Electronic Supporting Information (ESI)

Enhancing Magnetic Hardness by Ultrasonication Assisted Synthesis

of Heterometallic Carbonato Spin-glass

$Na[Ni(H_2O)_4Ru_2(CO_3)_4] \cdot 3H_2O$

Jing-Yu Li, Yu-Chen Tian, Li-Na Feng, Zi-Qin Zhou, Lin-Lin Wang, Jian-Hui Yang and Bin Liu*

^aKey Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry & Materials Science, Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Northwest University, Xi'an 710127, P. R. China¹

Experimental Section

Reagents and Physical Measurement: Na₃[Ru₂(CO₃)₄]·6H₂O was prepared according to the methods described previously.¹ All chemicals and solvents are of reagent grade and used as purchased. Powder X-ray diffraction measurements were recorded on a Rigaku RU200 diffractometer at 60 KV, 300 mA and Cu K α radiation ($\lambda = 1.5406$ Å) with a scan speed of 5°/min and a step size of 0.02° in 2 θ (Fig. S1—S4). Thermal analysis (N₂ atmosphere, heating rate: 5 °C·min⁻¹) was performed on an Netzsch STA 449C microanalyzer (Fig. S5). Magnetic measurements were carried out on the as-synthesized samples using a Quantum Design MPMS-XL7 SQUID magnetometer. AC susceptibility measurements were accomplished by using an oscillating AC field of 3.5 Oe (Fig. S8—S10). The data were corrected for the diamagnetic contributions of both the sample holder and the compound obtained from Pascal's constants.²

Crystallographic Data Collection and Refinement: Single-crystal diffraction data of compound **1** were collected on a Bruker SMART APEX II CCD diffractometer using graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) at room temperature. The data integration and reduction were processed with SAINT software. Multi-scan absorption correction was performed using SADABS program. The structures were solved by direct method of SHELXS-2008 and then refined by the full matrix least-squares technique on F² 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.

Typical synthesis procedure.

^{*} Corresponding author. Tel./fax: +86-029-88302604.

E-mail address: liubin@nwu.edu.cn (B. Liu).

The bulk samples of Na[Ni(H₂O)₄Ru₂(CO₃)₄]·3H₂O (**Bulk**) were accomplished by adding an aqueous solution of Ni(NO₃)₂·6H₂O (0.40 mmol, 0.140 g, 5 mL) to a solution of Na₃[Ru₂(CO₃)₄]·6H₂O (0.20 mmol, 0.124 g,) dissolved in 12 mL H₂O with vigorous stirring at 20°C for 2 h. After the mixture was filtered and kept at room temperature for an extended period of time (greater than 2 weeks). Red-brown block crystals of **1** were isolated (yield: 0.094 g, 73%, based on Ru). Anal. Calcd for C₄H₁₄O₁₉NaNiRu₂: C, 7.39; H, 2.17; Na, 3.54; Ni, 9.03; Ru, 31.10 Found C, 6.9; H, 2.2; Na, 3.8; Ni, 8.8; Ru, 30.7. **IR** (**KBr**, cm⁻¹) for **1**: 3431(br, s), 3254(s), 1816(w), 1628(m), 1510(s), 1269(m), 1068(m), 812(m), 762(w), 729(m), 413(m).

Sonication bath assisted synthesis at 20°C (SB-20°C).

The synthetic procedure for **SB-20°C** is similar to that of **Bulk**, then the reaction mixtures sealed in the flask were put into the ultrasonic cleaner (Ultrasonic frequency 40 kHz, power 200 W) and treated for the sonicating time 10, 20, 40, 60, 80, 120, and 160 minutes, respectively. Subsequently, the precipitates were filtered and washed with methanol and finally dried at room temperature.

Sonication bath assisted synthesis at 45°C (SB-45°C):

The synthetic procedure for SB-45°C is similar to that of SB-20°C, except for the heating temperature was increased to 45° C.

Ultrasonic disruption assisted synthesis at 20°C(USD-20°C):

The synthetic procedure for **USD-20°C** is similar to that of **Bulk-1**, then the resultant solutions were transferred into ultrasonic cell disruption device (Ultrasonic frequency 20 kHz, power 950 W) and sonicated at 20°C for several minutes, the yellow-brown solids precipitate immediately. Furthermore, the precipitates were treated for the sonicating time 10, 20, 30, and 40 minutes, respectively. Subsequently, the precipitates were filtered and washed with methanol several times and finally dried at room temperature.

