

Supporting Information

Uniform Spin-1/2 chain system with a weak interchain interaction

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Figure S1. Simulated (red line) and experimental (black line) powder X-ray (Cu K α) diffraction patterns of Lu₂Cu(SO₄)₂(OH)₃F·H₂O.

Figure S2. Oxygen-coordination environments for (a) Cu, (b) Lu1, (c) Lu2, (d) S1 and (e) S2 atoms in Lu₂Cu(SO₄)₂(OH)₃F·H₂O.

Figure S3. Infrared spectroscopy data (KBr cm⁻¹) for Lu₂Cu(SO₄)₂(OH)₃F·H₂O.

Figure S4. (a) UV-vis absorption spectra and (b) optical diffuse reflectance spectra for Lu₂Cu(SO₄)₂(OH)₃F·H₂O.

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Figure S6. The EPR spectrum of Lu₂Cu(SO₄)₂(OH)₃F·H₂O measured at 9.87GHz.

Table S1. Crystal data and structure refinement for Lu₂Cu(SO₄)₂(OH)₃F·H₂O.

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Table S5. Anisotropic displacement parameters for Lu₂Cu(SO₄)₂(OH)₃F·H₂O.

Table S6. Hydrogen bond lengths and bond angles of Lu₂Cu(SO₄)₂(OH)₃F·H₂O.

Experimental Section

Preparation of samples: Single crystals of Lu₂Cu(SO₄)₂(OH)₃F·H₂O were synthesized through a conventional hydrothermal method by using 0.8 mmol of Lu₂O₃ (3N, 0.3183g), 3.0 mmol of CuSO₄·5H₂O (AR, 0.75g), 0.8 mmol of NaF (AR, 0.034g) with 8 mL deionized water as starting materials. After sealing the mixture of the reactants in autoclaves, the autoclaves were put into a furnace. Then the furnace was heated at 230 °C and kept for seven days, and cooled down to room temperature within three days. Finally the products were washed using deionized water and ethanol (99%) for several times, and some light blue crystals were obtained. The purity of crystal was checked by powder X-ray diffraction (Figure S1) using a Rigaku Miniflex 600 powder diffractometer with graphite monochromatized Cu-K α radiation at room temperature.

X-ray crystallographic studies. Single crystal measurement of Lu₂Cu(SO₄)₂(OH)₃F·H₂O was performed on Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293K. The crystal structure was solved and refined by Olex-2.¹ The final structure parameters were refined and further checked by the PLATON program.² Structural refinements are listed in Table S1. Atomic coordinates and other structural information are provided in Supporting Information (Table S3 – S6).

Spectroscopic and thermal analyses. Infrared spectroscopy from 4000 to 400 cm⁻¹ was recorded by the KBr disk method on a VERTEX70 FT-IR spectrometer. Thermogravimetric analysis (TGA) was collected on NETZSCH STA 449C instrument with Al₂O₃ crucible from room temperature to 1000 °C at the rate of 15 °C/min under N₂ atmosphere. The UV-vis absorption spectra were recorded on a PE Lambda 900 UV–vis spectrophotometer in the wavelength range 200–1000 nm.

The infrared spectroscopy (KBr cm⁻¹) for CuLu₂(SO₄)₂(OH)₃F·H₂O is shown in Figure S3. The peaks around 3500 cm⁻¹ indicate the existence of OH⁻ and H₂O. The peaks at 1180 (s), 1126 (s), 1116 (s), 1016 (s), 885 (w), 786 (w), 715 (w)和 626 (s) cm⁻¹ indicate the existence of SO₄²⁻ group.³ These results are consistent with the single crystal structure analysis. UV-vis absorption spectra (Figure S4) reveals several

absorption peaks in the range of 200 - 1000 nm for Lu₂Cu(SO₄)₂(OH)₃F·H₂O. Optical diffuse reflectance spectra indicate a band gap of 2.17 eV. As shown in Figure S5, CuLu₂(SO₄)₂(OH)₃F·H₂O is stable below 235 °C with no changes of the weight in this temperature range, and then a weight loss of ~ 2.52 % is observed in the range of 235 – 365 °C, corresponding to the loss of one H₂O molecule (calculated: 2.59%). Upon heating, a rapid weight loss of 2.68 % is seen between 450 to 510 °C, indicating the loss of HF (calculated: 2.88 %). Further, a weight loss of 16.8 % is observed between 710 – 920 °C, indicating the release of 1SO₃ + 2OH⁻ (calculated: 16.4 %). The final residues of the compound were difficult to be characterized since they were melted with the Al₂O₃ crucible after heated to 1000 °C.

