. S3** . TG curve of compound **1**



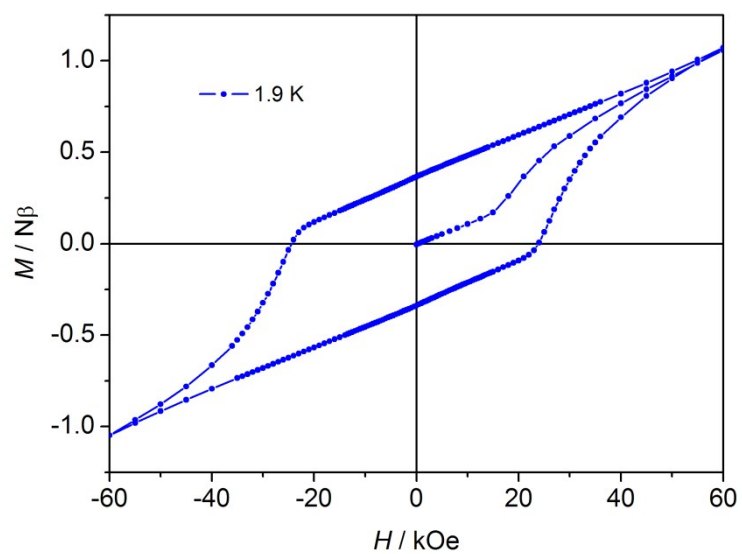
**Fig. S4**



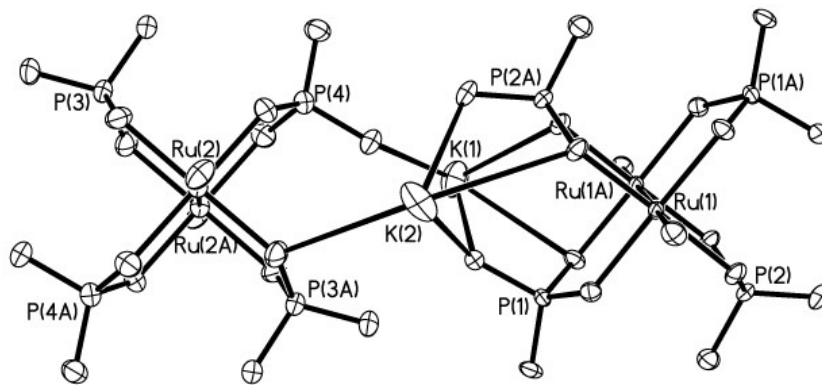
**Fig. S5** The frequency dependence of  $T_p$  on  $\chi_M'$  fitted in the Arrhenius law.



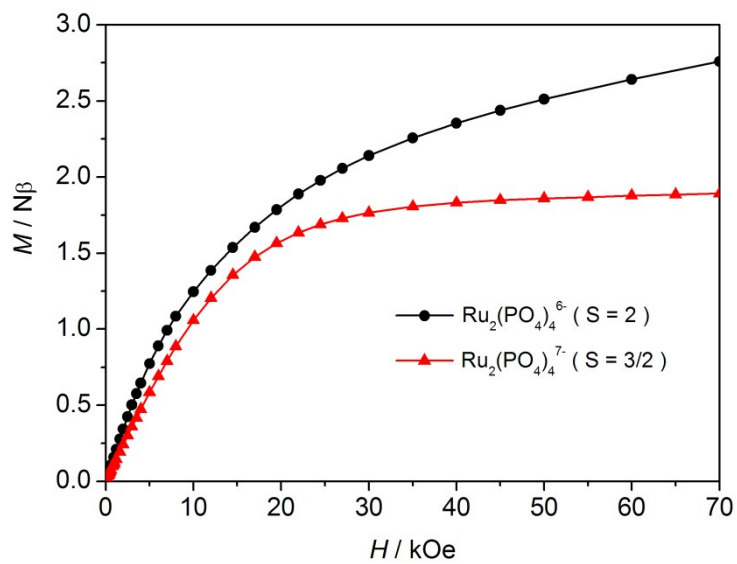
**Fig. S6**  $M$  vs  $H$  plots for compound **1**



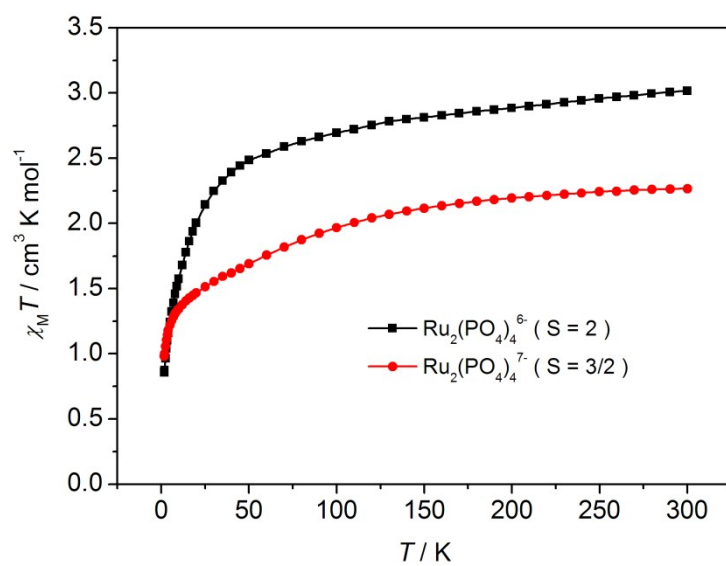
**Fig. S7** Magnetic hysteresis loop at 1.9 K for compound **1**



**Fig. S8** ORTEP representation (30% thermal probability ellipsoids) of the crystal structure of homo-valent compound  $\text{K}_2\text{Ru}_2(\text{HPO}_4)_4(\text{H}_2\text{O})_2$



**Fig. S9** Plots of magnetization  $M$  (in  $N\beta$  units) vs.  $H$  for homo-valent and mixed-valent diruthenium phosphates.



**Fig. S10** Plots of  $\chi_M T$  with respect to  $T$  for homo-valent and mixed-valent diruthenium phosphates.