

## Electronic Supporting Information (ESI)

# Grinding Enhances Magnetic Hardness of Heterometallic Diruthenium(II,III) Carbonates with Kagome Lattice Structure

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### Experimental Section

*Materials and Characterization Details*  $\text{Na}_3[\text{Ru}_2(\text{CO}_3)_4] \cdot 6\text{H}_2\text{O}$  was prepared according to the literature methods.[1] All chemicals and solvents (reagent grade) were used as purchased. Elemental analysis of C and H was performed on a PerkinElmer 2400C elemental analyzer. Metals Cs, Cd and Ru were analyzed on an IRIS Advantage ICP atomic emission spectrometer. IR (infrared spectrum) was recorded on a VECTOR 22 spectrometer with pressed KBr pellets (Fig. S1). Raman spectrum was collected with a 785 nm excitation line using a Renishaw inVia confocal microscopy Raman microscope (Fig. S2). PXRD (Powder X-ray diffraction) measurements were carried out on a RU200 diffractometer (Rigaku Co., Japan) at 60 KV, 300 mA and Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) with a scan speed of  $5^\circ/\text{min}$  and a step size of  $0.02^\circ$  in  $2\theta$  (Fig. S3). The thermogravimetric analysis ( $\text{N}_2$  atmosphere, heating rate:  $5^\circ\text{C} \cdot \text{min}^{-1}$ ) was performed on a STA 449C microanalyzer (Netzsch Co., Germany) (Fig. S4). Sorption measurement was performed on a Micrometrics ASAP 2020M physical sorption analyzer (Micrometrics Instrument Co., America) (Fig. S5). Magnetic measurements were carried out on the as-synthesized samples using a Quantum Design MPMS-XL7 SQUID magnetometer. The field dependence of magnetization (loop) measurement has been performed on the crystal samples using a scan mode of 10 Oe / step with scan speed  $\sim 3$  Oe/s near zero field. 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 $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) 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-2018 and then refined by the full matrix least-squares technique on  $F^2$  with anisotropic thermal parameters to

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describe the thermal motions of all nonhydrogen atoms. The hydrogen atoms were generated geometrically and refined isotropically through the riding model.

[1] F. A. Cotton, L. Labella and M. Shang, *Inorg. Chem.* 1992, 31, 2385-2389.

[2] G. A. Bain and J. F. Berry, *J. Chem. Educ.* 2004, 85 532-536.

### Typical synthesis procedure.

The perfect crystal samples of  $\text{Cs}_3\text{Cd}(\text{H}_2\text{O})_6[\{\text{Cd}(\text{H}_2\text{O})_3\}_2\{\text{Ru}_2(\text{CO}_3)_4\}_3]\cdot 10\text{H}_2\text{O}$  were accomplished by adding an aqueous solution of  $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$  (0.080 g, 0.026 mmol, 10 mL) to a solution of  $\text{Na}_3[\text{Ru}_2(\text{CO}_3)_4]\cdot 6\text{H}_2\text{O}$  (0.050 g, 0.008 mmol, 10 mL) with stirring for 5 min, then adding 10 mL of an aqueous solution of  $\text{CsCl}$  (0.100 g, 0.059 mmol) into the mixture and allowing the solution to stand at 20°C for a week, which produced red brown plate shape crystals with a yield of 73% (based on Ru). Anal. Calcd for  $\text{H}_{44}\text{C}_{12}\text{O}_{58}\text{Cs}_3\text{Cd}_3\text{Ru}_6$ : Cs, 16.22; Cd, 13.72; Ru, 24.66; Found Cs, 15.8; Cd, 14.0; Ru, 24.3%. **IR (KBr,  $\text{cm}^{-1}$ )** for **1**: 3572(m), 3572(m), 3264(br, s), 2537(w), 1765(w), 1643(m), 1550(vs), 1482(s), 1220(s), 1050(s), 819(s), 766(w), 707(m), 604(br, m), 496(m). **Roman shift ( $\text{cm}^{-1}$ )** for **1**: 182(m), 201(m), 333(vs), 390(vs), 739(w), 1072(s), 1290(w), 1331(m), 1464(s), 1543(m), 1641(w).

### Sonication bath assisted synthesis at 20°C.

The synthetic procedure is similar to the bulk samples of **1**, then the reaction mixtures sealed in the flask were put into the ultrasonic cleaner (Ultrasonic frequency 40 kHz, power 200 W) and treated with sonication power 10%, 20%, 40%, 60%, 80% and 100%, respectively. Subsequently, the precipitates were filtered and washed with methanol and finally dried at room temperature.

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

| Compound <b>1</b> |  |
|-------------------|--|
| Empirical formula | $\text{C}_{12}\text{H}_{44}\text{Cs}_3\text{Cd}_3\text{Ru}_6\text{O}_{58}$ |
| Formula weight    | 2458.82  |
| Crystal system    | Triclinic  |
| Space group       | $P\bar{1}$   |
| $a / \text{Å}$    | 10.2725(18)  |
| $b / \text{Å}$    | 12.332(2)  |
| $c / \text{Å}$    | 12.943(4)  |
| $\alpha / ^\circ$ | 106.574(4)   |
| $\beta / ^\circ$  | 107.651(4)   |
| $\gamma / ^\circ$ | 105.595(2)   |
| $V / \text{Å}^3$  | 1379.5(5)  |
| $Z$               | 1  |

|  |                |
|--|----------------|
| $\rho_{\text{calc}}$ (g · cm <sup>-3</sup> )                               | 2.960          |
| $\mu$ (mm <sup>-1</sup> )  | 4.811          |
| $F(000)$   | 1153           |
| Reflections collected  | 7877           |
| Reflections unique   | 5700           |
| parameters   | 376            |
| GOF on $F^2$   | 1.009          |
| $R_{\text{int}}$   | 0.029          |
| $R_1, wR_2^a [I > 2\sigma(I)]$   | 0.0488, 0.1312 |
| $R_1, wR_2^a$ (all data)   | 0.0710, 0.1511 |
| $(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}}$ [e/Å <sup>3</sup> ] | 1.879, -1.245  |

