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Electronic Supplementary Information

Spin coherence phenomena of a S = 1/2 copper(II) system in a polyoxometalate with a less-abundant nuclear-spin

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General information

Preparation of magnetic dilution sample

$[(n\text{-}C_4H_9)_4N]_4H_2[SiW_{11}O_{39}Cu_{0.01}Zn_{0.99}]$ (**1%dil.1**) was prepared according to the previous report.[refS1]

A mixture of $[(n\text{-}C_4H_9)_4N]_4H_2[SiW_{11}O_{39}Cu]$ (**1**) and its diamagnetic congener $[(n\text{-}C_4H_9)_4N]_4H_2[SiW_{11}O_{39}Zn]$, synthesized by the reported methods, in a molar ratio of 1 : 99 was dissolved in acetonitrile and filtered through Celite. The filtrate was concentrated on a rotary evaporator and dried under reduced pressure for several hours to give powder form of **1%dil.1**.

Electron spin resonance (ESR) measurements

Continuous-wave (CW) ESR measurements at between 4.35-291 K were performed on a JEOL JES-FA300 spectrometer at X-band (~9.0 GHz) frequency using a 5 mm quartz ESR tube. (typical conditions used: microwave frequency = 9.06 GHz; modulation frequency = 100 kHz; modulation amplitude = 0.3 mT; time constant = 0.03 s; and microwave power = 0.04 mW).

CW ESR measurement at room temperature and pulsed ESR measurements were performed on Bruker E680 spectrometer operated at X-band (~9.6 GHz) using a 5 mm quartz ESR tube. A Bruker standard dielectric resonator (ER4118X-MD5W) with TE011 mode was used. For pulsed ESR measurements, 1 kW amplified microwave irradiation was optimized to a fixed π/2 pulse of 16 ns. The echo decay measurements were conducted using a Hahn-echo (two-pulse) sequence. The pulse interval *τ* between the first π/2 pulse and the second π pulse was varied. T_M was obtained by stretched exponential fitting of decay curves. Inversion recovery measurements were conducted using a three-pulse spin echo sequence. The first π pulse was irradiated, with an interval τ before the second π/2 pulse being varied. The third pulse irradiated after 0.2 μs of interval, and then the echo signal followed after 0.2 μs of interval was observed. T_1 was obtained by stretched exponential fitting of recovery curves.

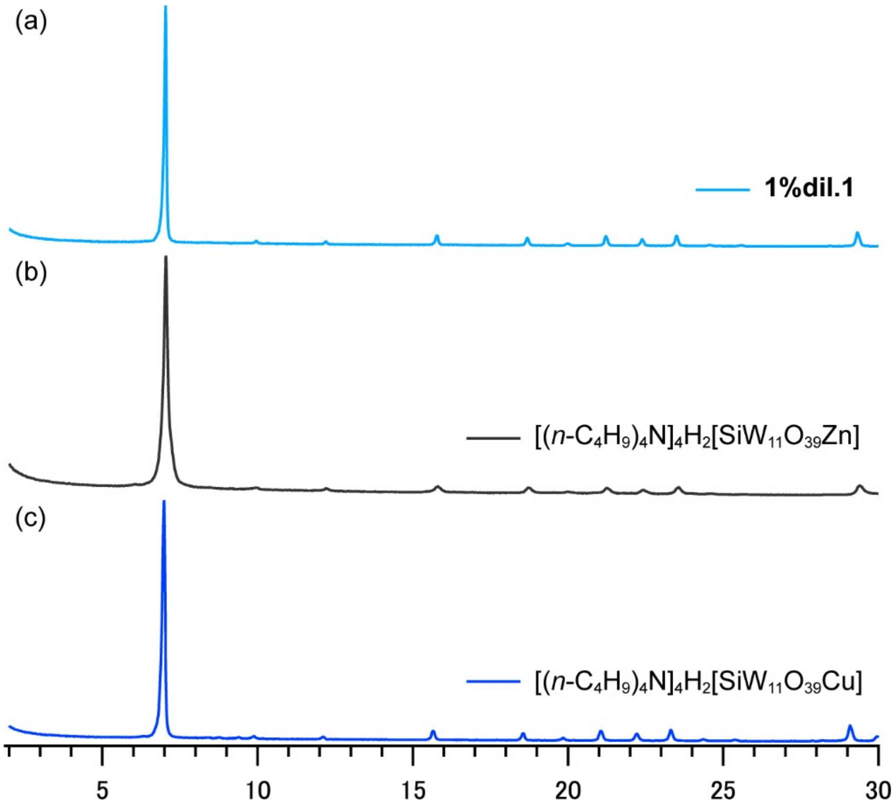

Figure S1 Powder X-ray diffraction patterns of (a) **1%dil.1** (light blue), (b) $[(n\text{-}C_4H_9)_4N]_4H_2[SiW_{11}O_{39}Zn]$ (black) and (c) $[(n\text{-}C_4H_9)_4N]_4H_2[SiW_{11}O_{39}Cu]$ (blue).