Magnetic measurements. Magnetic measurements were carried out by a commercial Quantum Design Physical Property Measurement System (PPMS) using powdered samples obtained by crushing small single crystals. Magnetic susceptibility (χ) was measured from 390 to 2 K at 0.1 T. Specific heat data was measured from 300 to 2 K under zero magnetic field. The EPR spectrum was collected at 293 K using a Bruker Biospin E-500 spectrometer with a frequency of 9.87 GHz. 1,1-diphenyl-2-picrylhydrazyl (DPPH) with $g = 2.0023$ was used as a standard sample for the resonance line of a field marker. A typical Lorentzian line-shape in Fig. 6S gives a g -factor of 2.12(1) using the equation of $h\nu = g m_B H$ with $H = \sim 3325$ Oe.⁴

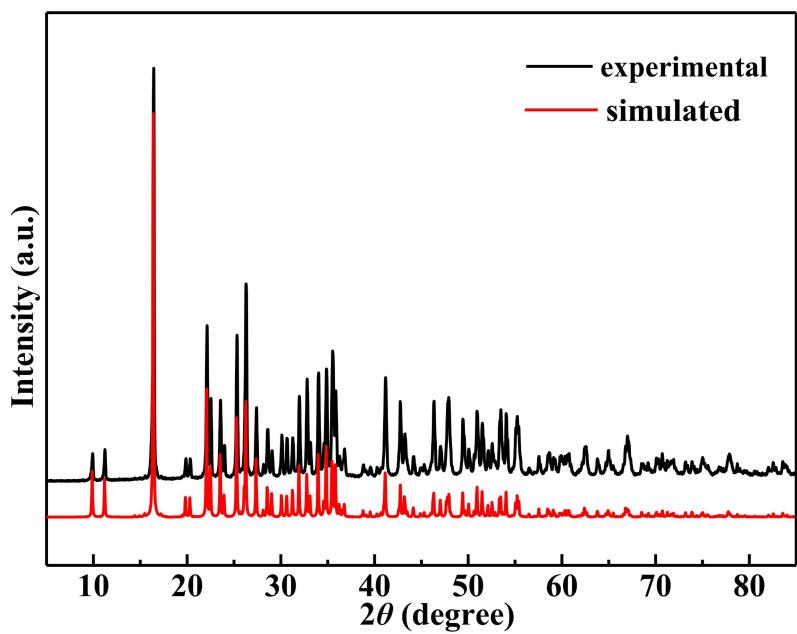


Figure S1. Simulated (red line) and experimental (black line) powder X-ray (CuK α) diffraction patterns of Lu₂Cu(SO₄)₂(OH)₃F·H₂O.