Table S2. Selected bond distances (Å) for compound **1**

| Selected bond distances (Å) |            |              |            |              |            |
|-----------------------------|------------|--------------|------------|--------------|------------|
| Ru(1)–Ru(1N)                | 2.2608(13) | Ru(2)–Ru(2K) | 2.2543(13) | Ru(3)–Ru(3J) | 2.2635(15) |
| Ru(1)–O(1)                  | 2.033(9)   | Ru(2)–O(7)   | 2.007(8)   | Ru(3)–O(13)  | 2.025(8)   |
| Ru(1)–O(4)                  | 2.035(8)   | Ru(2)–O(9K)  | 2.028(7)   | Ru(3)–O(14J) | 1.999(8)   |
| Ru(1)–O(2N)                 | 2.032(9)   | Ru(2)–O(10)  | 2.011(9)   | Ru(3)–O(16)  | 2.026(9)   |
| Ru(1)–O(5N)                 | 2.033(8)   | Ru(2)–O(11K) | 2.015(9)   | Ru(3)–O(17J) | 2.026(8)   |
| Ru(1)–O(8)                  | 2.241(7)   | Ru(2)–O(15)  | 2.294(7)   | Ru(3)–O(6D)  | 2.245(9)   |
| Cd(1)–O(3C)                 | 2.262(8)   | Cd(2)–O(22)  | 2.290(12)  | C(3)–O(9)    | 1.294(13)  |
| Cd(1)–O(12K)                | 2.270(7)   | Cd(2)–O(22L) | 2.290(12)  | C(4)–O(10)   | 1.306(13)  |
| Cd(1)–O(18)                 | 2.205(9)   | Cd(2)–O(23)  | 2.272(11)  | C(4)–O(11)   | 1.293(14)  |
| Cd(1)–O(19)                 | 2.298(9)   | Cd(2)–O(23L) | 2.272(11)  | C(4)–O(12)   | 1.254(15)  |
| Cd(1)–O(20)                 | 2.308(9)   | Cd(2)–O(24)  | 2.289(11)  | C(5)–O(13)   | 1.294(14)  |
| Cd(1)–O(21)                 | 2.381(9)   | Cd(2)–O(24L) | 2.289(11)  | C(5)–O(14)   | 1.300(13)  |
| C(1)–O(1)                   | 1.327(12)  | C(2)–O(5)    | 1.315(14)  | C(5)–O(15)   | 1.274(13)  |
| C(1)–O(2)                   | 1.277(13)  | C(2)–O(6)    | 1.272(15)  | C(6)–O(16)   | 1.295(15)  |
| C(1)–O(3)                   | 1.266(16)  | C(3)–O(7)    | 1.304(11)  | C(6)–O(17)   | 1.318(15)  |
| C(2)–O(4)                   | 1.282(12)  | C(3)–O(8)    | 1.282(13)  | C(6)–O(18)   | 1.265(15)  |

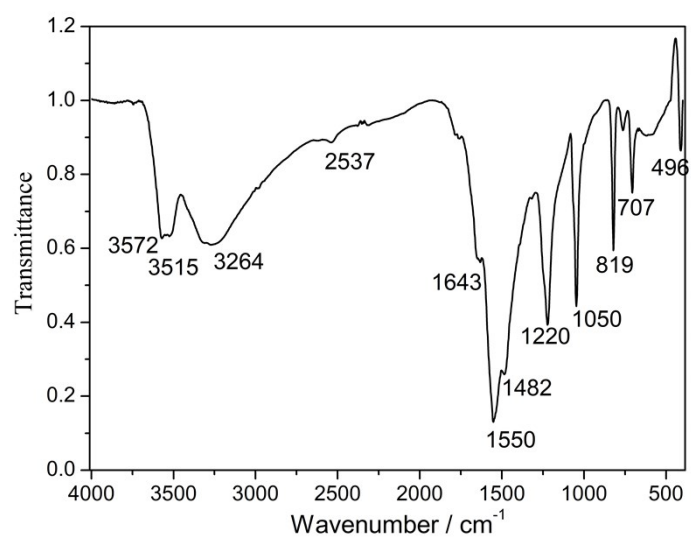
Symmetry codes: D x, y, -1+z; J 1-x, -y, -z; K 1-x, -y, 1-z; L 1-x, 1-y, 1-z; N 2-x, 1-y, 2-z.

Table S3. Selected angles (°) for compound **1**

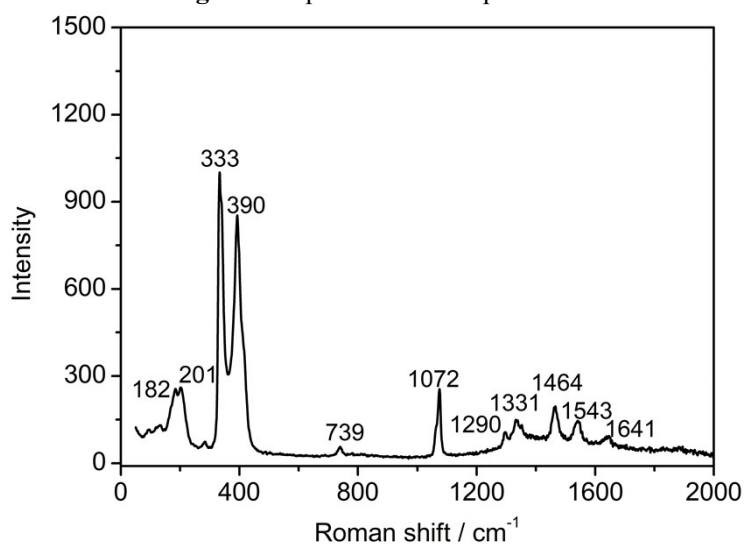
|                    |          |                     |            |
|--------------------|----------|---------------------|------------|
| Ru(1N)–Ru(1)–O(1)  | 90.7(2)  | Ru(2K)–Ru(2)–O(7)   | 90.3(2)    |
| Ru(1N)–Ru(1)–O(2N) | 89.5(2)  | Ru(2K)–Ru(2)–O(9K)  | 89.8(2)    |
| Ru(1N)–Ru(1)–O(5N) | 89.1(2)  | Ru(2K)–Ru(2)–O(11K) | 90.1(2)    |
| Ru(1N)–Ru(1)–O(4)  | 91.1(2)  | Ru(2K)–Ru(2)–O(10)  | 89.7(2)    |
| Ru(1N)–Ru(1)–O(8)  | 171.7(2) | Ru(2K)–Ru(2)–O(15)  | 170.33(19) |
| O(1)–Ru(1)–O(5N)   | 93.9(3)  | O(7)–Ru(2)–O(10)    | 87.2(3)    |
| O(1)–Ru(1)–O(4)    | 86.2(3)  | O(7)–Ru(2)–O(15)    | 80.9(3)    |