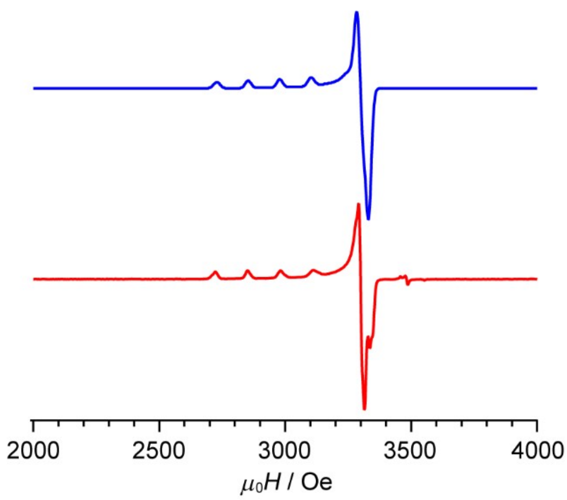

Figure S2 (red line) X-band (9.65 GHz) continuous-wave electron spin resonance spectrum of **1%dil.1** measured at room temperature and (blue line) the simulation using the following parameters: $g_{//}$ = 2.34, $g_{\perp}$ = 2.07, $A_{//}$ = 411 MHz, $A_{\perp}$ = 8 MHz.

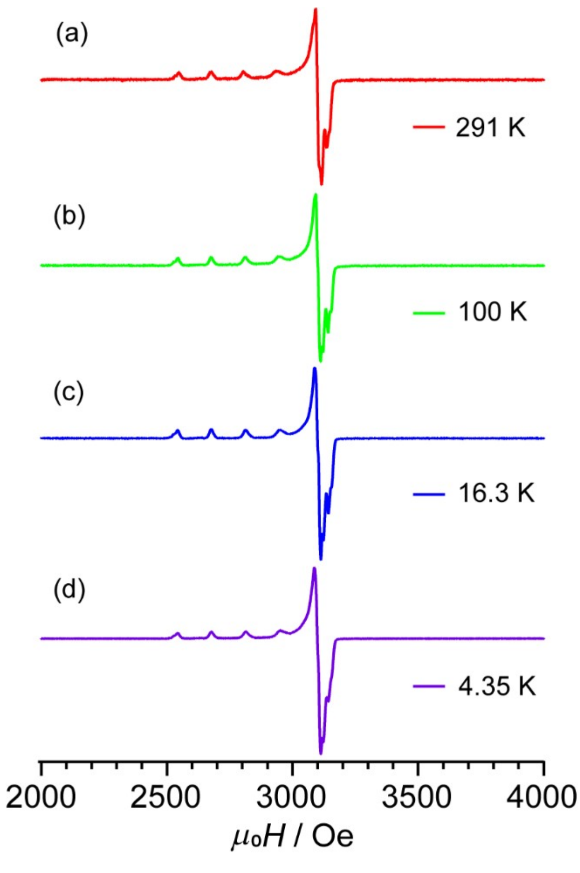

Figure S3 X-band (9.0 GHz) continuous-wave electron spin resonance spectrum of an independently prepared sample of **1%dil.1** measured at (a) 291 K, (b) 100 K, (c) 16.3 K, and (d) 4.35 K.

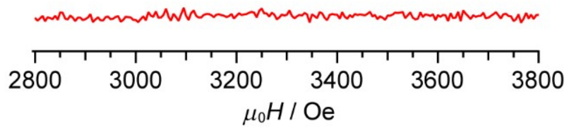

Figure S4 Echo-detected field-swept ESR spectrum of **1%dil.1** measured at room temperature.

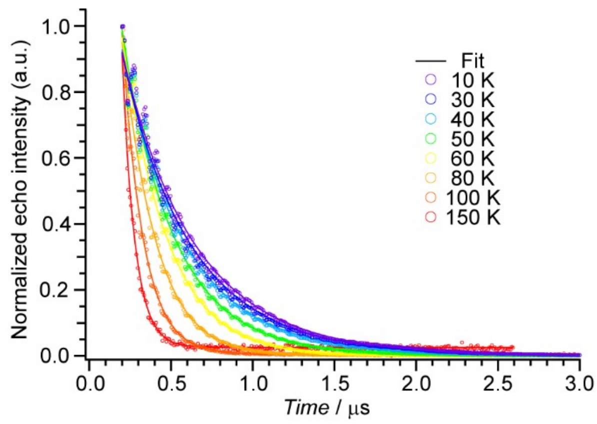

Figure S5 Spin-echo decays of **1%dil.1** obtained by performing the Hahn echo sequence on the transition of 3330 Oe at the indicated temperatures, and the corresponding fitting curves.