Compound 1			
Empirical formula	C4H14NaNiRu2O19		
Formula weight	649.97		
Crystal system	Orthorhombic		
Space group	Pccn		
a /Å	18.251(3)		
b /Å	9.2828(16)		
c /Å	10.1645(17)		
$\alpha/^{\circ}$	90		
$eta / ^{\circ}$	90		
$\gamma^{/\circ}$	90		
$V/Å^3$	1722.1(5)		
Ζ	4		
$\rho_{\text{calc}}(\text{g}\cdot\text{cm}^{-3})$	2.484		
μ (mm ⁻¹)	2.935		
$F\left(000 ight)$	1244		
Reflections collected	8614		
Reflections unique	1714		
parameters	150		
GOF on F^2	1.059		
Rint	0.058		
$R_1, wR_2^a[I > 2\sigma(I)]$	0.0368, 0.0991		
R_1 , wR_2^a (all data)	0.0530, 0.1080		
$(\Delta \rho)_{\text{max}}, (\Delta \rho)_{\text{min}} [e/Å^3]$	1.467, -0.626		

Table S1. Crystal data and structural refinement parameters for compound 1

Table S2. Selected bond distances (Å) and angles (°) for compound $\boldsymbol{1}$

Selected bond distances (Å)						
Ru(1)–Ru(1A)	2.2611(7)	C(1)–O(1)	1.290(7)			
Ru(1)–O(1A)	2.022(4)	C(1)–O(2)	1.300(7)			
Ru(1)–O(2)	2.028(4)	C(1)–O(3)	1.253(7)			
Ru(1)–O(4)	2.032(4)	C(2)–O(4)	1.290(8)			
Ru(1)–O(5A)	2.012(4)	C(2)–O(5)	1.308(7)			
Ru(1)–O(6B)	2.273(4)	C(2)–O(6)	1.256(8)			
Ni(1)–O(3)	2.035(4)					
Ni(1)–O(7)	2.034(6)					
Ni(1)–O(8)	2.103(5)					
Selected bond angles (°)						
Ru(1A)–Ru(1)–O(2)	89.56(12)	O(3)-Ni(1)-O(7)	90.8(2)			
Ru(1A)–Ru(1)–O(4)	90.36(12)	O(3)–Ni(1)–O(8)	89.66(18)			
Ru(1A)-Ru(1)-O(1A)	89.97(12)	O(3)–Ni(1)–O(3C)	88.68(17)			
Ru(1A)–Ru(1)–O(5A)	89.22(11)	O(3)–Ni(1)–O(7C)	176.0(2)			

Ru(1A)-Ru(1)-O(6B)	174.48(12)	O(3)–Ni(1)–O(8C)	88.99(18)
O(2)-Ru(1)-O(4)	89.62(17)	O(7)–Ni(1)–O(8)	95.0(2)
O(2)-Ru(1)-O(5A)	91.50(16)	O(7)-Ni(1)-O(7C)	89.9(2)
O(2)-Ru(1)-O(6B)	92.74(18)	O(7)-Ni(1)-O(8C)	86.3(2)
O(2)-Ru(1)-O(1A)	178.97(19)	O(8)-Ni(1)-O(3C)	88.99(18)
O(4)-Ru(1)-O(1A)	89.47(17)	O(8)–Ni(1)–O(7C)	86.3(2)
O(4)-Ru(1)-O(6B)	84.64(17)	O(8)-Ni(1)-O(8C)	178.1(2)
O(4)-Ru(1)-O(5A)	178.80(15)	O(3C)-Ni(1)-O(7C)	90.8(2)
O(1A)-Ru(1)-O(5A)	89.41(16)	O(3C)-Ni(1)-O(8C)	89.66(18)
O(1A)-Ru(1)-O(6B)	87.65(18)	O(7C)-Ni(1)-O(8C)	95.0(2)
O(5A)-Ru(1)-O(6B)	95.72(16)	Ni(1)-O(3)-C(1)	129.4(4)
Ru(1)–O(2)–C(1)	120.1(4)	Ru(1A)–O(1)–C(1)	120.2(3)
Ru(1)-O(4)-C(2)	119.4(4)	Ru(1A)–O(5)–C(2)	121.1(4)

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



Fig. S1 Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and the as-synthesized bulk samples of 1.



Fig. S2 Comparison of XRPD patterns of the as-synthesized product of SB-20°C.



Fig. S3 Comparison of XRPD patterns of the as-synthesized product of SB-45°C



Fig. S4 Comparison of XRPD patterns of the as-synthesized product of USD-20°C.



Fig. S5 Comparison of XRPD patterns of grinding samples of 1 for 0, 20,40, 60, 80, 100 and 120 minutes, respectively.



Fig. S6 SEM images of SB-45 $^\circ\!\mathrm{C}$ samples of 1.



Fig. S7 SEM images of grinding samples of **1** for (a) 0, (b) 20, (c) 40, (d) 60, (e) 80, (f) 100 and (g)

120 minutes, respectively.



Fig. S8 ORTEP representation (30% thermal probability ellipsoids) of the crystal structure of 1



Fig. S9 TG curves of compound 1 synthesized by different methods.



Fig S10. Nitrogen gas sorption-desorption isotherms at 77 K for SB-20°C samples



Fig S11. Nitrogen gas sorption-desorption isotherms at 77 K for SB-45 °C samples



Fig S12. Nitrogen gas sorption-desorption isotherms at 77 K for USD-20°C samples



Fig S13. χ_M and $\chi_M T$ vs *T* plots for 1.