|                     |          |                     |          |
|---------------------|----------|---------------------|----------|
| O(1)–Ru(1)–O(8)     | 91.4(3)  | O(7)–Ru(2)–O(11K)   | 91.2(3)  |
| O(1)–Ru(1)–O(2N)    | 179.2(3) | O(7)–Ru(2)–O(9K)    | 179.5(3) |
| O(5N)–Ru(1)–O(8)    | 82.8(3)  | O(10)–Ru(2)–O(15)   | 85.9(3)  |
| O(2N)–Ru(1)–O(5N)   | 86.9(3)  | O(9K)–Ru(2)–O(11K)  | 89.3(3)  |
| O(2N)–Ru(1)–O(4)    | 93.0(3)  | O(9K)–Ru(2)–O(10)   | 92.3(3)  |
| O(4)–Ru(1)–O(5N)    | 179.8(3) | O(10)–Ru(2)–O(11K)  | 178.4(3) |
| O(2N)–Ru(1)–O(8)    | 88.6(3)  | O(9K)–Ru(2)–O(15)   | 99.0(3)  |
| O(4)–Ru(1)–O(8)     | 97.1(3)  | O(11K)–Ru(2)–O(15)  | 94.0(3)  |
| Ru(3J)–Ru(3)–O(13)  | 90.0(2)  | Ru(1)–O(1)–C(1)     | 117.7(7) |
| Ru(3J)–Ru(3)–O(14J) | 89.8(2)  | Ru(1N)–O(2)–C(1)    | 120.2(7) |
| Ru(3J)–Ru(3)–O(17J) | 89.6(2)  | Ru(1)–O(4)–C(2)     | 117.8(7) |
| Ru(3J)–Ru(3)–O(16)  | 90.3(2)  | Ru(1N)–O(5)–C(2)    | 119.2(6) |
| Ru(3J)–Ru(3)–O(6D)  | 171.0(2) | Ru(1)–O(8)–C(3)     | 134.1(7) |
| O(13)–Ru(3)–O(16)   | 88.1(3)  | Ru(2)–O(7)–C(3)     | 119.6(7) |
| O(13)–Ru(3)–O(17J)  | 91.2(3)  | Ru(2K)–O(9)–C(3)    | 119.4(6) |
| O(13)–Ru(3)–O(6D)   | 85.0(3)  | Ru(2)–O(10)–C(4)    | 120.2(7) |
| O(13)–Ru(3)–O(14J)  | 179.2(3) | Ru(2K)–O(11)–C(4)   | 119.9(7) |
| O(6D)–Ru(3)–O(16)   | 82.1(3)  | Ru(2)–O(15)–C(5)    | 122.5(7) |
| O(14J)–Ru(3)–O(17J) | 88.0(3)  | Ru(3E)–O(6)–C(2)    | 136.2(7) |
| O(16)–Ru(3)–O(17J)  | 179.3(3) | Ru(3)–O(13)–C(5)    | 119.0(7) |
| O(14J)–Ru(3)–O(16)  | 92.7(3)  | Ru(3J)–O(14)–C(5)   | 120.4(7) |
| O(6D)–Ru(3)–O(17J)  | 98.0(3)  | Ru(3)–O(16)–C(6)    | 120.0(8) |
| O(6D)–Ru(3)–O(14J)  | 95.4(3)  | Ru(3J)–O(17)–C(6)   | 120.1(7) |
| O(18)–Cd(1)–O(20)   | 166.8(3) | O(22)–Cd(2)–O(24L)  | 89.8(4)  |
| O(18)–Cd(1)–O(19)   | 110.8(3) | O(22)–Cd(2)–O(23)   | 94.6(4)  |
| O(12K)–Cd(1)–O(19)  | 89.1(3)  | O(22)–Cd(2)–O(24)   | 90.3(4)  |
| O(20)–Cd(1)–O(21)   | 81.2(3)  | O(22)–Cd(2)–O(22L)  | 180.00   |
| O(3C)–Cd(1)–O(20)   | 92.8(3)  | O(22)–Cd(2)–O(23L)  | 85.4(4)  |
| O(12K)–Cd(1)–O(20)  | 87.0(3)  | O(22)–Cd(2)–O(24L)  | 180.00   |
| O(3C)–Cd(1)–O(21)   | 97.1(3)  | O(22L)–Cd(2)–O(23L) | 94.6(4)  |
| O(12K)–Cd(1)–O(21)  | 77.3(3)  | O(22L)–Cd(2)–O(23L) | 90.3(4)  |
| O(3C)–Cd(1)–O(12K)  | 174.4(3) | O(23L)–Cd(2)–O(24L) | 94.5(4)  |
| O(12K)–Cd(1)–O(18)  | 88.3(3)  | O(23)–Cd(2)–O(23L)  | 180.00   |
| O(19)–Cd(1)–O(20)   | 81.4(3)  | O(23)–Cd(2)–O(24L)  | 85.5(4)  |
| O(19)–Cd(1)–O(21)   | 158.4(3) | O(22L)–Cd(2)–O(24)  | 89.8(4)  |
| O(3C)–Cd(1)–O(19)   | 96.3(3)  | O(23L)–Cd(2)–O(24)  | 85.5(4)  |
| O(18)–Cd(1)–O(21)   | 85.8(3)  | O(23)–Cd(2)–O(24)   | 94.5(4)  |
| O(3C)–Cd(1)–O(18)   | 90.7(3)  | O(22L)–Cd(2)–O(23)  | 85.4(4)  |