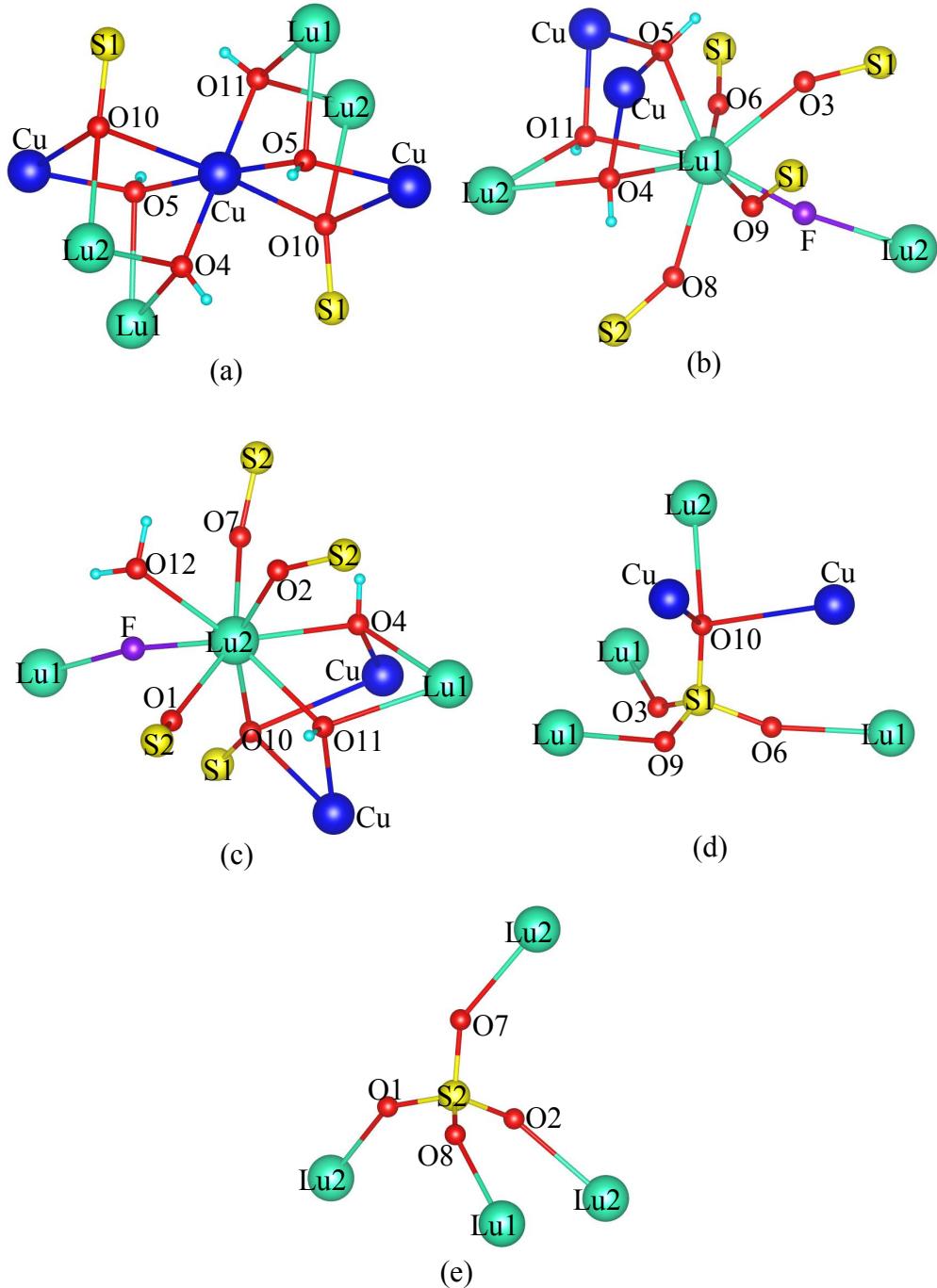


Figure S2. Oxygen-coordination environments for (a) Cu, (b) Lu1, (c) Lu2, (d) S1 and (e) S2 atoms in $\text{Lu}_2\text{Cu}(\text{SO}_4)_2(\text{OH})_3\text{F}\cdot\text{H}_2\text{O}$.

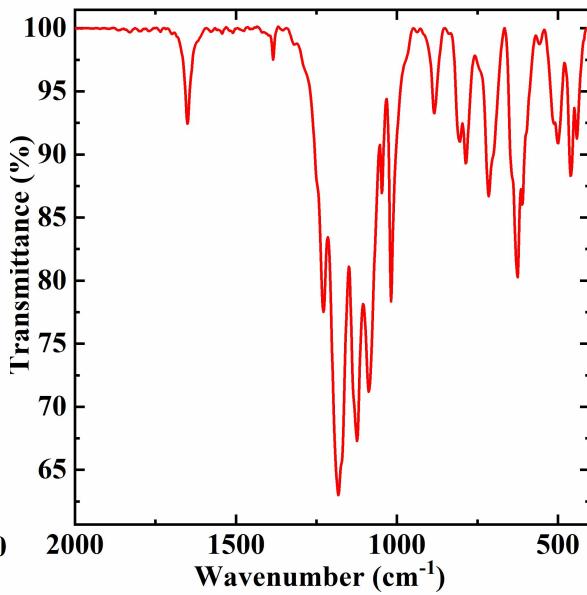
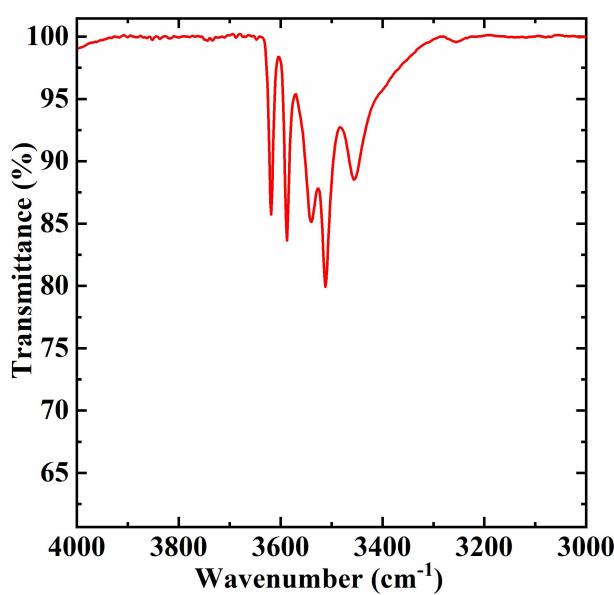
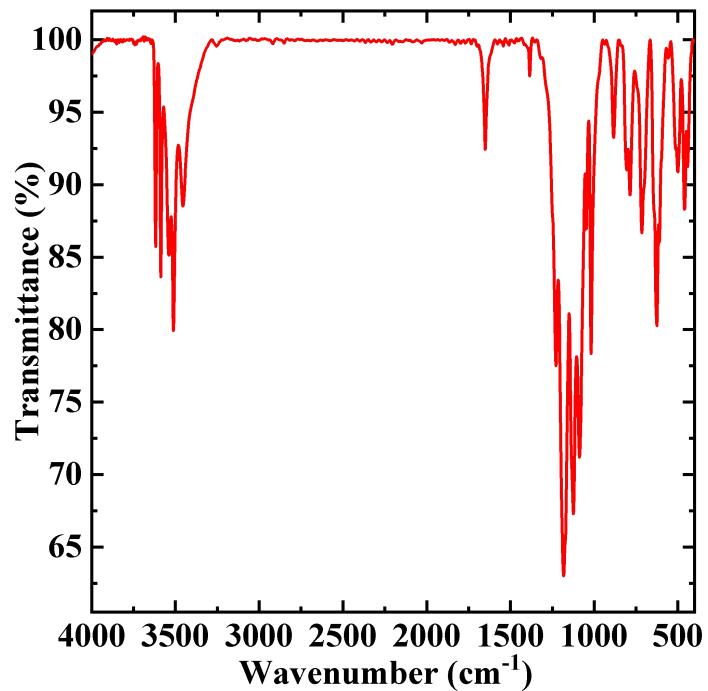