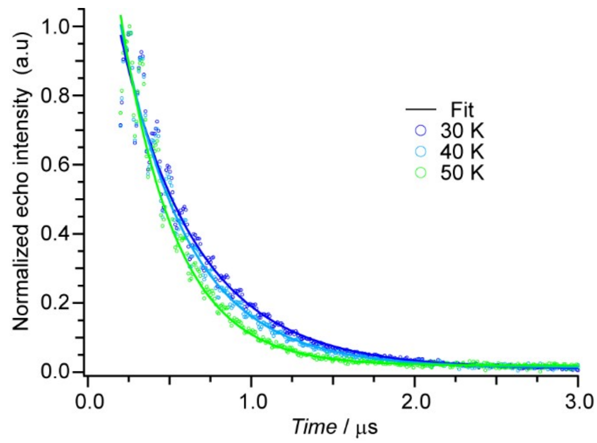

Figure S6 Spin-echo decays of **1%dil.1** obtained by performing the Hahn echo sequence on the transition at 2760 Oe at the indicated temperatures, along with the corresponding fitting curves.

Table S1 Fitting parameters used in the stretched monoexponential decay (eq. 1) of the transition of **1%dil.1** at 3330 Oe.

T / K	I_0	A	T_M / μs	β_M
10	0.00045 ± 0.00005	1.50 ± 0.01	0.425 ± 0.01	0.955 ± 0.005
30	0.0006 ± 0.001	1.57 ± 0.1	0.390 ± 0.02	0.93 ± 0.02
40	0.00074 ± 0.0001	1.67 ± 0.07	0.355 ± 0.015	0.93 ± 0.02
50	0.00085 ± 0.0001	1.98 ± 0.3	0.294 ± 0.04	0.94 ± 0.06
60	0.0011 ± 0.0001	1.84 ± 0.2	0.300 ± 0.03	1.08 ± 0.06
80	0.0019 ± 0.0002	2.20 ± 0.3	0.234 ± 0.03	1.11 ± 0.07
100	0.0040 ± 0.0004	4.80 ± 1.7	0.125 ± 0.04	0.99 ± 0.11
150	0.026 ± 0.002	12.0 ± 4.0	0.077 ± 0.017	1.00 ± 0.10

Table S2 Fitting parameters used in the stretched monoexponential decay (eq. 1) of the transition of **1%dil.1** at 2760 Oe.

T / K	I_0	A	T_M / μs	β_M
30	0.008 ± 0.0010	1.55 ± 0.20	0.445 ± 0.055	0.94 ± 0.06
40	0.013 ± 0.0015	1.66 ± 0.24	0.400 ± 0.070	0.96 ± 0.09
50	0.019 ± 0.0010	1.79 ± 0.01	0.346 ± 0.024	1.03 ± 0.05

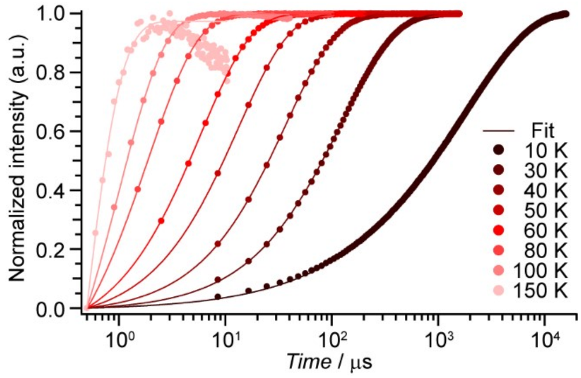

Figure S7 Inversion recovery traces obtained for the transition of **1%dil.1** at 3330 Oe at the indicated temperatures, along with the corresponding fitting curves.

Table S3 Fitting parameters used in the stretched monoexponential decay (eq. 2) of the transition of **1%dil.1** at 3330 Oe.

T / K	I_0	A	T_1 / μs	β_1
10	1.025 ± 0.001	-1.032 ± 0.001	1680 ± 20	0.62 ± 0.01
30	1.001 ± 0.001	-1.009 ± 0.001	124 ± 0.5	0.85 ± 0.03
40	0.998 ± 0.001	-1.019 ± 0.001	37.1 ± 0.01	0.90 ± 0.02
50	0.999 ± 0.001	-1.051 ± 0.001	13.3 ± 0.001	0.91 ± 0.01
60	0.999 ± 0.001	-1.111 ± 0.001	5.88 ± 0.06	0.91 ± 0.002
80	0.998 ± 0.005	-1.33 ± 0.001	1.89 ± 0.01	0.93 ± 0.04
100	0.997 ± 0.002	-1.641 ± 0.04	0.998 ± 0.05	1.01 ± 0.02
150	0.974 ± 0.020	-4.09 ± 0.01	0.349 ± 0.01	1.01 ± 0.002

Ref. S1 T. Ishizaki and T. Ozeki, *Dalton Trans.*, 2023, **52**, 4678.