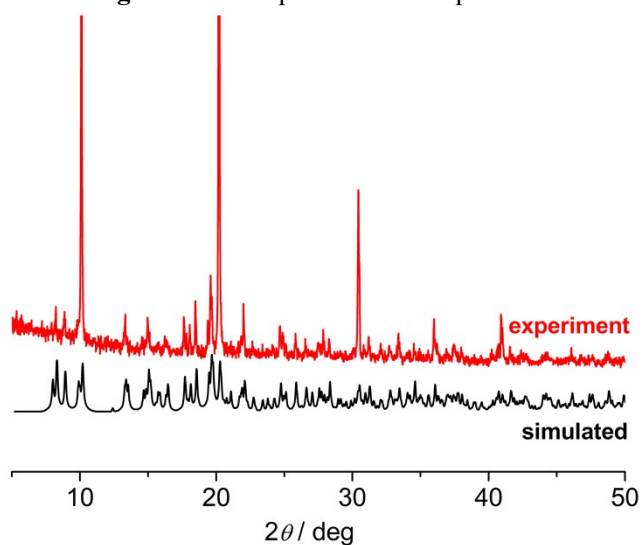
Symmetry codes: D x, y, -1+z; J 1-x, -y, -z; K 1-x, -y, 1-z; L 1-x, 1-y, 1-z; N 2-x, 1-y, 2-z.



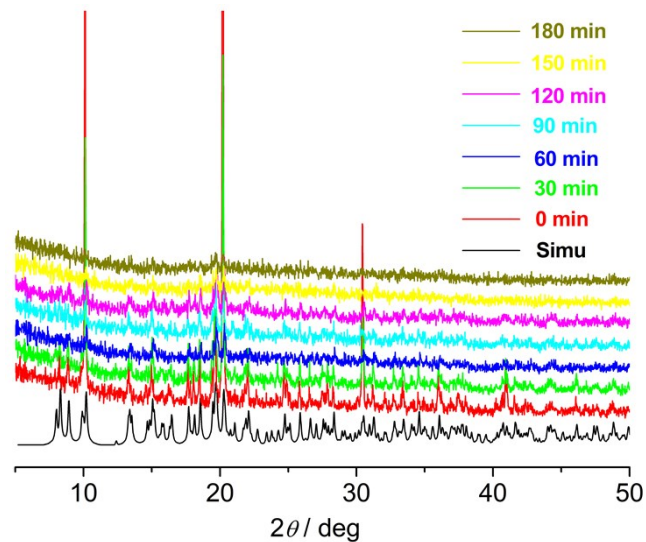
**Fig. S1** IR spectrum of compound **1**.



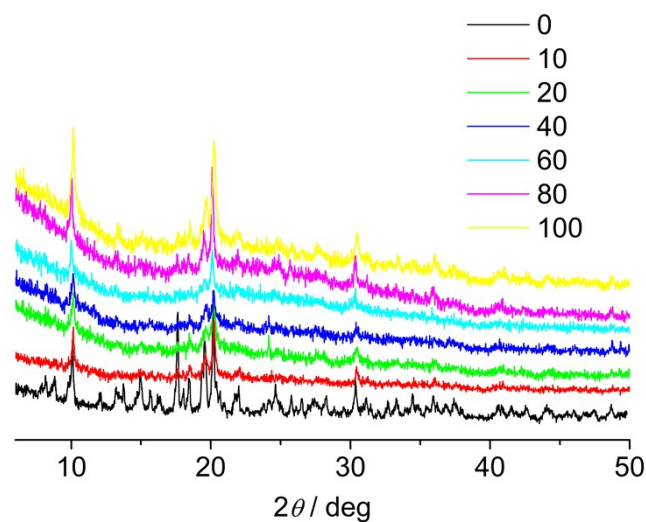
**Fig. S2** Raman spectrum of compound **1**.



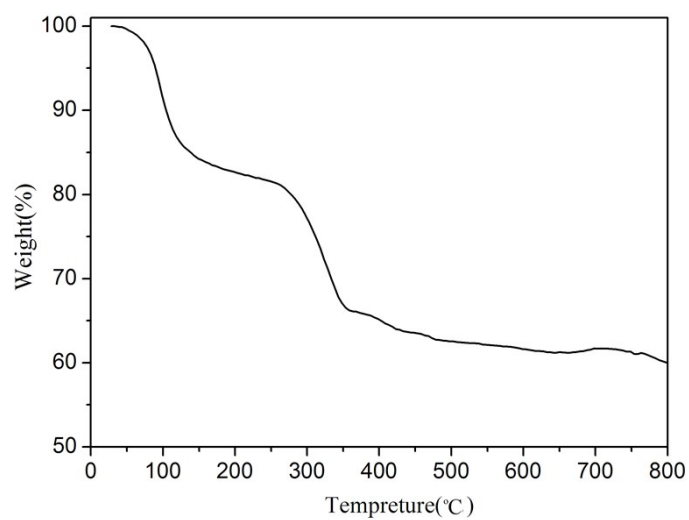
**Fig. S3** Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and the as-synthesized bulk samples of **1**.