Figure S3. Infrared spectroscopy data (KBr cm⁻¹) for Lu₂Cu(SO₄)₂(OH)₃F·H₂O.

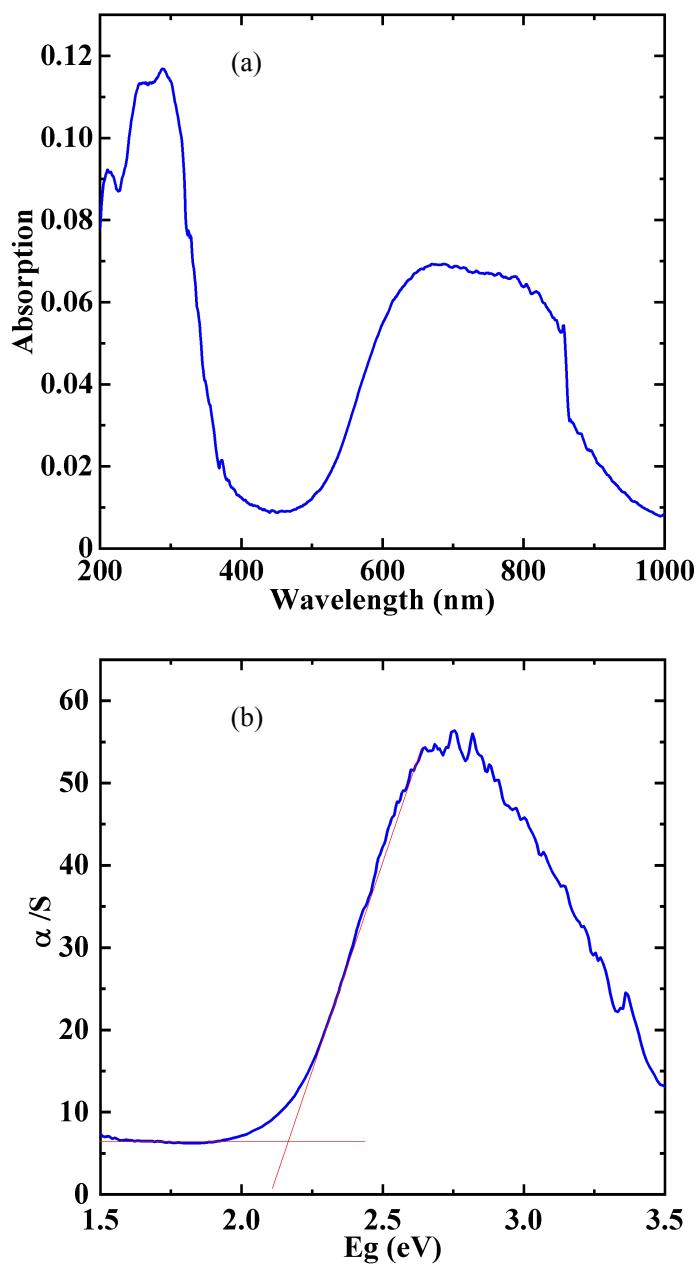


Figure S4. (a) UV-vis absorption spectra and (b) optical diffuse reflectance spectra for $\text{Lu}_2\text{Cu}(\text{SO}_4)_2(\text{OH})_3\text{F}\cdot\text{H}_2\text{O}$.