	Particle size (d)	H_{c}	$M_{ m r}$	$T_C(FC/ZFC)$
	μm	Oe	Nβ	K
Bulk	>200	50	0.35	3.8
SB-20°C/10min	3.0	159	0.83	4.0
SB-20°C/20min	—	305	1.23	4.1
SB-20°C/40min	2.0	298	1.22	4.0
SB-20°C/60min	—	240	1.10	4.2
SB-20°C/80min	1.0	222	1.08	4.0
SB-20°C/100min	—	340	1.29	4.2
SB-20°C/120min	1.1	339	1.28	4.1
SB-45°C/0min	2.5	111	0.67	4.0
SB-45°C/20min	1.5	208	1.22	4.4
SB-45°C/40min	1.0	130	0.81	4.4
SB-45°C/60min	0.8	149	0.87	4.3
SB-45°C/80min	0.7	176	0.95	4.2
SB-45°C/100min	0.5	145	0.88	4.3
SB-45°C/120min	0.2	252	1.24	4.2
USD-20°C/0min	2.1	743	1.55	4.0
USD-20°C/10min	1.6	280	1.37	4.3
USD-20°C/20min	1.8	370	1.44	4.4
USD-20°C/30min	1.5	386	1.48	4.5
USD-20°C/40min	1.9	330	1.47	5.2
Grinding-0min	3.0	187	1.27	4.1
Grinding-20min	2.5	172	1.10	—
Grinding-40min	2.0	149	1.00	4.0
Grinding-60min	1.8	136	0.97	—
Grinding-80min	1.5	135	0.89	3.9

Table S3. Comparison of the magnetism parameters for 1 in different synthesis conditions

Grinding-100min	0.5	136	0.80	—
Grinding-120min	0.4	133	0.77	4.1

	d	$\Delta E/k_{\rm B}$	$ au_0$	ϕ	$T_{\max}(\chi')$	$T_{\max}(\chi")$
	μm	K	S		Κ	Κ
Bulk	>200	219	6.6 × 10 ⁻³⁴	0.034	3.7	2.9
SB-20°C/10min	3.0	181	2.4×10^{-31}	0.034	3.8	2.7
SB-20°C/120min	1.1	195	5.1 × 10 ⁻³⁵	0.029	3.7	2.6
SB-45°C/0min	2.5	221	1.6 × 10 ⁻³⁷	0.028	3.7	2.7
SB-45°C/120min	0.2	205	6.5 × 10 ⁻³⁵	0.029	3.8	2.7
USD-20°C/0min	2.1	199	8.2 × 10 ⁻³⁶	0.029	3.7	2.5
USD-20°C/10min	1.6	220	8.8 × 10 ⁻³⁸	0.027	3.7	2.7
USD-20°C/20min	1.8	261	5.5 × 10 ⁻³⁹	0.026	4.0	3.0
USD-20°C/30min	1.5	286	2.7 × 10 ⁻³⁹	0.027	4.3	3.3
USD-20°C/40min	1.9	292	5.6 × 10 ⁻⁴¹	0.025	4.2	3.2

Table S4. Comparison of the slow relaxation parameters for 1 in different synthesis conditions



Fig S14. In-phase (χ_M ') and out-of-phase (χ_M '') components for Bulk sample with increasing frequencies



Fig S15. In-phase (χ_M ') and out-of-phase (χ_M '') components for samples of SB-20°C/0min, SB-20°C/120min, SB-45°C/0min and SB-45°C/120min with increasing frequencies.



Fig S16. In-phase (χ_M') and out-of-phase (χ_M'') components for samples of USD-20°C/0min, USD-20°C/10min, USD-20°C/20min, USD-20°C/30min and USD-20°C/40min with increasing frequencies



Fig S17. Arrhenius plot of the relaxation time τ vs reciprocal temperature for Bulk samples (The solid line represents the least-squares fitting of the experimental data).



Fig S18. Arrhenius plot of the relaxation time τ vs reciprocal temperature for SB-20 0min samples.



Fig S19. Arrhenius plot of the relaxation time τ vs reciprocal temperature for SB20-120min



Fig S20. Arrhenius plot of the relaxation time τ vs reciprocal temperature for SB45-0min samples.



Fig S21. Arrhenius plot of the relaxation time τ vs reciprocal temperature for SB45-120min



Fig S22. Arrhenius plot of the relaxation time τ vs reciprocal temperature for USD20-0min



Fig S23. Arrhenius plot of the relaxation time τ vs reciprocal temperature for USD20-10min



Fig S24. Arrhenius plot of the relaxation time τ vs reciprocal temperature for USD20-20min



Fig S25. Arrhenius plot of the relaxation time τ vs reciprocal temperature for USD20-30min



Fig S26. Arrhenius plot of the relaxation time τ vs reciprocal temperature for USD20-40min



Fig S27. FC/ZFC versus *T* plots for SB-20 $^{\circ}$ C samples.







Fig S29. FC/ZFC versus *T* plots for USD-20°C samples.



Fig S30. FC/ZFC versus *T* plots for the ground samples.