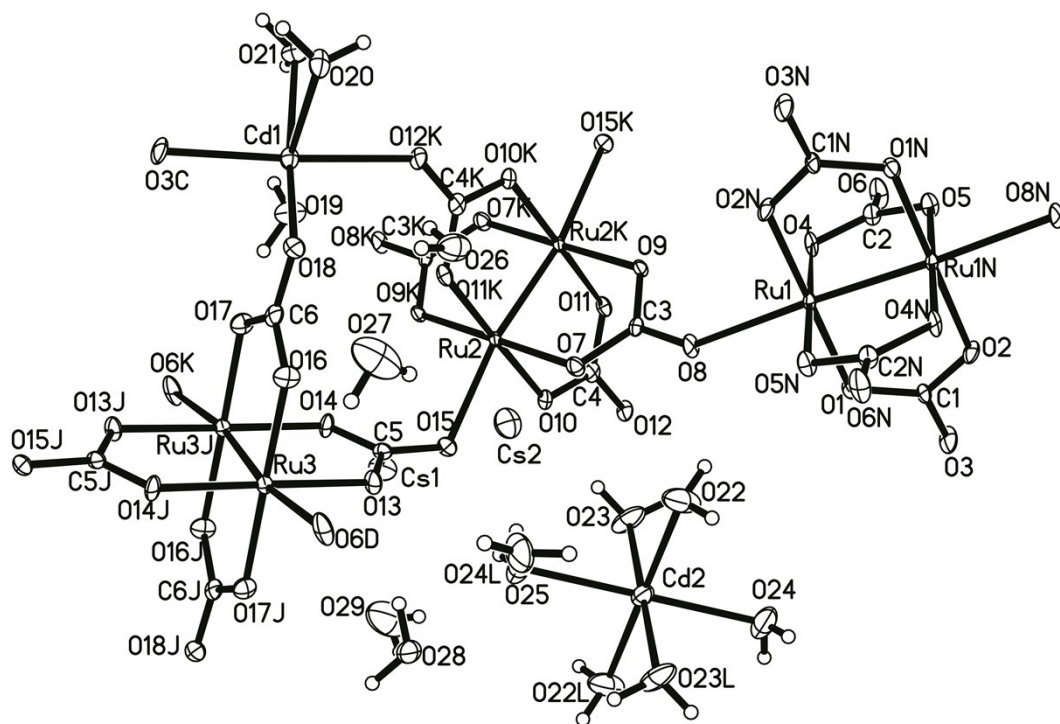
**Fig. S4** Comparison of XRPD patterns of the different grinding time samples of **1**.



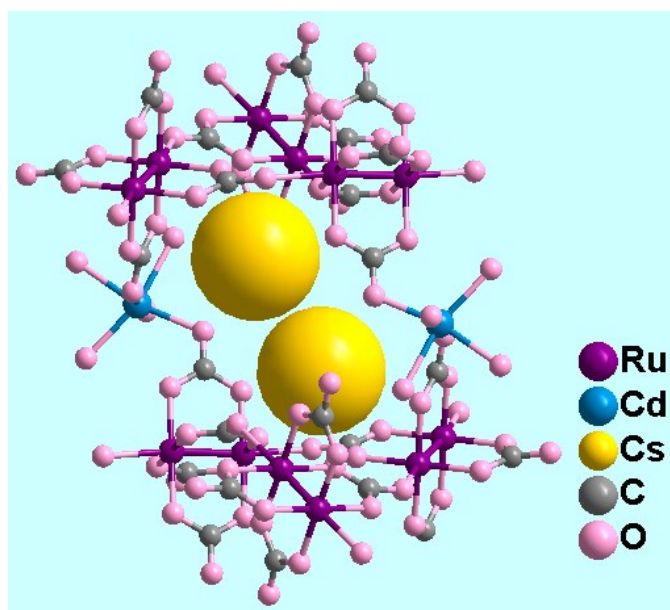
**Fig. S5** Comparison of XRPD patterns of the sonication bath assisted synthesized products of **1**.



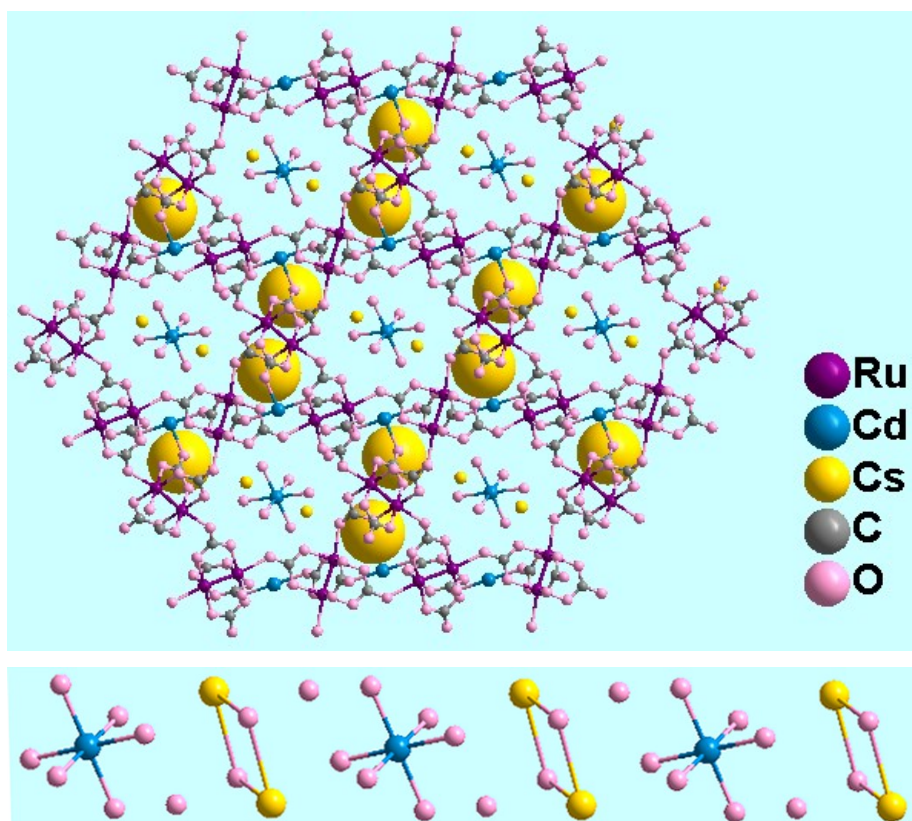
**Fig. S6** TG curve of compound **1**.