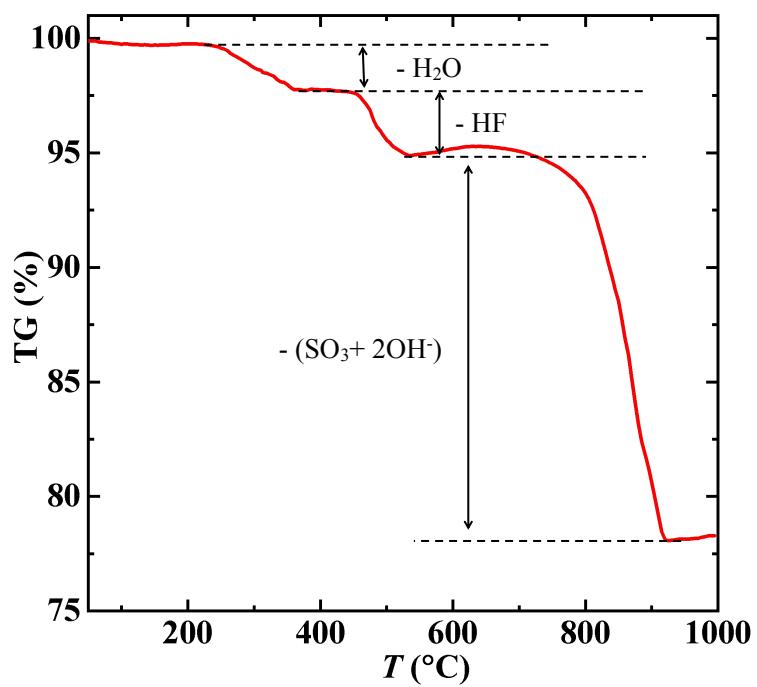


Figure S5. Thermogravimetric analysis of $\text{Lu}_2\text{Cu}(\text{SO}_4)_2(\text{OH})_3\text{F}\cdot\text{H}_2\text{O}$.

