Supplementary Information

Humidity dependency of the thermal phase transition of a cyano-bridged Co-W bimetal assembly

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§1. The results of Rietveld analyses and the atomic coordinates

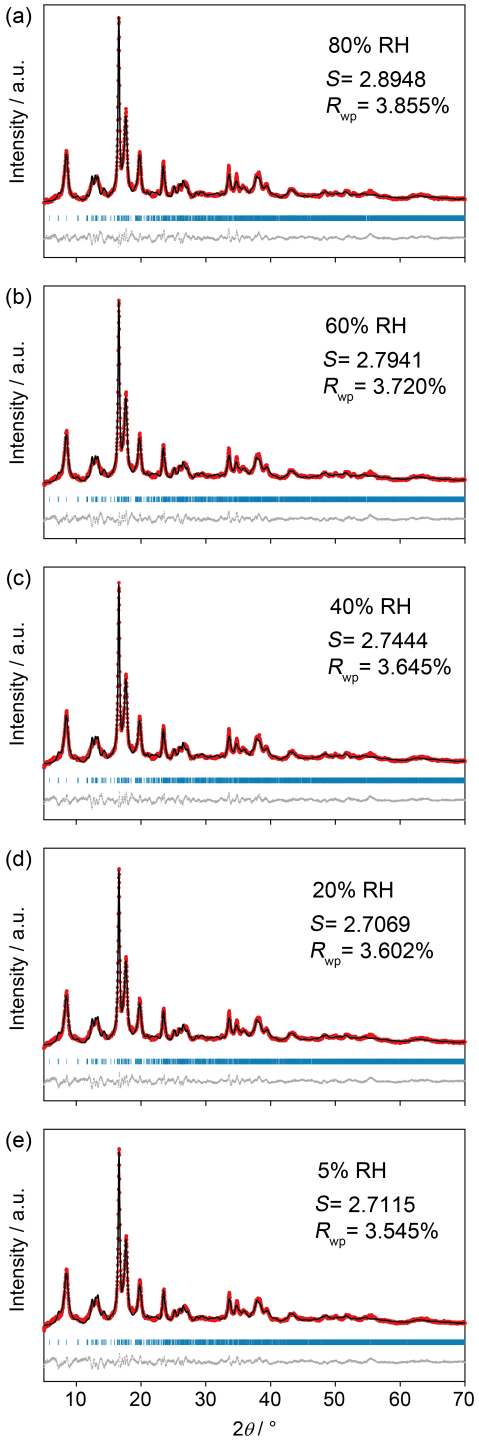

Fig. S1 XRD patterns and Rietveld analyses of $Co_3[W(CN)_8]_2(4\text{-methylpyridine})_2(\text{pyrimidine})_2{\cdot}xH_2O$ for (a) 80% RH, (b) 60% RH, (c) 40% RH, (d) 20% RH, and (e) 5% RH. Black points, red lines, blue bars, and gray points indicate the observed patterns, calculated patterns, Bragg peak positions, and residual curves, respectively.

Table S1. Atomic coordinates of $Co_3[W(CN)_8]_2(4\text{-methylpyridine})_2(pyrimidine)_2 \cdot xH_2O$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co1	0.55	0.90	0.74	C31	0.48	0.58	0.88
Co2	0.54	0.42	0.78	C32	0.65	0.62	0.99
Co3	0.50	0.50	0.50	C33	0.78	0.56	0.98
Co4	0.00	0.00	0.00	C34	0.76	0.50	0.92
W1	0.03	0.15	0.74	C35	0.50	0.63	0.94
W2	0.98	0.65	0.69	C36	0.67	0.67	0.05
C1	0.89	0.29	0.77	N1	0.81	0.35	0.79
C2	0.91	0.02	0.75	N2	0.84	0.96	0.75
C3	0.09	0.08	0.85	N3	0.09	1.04	0.90
C4	0.28	0.06	0.77	N4	0.40	0.01	0.78
C5	0.27	0.14	0.83	N5	0.41	0.12	0.86
C6	0.91	0.16	0.66	N6	0.86	0.17	0.61
C7	0.09	0.25	0.84	N7	0.12	0.31	0.88
C8	0.24	0.27	0.79	N8	0.36	0.32	0.81
C9	0.15	0.78	0.71	N9	0.25	0.84	0.73
C10	0.20	0.55	0.74	N10	0.31	0.50	0.75
C11	0.73	0.61	0.63	N11	0.62	0.59	0.58
C12	0.12	0.65	0.81	N12	0.17	0.66	0.86
C13	0.14	0.52	0.66	N13	0.24	0.47	0.64
C14	0.79	0.57	0.73	N14	0.70	0.54	0.75
C15	0.82	0.77	0.63	N15	0.73	0.83	0.61
C16	0.78	0.75	0.71	N16	0.66	0.79	0.71
C17	0.51	0.80	0.86	N17	0.76	0.91	0.94
C18	0.70	0.93	0.87	N18	0.62	0.87	0.83
C19	0.55	0.78	0.93	N19	0.51	0.39	0.58
C20	0.68	0.83	0.97	N20	0.53	0.36	0.69
C21	0.54	0.28	0.67	N21	0.49	0.95	0.65
C22	0.52	0.42	0.64	N22	0.58	0.51	0.88
C23	0.54	0.25	0.61	O1	0.58	0.05	0.95
C24	0.53	0.31	0.56	O2	0.90	0.26	0.51
C25	0.53	0.05	0.64	O3	0.34	0.69	0.97
C26	0.42	0.05	0.54	O4	0.78	0.70	0.45
C27	0.36	0.95	0.54	O5	0.10	0.93	0.55
C28	0.40	0.91	0.60	O6	0.99	0.39	0.97
C29	0.50	0.09	0.59	O7	0.15	0.87	1.00
C30	0.39	0.10	0.47	O8	0.78	0.45	0.47