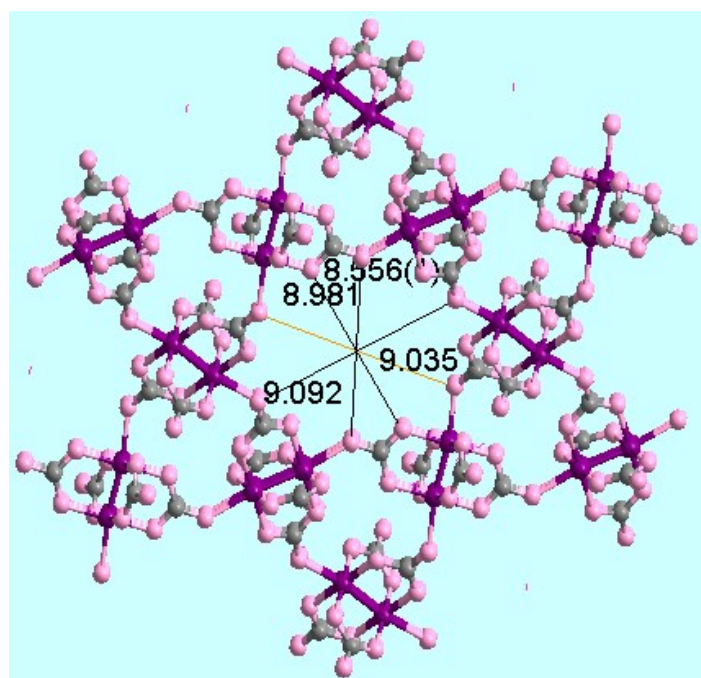
**Fig. S7** ORTEP representation (30% thermal probability ellipsoids) of the crystal structure of **1**.



**Fig. S8.** Local environment of Cs1<sup>+</sup> in compound **1**.

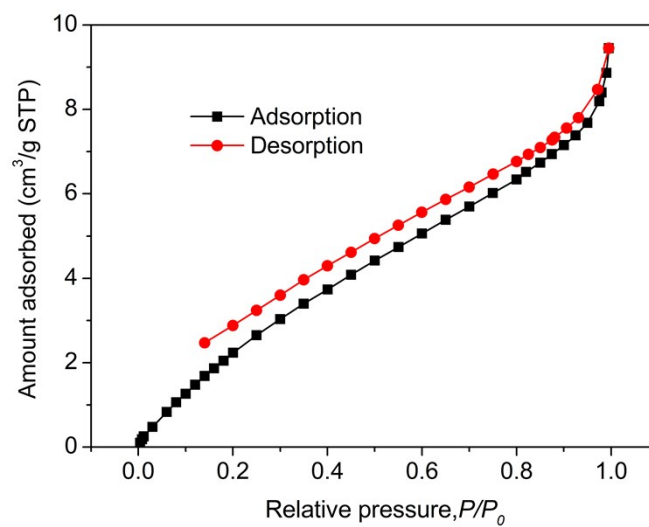


**Fig. S9.** Top: Kagome lattice structure viewed along the *a* axis. Bottom: Local environment of Cd(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>, Cs<sup>2+</sup> and lattice water located within the channels.