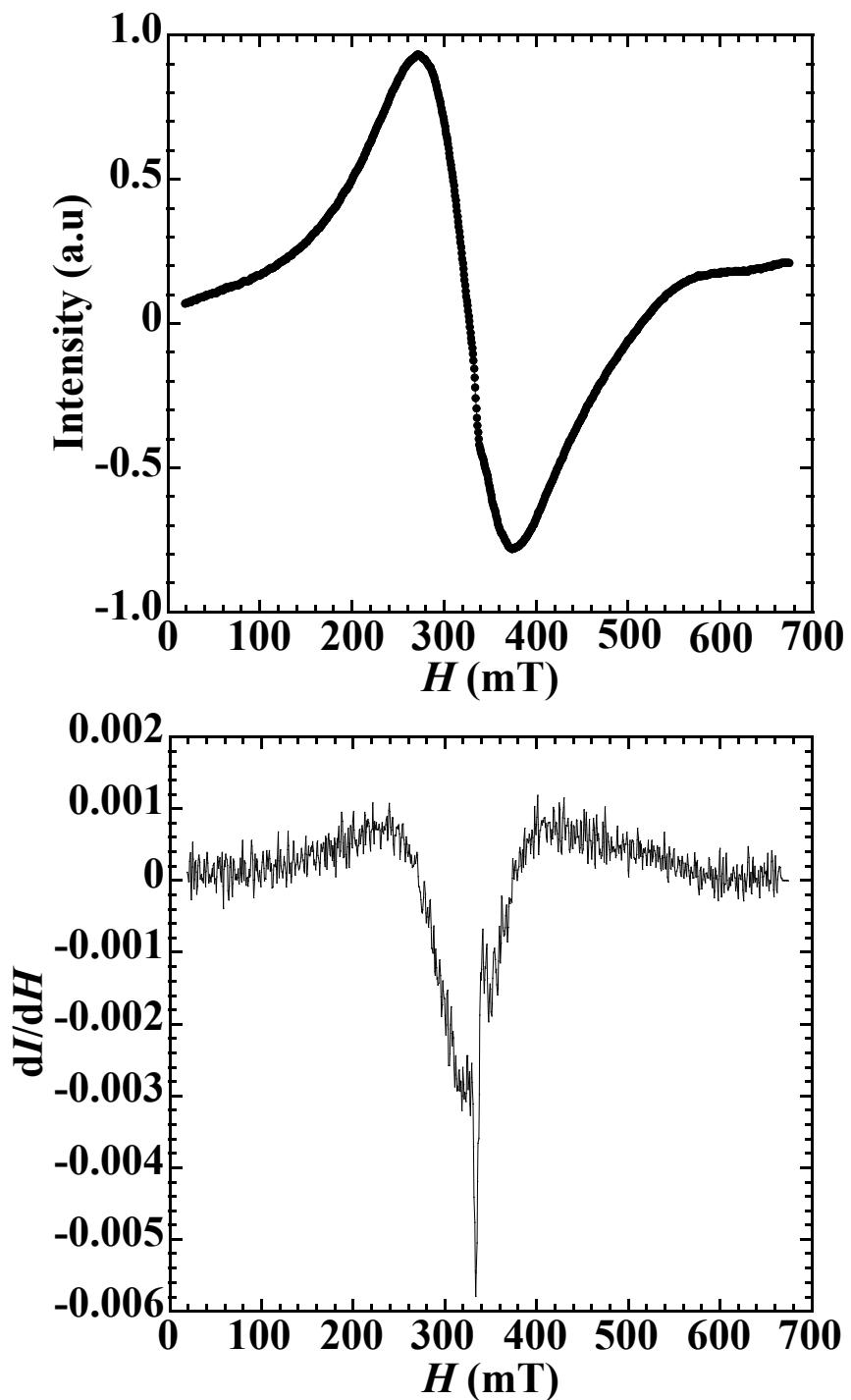


Figure S6. The EPR spectrum of $\text{Lu}_2\text{Cu}(\text{SO}_4)_2(\text{OH})_3\text{F}\cdot\text{H}_2\text{O}$ measured at 9.87 GHz.

The derivation of intensive by the resonance field is seen.

References:

- (1) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl.Cryst.* **2009**, *42*, 339-341.
- (2) Spek, A. L. Single-crystal structure validation with the program PLATON. *J. Appl.Crystallogr.* **2003**, *36*, 7-13.
- (3) Fillaux, F.; Lautié, A.; Tomkinson, J.; Kearley, G. J. Proton-transfer dynamics in the hydrogen-bond inelastic neutron-scattering, infrared and raman-spectra of $\text{Na}_3\text{H}(\text{SO}_4)_2$, $\text{K}_3\text{H}(\text{SO}_4)_2$ and $\text{Rb}_3\text{H}(\text{SO}_4)_2$, *Chem. Phys.*, **1991**, *154*, 135-144.
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Table S1. Crystal data and structure refinement for $\text{Lu}_2\text{Cu}(\text{SO}_4)_2(\text{OH})_3\text{F}\cdot\text{H}_2\text{O}$

Formula	$\text{Lu}_2\text{Cu}(\text{SO}_4)_2(\text{OH})_3\text{F}\cdot\text{H}_2\text{O}$
Fw	693.67
T, K	Room temperature
Space group	$P2_1/c$
a/Å	11.533(4)
b/Å	6.785(2)
c/Å	15.838(4)
β/deg	129.072(16)
V/Å ³	962.2(5)
Z	4
$\rho_{\text{calc}}/\text{g/cm}^3$	4.789
GOF on F^2	1.037
R1, wR2 [$I > 2\sigma(I)$] ^a	0.0242, 0.0596
R1, wR2 [all data]	0.0294, 0.0622

^a $R1 = \sum ||\mathbf{F}_0| - |\mathbf{F}_c|| / \sum |\mathbf{F}_0|$, and $wR2 = [\sum w(\mathbf{F}_{02} - \mathbf{F}_{c2})^2 / \sum w(\mathbf{F}_{02})^2]^{1/2}$

Table S2. The bond valence sum (BVS) calculations of all atoms for $\text{Lu}_2\text{Cu}(\text{SO}_4)_2(\text{OH})_3\text{F}\cdot\text{H}_2\text{O}$.