* The atomic coordinates are the same for all humidities.

§2. Phase transition temperatures

Table S2 Humidity dependence of the transition temperatures and thermal hysteresis

	100% RH	80% RH	60% RH	40% RH	20% RH	5% RH
$T_{1/2\downarrow}$ / K	147	152	157	168	174	191
$T_{1/2\uparrow}$ / K	242	239	236	236	239	245
T_p / K	195	196	197	202	207	218
ΔT / K	95	87	79	68	65	54

§3. DSC measurements

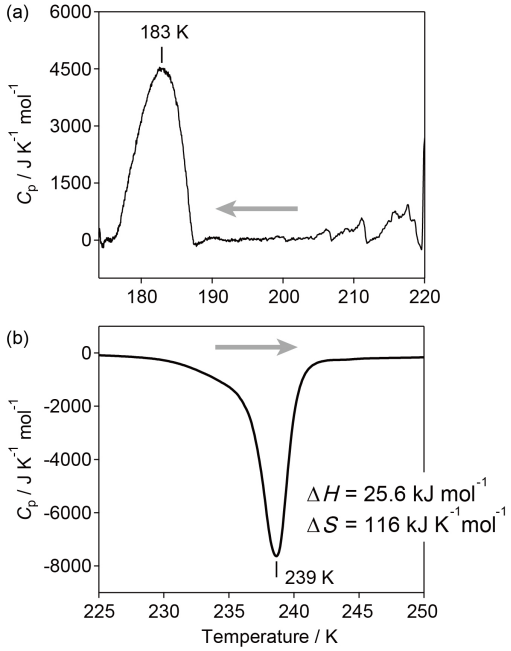

Fig. S2 The DSC charts of $Co_3[W(CN)_8]_2$(4-methylpyridine)$_2$(pyrimidine)$_2$·xH$_2$O in (a) cooling and (b) warming processes.

§4. Spin entropy change due to a phase transition

The change in the spin entropy (ΔS_{spin}) is calculated from the orbital degeneracy and the spin multiplicity. In the present complex, Co has an octahedral (D_{4h}) symmetry. The electronic states of Co^{II} and Co^{III} are ^4E_g and $^1A_{1g}$, respectively. On the other hand, W has a dodecahedron (C_{2v}) symmetry, and the electronic states of W^V and W^{IV} are $^2B_1$ and $^1A_1$, respectively. Therefore, the electronic states are:

HT phase: $3D_{4h}Co^{II}(^4E_g)$-$2C_{2v}W^V(^2B_1)$
LT phase: $2D_{4h}Co^{III}(^1A_{1g})$-$D_{4h}Co^{II}(^4E_g)$-$2C_{2v}W^{IV}(^1A_1)$

The degeneracy of each phase is expressed by the product of the orbital degeneracy and the spin multiplicity. $D_{4h}Co^{III}(^1A_{1g})$ is 1 × 1, $C_{2v}W^{IV}(^1A_1)$ is 1 × 1, $D_{4h}Co^{II}(^4E_g)$ is 2 × 4, and $C_{2v}W^V(^2B_1)$ is 1 × 2. Therefore, the degeneracies are:

HT phase: $(2 \times 4)^3 \times (1 \times 2)^2 = 2048$
LT phase: $(1 \times 1)^2 \times (2 \times 4)^1 \times (1 \times 1)^2 = 8$

Thus, the spin entropy of the HT and LT phases are $S_{spin,\,LT} = R\ln 8$, $S_{spin,\,HT} = R\ln 2048$, respectively. Taking the difference of these values, ΔS_{spin} is

$$\begin{aligned}\Delta S_{spin} &= S_{spin,\,HT} - S_{spin,\,LT} \\ &= R\ln 2048 - R\ln 8 \\ &= R\ln 256 \\ &= 46\ \mathrm{J\ K^{-1}\ mol^{-1}}\end{aligned}$$

This value is constant unless the orbital degeneracy and spin multiplicity change. In the present compound, these values are not affected by humidity.