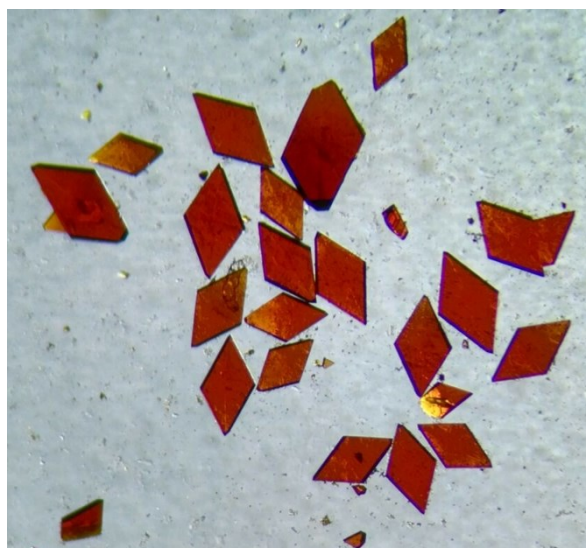


**Fig. S10.** The structure of the hexagonal channels in compound **1**.

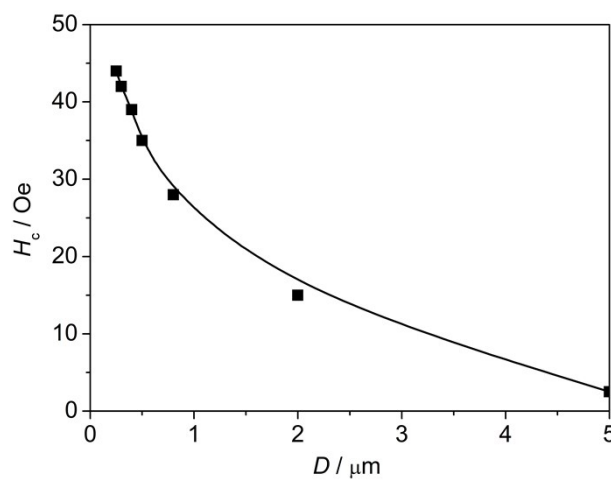




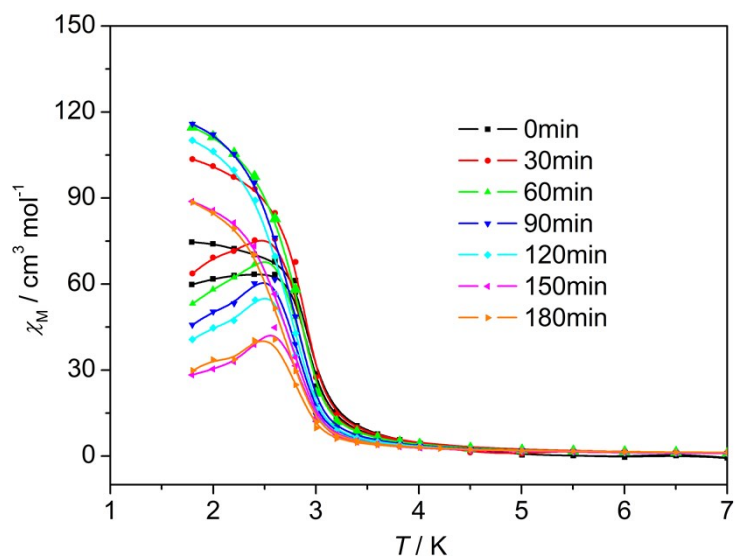
**Fig S11.** Nitrogen gas sorption–desorption isotherms at 77 K for the partially dehydrated samples of compound **1**.



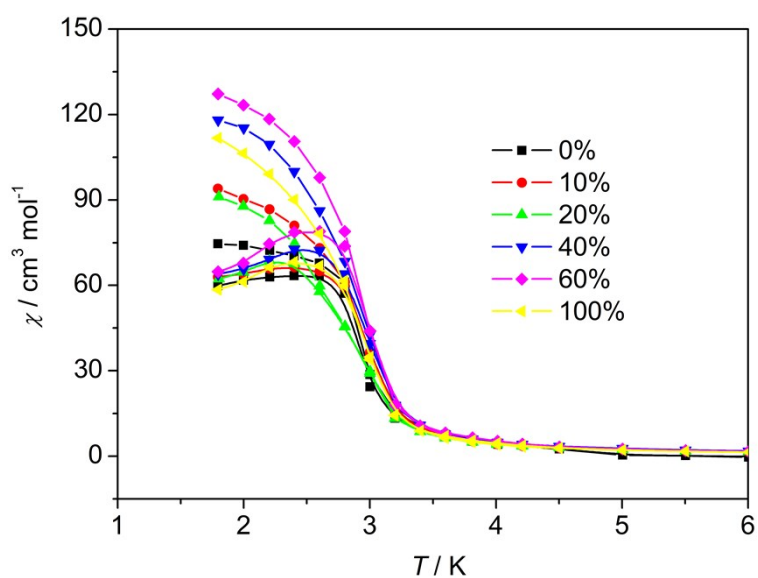
**Fig. S12.** Photographs of the perfect crystals of **1**.



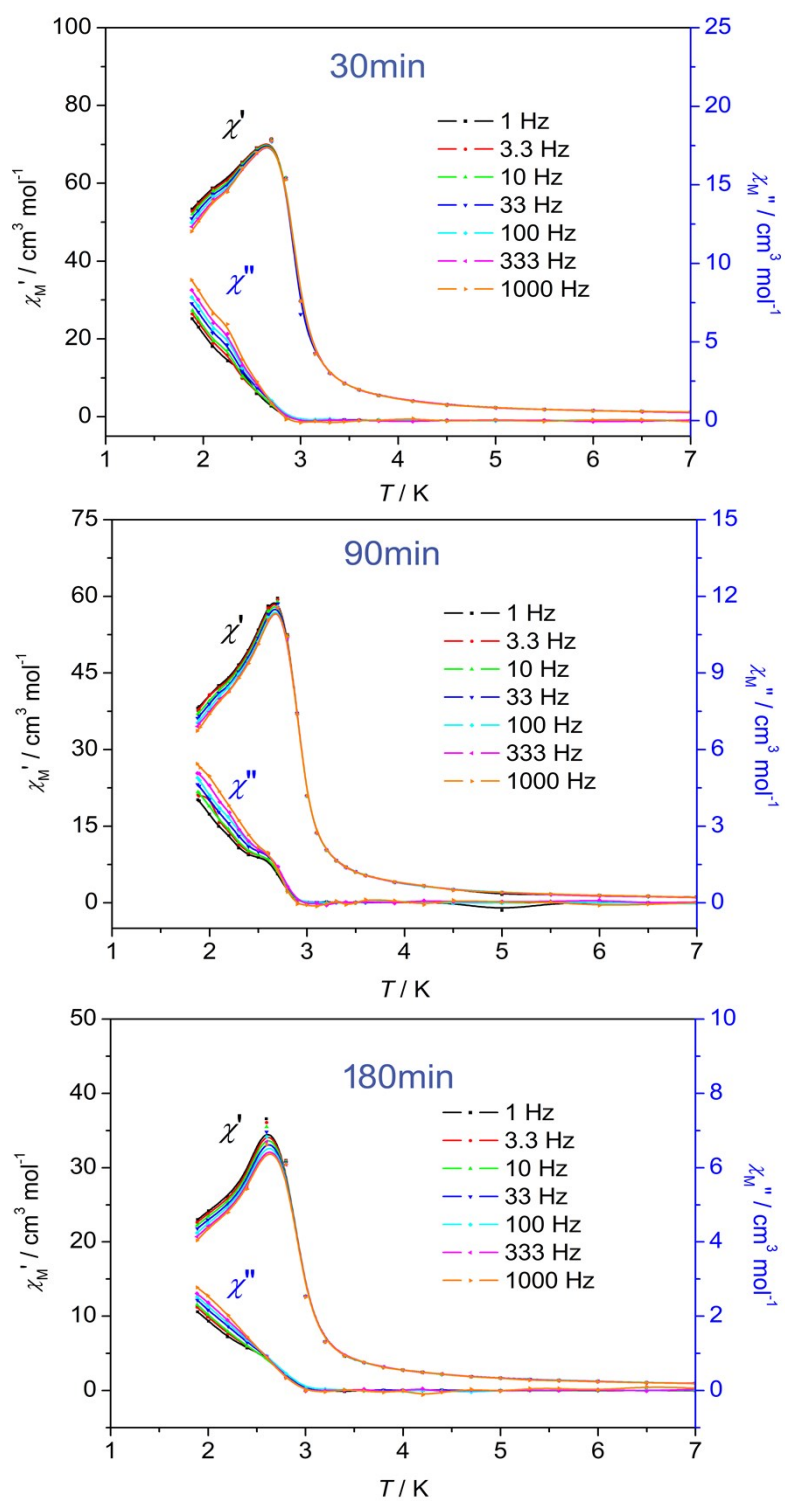
**Fig S13.** The coercive field  $H_c$  vs ground sample particles diameter  $D$  plot of **1**.