Atom	BVS	Valence	Atom	BVS	Valence
Lu1	3.275	+3	O4	1.153	-2 (OH)
Lu2	3.047	+3	O5	1.287	-2(OH)
Cu	2.009	+2	O6	2.037	-2
S1	6.125	+6	O7	1.987	-2
S2	6.233	+6	O8	2.074	-2
F	0.998	-1	O9	1.861	-2
O1	1.991	-2	O10	1.994	-2
O2	1.914	-2	O11	1.105	-2(OH)
O3	1.981	-2	O12	0.307	-2(H_2O)

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Lu}_2\text{Cu}(\text{SO}_4)_2(\text{OH})_3\text{F}\cdot\text{H}_2\text{O}$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	U(eq)
Lu(1)	1852(1)	-2513(1)	-3056(1)	5(1)
Lu(2)	3106(1)	-2397(1)	-5066(1)	6(1)
Cu(1)	-50(1)	-4889(1)	-7509(1)	8(1)
S(1)	-720(2)	-2395(2)	-5978(1)	6(1)
S(2)	5654(2)	-2409(2)	-643(1)	7(1)
F(1)	2688(4)	-2499(4)	-3922(3)	16(1)
O(1)	6555(5)	-4148(6)	-413(4)	15(1)
O(2)	5171(5)	-2456(5)	27(4)	14(1)
O(3)	-171(5)	-2131(6)	-4868(3)	11(1)
O(4)	2060(4)	-740(6)	-1664(3)	9(1)
O(5)	-318(5)	-2600(5)	-3265(3)	8(1)
O(6)	-1422(5)	-4319(6)	-6395(3)	18(1)
O(7)	6584(5)	-681(6)	-364(4)	15(1)
O(8)	4356(6)	-2339(6)	-1782(4)	17(1)
O(9)	-1848(4)	-876(5)	-6698(3)	11(1)
O(10)	484(6)	-2190(7)	-6055(4)	23(1)
O(11)	2164(4)	-4478(6)	-1663(3)	7(1)
O(12)	5371(5)	-2253(6)	-3209(4)	21(1)

Table S4. Selected bond lengths (Å) and bond angles (°) of Lu₂Cu(SO₄)₂(OH)₃F·H₂O.

Lu1- F1	2.117(4)	Lu2- O2 ⁶	2.294(5)	Cu1-O10 ⁸	2.535(5)
Lu1- O3	2.304(4)	Lu2- O4 ⁶	2.368(4)	Cu1-O10	2.692(5)
Lu1- O4	2.387(4)	Lu2- O7 ⁷	2.291(4)	S1- O3	1.456(5)
Lu1- O5	2.309(5)	Lu2- O10	2.376(5)	S1- O6	1.457(4)
Lu1- O6 ¹	2.253(4)	Lu2- O11 ⁶	2.394(4)	S1- O9	1.478(4)
Lu1- O8	2.254(5)	Lu2- O12	2.408(5)	S1- O10	1.475(6)
Lu1- O9 ³	2.332(4)	Cu1- O4 ⁶	1.946(4)	S2- O1	1.459(4)
Lu1- O11	2.402(4)	Cu1- O5 ⁶	1.978(4)	S2- O2	1.475(5)
Lu2- F1	2.150(4)	Cu1- O5 ¹	1.983(4)	S2- O7	1.458(4)
Lu2- O1 ⁵	2.284(4)	Cu1- O11 ¹	1.955(4)	S2- O8	1.448(5)
F1-Lu1-O3	73.08(2)	F1-Lu2-O10	71.89(16)	O5 ¹ -Cu1-O10 ⁸	82.51(16)
F1-Lu1-O6 ¹	80.40(1)	F1-Lu2-O12	67.59(16)	O5 ¹ -Cu1-O10	102.17(16)
F1-Lu1-O8	74.30(2)	O1 ⁵ -Lu2-O2 ⁶	93.87(14)	O5 ⁶ -Cu1-O10	78.55(16)
F1-Lu1-O9 ³	80.84(13)	O1 ⁵ -Lu2-O10	92.42(16)	O5 ⁶ -Cu1-O10 ⁸	96.65(17)
O3-Lu1-O5	70.69(16)	O1 ⁵ -Lu2-O11 ⁶	72.95(14)	O11 ¹ -Cu1-O5 ⁶	97.38(17)
O3-Lu1-O9 ³	77.70(14)	O1 ⁵ -Lu2-O12	74.22(15)	O11 ¹ -Cu1-O5 ¹	85.18(17)
O4-Lu1-O11	64.04(14)	O2 ⁶ -Lu2-O4 ⁶	81.63(15)	O11 ¹ -Cu1-O10	103.84(16)
O5-Lu1-O4	67.31(14)	O2 ⁶ -Lu2-O11 ⁶	81.50(15)	O11 ¹ -Cu1-O10 ⁸	78.77(16)
O5-Lu1-O9 ³	96.51(13)	O2 ⁶ -Lu2-O12	68.93(17)	O3-S1-O6	110.6(3)
O5-Lu1-O11	68.87(14)	O4 ⁶ -Lu2-O10	75.38(15)	O3-S1-O9	110.3(3)
O6 ¹ -Lu1-O3	79.79(15)	O4 ⁶ -Lu2-O11 ⁶	64.44(15)	O3-S1-O10	111.9(3)
O6 ¹ -Lu1-O5	88.02(15)	O7 ⁷ -Lu2-O2 ⁶	88.70(14)	O6- S1-O9	107.9(3)
O6 ¹ -Lu1-O8	103.97(15)	O7 ⁷ -Lu2-O4 ⁶	71.18(15)	O6- S1-O10	109.3(3)
O6 ¹ -Lu1-O11	72.19(15)	O7 ⁷ -Lu2-O10	98.55(16)	O7- S2- O1	107.6(3)
O8-Lu1-O4	79.69(15)	O7 ⁷ -Lu2-O12	80.24(15)	O7- S2- O2	109.8(2)
O8-Lu1-O9 ³	87.95(14)	O10-Lu2-O11 ⁶	74.39(15)	O8- S2- O1	110.6(3)
O8-Lu1-O11	80.88(15)	O4 ⁶ -Cu1-O5 ⁶	83.13(17)	O8- S2- O2	109.6(3)
O9 ³ -Lu1-O4	69.26(14)	O4 ⁶ -Cu1-O5 ¹	94.32(17)	O8- S2- O7	109.6(3)
F1-Lu2-O1 ⁵	80.40(13)	O4 ⁶ -Cu1-O10	75.50(16)		
F1- Lu2-O7 ⁷	78.11(13)	O4 ⁶ -Cu1-O10 ⁸	101.94(17)		

Symmetry transformations: ¹, X -1-Y, -1-Z; ²+X, -1/2-Y, 1/2+Z; ³-X, -Y, -1-Z; ⁴-X, 1/2+Y, -3/2-Z; ⁵1-X, 1/2+Y, -1/2-Z; ⁶+X, -1/2-Y, -1/2+Z; ⁷1-X, -1/2+Y, -1/2-Z; ⁸-X, -1/2+Y, -3/2-Z

Table S5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Lu}_2\text{Cu}(\text{SO}_4)_2(\text{OH})_3\text{F}\cdot\text{H}_2\text{O}$. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^{*} b^{*} U_{12}]$

atom	U11	U22	U33	U23	U13	U12
Lu1	5(1)	7(1)	3(1)	0(1)	3(1)	0(1)
Lu2	6(1)	9(1)	4(1)	0(1)	3(1)	0(1)
Cu1	7(1)	9(1)	8(1)	1(1)	5(1)	-2(1)
S1	7(1)	7(1)	3(1)	0(1)	3(1)	1(1)
S2	6(1)	11(1)	5(1)	0(1)	4(1)	0(1)
F1	9(2)	27(2)	13(2)	-1(1)	8(2)	0(1)
O1	21(2)	11(2)	14(2)	1(2)	12(2)	5(2)
O2	16(3)	24(3)	7(2)	0(2)	9(2)	0(2)
O3	9(2)	17(2)	4(2)	-1(2)	2(2)	-2(2)
O4	6(2)	11(2)	7(2)	2(2)	3(2)	2(2)
O5	5(2)	10(2)	3(2)	-1(1)	0(2)	-1(1)
O6	26(3)	9(2)	15(2)	-3(2)	11(2)	-2(2)
O7	22(2)	9(2)	15(2)	-2(2)	12(2)	-4(2)
O8	13(3)	30(3)	3(2)	-3(2)	3(2)	0(2)
O9	10(2)	11(2)	7(2)	3(2)	4(2)	2(2)
O10	18(3)	42(3)	13(3)	4(2)	12(2)	5(2)
O11	6(2)	9(2)	5(2)	-1(2)	2(2)	-2(2)
O12	9(2)	38(3)	12(3)	1(2)	5(2)	10(2)

Table S6. Hydrogen bond lengths (\AA) and bond angles ($^\circ$) of $\text{Lu}_2\text{Cu}(\text{SO}_4)_2(\text{OH})_3\text{F}\cdot\text{H}_2\text{O}$.

D–H…A	d(D–H) / \AA	d(H…A) / \AA	d(D…A) / \AA	$\angle\text{DHA}/^\circ$
O4–H4…S2 ¹	0.83	2.97	3.566(4)	130.9
O5–H5…S2 ²	0.83	2.96	3.703(5)	149.8
O11–H11…S2 ³	0.82	2.96	3.542(4)	130.0
O12–H12B…O9 ⁴	0.87	2.15	2.820(6)	132.9

Symmetry codes: ¹ 1-X,-Y,-Z; ² -1+X,-1/2-Y,-1/2+Z; ³ 1-X,-1-Y,-Z; ⁴ 1+X, -1/2-Y, 1/2+Z