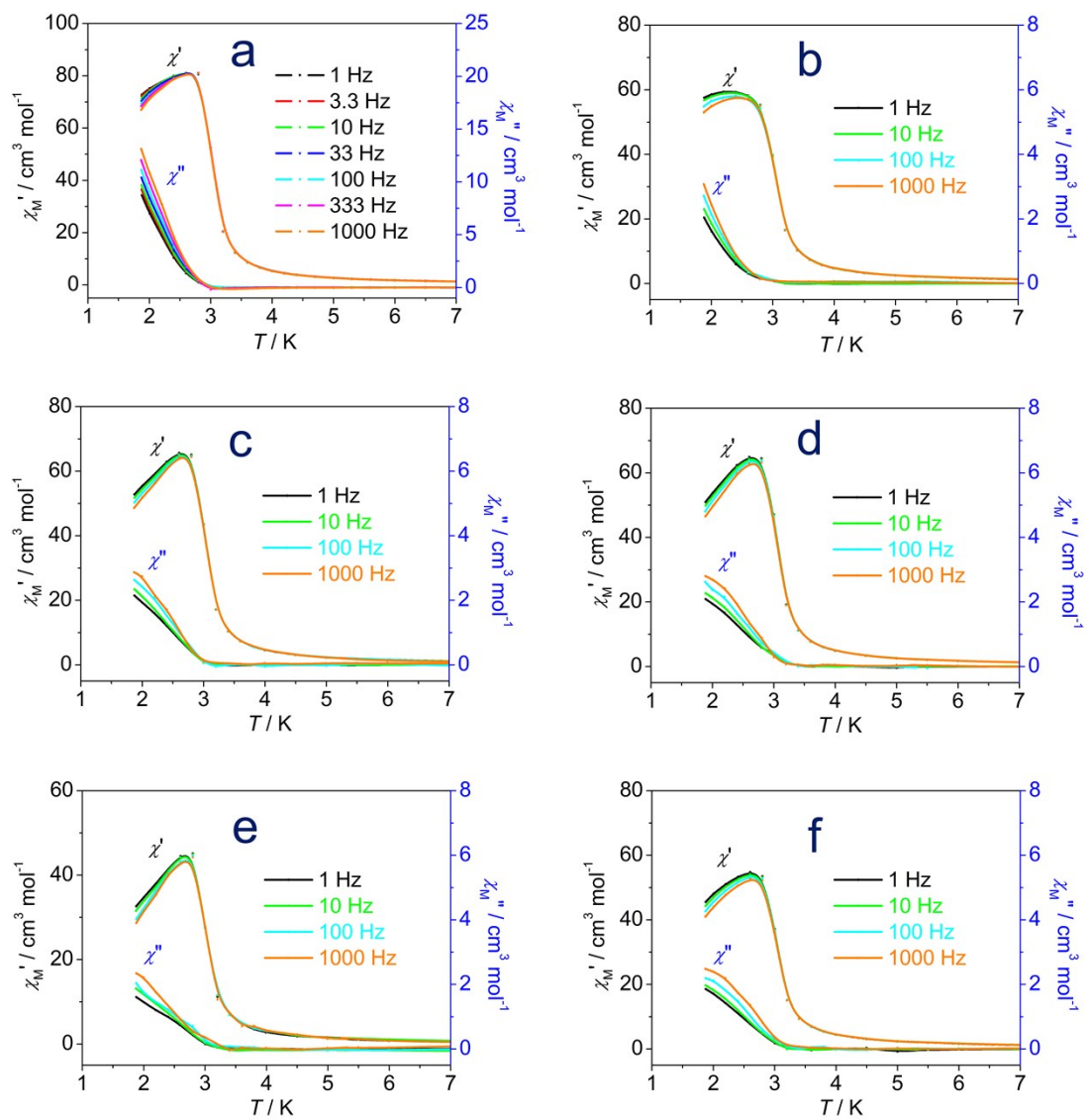
**Fig S14.** FC/ZFC versus  $T$  plots for grinding treatment samples of **1**.



**Fig S15.** FC/ZFC versus  $T$  plots for sonication bath assisted synthesized samples of **1**.



**Fig S16.** In-phase ( $\chi_M'$ ) and out-of-phase ( $\chi_M''$ ) components for ground samples of **1**.



**Fig S17.** In-phase ( $\chi''$ ) and out-of-phase ( $\chi'$ ) components for sonication bath samples of **1**: a: perfect crystals; b-f: the powder samples with sonication bath power 10%, 20%, 40%, 60%, 80% and 100%, respectively.